ENGINEERING SCIENCES AND TECHNOLOGIES RESEARCHES

Editors

Halil Ibrahim KURT
Engin ERGUL

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Engineering Sciences and Technologies Researches

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PREFACE

Engineering is a basic subject that combines science with other areas and technologies. Research in this field plays an important role in providing solutions to problems and difficulties. This book, "Engineering Sciences and Technologies Researches", aims to explore the wide range of topics that science has to offer. The book brings together the efforts of researchers and scientists from different engineering disciplines. It presents innovations in engineering sciences and technologies to readers. Each chapter and/or paper was/were prepared with the efforts of academics or scientists. Theoretical knowledge is combined with practical applications to produce basic knowledge and solutions in the field of engineering. This book also intends to increase interest in engineering sciences and technologies.

Best Regards,

Assoc. Prof. Dr. Halil Ibrahim Kurt
Ph.D Engin Ergul

CONTENT

CHAPTER I

ADSORPTION STUDIES OF CR(III) INTO BENTONITE CLAY

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1. Introduction

The constant increase in the world population and the addition of new technological developments every day lead to an increase in industrial activities in quality and quantity. Rapidly increasing production of industries not only leads to depletion of natural resources, but also causes water, air and soil pollution (Dinh et al., 2022). Wastewater from industries differs greatly from domestic wastewater in terms of source, quantity and character. The effects of industrial wastewater on nature are much more significant, changing the natural balance, and in some cases, irreversible. For this reason, the factors that cause environmental pollution must be controlled and the effluent of the industrial facility must be treated to prevent it from polluting the natural water environment. Metals used in various fields in industry spread to the environment through wastewater and pollutant emissions and accumulate in nature. Metals, which are in a constant cycle in the air, water and soil and have toxic effects on living things, also hold an important place among water pollutants (Vezentsev et al., 2022).

The most important heavy metal sources in the environment are; Process and wastewater of industries such as metal production, paints, battery production, metal finishing, mining and mineral processing, coal mining and oil refinery. It is not possible for heavy metals, which are in the primary toxic pollutant class, have high atomic density and toxicity, and are thought to be responsible for groundwater pollution, to be transformed into harmless compounds by biochemical methods, such as organic pollutants found in water (Acar et al., 2023). One of the heavy metals that pose a problem in terms of environmental pollution is chromium. Chromium; It can be found as +6 and +3 in wastewater from industries such as coating, leather tanning, wood preservative production, stainless steel production. Release of Cr (VI) into the environment can cause serious health problems. For this reason, different methods have been developed for the treatment of wastewater containing Cr(VI). The most commonly used method is to reduce Cr(VI) to Cr(III) and precipitate it as $Cr(OH)_3$ by increasing the pH of the environment. However, the sludge generated in this method creates an important secondary waste. Apart from these, methods such as ion exchange, electrocoagulation, membrane techniques and adsorption can be applied.

Among these methods, adsorption attracts attention in terms of ease of application and economy (Baran, et al., 2006; Aksu, et al., 2002). However, in order for this method to be used efficiently, it is of particular importance that the material chosen as the adsorbent is cheap and effective. Adsorbents used in heavy metal removal; clays, activated carbon, gels, alumina, silica, zeolites and resins. Recently, activated carbon has been replaced by cheap, effective, easy to obtain, abundant, natural materials and various industrial by-products in heavy metal removal. One of the natural adsorbents that has an important place in wastewater treatment by adsorption method is clay (Tahir and Naseem, 2007). Clays found in soil are important inorganic compounds. Its sorption is due to their large surface area and ion exchange capacity. Clay minerals affect metal ions thanks to the negative charge in their structure (Anonymous). In our study, it is aimed to remove chromium ion, which is an important pollutant and a heavy metal in industrial wastewater, by using bentonite clay as an adsorbent by adsorption method, and to examine the effect of parameters such as chromium concentration, adsorbent dose, pH on adsorption efficiency and to determine the compliance of adsorption with the equilibrium isotherm equations.

2. Materyal and Methods

2.1. Batch Adsorption Studies:

The solutions used in the experiments were prepared by diluting the 1000 mg/L Cr^{3+} stock solution from $Cr(NO_3)_3.9H_2O$ salt. The initial concentrations of the Cr^{3+} solutions used for the analyzes and the concentrations of the samples obtained after adsorption were determined with the Perkin Elmer AAS (Atomic Absorption Spectrometer) device.

The bentonite used in the experimental study was obtained from Kütahya Magnezit İşletmeleri A.Ş. The chemical composition of bentonite (XRF result) is given in Table 1.

Before starting the experiments, the bentonite used as an adsorbent was sieved and its particle sizes were determined and separated to be used in the experiments. As a result of the sieving process, the particle diameter of the adsorbent material was determined as 270 mesh< Dp< 400 mesh (53µm-38µm). Then, it was kept in a 70°C oven for 24 hours and brought to a constant weight.

For adsorption experiments, certain amounts of bentonite were weighed and placed in polyethylene tubes. A shaking water bath was used to keep the temperature (25°C) constant in the experiments. 25 mL of Cr^{3+} solution (100 mg/L) at a certain pH was taken and added to the tubes containing bentonite. After a certain time, the tubes were taken from the water bath and placed in the centrifuge. Samples were processed at 5000 rpm for 7 min. Adsorbent substances were precipitated by centrifugation. The clear part of the solutions taken from the centrifuge was separated from the precipitate by decantation and analyzed on the AAS device to determine the equilibrium concentrations. % Adsorption values were calculated from the difference between the initial concentration and the concentration remaining in the solution (equilibrium concentration). The same processes were repeated for each parameter.

Table 1. Chemical composition of bentonite used in experiments (XRF results)

Component Amount	% by weight
Na_2O	1.18
MgO	9.05
Al_2O_3	11.80
SiO_2	43.05
P_2O_5	0.16
SO_3	0.17
K_2O	1.13
CaO	8.96
TiO_2	1.39
Cr_2O_3	0.29
MnO	0.16
Fe_2O_3	9.63
Loss of Glow	13.00

3. Results and Discussion

3.1. Effect of pH

When Figure 1 is examined, it is observed that the adsorption is maximum at pH 4 with 95.89% in the experiments conducted with bentonite. As can be seen, adsorption efficiency increased as pH increased. The reason why adsorption increases as the pH of the Cr^{3+} solution increases can be explained as follows. The surface of bentonite samples contains a large number of active centers and is charged (+) at low pH. Thus, the competition between H^+ and metal ions for available adsorption centers increases. However, as pH increases, this competition decreases as the active surfaces become more negatively charged. As a result, the adsorption of (+) charged metal ions increases due to the electrostatic attraction force (Unuabonah et al., 2008).

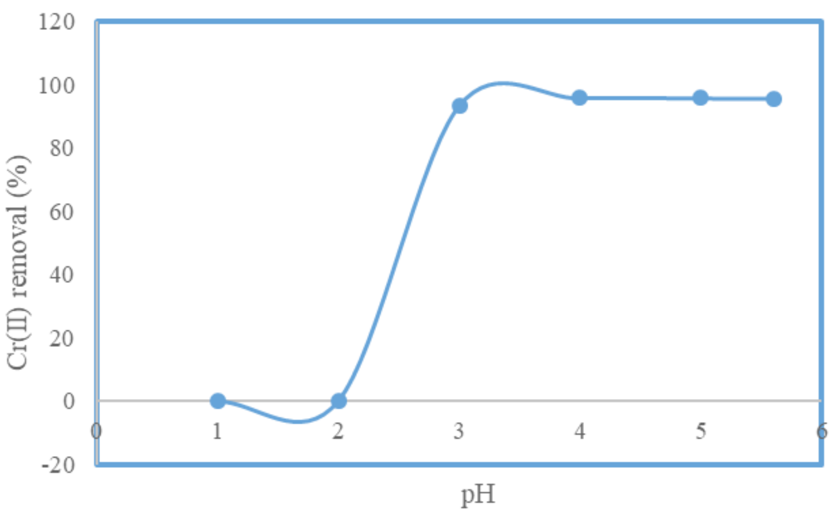

Figure 1. Effect of pH on Cr(III) Adsorption

3.2. Effect of adsorbent dose

The effect of various adsorbent doses on chromium adsorption is given in Figure 2. As seen in Figure 2, it was observed that as the adsorbent dose increased, the amount of adsorbed substance increased up to a certain point and then remained constant. Accordingly, % adsorption values increased. The reason for this can be shown as the increase in the surface area to which the substance adheres as the amount of adsorbent increases.

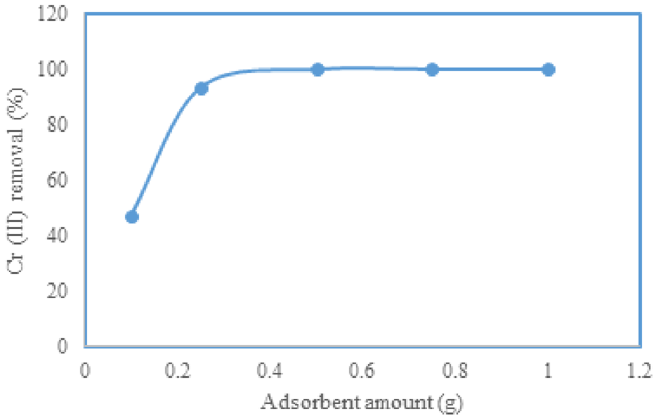

Figure 2. Effect of adsorbent amount on Cr(III) Adsorption

3.3. Effect of Initial Cr(III) Concentration

Figure 3 shows the effect of initial chromium concentration on adsorption efficiency. When Figure 3 is examined, as the initial Cr(III) concentration increases, the sorption efficiency of Cr(III) decreases, although the amount of Cr(III) sorbed per unit adsorbent increases. The reason for this is that as the initial Cr(III) ion concentration increases, the number of empty centers to which the metal will bind decreases and the adsorbent reaches saturation, especially at high concentrations.

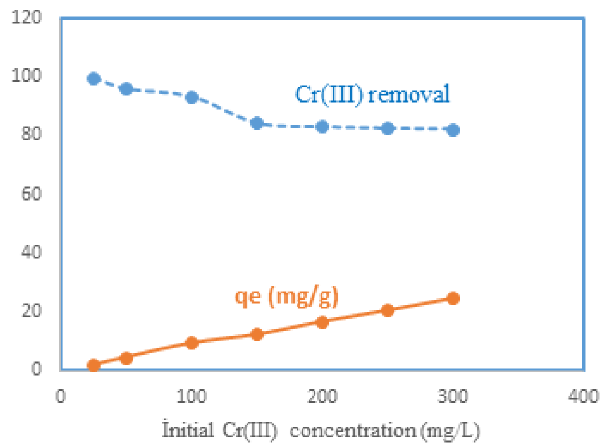

Figure 3. Effect of Initial Cr(III) Concentration on Cr(III) Adsorption

3.4. Adsorption Isotherm Results

To quantify the agreement between the sorption models and experimental observations for the behaviour of the Cr(III)–bentonite system, two different sorption models, Langmuir and Freundlich, were used. The most widely used isotherm equation for modeling of the sorption equilibrium data is the Langmuir and Freundlich equation (Aşçı et al., 2007). The adsorption model constants were estimated from the adsorption data of Cr(III) ions on bentonite by using a Curve Expert computer program (Table 2). The Langmuir and Freundlich sorption isotherms obtained at pH 3.0 for Cr(III) ions are shown in Fig. 4.

Table 2. Isotherm constants obtained using Langmuir and Freundlich models

Lngmuir model	**q_m (mg.g^{-1})**	**K (L.g^{-1})**	**R^2**
	29.941	0.051	0.9247
Freundlich Model	**K_F (mg^n g^{-1} L^n)**	**n**	**R^2**
	2.78	1.876	0.9564

Considering the regression coefficients (R^2) obtained for the isotherms, it was seen that chromium(III) adsorption to bentonite fits both isotherms, but it fits the Freundlich isotherm better than the Langmuir isotherm. The Freundlich constant n>1 indicates a desired level of sorption, and the closer the value of n is to zero, the more heterogeneous the system is. The Langmuir constant q_m is the sorption capacity when the surface is completely saturated with metal ions. The Langmuir constant K indicates the strength of the bond between Cr(III) ions and the sorbent. A large K indicates that the binding of metal ions is irreversible and strong. In the study conducted by Ghorbel-Abid et al. (2009), Cr(III) was removed from aqueous solution by adsorption using bentonite and it was emphasized that the experimental data fit better with the Freundlich isotherm for natural bentonite clay.

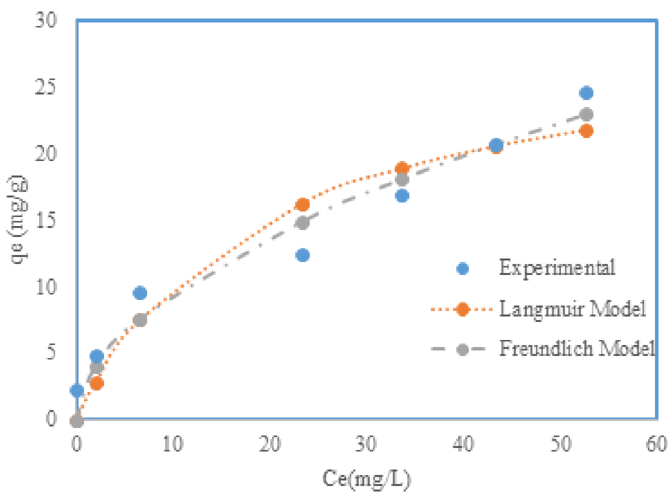

Figure 4. Comparison of Langmuir and Freundlich isotherms

4. Conclusion

In this study, batch adsorption experiments for the removal of Cr(III) from aqueous solution by using bentonite clay have been carried out. The effects of pH, adsorbent dose and initial Cr(III) concentration on adsorption were investigated and finally, the compatibility of sorption with Langmuir and Freundlich isotherms was examined.

When the pH changed between 1 and 5.6, the maximum efficiency was obtained as 95.89% at pH=4, 0.25 g clay amount and 100 mg/L initial Cr(III) concentration. The sorption efficiency of Cr(III) to the bentonite varied between as 100 and 82.47 % in the range of 25 and 300 mg/L initial Cr(III) concentration. Sorption of Cr(III) to the bentonite was non-linear and the bentonite-Cr(III) isotherms fitted well the Freundlich model and have similar shapes (n-values > 1, showing favorable sorption). The highest Cr(III) sorption capacity, K_F (2.78 $mg^n\ g^{-1}\ L^n$) and intensity, n (1.876), were obtained for the bentonite.

5. References

Acar, B. Ç., Oku, Z. Y. (2023). Deri Endüstrisinde Krom Kullanımı ve Biyolojik Yöntemlerle Krom Giderimi, Journal of The Institute of Science and Technology, 6(1): 1006-1029.

Aksu, Z., Gönen, F., Demircan, Z. (2002). Biosorption of chromium (VI) ions by motiwal B30H resin immobilized activated sludge in a packed bed: comparasion with granular activated carbon, Process Brachem., 38, 175-186.

Aşçı, Y., Nurbaş, M., Açıkel, Y.S. (2007). Sorption of Cd (II) onto kaolin as a soil component and desorption of Cd (II) from kaolin using rhamnolipid biosurfactant, Journal of Hazardous Materials, 139 (1), 50-56.

Baran, A., Bıçak, E., Hamarat- Baysel, Ş., Önal, S. (2006). Comparative studies on the adsorptions of Cr(VI) ions on to various sorbents, Bioresource Technol., 98, 661-665.

Dinh et al., (2022). HTDMA-modified bentonite clay for effective removal of Pb(II) from aqueous solution. Chemosphere 286, 131766.

Ghorbel-Abid I., Jrad, A., Nahdi, K. and Trabelsi-Ayadi. M. (2009). Sorption of chromium (III) from aqueous solution using bentonitic clay, Desalination, 246, 595–604.

Tahir, S.S. and Naseem, R. (2007) Removal of Cr(III) from tannery wastewater by adsorption onto bentonite clay, Separation and Purification Technology, 53 312–321.

Unuabonah, E.I., Adebowale, K.O., Olu-Owolabi, B.I., Yang, L.Z., Kong, L.X. (2008). Adsorption of Pb (II) and Cd (II) from aqueous solutions onto sodium tetraboratemodified Kaolinite clay: Equilibrium and thermodynamic studies, Hydrometallurgy, 93(1-2) 1-9.

Vezentsev A. I., Gorbunova N. M., Sokolovskiy, P. V., Mar´inskikh, S. G., Chub, A. V., Chau, N. H. and Greish, A. A. (2022). On the adsorption mechanism of copper ions on bentonite clay, Russian Chemical Bulletin, 71 (4) 651—655.

CHAPTER II

EVALUATION OF THE EFFECT OF PROCESS PARAMETERS AND ADSORBENT PROPERTIES ON THE REMOVAL OF METAL IONS WITH BIOCHAR-BASED ADSORBENTS: A MACHINE LEARNING APPLICATION

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1. Introduction

1.1. Evaluation of Heavy Metal Ions Pollution and Removal Methods

Metal ions are used in many industrial productions, including chromium plating, battery manufacturing, glass industries, agricultural activities, inorganic pigment production, plastic and rubber production, household waste, and pharmaceutical industrial processes (Singh & Mishra, 2021). Since heavy metal ions are not biodegradable, they tend to accumulate in living organisms. Heavy metal ions such as cadmium, chromium and lead, which are known to be potentially toxic even at low concentrations, pose a significant threat to the aquatic ecosystem. For these heavy metals expressed, the maximum allowable concentration in drinking water established by the US Environmental Protection Agency (USEPA) is

0.10 mg/L for Cr (total) (mg/L); It is 0.005 mg/L for Cd (II) and 0.015 mg/L for Lead (II) (Fu & Wang, 2011). Drinking water containing heavy metals above the permissible upper limit has various toxic effects on humans and living things. Some heavy metals such as cadmium, chromium and lead, mercury and arsenic are considered as potential carcinogens (Balali-Mood vd., 2021). For this reason, the wastewater of the industries mentioned above, which constitutes heavy metal pollution, should be treated before being discharged into the receiving environment (Liu vd., 2022). To remove the heavy metal ions from ındustrial wastewater are used in different physicochemical processes such as; adsorption, membrane filtration, electrodialysis, the reverse osmosis method, the ion exchange method, photocatalysis, and the ferrite method (Abraham vd., 2017; Z. Chen vd., 2021; Khulbe & Matsuura, 2018; Mariana vd., 2021). Among these methods, the best and most effective technique is the adsorption process (Lakherwal, t.y.). The cost of the adsorbent used in the adsorption process, the regeneration ability of the adsorbent, and the adsorption capacity are the most important factors affecting the process efficiency. Many materials such as natural or modified clay and oxide minerals (Jiménez-Castañeda & Medina, 2017), commercial activated carbon (Shahrokhi-Shahraki vd., 2021), carbon nanotubes(Baghayeri vd., 2021; Kumar vd., 2015), graphene oxide (X. Chen vd., 2016) , chitosan-based polymeric sorbent (Y.-W. Chen & Wang, 2016) and natural biomaterials (Taşar vd., 2014) have used as an sorbent to the removal of the heavy metal ions from wastewater. However, these materials are disadvantageous because they have low adsorption capacity or have high costs. Therefore, it is tried to develop both effective and cheap, and easily available adsorbents to increase the efficiency and effectiveness of the adsorption process (Dhyani & Bhaskar, 2018; Shaheen vd., 2019). And especially biochars, which are seen as an alternative adsorbent for the removal of pollutions in wastewater, are attracted attention due to their porous structure, abundant surface functional groups, and ease available (Tran vd., 2020). The use of biochar as an adsorbent both contributes to the recycling of wastes and is cheaper than another adsorbent since it was produced from waste biomass sources. The range of waste biomass resources (woody waste, agricultural waste, municipal solid waste, industrial waste, animal waste, etc.) is quite wide and it is known that significantly changes the adsorption capacity of the produced bio-char (Zhang vd., 2020). The properties (such as porosity) of biochar depend on the structure of the biomass (ultimate and proximate content) and sorbent production conditions.

1.2. The Aim of the Studies and The Gap of the Literature

Adsorption of heavy metals on biochars depends on many factors. These are biochar properties, environmental conditions, metal ion properties and initial metal ion concentration etc.(Gao vd., 2019; Shaheen vd., 2019). However, it is best to consider biochar properties such as particle size, surface area, cation exchange capacity, and total carbon mass percentage with holistic adsorption mechanisms. Studies are carried out by using solutions prepared in simulated laboratory conditions and by considering the relative contribution of each effect factor to the adsorption efficiency separately. The achieved removal success cannot be achieved when real wastewater samples containing heavy metals are used, that is, it does not give realistic and successful results. Therefore, it is important to evaluate the effect of all variables on adsorption with a holistic approach and to determine their feature importance.

Many empirical adsorption kinetic and isotherm equations have been derived to model the adsorption process. However, these equations are usually static models derived to model the adsorption process under certain stable operating conditions. Therefore, models based on conventional adsorption equations have limitations in both kinetics and isotherms (Largitte & Pasquier, 2016). Conventional model equations based on examining the effect of only one parameter at a time do not reveal the effect of the interaction between variable parameters on the adsorption capacity (Rodríguez-Romero vd., 2020). Therefore, models that can reveal the multidimensional structure of adsorption are needed. For these reasons, machine learning (ML) methods were used in this study to model the adsorption behavior of heavy metals on biochars and to solve the problems expressed by learning.

Machine learning (ML) regressions are capable of modeling and predicting the complex and nonlinear mathematical relationship between independent and dependent variables. For this reason, researchers have used machine learning methods, especially in engineering applications (such as adsorption) where many variables must be evaluated simultaneously. In this way, many new methods have been included in traditional engineering research. Thus, acceptable estimation results for engineering applications began to be obtained. Especially, in the last five years, studies on the modeling of artificial neural networks (ANN) and machine learning techniques and the adsorption process have started to attract the attention of those working in the field (Aftab vd., 2022; Li vd., 2023; Rodríguez-Romero vd., 2020; Taşar, 2022). In the mentioned studies, the effect of environmental factors affecting the adsorption capacity such as the initial pH of the solution, the initial concentration of heavy metal ions, ionic strength, and adsorption temperature has been evaluated. Only one heavy metal ion was simulated in the studies. In the adsorption process of heavy metal ions on biochar, the pH, surface charge, surface area, porosity, functional groups, and mineral content of the adsorbent, etc. are determined plays an important role. And in the studies conducted by previous researchers, the type of adsorbent and its properties have a great effect on the adsorption capacity.

Therefore, in this study, the success of the decision tree (DT), Gaussian method (GM), Random forest (RF) and Multi-Layer Sensing (MLP) machine learning methods in estimating the adsorption efficiency were comparatively examined.in single, double, and triple systems. While modeling, in addition to adsorption parameters (pH, temperature, initial concentration), adsorbent properties (particle size, average pore surface area, proximate and ultimate composition, etc.) were also taken into account. The relative importance of each variable parameter on the target variable was revealed.

2. Material and Methods

2.1. Dataset and Data Preprocessing

In this study, the adsorption capacity of biochars for heavy metals was investigated and adsorption process was modeled. A dataset was used that summarizes the experimental data (350 pieces) on the adsorption of heavy metals such as As^{3+}, Cd^{2+}, Cu^{2+}, Ni^{2+} , Pb^{2+} and Zn^{2+} to biochars. The dataset is presented in the supporting information document. In the data set, only biochar samples (44 pieces) were taken into account as adsorbents. The biochar samples considered in the data set were produced from different biomass types (24 pieces) with lignocellulosic structures in the temperature range of 300-700 °C. The characteristic features of biochars are summarized in Table S1 in the supplementary dossier.

In the dataset, there were used three major categories in which to classify variables; (i) biochar properties: particle size, surface area (SA, m^2/g), and the cation exchange capacity (CEC, $cmol^{(+)}/kg$) of biochar are all measured in terms of pH in water (pHH_2O), total carbon mass percentage (C%, (O+N)/C, (O/C), and (H/C). (ii) The adsorption process's parameters: The initial pH (pH_{sol}) of the wastewater and adsorption temperature (T), the initial heavy metal concentration of wastewater (C_0, mmol/g). (iii) Adsorbate properties: properties of heavy metals, such as charge density (N_{charge}).

The expressed variables, data ranges, and adsorption efficiency were presented in Table S2 in the supplementary document. For this, a box plot was developed as a data representation method. Using the Pearson correlation coefficient (PCC), the linear relationship between any two factors in the datasets was determined (Equation 1).

$$r = \frac{Cov(X,Y)}{\sigma_X \sigma_Y} \tag{1}$$

The covariance between X and Y was cov(X,Y); σ_Y and σ_X are the standard deviations of Y and X.

A two-tailed t-distribution with (N-2) degrees of freedom was used to compute a statistical value using Equation 2. r is the PCC and N is the number of related samples in Equation 2.

$$t = \frac{r}{\sqrt{\frac{1-r^2}{N-2}}} \tag{2}$$

2.2. Regression Methods

2.2.1. Multiple Linear Regression (MLR)

Multiple linear regression (MLR) is the most basic regression model used to describe linear relationships between multiple variables. In the MLR regression model, the relationships are defined as in Equation (3).

$$y_i = \beta_0 + \beta_1 X_{i1} + \beta_2 X_{i2} + \cdots + \beta_k X_{ik} + \epsilon_{ij} \tag{3}$$

The term X_{ij} is *j.* of the independent variable *i.* represents the level value. Observation of y_i dependent variable i. represents its value. $\in_{ij}$ error term and β_j j. regression coefficient and *k* is the number of independent variables. In the multiple regression model, the regression coefficients are calculated using the least squares method.

2.2.2. Decision Tree Regression (DT)

The decision tree regression is a binary recursive partitioning process that splits the input data into partitions/branches. As it progresses from each branch upwards, it continues to be divided into smaller groups according to the data feature. At this stage, the algorithm uses the partitioning method, which minimizes the sum of the squares of the deviations from the mean in two separate sections. In the regression tree method, the minimization (reduction) deviation at each node is solved by the equation in Equation (4) (Taşar, 2022).

$$\arg\min[P_l Var(Y_l) + P_r Var(Y_r)] \qquad x_j = x_j^R, j = 1,2,3 \ldots, M \tag{4}$$

P_l and P_r are the probabilities of the left and right nodes, respectively. $Var(Y_l)$, $Var(Y_r)$ are the responsible vectors for the mutual right and left child nodes. $x_j = x_j^R, j = 1,2,3\ldots,M$ stands for optimal discrimination query. x_j represents the x_j^R the best discrimination value. M is the number of variables in the training set.

2.2.3. Gaussian Process Regression (GPR)

GPRs are non-parametric machine learning models used to estimate the value of the continuous response variable. The output variable is modeled as a Gaussian process using covariances with the input variables. The most important feature of the GSR is that it has a variety of covariance functions that enable the most accurate option to be determined by providing the ability to create functions at different degrees. The Gaussian process is a generalization of the gaussian distribution. While the Gaussian distribution is the spread between random changes, the Gaussian process is explained as the distribution between functions. The Gaussian process function (x) is defined by the covariance and mean (x). The mathematical relationship between them can be expressed by the following equation.

$$m(x) = E(f(x)) \tag{5}$$

$$k\ (x, x') = E(f(x) - m(x))\ (f(x') - m\ (x'))) \tag{6}$$

Here, (x, x') stands for kernel or covariance function. The (x) function can be defined as:

$$f(x) = G\mathrm{P}(m(x), k(x.\ x')) \tag{7}$$

Usually, for simplification, the mean function value is assumed to be zero. The relationship between the input vector and the objective vector in the Gaussian process is as follows:

$$y_i = f(x_i) + \varepsilon \tag{8}$$

where $f(x)$ and ε denote the regression function and the noise value of the gaussian distribution, respectively. Also, the covariance matrix can be given as follows. ki is the covariance determined between the hidden functions (xi) and (xj).

$$k_{i.\,j} = k\ (x_i, x_j) \tag{9}$$

$$k = \begin{pmatrix} k(x_1, x_1) & k(x_1, x_2) & k(x_1, x_n) \\ \vdots & \vdots & \vdots \\ k(x_n, x_1) & \dots & k(x_n, x_n) \end{pmatrix} \tag{10}$$

2.2.4. Random Forest Regression (RF)

The random forest (RF) regression is a technique for constructing a decision ensemble (forest) consisting of many decision trees. In this method, multiple regression trees are created and the final regression result is calculated by taking a combination of the predictions from the regression trees to calculate the final estimate.

2.2.5. Supported Vector Regression (SVR)

Support vector machines are the supervised learning techniques used in classification and regression. The general statement about the regression adaptation of the support vector machine is:

$$D = \{(x_1, y_1), (x_2, y_2), \dots, (x_l, y_l)\} \tag{11}$$

where x_i is each of the *N*-dimensional input variables and y_i is the output variable.

$$f(x) = \langle w, x \rangle + b \tag{12}$$

It is desired to calculate the value of the function presented in Eq. (12). In this case, *w* is referred to as the normal vector, *x* is the input vector, and the vector product is iso-dimensional. In the SVR method, our goal is to find a function *f*(*x*) such that the actual y_i output values are estimated with a deviation of at most ε, and the distance between the two planes that are parallel to the found function and contain the training inputs is minimum. In order to find the *f*(*x*) function; a minimum vector *w* is sought. In this, the norm of the vector *w* is minimized. It is possible to formulate as a convex optimization problem:

$$min \frac{1}{2} \|w\|^2 + C \sum_{i-1}^{l} (\xi_i + \xi_i^*) \tag{13}$$

$$y_i - \langle w, x_i \rangle - b \leq \varepsilon + \xi_i \tag{14}$$

$$\langle w, x_i \rangle + b - y_i \leq \varepsilon + \xi_i^* \tag{15}$$

$$\xi_i, \xi_i^* \geq 0 \tag{16}$$

where constant C is a number greater than 0, and it reconciles the amount of deviations greater than the e with the distance between two parallel planes in which the $f(x)$ function takes place. Compared to the traditional supervised learning methods of neural networks, the SVR also uses the principle of inherent risk minimization, which aims to reduce not only the experimental measurement error but also the upper bound of the generalization error.

2.2.6. Multi-Layer Perception (MLP) Model

Multilayer perceptron networks (MLPs) are a type of artificial neural network that uses at least one layer between the input and output layers. Unlike the single-layer perceptron, MLPs can solve nonlinear problems, so they are the most popular type of neural network in widespread use. This MLP architecture consists of the input layer, output layer, k hidden layers, and 2 neurons in each hidden layer. The input layer consists of a large number of neurons corresponding to each independent variable. The hidden layer provides the capture of non-linear relationships between variables. The output layer also corresponds to the predicted classification or recommendation. While the MLP method performs a forward transmission, it also uses a backpropagation algorithm to minimize the error. Forward transmission is when the input applied to the network advances from the previous layer to the next layer in sequence and reaches the output layer. The error signal is the difference between the input signal reaching the output layer and the desired value. The error signal moves from the output layer to the input layer and aims to minimize the error value by updating the weight values. Each hidden volume has an activation function that is generally non-linear and the same for all hidden volumes. The output of a hidden unit is determined by applying the activation function to the sum of the weighted signals from the previous layer and a discrete bias.

The working structure of multi-layer perceptrons consists of two stages: forward computation, where the output of the network is calculated, and backward computation, where the weights are updated. The main purpose of the forward calculation is to estimate the output value for the given input values and calculate the error using the target value. While the information in the input cells is transferred to the middleware cells, it is multiplied by the relevant weights, and the NET input of each middleware cell is calculated according to the weighted sum function:

$$NET_p = \sum_i w_{ip} x_i \tag{17}$$

Here the *NET*p middleware p. the entry into his cell; Wip input layer i. cell, p. the weight that attaches to the cell; i in the xi input layer. represents the output of the cell. The *NET* input found is passed through an activation function, and the output of the middleware cells is found.

$$F_p = f(NET_p) \tag{18}$$

Here is the p of the F_p intermediate layer shows the activation function of the cell. The activation function to be used must be differentiable. After this stage, the error calculation is made using the target value and the value in the output cell. Error calculation:

$$\varepsilon_p = (T_p) - (F_p) \tag{19}$$

εp the error made; T_p is the target output value; F_p. Displays the calculated value of the cell. In the second stage, backward calculation, the weights are updated to minimize the error rate. For this, the error values are propagated backwards and the update rules of the weights are created. The error is primarily the weight values between the output layer and the middle layer; Then, the weight values between the middleware and the input layer are calculated and proceed backwards.

2.2.7. Performance Evaluation

The coefficient of determination (R^2), mean squared error (MSE), mean absolute error (MAE), and root mean square error (RMSE) were used to discuss the performance of machine learning models and evaluate the model's accuracy and the model's compatibility with the dataset used. For this reason, the coefficients were calculated using Equations 20 through Equation 23, respectively (Taşar, 2022).

$$R^2 = 1 - \frac{\Sigma(y_i - \hat{y})^2}{\Sigma(y_i - \bar{y})^2} \tag{20}$$

$$MSE = \frac{1}{N}\sum_{i=1}^{N}(y_i - \hat{y})^2 \tag{21}$$

$$MAE = \frac{1}{N}\sum_{i=1}^{N}|y_i - \hat{y}| \tag{22}$$

$$RMSE = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(y_i - \hat{y})^2} \tag{23}$$

3. Result and Discussion

3.1. Analysis of The Dataset and Pearson Correlation Matrix

Biochar's pH in water (pHH_2O), carbon mass percentage (C, percent), molar oxygen/carbon ratio (O/C), molar hydrogen/carbon ratio (H/C), ash content (ash, percent), particle size (PS, mm), biochar surface area (SA, m^2/g), and cation exchange capacity (CEC, $cmol^{(+)}/kg$) are all considered characteristic features. It was shown in Figure 1 as a box graphic that the biochar's characteristic properties changed depending on the pyrolysis conditions.

Figure 1 presents a statistical distribution of properties of 44 biochar samples produced from lignocellulosic biomass by thermal degradation. By dividing the data set into quarters, the interquartile range was used to measure data variability. The minimum, first quartile, median, third quartile, and maximum statistical data were represented by five rows from bottom to top in each boxplot. In other words, the bottom and top of each box, for instance, correspond to the 25^{th} and 75^{th} percentiles. The distance between each box's bottom and the top is referred to as the interquartile range. The red line in each box's center represents the sample median. Sample skewness is depicted on a graph if the median is not in the center of the box. Whiskers refer to the lines that cross above and below each box. Whiskers range from the farthest observation of the interquartile range to the farthest observation of the whisker length (adjacent value). Considered to be outliers are observations that exceed the whisker. By default, an outlier is a value that exceeds 1.5 times the interquartile range from the bottom or top of the box. A red plus sign is used to denote outliers. Comparing boxplot medians is analogous to a t-test for means or other visual hypothesis tests.

In order to increase the reliability of machine learning models, data must be analyzed before developing the models. It has been determined that the biochar samples are generally basic character (Figure 1). This can be explained by the reduction of acidic functional groups in the biomass structure during thermal degradation and the accumulation of alkaline cations such as Ca^{2+}, K^+, Mg^{2+}, and Na^+ (S. Wang vd., 2015). In the few examples of biochars showing acidic character; It can be thought that organic acids are formed by the decomposition of hemicellulose and cellulose, which are the main components of biomass. In addition, it was thought that at low temperatures depending on the chemical structure of the biomass a small amount of alkali salt release/ accumulation occurs (X. Chen vd., 2011).

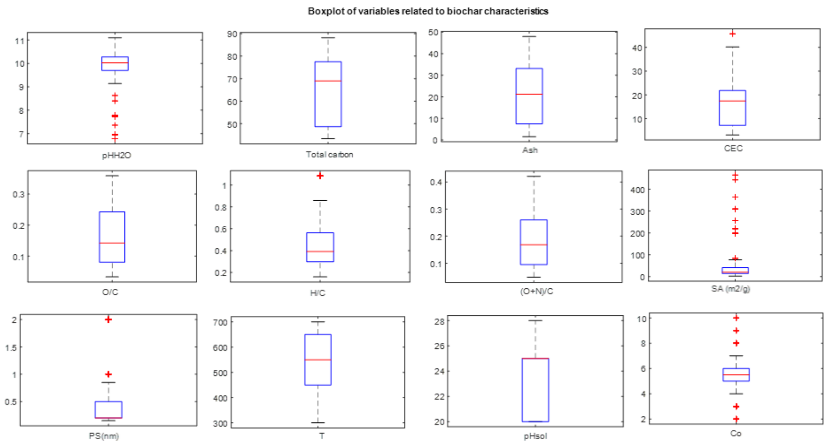

Figure 1. Boxplot of variables related to bio-char characteristic and adsorption conditions characteristic

The inorganic contents and compositions of biomass resources are not the same, thus these results are understandable. When Figure 1 is examined, it is seen that the elemental compositions of biochar resources are relatively different from each other. This difference depends on the thermal decomposition conditions (especially the temperature) and the nature of the lignocellulosic raw material from which the biochar is produced (type, age, growing conditions, etc.). The main purpose of biochar production with the thermal decomposition process is to obtain a more porous and carbon-rich, high-strength material while removing the volatile components from the raw material structure. It is known that while the structure is enriched with carbon during thermal decomposition, the moisture and oxygen content also decreases. In this context, it is expected that the carbon contents of biochar samples will increase depending on the carbonization temperature and generally vary between 40% and 90%.

The ash content of biochars affects on physicochemical properties and the distribution of organic matter (Sun vd., 2013). However, how the ash content affects the adsorption process and its interaction with the adsorbent to be sorbed is a controversial issue (Abbas vd., 2018; R.-Z. Wang vd., 2018). For this reason, in this study, biochar samples varying between 1% and 50% are especially included. It is thought that the selected range will contribute to a more efficient interpretation of this effect.

The O/C, H/C and (O+N)/C ratios of biochars are an indication of the abundance of oxygen-containing functional groups and the hydrophilicity of biochars, biochar surface aromaticity, and concentration of polar surface functional groups, respectively (Cui vd., 2016; Shaheen vd., 2019; Zama vd., 2017). Therefore, these parameters are important for adsorption applications, thus bio-chars can be compared in terms of these parameters. When the median of the O/C, H/C, and (O+N)/C molar ratios of the biochar samples which was used in this study are examined, it is seen that they are 0.14, 0.4, and 0.15, respectively.

It is seen that the average surface areas of biochars are concentrated in the range of 1-75 m^2/g. Although carbonization is known to increase the porosity of biochar, it has been determined that the surface areas of the obtained biochars are generally much lower than commercial activated carbon (up to 1000 m^2/g). The surface area of only a few biochar samples could be reached 450 m^2/g. However, porosity is not the only parameter that affects the efficiency of the adsorption process. Although the surface area of biomass sources is low, heavy metal ion removal efficiencies are higher than expected (Kołodyńska vd., 2017). Because the CEC and inorganic contents of biochars also play an active role in the adsorption of heavy metals (Deng vd., 2019). The CEC value represents the ability to retain cations on the biochar surface. As the CEC value increases, the adsorption efficiency of metal pollutants increases. Figure 1 shows that the CEC values of biochars are in the range of 5-40 $cmol^{(+)}/kg$.

3.2. Pearson Correlation Matrix Analysis

In this section, the relationships between PCC analysis and biochar properties were investigated and interpreted. According to the Pearson correlation matrix presented in Figure 2, the comments presented below were reached.

(i) The surface area of biochars expresses a positive correlation with the carbon content. Considering that there is a linear relationship between the carbon content and the thermal decomposition temperature, it is understood that the relationship between the thermal decomposition temperature and the surface area of biochars indicates a positive correlation.

(ii) There is an inverse correlation between the ash content and the surface area of the biochar. This can be interpreted as the clogging/filling of the micropores formed by the removal of volatile components during thermal decomposition by ash.

(iii) It was determined that biochars showed close positive relationships with CEC, (O+N)/C, O/C, pHH_2O, and ash. This proved that the CEC values of biochars and their functional groups and mineral contents are closely related.

(iv) Adsorption efficiency of heavy metals was negatively correlated with carbon content, surface area, N_{Chance} and positively correlated with other variable parameters.

Multilinear regression methods were used in the study to investigate the deep relationship between adsorption efficiency and variable parameters. The data obtained are discussed in the next sections.

3.3. Performance Predictions for The Adsorption Efficiency Using The Regression Models

The data were modeled using the Random Forest Regression (RF), Gaussian Regression (GM), Decision Tree Regression (DT), Supported Vector Regression (SVR) ve Multi Layer Perception (MLP). Table 1 lists the ideal hyperparameters that were found for each regression. 10-fold cross-validation rate used in this study.

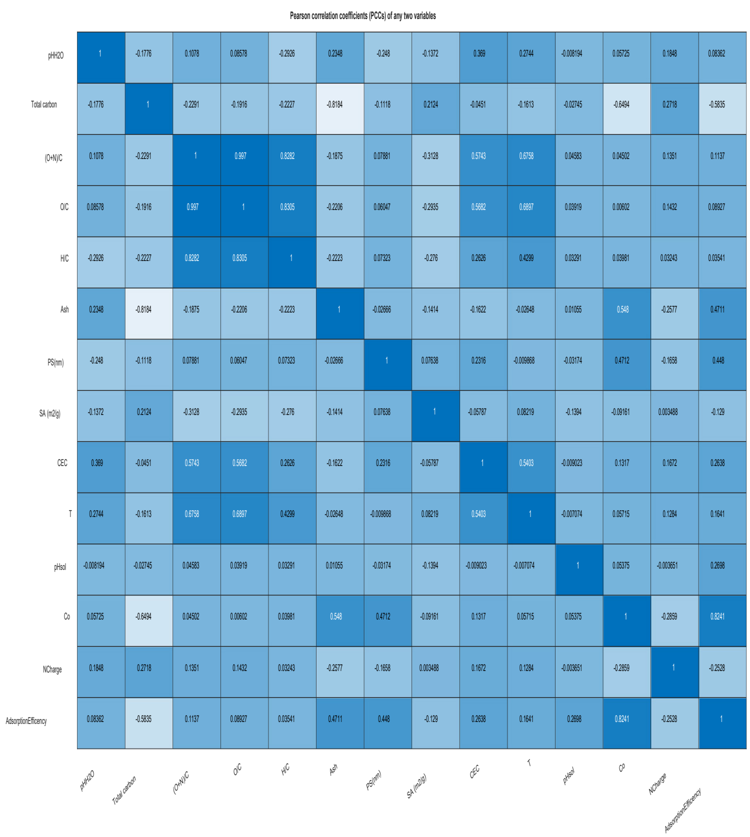

Figure 2. Pearson correlation coefficients matrix

Table 1. Optimum hyper-parameters of methods

<table>
<tr><th>Regression</th><th>Parameter</th></tr>
<tr><td>MLR (Method 1)</td><td>Linear</td></tr>
<tr><td>DT (Method 2)</td><td>max depth: 5</td></tr>
<tr><td>GM (Method 3)</td><td><table><tr><th>Basıc Function</th><th>Kernel Function</th><th>Kernel Scala</th><th>Standard Deviation</th><th>Sigma</th></tr><tr><td>Constant</td><td>Quadratic</td><td>9.2584</td><td>0.2439</td><td>0.2439</td></tr></table></td></tr>
<tr><td>RF (Method 4)</td><td>Tree number: 200, max depth: 5</td></tr>
<tr><td>SVR (Model 5)</td><td>Preset: Linear SVM; Kernel function: Linear;Kernel scale: Automatic; Box constraint: Automatic;Epsilon: Automatic; Standardize data: true</td></tr>
<tr><td>MLP (Method 6)</td><td>Preset: Wide Neural Network; Number of fully connected layers: 1; First layer size: 100; Activation: ReLU; Iteration limit: 1000; Regularization strength (Lambda): 0</td></tr>
</table>

Figure 3 compares the experimental and predictive results of the MLR(a), DT(b), GM(c), RF(d), SVR(e) and MLP(f) regressions. The x-axis and y-axis displays experimental data and the estimated value, respectively. The best prediction scenario is displayed by the straight line. Prediction rate, training time, and regression scores are all included in Table 2, which shows the R^2, RMSE, MSE, and MAE. The MLR performed less well than the other regressions in this study because the regression coefficient of the MLR regression was found to be smaller than the coefficients of the other regressions studied. As shown in Table 2, when the regression coefficients for the DT; GM; RF; SVM and MLP regressions regression coefficients were found to be 0.90; 0.97; 0.98; 0.76 and 0.95 respectively. In addition, the RMSE coefficient for the RF regression was obtained at 0.04929. Since the RMSE value of the RF regression is at least 15% lower than the other regressions. The root means square error (RMSE) is very close to zero, indicating that the RF regression performs satisfactorily. As a result, it was determined that the RF regression had the best performance. It was concluded as a result that RF regression is required to ascertain the intricate relationship between factors and targets.It was revealed that the success rate obtained in the study was higher than all of the regression methods (El Hanandeh vd., 2021; Ke, Nguyen, Bui, Bui, Choi, vd., 2021; Ke, Nguyen, Bui, Bui, &

Nguyen-Thoi, 2021; Yang vd., 2014; Zhu vd., 2019) presented in the literature. The general estimation ability is far superior to the studies in the literature and the regressions used in this study.

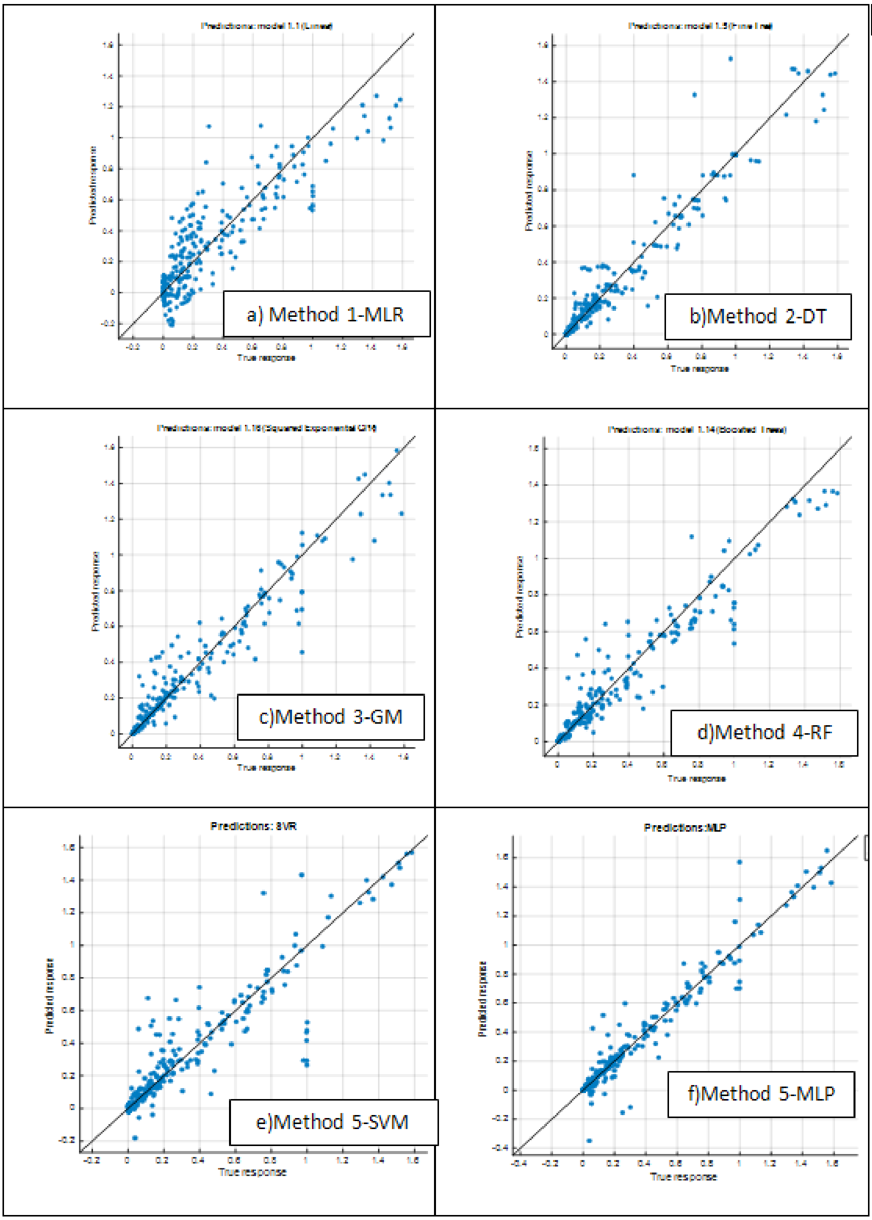

Figure 3. Prediction and actual response graph all of the regressions for adsorption efficiency

Table 2. Performance metrics of Regressions

Regression	RMSE	R^2	MSE	MAE	Prediction Speed (obs/sec)	Training Time (sec)
MLR	0.15686	0.79	0.024606	0.10987	6600	0.5517
DT	0.10902	0.90	0.011885	0.045542	17000	0.38394
GM	0.06111	0.97	0.0037343	0.028098	11000	4.3655
RF	0.04929	0.98	0.0024299	0.023042	820	10.603
SVM	0.16888	0.76	0.028521	0.10216	5500	2.1505
MLP	0.08046	0.95	0.0064737	0.03502	7300	17.396

3.4. Feature Importance

In this step of the study, feature importance information was tried to create for the adsorption process. The feature importance values of the variable parameters discussed were tried to be presented in pie charts in detail and presented in Figure 4. It was determined that the initial metal ion concentration is the most critical parameter affecting the adsorption efficiency. This parameter was followed by the CEC and total carbon values of the adsorbent and the particle size of the adsorbent.

When examined in Figure 4, it is understood that the biochar properties affect the adsorption efficiency by 67%, the ambient conditions by 13%, and the initial heavy metal ion concentration by 20%. Considering the feature's importance, it was concluded that first of all, attention should be paid to the selection of adsorbent for process efficiency.

When the biochar properties are evaluated within themselves, the outstanding parameters are CEC (21%), total carbon content (15%), particle size (15%), ash (13%), and pHH_2O (10%). The relatively higher contribution of CEC is because the adsorbent is a function/result of both ion exchange (eg, Ca^{2+}, K^+, Mg^{2+}, and Na^+) and surface functional groups (eg phenolic carboxyl, and carbonyl groups) (Mohan vd., 2014). The total contribution of (O+N)/C and H/C to the molar ratio was determined as 12%. This indicates the role of oxygen-containing functional groups and aromatic structures in adsorption (Alam vd., 2018).

In addition, contrary to what is generally expected (Ke, Nguyen, Bui, Bui, Choi, vd., 2021), the importance property value of the surface area of the adsorbent was determined to be relatively low (6%). This situation revealed that the chemical adsorption process, in which functional groups are active, is predominant in the adsorption process of metal ions.

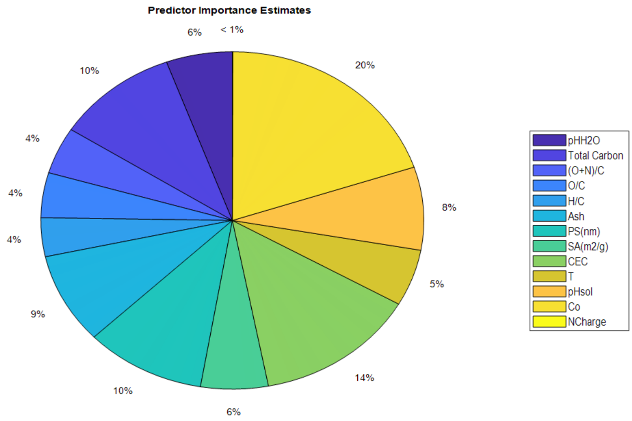

Figure 4. The feature importance of variable parameters on the adsorption efficiency

Besides, the contribution of N_{charge} and electronegativity in the adsorption process is almost negligible (<1%). It was also reported in Zhu et al., (2019) that heavy metal properties such as ion radius, charge number and electronegativity do not have a significant effect on the adsorption capacity. The initial metal ion concentration feature importance value is in agreement with the PCC coefficient (0.8241) shown in Figure 2. Studies in the literature emphasize the importance of initial metal ion concentration on sorption (Zhou vd., 2017).

It is known that the adsorption conditions, including the initial pH of the solution and the adsorption temperature, are critical for adsorption efficiency (Meng vd., 2014; Samsuri vd., 2013). It is emphasized that the initial pH value of the solution affects the ion exchange capacity of biochar and the biochar surface charge distribution. The precipitation or adsorption of heavy metals on the adsorbent surface is closely related to the pH value of the solution (Ho vd., 2017; Ma vd., 2016). The obtained importance attribute value (8%) proves this.

3.5. Partial Dependence Analysis for Adsorption Efficiency

Adsorption efficiency is the primary goal of partial dependency analysis, which focuses on the impact of a single parameter on the target variable (adsorption efficiency) and restricts other parameters to mean values. In this step, we attempted to use partial dependence analysis to reveal the type and magnitude of the effects that the parameters whose effects were looked at had on the adsorption efficiency. A thorough partial dependency analysis was also conducted to thoroughly examine the connections between the biomass composition, the surrounding environment, the initial metal ion concentration, and the adsorption effectiveness. A partial dependency analysis data set was produced as a result of 350 adsorption studies, and it was valuable because it offered all-encompassing and general results.

In Figure 5 and Figure 6, the effects of variable parameters on adsorption efficiency are presented as a result of one-way and two-way partial dependence analysis, respectively. A two-way partial dependence analysis was created by considering the effect of other parameters against initial metal ion concentration, which is the most effective parameter on adsorption efficiency. In addition, it is seen that as the initial metal ion concentration increases, the adsorption efficiency increases up to the critical value and then stabilizes. The difference in concentration between the two phases, which serves as their driving force, is what causes this. The saturation of the active sites on the biochar surface can be used to explain the stabilization of the sorption efficiency.

One-way partial dependency analyses and PCC values presented in Figure 2 were found to be in agreement. Accordingly, there is a negative relationship between the adsorption efficiency of heavy metals and the carbon content and surface area of biochar. Other variables show a positive correlation with adsorption efficiency.

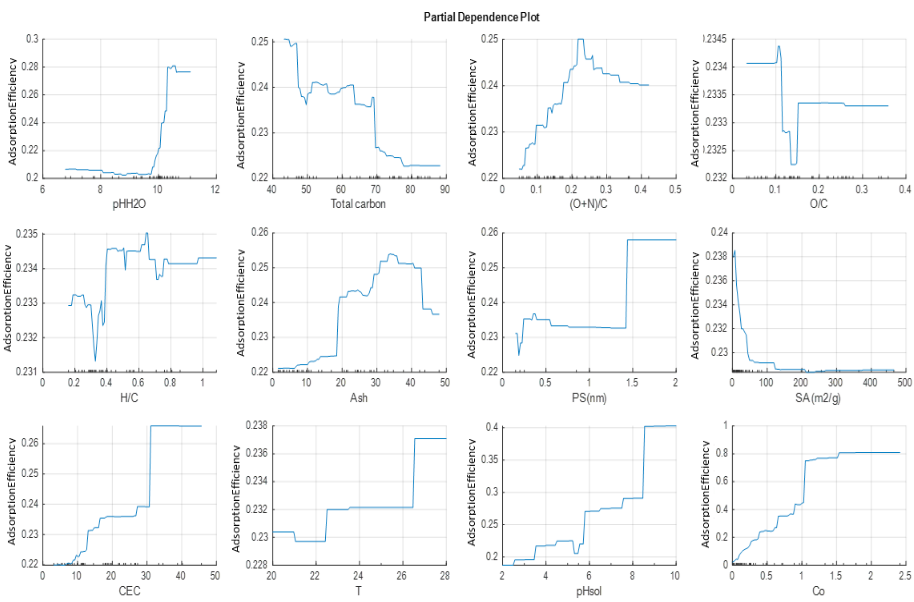

Figure 5. Regression of adsorption efficiency with one-way partial dependence plot.

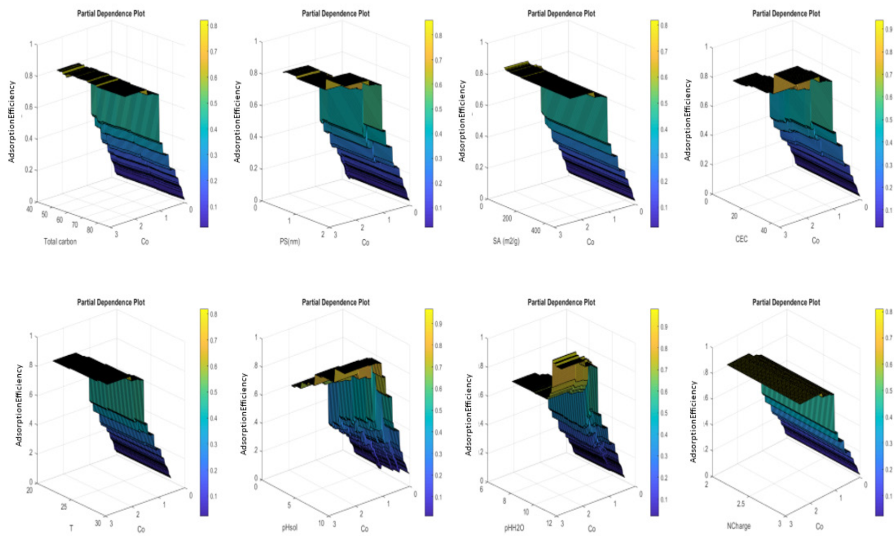

Figure 6. Regression of adsorption efficiency with two-way partial dependence plot

4. Conclusion

In the study, which was designed to discuss the adsorption efficiency of heavy metal ions on biochars in aqueous solutions, the data set consisting of 350 experimental data was evaluated by machine learning methods. The effect of variable parameters on adsorption efficiency was investigated by considering linear and non-linear relationships. As a result, the following conclusions were reached;

- The result of the study; multiple linear regression and Pearson correlation coefficient (PCC) analysis were found to be insufficient for analyzing the relationships.
- The random forest (RF) regression was found to have a high success rate (98%) for predicting the adsorption efficiency. In addition, the prediction success of the RF regression was proven to be higher than the ANN presented in the literature.
- The partial dependency analysis was performed to specifically reveal and interpret nonlinear relationships in the study. It was seen that PCC analyses and importance feature data and partial dependency analyses gave consistent results.
- According to the importance property evaluations, the effect of biochar properties on adsorption efficiency is 67%, and the effect of ambient conditions

%CEC, total carbon, particle size and pHH_2O values of biochars have more effective importance compared to other biochar properties. Contrary to expectations, the effect of the surface area of biochars is low.

As a result, it is thought that this study will shed light on the literature within the scope of discussing the adsorption efficiency depending on the biomass composition, ambient conditions, and metal ion concentration. It is thought that the inferences obtained in this study can direct the biochar production process as an adsorbent. For metal ion adsorption studies, it is predicted that it will protect researchers from unnecessary repetition, time losses, and chemical losses.

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DECLARATIONS

Ethical Approval: Not include human or animal studies. Ethical approval is not required.

Competing interests: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Authors' contributions: Beyda Taşar: Methodology, Analysis, Project administration, Şeyda Taşar: Writing − original draft, Visualization, Preparation.

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Availability of data and materials: In this study, a dataset was created that summarizes the experimental data (350 pieces) on the adsorption of heavy metals such as As^{3+}, Cd^{2+}, Cu^{2+}, Ni^{2+} , $Pb^{2+}$and Zn^{2+} to biochars. The references used while creating the dataset are presented in the supporting information document. The characteristic features of biochars are summarized in Table S1 in the supplementary dossier.

REFERENCES

Abbas, Z., Ali, S., Rizwan, M., Zaheer, I. E., Malik, A., Riaz, M. A., Shahid, M. R., Rehman, M. Z. U., & Al-Wabel, M. I. (2018). A critical review of mechanisms involved in the adsorption of organic and inorganic contaminants through biochar. *Arabian Journal of Geosciences*, *11*(16), 448. https://doi.org/10.1007/s12517-018-3790-1

Abraham, J., Vasu, K. S., Williams, C. D., Gopinadhan, K., Su, Y., Cherian, C. T., Dix, J., Prestat, E., Haigh, S. J., Grigorieva, I. V., Carbone, P., Geim, A. K., & Nair, R. R. (2017). Tunable sieving of ions using graphene oxide membranes. *Nature Nanotechnology*, *12*(6), 546-550. https://doi.org/10.1038/nnano.2017.21

Aftab, R. A., Zaidi, S., Danish, M., Ansari, K. B., & Danish, M. (2022). Novel Machine Learning (ML) models for predicting the performance of multi-metal binding green adsorbent for the removal of Cd (II), Cu (II), Pb (II) and Zn (II) ions. *Environmental Advances*, *9*, 100256. https://doi.org/10.1016/j.envadv.2022.100256

Alam, Md. S., Gorman-Lewis, D., Chen, N., Flynn, S. L., Ok, Y. S., Konhauser, K. O., & Alessi, D. S. (2018). Thermodynamic Analysis of Nickel(II) and Zinc(II) Adsorption to Biochar. *Environmental Science & Technology*, *52*(11), 6246-6255. https://doi.org/10.1021/acs.est.7b06261

Baghayeri, M., Amiri, A., Karimabadi, F., Di Masi, S., Maleki, B., Adibian, F., Pourali, A. R., & Malitesta, C. (2021). Magnetic MWCNTs-dendrimer: A potential modifier for electrochemical evaluation of As (III) ions in real water samples. *Journal of Electroanalytical Chemistry*, *888*, 115059. https://doi.org/10.1016/j.jelechem.2021.115059

Balali-Mood, M., Naseri, K., Tahergorabi, Z., Khazdair, M. R., & Sadeghi, M. (2021). Toxic Mechanisms of Five Heavy Metals: Mercury, Lead, Chromium, Cadmium, and Arsenic. *Frontiers in Pharmacology*, *12*, 643972. https://doi.org/10.3389/fphar.2021.643972

Chen, X., Chen, G., Chen, L., Chen, Y., Lehmann, J., McBride, M. B., & Hay, A. G. (2011). Adsorption of copper and zinc by biochars produced from pyrolysis of hardwood and corn straw in aqueous solution. *Bioresource Technology*, *102*(19), 8877-8884. https://doi.org/10.1016/j.biortech.2011.06.078

Chen, X., Zhou, S., Zhang, L., You, T., & Xu, F. (2016). Adsorption of Heavy Metals by Graphene Oxide/Cellulose Hydrogel Prepared from NaOH/Urea Aqueous Solution. *Materials*, *9*(7), 582. https://doi.org/10.3390/ma9070582

Chen, Y.-W., & Wang, J.-L. (2016). Removal of cesium from radioactive wastewater using magnetic chitosan beads cross-linked with glutaraldehyde. *Nuclear Science and Techniques*, *27*(2), 43. https://doi.org/10.1007/s41365-016-0033-6

Chen, Z., Tang, B., Niu, Y., Chen, H., Liu, Y., Wang, A., & Bai, L. (2021). Synthesis of silica supported thiosemicarbazide for Cu(II) and Zn(II) adsorption from ethanol: A comparison with aqueous solution. *Fuel*, *286*, 119287. https://doi.org/10.1016/j.fuel.2020.119287

Cui, X., Hao, H., Zhang, C., He, Z., & Yang, X. (2016). Capacity and mechanisms of ammonium and cadmium sorption on different wetland-plant derived biochars. *Science of The Total Environment*, *539*, 566-575. https://doi.org/10.1016/j.scitotenv.2015.09.022

Deng, Y., Huang, S., Laird, D. A., Wang, X., & Meng, Z. (2019). Adsorption behaviour and mechanisms of cadmium and nickel on rice straw biochars in single- and binary-metal systems. *Chemosphere*, *218*, 308-318. https://doi.org/10.1016/j.chemosphere.2018.11.081

Dhyani, V., & Bhaskar, T. (2018). A comprehensive review on the pyrolysis of lignocellulosic biomass. *Renewable Energy*, *129*, 695-716. https://doi.org/10.1016/j.renene.2017.04.035

El Hanandeh, A., Mahdi, Z., & Imtiaz, M. S. (2021). Modelling of the adsorption of Pb, Cu and Ni ions from single and multi-component aqueous solutions by date seed derived biochar: Comparison of six machine learning approaches. *Environmental Research*, *192*, 110338. https://doi.org/10.1016/j.envres.2020.110338

Fu, F., & Wang, Q. (2011). Removal of heavy metal ions from wastewaters: A review. *Journal of Environmental Management*, *92*(3), 407-418. https://doi.org/10.1016/j.jenvman.2010.11.011

Gao, L.-Y., Deng, J.-H., Huang, G.-F., Li, K., Cai, K.-Z., Liu, Y., & Huang, F. (2019). Relative distribution of Cd2+ adsorption mechanisms on biochars derived from rice straw and sewage sludge. *Bioresource Technology*, *272*, 114-122. https://doi.org/10.1016/j.biortech.2018.09.138

Ho, S.-H., Chen, Y., Yang, Z., Nagarajan, D., Chang, J.-S., & Ren, N. (2017). High-efficiency removal of lead from wastewater by biochar derived from anaerobic digestion sludge. *Bioresource Technology*, *246*, 142-149. https://doi.org/10.1016/j.biortech.2017.08.025

Jiménez-Castañeda, M., & Medina, D. (2017). Use of Surfactant-Modified Zeolites and Clays for the Removal of Heavy Metals from Water. *Water*, *9*(4), 235. https://doi.org/10.3390/w9040235

Ke, B., Nguyen, H., Bui, X.-N., Bui, H.-B., Choi, Y., Zhou, J., Moayedi, H., Costache, R., & Nguyen-Trang, T. (2021). Predicting the sorption efficiency of heavy metal based on the biochar characteristics, metal sources, and environmental conditions using various novel hybrid machine learning models. *Chemosphere*, *276*, 130204. https://doi.org/10.1016/j.chemosphere.2021.130204

Ke, B., Nguyen, H., Bui, X.-N., Bui, H.-B., & Nguyen-Thoi, T. (2021). Prediction of the sorption efficiency of heavy metal onto biochar using a robust combination of fuzzy C-means clustering and back-propagation neural network. *Journal of Environmental Management*, *293*, 112808. https://doi.org/10.1016/j.jenvman.2021.112808

Khulbe, K. C., & Matsuura, T. (2018). Removal of heavy metals and pollutants by membrane adsorption techniques. *Applied Water Science*, *8*(1), 19. https://doi.org/10.1007/s13201-018-0661-6

Kołodyńska, D., Krukowska, J., & Thomas, P. (2017). Comparison of sorption and desorption studies of heavy metal ions from biochar and commercial active carbon. *Chemical Engineering Journal*, *307*, 353-363. https://doi.org/10.1016/j.cej.2016.08.088

Kumar, R., Chawla, J., & Kaur, I. (2015). Removal of cadmium ion from wastewater by carbon-based nanosorbents: A review. *Journal of Water and Health*, *13*(1), 18-33. https://doi.org/10.2166/wh.2014.024

Lakherwal, D. (t.y.). *Adsorption of Heavy Metals: A Review*.

Largitte, L., & Pasquier, R. (2016). A review of the kinetics adsorption models and their application to the adsorption of lead by an activated carbon. *Chemical Engineering Research and Design*, *109*, 495-504. https://doi.org/10.1016/j.cherd.2016.02.006

Li, H., Chen, J., Zhang, W., Zhan, H., He, C., Yang, Z., Peng, H., & Leng, L. (2023). Machine-learning-aided thermochemical treatment of biomass: A review. *Biofuel Research Journal*, *10*(1), 1786-1809. https://doi.org/10.18331/BRJ2023.10.1.4

Liu, X., Zhao, X., Liu, Y., & Zhang, T. (2022). Review on preparation and adsorption properties of chitosan and chitosan composites. *Polymer Bulletin*, *79*(4), 2633-2665. https://doi.org/10.1007/s00289-021-03626-9

Ma, F., Zhao, B., & Diao, J. (2016). Adsorption of cadmium by biochar produced from pyrolysis of corn stalk in aqueous solution. *Water Science and Technology*, *74*(6), 1335-1345. https://doi.org/10.2166/wst.2016.319

Mariana, M., H.P.S., A. K., Mistar, E. M., Yahya, E. B., Alfatah, T., Danish, M., & Amayreh, M. (2021). Recent advances in activated carbon modification techniques for enhanced heavy metal adsorption. *Journal of Water Process Engineering*, *43*, 102221. https://doi.org/10.1016/j.jwpe.2021.102221

Meng, J., Feng, X., Dai, Z., Liu, X., Wu, J., & Xu, J. (2014). Adsorption characteristics of Cu(II) from aqueous solution onto biochar derived from swine manure. *Environmental Science and Pollution Research*, *21*(11), 7035-7046. https://doi.org/10.1007/s11356-014-2627-z

Mohan, D., Sarswat, A., Ok, Y. S., & Pittman, C. U. (2014). Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent – A critical review. *Bioresource Technology*, *160*, 191-202. https://doi.org/10.1016/j.biortech.2014.01.120

Rodríguez-Romero, J. A., Mendoza-Castillo, D. I., Reynel-Ávila, H. E., De Haro-Del Rio, D. A., González-Rodríguez, L. M., Bonilla-Petriciolet, A., Duran-Valle, C. J., & Camacho-Aguilar, K. I. (2020). Preparation of a new adsorbent for the removal of arsenic and its simulation with artificial neural network-based adsorption models. *Journal of Environmental Chemical Engineering*, *8*(4), 103928. https://doi.org/10.1016/j.jece.2020.103928

Samsuri, A. W., Sadegh-Zadeh, F., & Seh-Bardan, B. J. (2013). Adsorption of As(III) and As(V) by Fe coated biochars and biochars produced from empty fruit bunch and rice husk. *Journal of Environmental Chemical Engineering*, *1*(4), 981-988. https://doi.org/10.1016/j.jece.2013.08.009

Shaheen, S. M., Niazi, N. K., Hassan, N. E. E., Bibi, I., Wang, H., Tsang, D. C. W., Ok, Y. S., Bolan, N., & Rinklebe, J. (2019). Wood-based biochar for the removal of potentially toxic elements in water and wastewater: A critical review. *International Materials Reviews*, *64*(4), 216-247. https://doi.org/10.1080/09506608.2018.1473096

Shahrokhi-Shahraki, R., Benally, C., El-Din, M. G., & Park, J. (2021). High efficiency removal of heavy metals using tire-derived activated carbon vs commercial activated carbon: Insights into the adsorption mechanisms. *Chemosphere*, *264*, 128455. https://doi.org/10.1016/j.chemosphere.2020.128455

Singh, V., & Mishra, V. (2021). Microbial removal of Cr (VI) by a new bacterial strain isolated from the site contaminated with coal mine effluents. *Journal of Environmental Chemical Engineering*, *9*(5), 106279. https://doi.org/10.1016/j.jece.2021.106279

Sun, K., Kang, M., Zhang, Z., Jin, J., Wang, Z., Pan, Z., Xu, D., Wu, F., & Xing, B. (2013). Impact of Deashing Treatment on Biochar Structural Properties and Potential Sorption Mechanisms of Phenanthrene. *Environmental Science & Technology*, *47*(20), 11473-11481. https://doi.org/10.1021/es4026744

Taşar, Ş. (2022). Estimation of pyrolysis liquid product yield and its hydrogen content for biomass resources by combined evaluation of pyrolysis conditions with proximate-ultimate analysis data: A machine learning application. *Journal of Analytical and Applied Pyrolysis*, *165*, 105546. https://doi.org/10.1016/j.jaap.2022.105546

Taşar, Ş., Kaya, F., & Özer, A. (2014). Biosorption of lead(II) ions from aqueous solution by peanut shells: Equilibrium, thermodynamic and kinetic studies. *Journal of Environmental Chemical Engineering*, *2*(2), 1018-1026. https://doi.org/10.1016/j.jece.2014.03.015

Tran, H. N., Tomul, F., Thi Hoang Ha, N., Nguyen, D. T., Lima, E. C., Le, G. T., Chang, C.-T., Masindi, V., & Woo, S. H. (2020). Innovative spherical biochar for pharmaceutical removal from water: Insight into adsorption mechanism. *Journal of Hazardous Materials*, *394*, 122255. https://doi.org/10.1016/j.jhazmat.2020.122255

Wang, R.-Z., Huang, D.-L., Liu, Y.-G., Zhang, C., Lai, C., Zeng, G.-M., Cheng, M., Gong, X.-M., Wan, J., & Luo, H. (2018). Investigating the adsorption behavior and the relative distribution of Cd2+ sorption mechanisms on biochars by different feedstock. *Bioresource Technology*, *261*, 265-271. https://doi.org/10.1016/j.biortech.2018.04.032

Wang, S., Gao, B., Zimmerman, A. R., Li, Y., Ma, L., Harris, W. G., & Migliaccio, K. W. (2015). Physicochemical and sorptive properties of biochars derived from woody and herbaceous biomass. *Chemosphere*, *134*, 257-262. https://doi.org/10.1016/j.chemosphere.2015.04.062

Yang, Y., Lin, X., Wei, B., Zhao, Y., & Wang, J. (2014). Evaluation of adsorption potential of bamboo biochar for metal-complex dye: Equilibrium, kinetics and artificial neural network modeling. *International Journal of Environmental Science and Technology*, *11*(4), 1093-1100. https://doi.org/10.1007/s13762-013-0306-0

Zama, E. F., Zhu, Y.-G., Reid, B. J., & Sun, G.-X. (2017). The role of biochar properties in influencing the sorption and desorption of Pb(II), Cd(II) and As(III) in aqueous solution. *Journal of Cleaner Production*, *148*, 127-136. https://doi.org/10.1016/j.jclepro.2017.01.125

Zhang, P., O'Connor, D., Wang, Y., Jiang, L., Xia, T., Wang, L., Tsang, D. C. W., Ok, Y. S., & Hou, D. (2020). A green biochar/iron oxide composite for methylene blue removal. *Journal of Hazardous Materials*, *384*, 121286. https://doi.org/10.1016/j.jhazmat.2019.121286

Zhou, N., Chen, H., Xi, J., Yao, D., Zhou, Z., Tian, Y., & Lu, X. (2017). Biochars with excellent Pb(II) adsorption property produced from fresh and dehydrated banana peels via hydrothermal carbonization. *Bioresource Technology*, *232*, 204-210. https://doi.org/10.1016/j.biortech.2017.01.074

Zhu, X., Wang, X., & Ok, Y. S. (2019). The application of machine learning methods for prediction of metal sorption onto biochars. *Journal of Hazardous Materials*, *378*, 120727. https://doi.org/10.1016/j.jhazmat.2019.06.004

CHAPTER III

MUNICIPAL SOLID WASTE LANDFILL LEACHATE CHARACTERISTICS AND TREATMENT OPTIONS

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1. Introduction

Landfills are an essential element of waste management in modern societies (Kjeldsen et al., 2002). As waste disposal sites, landfills often contain various residual waste materials and incineration residues. Leachate, a severe issue related to landfill operations, is known to harm environmental quality considerably (Nika et al., 2020; Bandala et al., 2021; Viegas et al., 2021). Leachates pose serious environmental pollution risks, mainly underground and surface water resources (Costa et al., 2019). These leachates can contain high amounts of organic and inorganic compounds. These compounds can have toxic effects and damage water resources (Sewwandi et al., 2012).

Leachates have a complex composition, and these pollutants include organic and inorganic compounds, metals, toxic and pathogenic substances (Bandala et al., 2021). Heavy metals (Esfahani et al., 2021), pesticides (Wang et al., 2020a), polycyclic aromatic hydrocarbons (PAHs) (Ateş & Argun, 2021) and microplastics (Rodriguez-Narvaez et al., 2021) are just a few of the toxic pollutants discovered in landfill leachate in previous studies. In addition, parameters such as pH, conductivity, dissolved oxygen, chemical oxygen demand, biochemical oxygen demand, dissolved solids, suspended solids, ammonium, nitrate, phosphate, sodium, chloride, sulfide, and sulfate can be found in the composition of leachate (Siddiqi et al., 2022).

Leachate composition depends on the design and operation methods of the landfill and the waste composition. Methane gas, formed due to the decomposition of organic materials contained in wastes, can reduce the amount of dissolved oxygen in leachate and cause anaerobic conditions. If these conditions continue, substances such as ammonia, sulfur and methane gas may increase leachate composition (Ma et al., 2022).

The parameters in the leachate composition also impact environmental impacts and treatment methods. For example, low pH values of leachate may increase toxic metals' solubility and environmental impact (Guo et al., 2010). In addition, the high organic matter in leachate may increase treatment costs and make it challenging to implement alternative solutions such as recycling or recovery (Chen et al., 2021).

Treatment methods can be used to minimize the damage of leachate (Costa et al., 2019). These methods may vary according to the chemical composition, amount, and source of leachate (Kamaruddin et al., 2017). Various technologies have been developed to treat landfill leachate, including biological treatments (e.g., activated sludge and fluidized bed reactor processes) (Salam & Nilza, 2021), chemical treatments (e.g., chemical precipitation, Fenton process) (de Oliveira et al., 2019), and physical-chemical treatments (e.g., adsorption and membrane processes) (Foo & Hameed, 2010; Reshadi et al., 2020). However, it is usually necessary to strike a compromise between the effectiveness of the treatment and the expense of using these techniques. For landfill leachate treatment, a thorough understanding of the composition of landfill leachate, as well as its variation and degradation characteristics, is crucial.

Each method has different advantages and disadvantages, and the method to be applied may vary depending on the type of compounds in the leachate (Kjeldsen et al., 2002). For example, membrane filtration is highly effective in removing organic matter, nitrogen, and phosphorus but often requires maintenance due to membrane fouling (Foo & Hameed, 2010). While the chemical precipitation method produces a non-toxic precipitate, it can cause a high amount of sludge formation (Ye et al., 2016). While biological treatment provides high efficiency with low operating costs, it performs poorly in removing heavy metals (Salam & Nilza, 2021). The adsorption method can remove a wide range of compounds using different adsorbents, but the recovery of adsorbents can be challenging (Reshadi et al., 2020).

This article aims to examine in depth the properties of leachate, which is one of the most important environmental effects of solid waste landfills, and the methods that can be used to treat these waters. The article will provide information on the composition, toxic pollutants and environmental impacts of landfill leachate based on an extensive literature review. It will also provide a detailed analysis of the advantages, disadvantages, effectiveness and efficiency of different treatment technologies in treating leachate. The article's main objective is to provide a scientific depth on landfill leachate and to promote the use of effective treatment methods to reduce the environmental impact of leachate.

2. Characteristics of Leachate

In general, landfill leachate is characterized by conventional parameters such as Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total Organic Carbon (TOC), pH, ammonia (NH_4^+-N), heavy metal concentrations and suspended solids. BOD_5/COD and COD/TOC ratios are typical indicators for the biodegradability of organic compounds and the oxidized state of organic carbon. The quality of landfill leachate is affected by various factors such as waste type, landfill age, climate, operating conditions and hydrogeology (Dabaghian et al., 2018). Concentrations of common pollutants in landfill leachate are given in Table 1.

Table 1. Concentrations of common pollutants in landfill leachate (Kjeldsen et al., 2002; Costa et al., 2019; Luo et al., 2019).

Common Pollutant	Pollutant Type	Concentration (mg/L)
COD	Macro organics (dissolved organic matter)	0.0014-1.52 x 10^5
BOD_5		0.001-5.7 x 10^4
NH_4^+- N	Inorganic macrocomponents (nitrogen compounds and salts)	0.05-2.5 x 10^3
Cl^-		0.03-4.5 x 10^3
HCO_3^-		0.61-7.3 x 10^3
SO_4^{2-}		0.008-7.8 x 10^3
Cd	Trace inorganics (heavy metals)	0-0.4
Cr		0.02-1.5
Cu		0.001-10
Pb		0.001-5
Ni		0.015-13
Zn		0.03-1000
POPs	Trace organics	<1

Type and Composition of Accumulated Urban Solid Waste: The chemical composition of leachate is directly related to the type and composition of the waste. For example, gases such as ammonia, methane, hydrogen sulfide and carbon dioxide released as a result of the decomposition of organic wastes affect the chemical composition of the leachate (Luo et al., 2020). In addition, the type and composition of municipal solid waste can affect the chemical composition of leachate. For example, heavy metals in the waste can be found in high concentrations in the chemical composition of the leachate. Also, some effluents may have high or low pH values, causing the leachate to become acidic or alkaline. As a result, the chemical composition of the leachate during the storage of municipal solid waste is directly related to the type and composition of the waste. Therefore, proper waste management is essential for reducing leachate generation and preventing environmental pollution (Coffin et al., 2022).

Waste Degradation Stage: The waste degradation stage also affects changes in the chemical composition of the leachate. In the aerobic decomposition stage, CO_2 and water are released due to the decomposition of organic wastes under aerobic conditions. In the anaerobic acid phase, hydrogen sulfide, ammonia and organic acids are released due to the decomposition of organic wastes under anaerobic conditions. In the methanogenic phase, organic acids are converted to methane. In the stabilization phase, most of the organic wastes decomposed and the waste volume decreased (Anqi et al., 2020). The leachate characteristics according to the waste degradation stages are given in Table 2.

Table 2. Waste Decomposition Stages and Leachate Characteristics (Li ve ark., 2011; Bhalla ve ark., 2013; Ho ve ark., 2018; Sharma & Gupta, 2022; De Almeida et al., 2023)

Parameter	**Stage I Beginning**	**Stage II Transition**	**Stage III Acid Formation**	**Stage IV Methane Formation**	**Stage V Maturation**
BOD (mg/L)	150-300	100-10000	1000-57000	600-3400	4-120
COD (mg/L)	1000-3000	480-18000	1500-71000	580-9760	31-900
Total Volatile Acid (mg/L) (Acetic acid)	0	100-3000	3000-18800	250-4000	0
BOD/COD (mg/L)	0.05-0.2	0.23-0.87	0.4-0.8	0.17-0.64	0.02-0.13
Ammonia (mg/L-N)	0-30	120-125	2-1030	6-430	6-430
pH	7-8	6.7	4.7-7.7	6.3-8.8	7.1-8.8
Total Dissolved Solids (TDS)	Low	Low	Low	Low	Very low
Amount of Organic Matter	Low	High	Low	Lower	Very low
Amount of Organic Acid	Low	High	Low	High	Very low
Electrical Conductivity	Low	High	Low	Lower	Lower

***Decomposition Rate*:** Waste degradation rate is another factor affecting changes in the chemical composition of leachate. The degradation rate depends on the composition of the waste, humidity, temperature and other environmental factors. A faster degradation rate results in more gaseous emissions and, therefore, higher chemical composition (Liu et al., 2015).

Scientific studies show that the waste degradation rate significantly impacts the distribution and quality of components in leachate. For example, a study by Lim (1999) found that leachate had higher levels of dissolved organic matter and nitrogen compounds as the rate of waste degradation increased. In addition, the increased rate of waste degradation may result in lower pH values and highly toxic substances in leachate. Another study was done by Abdel-Shafy and Mansour (2018). This study investigated leachate from a landfill with a low waste degradation rate. The results showed that a high amount of organic matter accumulates in the leachate, and these substances damage the aquatic ecosystem. However, the impact of the rate of waste degradation on the distribution and quality of components in the leachate depends on the composition of the waste and environmental conditions. Therefore, determining leachate characteristics and controlling the waste degradation rate is essential for environmental management (Top et al., 2019).

***Age of the Landfill*:** The age of the landfill is another factor that affects changes in the chemical composition of the leachate. The older the landfill, the more decomposed the waste and the more different the leachate composition (Lindamulla et al., 2022). Landfill leachate is classified into three types based on landfill age. According to Table 3, young leachate is less than five years old, medium leachate is 5-10 years old, and old leachate has been created for more than a decade (Miao et al., 2019). Young landfill leachate mainly comprises low molecular weight hydrophilic organic matter with a low pH value and high biodegradation index (BOD_5/COD). By comparison, high molecular weights humic acid (HA) and fulvic acid (FA) are the predominant components of old landfill leachate, resulting in a high pH value and low biodegradation index. Heavy metal concentrations, in particular, tend to decrease with ageing, as increasing pH decreases the solubility of metals.

Table 3. Changes in storage leachate classification with age (Renou et al., 2008; Zhao et al., 2019)

No.	Parameter	Unit	Type of landfill leachate		
			Young (< 5 years)	**Intermediate (5-10years)**	**Stabilized (> 10 years)**
1	PH		<6.5	6.5-7.5	>7.5
2	COD	mg/L	>10000	4000-10000	<4000
3	BOD_5/COD		0.5-1.0	0.1-0.5	<0.1
4	Organic compound		80% VF[A]a	5-30% VFA[a] + HFA[b]	HF[A]b
5	NH_3-N	mg/L	<400	NA[c]	>400
6	TOC/COD		<0.3	0.3 -0.5	>0.5
7	Kjeldahl nitrogen	g/L	0.1-0.2	NA[c]	NA[c]
8	Heavy metals	mg/L	Low to medium	Low	Low
9	Biodegradability		Important	Medium	Low

[a] = Volatile fatty acids, [b]=Humic and fulvic acids, and [c]= Not available

Hydrogeology of the Landfill: The chemical composition of the leachate is also related to the hydrogeology of the landfill. The soil type in the area where the landfill is located, the movement of groundwater and the height of the site are among the factors affecting the composition of the leachate (Wiszniowski et al., 2006; Bove et al., 2015).

Area and Climatic Conditions: The characteristics of leachate also depend on the area and climatic conditions of the landfill. Leachate from precipitation often contains high organic matter, nitrogen, phosphorus, COD, BOD_5, TOC, chloride and heavy metals. The densities of these components depend on the conditions of the landfills where the leachate originates (Lindamulla et al., 2022). Lower COD and Dissolved Organic Carbon (DOC) concentrations in summer result from higher temperatures, although pH, total nitrogen, and electrical conductivity are typically greater in winter than in summer. In contrast, there is little seasonal change in the oxidation-reduction potential, metal concentrations, total suspended solids, and volatile suspended solids (Zhao et al., 2013). The amount of aromaticity in landfill leachate is indicated by the absorbance ratio to TOC concentration at 254 nm (SUVA254), which exhibits substantial seasonal change and is greater in the summer than the winter (Yang et al., 2019). Because of this, Dissolved Organic Matter (DOM) formed from leachate has a greater proportion of aromatic compounds in the summer. This is presumably because higher temperatures make landfill biodegradation more effective in the summer.

In addition, leachates are often characterized by high temperatures and pH values. The reason for this is related to the heat generated by the biochemical reactions occurring during the degradation process and the high pH levels of the materials inside the tank (Wiszniowski et al., 2006; Bove et al., 2015).

Due to their prevalence in landfill leachates, emerging organic contaminants (EOCs) such as persistent organic pollutants, endocrine disruptors, pharmaceuticals, personal care products, antibiotic resistance genes, and disinfection byproducts have lately attracted much attention. These contaminants have the potential to have negative effects on both human health and the environment. Leachate from landfills included 17 different kinds of microplastics, with concentrations ranging from 0.42 to 24.58 items/L (He et al., 2019). Additionally, landfill leachate included significant amounts (>10 mg/L) of phenolic chemicals, particularly Bisphenol A and 2,4-Di-tert-butylphenol (Aziz et al., 2018). Over the past 20 years, 172 pharmaceutical and personal care products (PPCPs), including beta-blockers, antibiotics, and anti-inflammatories, have been notified in landfill leachate worldwide (Yu et al., 2020). In addition, there are high levels of antibiotic-resistance genes in landfill leachate. The presence of these genes enables leachate to be considered a reservoir of antibiotic resistance. As a result, landfill leachate is a significant EOC source, making treatment more urgent.

3. Environmental Effects of Leachate

In research on the environmental effects of waste landfill leachate, it has been observed that waste landfills severely affect the environment and human health. According to studies on this subject, leachate causes many environmental effects, such as groundwater pollution, surface water pollution, soil pollution, atmospheric effects, loss of biodiversity, and harmful effects on human health.

Many studies have examined the environmental effects of leachate. For example, a study by Abd El-Salam and Abu-Zuid (2015) examined the environmental effects of water leaking from a landfill in Egypt. They found that leachate can contain high levels of heavy metals, organic compounds and nutrients that can contaminate groundwater and make it unsuitable for drinking and agricultural use. The authors also noted that leachate can cause soil salinization and reduce soil fertility. Also, a study by Alemayehu et al. (2019) showed that water leaking from a landfill in Ethiopia harms the environment and human health. The authors noted that leachate might contain high levels of organic and inorganic pollutants that can lead to the eutrophication of surface water bodies and the growth of harmful algae. This study reveals that leachate contains toxic chemicals and that the water resources in the region are polluted.

The environmental effects of leachate affect not only groundwater but also soil. In a study by Rezapour et al. (2018), it was reported that water leaking from a landfill in Iran has adverse effects on the soil; chemical contamination of the soil causes adverse effects on plant growth and adversely affects agricultural activities in the region.

Sauve and Van Acker (2020) conducted a life cycle assessment of European municipal landfills and found that leachate can significantly impact human health and the environment. Their study stated that leachate may contain high levels of pathogens, toxins, and pollutants that can cause water, air, and soil pollution. They also noted that leachate could contribute to greenhouse gas emissions and climate change by releasing methane and other volatile organic compounds.

One of the important problems in landfills is geotextile blockage. In the study by Ko et al. (2019), they investigated the factors that cause geotextile clogging due to the co-storage of waste ash in municipal solid waste landfills at different stages. As a result of the research, it has been reported that insoluble solids are formed during the storage of waste ash, and factors such as liquid permeability values and leachate properties in the process cause geotextile clogging. Similarly, Wu et al. (2018) examined the characteristics of geotextile clogging during the storage of MSW wastes and municipal solid waste incineration (MSWI) bottom ash, and it was determined that the geotextile clogging problem depends on the leachate properties, the pH value of the water, and the amount of waste ash.

In conclusion, studies on landfills' environmental impacts highlight leachate's severe effects on groundwater, surface water, soil, and human health. Landfills' design, operation, maintenance, and leachate management should be strictly regulated to prevent these effects.

4. Treatment of Landfill Leachate

Laboratory-scale studies on the treatment process of landfill leachate have been reported in the last 50 years. Conventional techniques (such as recirculation to landfills and transmission to sewage facilities) and biological, physical-chemical, and chemical technologies can all be used to remediate landfill leachate. A comparison of landfill leachate treatment techniques is shown in Table 4 and Figure 1, and combinations are shown in Figure 2. The efficiency of the treatment types according to the age of the leachate is shown in Table 5.

Table 4. Comparison of landfill leachate treatment techniques (Teng et al., 2021)

Treatment Methods	Explanation	Advantages	Disadvantages
Physical Treatment	Treatment by methods such as precipitation, filtration, retention of particles in wastewater on the surface	- Simple and low cost - Low energy consumption	- Can only remove large particles, not organic and inorganic pollutants
Biological Treatment	Treatment using microorganisms that naturally clean the wastewater	- Natural process - Low operating costs - Removal of organic pollutants	- May be insufficient for some pollutants - Long treatment times - Requires maintenance and management
Chemical Treatment	Treatment using chemical substances	- High efficiency - Removes inorganic pollutants	- High operating costs - Storage and disposal of chemicals - Toxic by-products
Adsorption	Retention and removal of pollutants on a surface	- Low operating costs - High pollutant removal efficiency	- Inadequate treatment performance - Waste may be generated after the adsorbent material reaches saturation
Reverse Osmosis	Passage of wastewater water through a membrane by applying pressure	- High treatment efficiency - Removal of high pollutants	- High operating costs - Energy intensity - Increased salt concentration in leachate - Easy clogging of membranes
Electrochemical Treatment	Removal of pollutants using electric current	- High efficiency - Removes organic and inorganic pollutants	- High operating costs - The problem of reuse of electrolytes - Requires regular maintenance

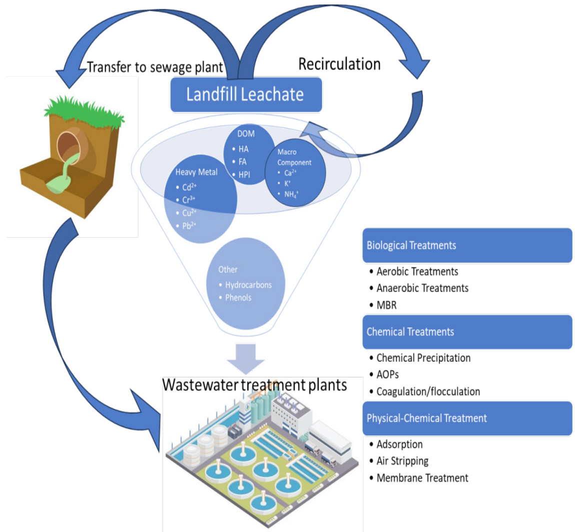

Figure 1. Landfill leachate treatment techniques (Teng et al., 2021)

Table 5. The efficiency of treatment types according to the age of leachate (Renou et al., 2008; Costa et al., 2019)

Treatment Type	**Age of leachate (Year)**			**Average removal (%)**		
	Young (<5)	**Medium (5-10)**	**Old (>10)**	**BOD**	**COD**	**TKN**
Domestic + Sewerage	Good	Fair	Poor	Depending on the domestic wastewater treatment plant		
Recycling	Good	Fair	Poor	60-80	-	-
Aerobic processes	Good	Fair	Poor	>80	60-90	>80
Anaerobic processes	Good	Fair	Poor	>80	60-80	>80
Coagulation/ flocculation	Poor	Fair	Fair	-	40-60	<30
Chemical precipitation	Poor	Fair	Poor	-	<30	<30
Adsorption	Poor	Fair	Good	>80	70-90	-
Oxidation	Poor	Fair	Fair	-	30-90	-
Stripping	Poor	Fair	Fair	-	<30	>80
Ultrafiltration	Poor–Fair	-	-	-	50	60-80
Nanofiltration	Good	Good	Good	80	60-80	60-80
Reverse osmosis	Good	Good	Good	>90	>90	>90

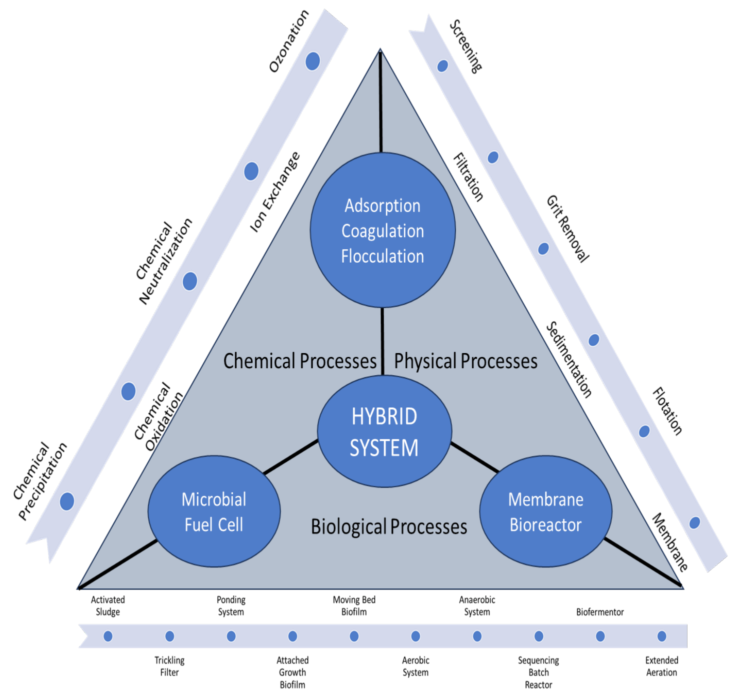

Figure 2. Leachate treatment processes and combinations (Tee et al., 2016)

4.1. Traditional Removal Methods

Techniques such as conventional methods, recycling, and transfer to sewage plants are used to treat water leaking from landfills. Landfill leachate recycling has been widely used in previous years because it is easy and requires low operating costs. However, the main factors influencing the effectiveness of this system are the frequency and volume of recirculation. Multiple recirculation cycles can result in the buildup of refractory materials in landfill leachate, compromising the integrity of the landfill system and making it more challenging to remediate the leachate later (Chugh et al., 1998). Transferring landfill leachate to sewage facilities necessitates both biological and chemical treatment, depending on the sewage treatment facility receiving the leachate.

Disposing of landfill leachate at wastewater treatment plants (WWTPs) is easy and affordable. However, adding leachate with high levels of organic matter hurts the success of future treatment steps and lowers treatment efficiency overall (Deng et al., 2018). Furthermore, persistent organic compounds have been found to be resistant to biodegradation as they pass through wastewater treatment plants. Furthermore, intact organic substances, particularly persistent UV Dissolved Organic Matter (DOM), can seriously hinder UV disinfection in WWTPs (Zhao et al., 2012). Consequently, an efficient pre-treatment should be performed to remove UV-quenched materials to lessen the detrimental effects of landfill leachate on UV disinfection.

4.2. Physical-Chemical Treatment

4.2.1. Coagulation / Flocculation

The coagulation/flocculation process is a physicochemical treatment method. In this method, chemicals called coagulants are added to the leachate. Coagulants neutralize the colloidal particles in the water, allowing them to coalesce (Djeffal et al., 2021). Thus, more extensive and heavier particles are formed. These particles come together in the form of balls called flocs and are separated from the leachate in the settling tank (Abbas et al., 2009). The coagulation/flocculation processes can effectively remove organic pollutants and heavy metals. However, its effect on ammonium nitrogen (NH_4^+-N) is very low (Duran & Cuci, 2016).

The coagulation/flocculation process success depends on the coagulant type, dose, pH value, mixing speed and duration (Djeffal et al., 2021). Aluminium sulfate ($Al_2(SO_4)_3$), ferrous sulfate ($FeSO_4$), ferric chloride ($FeCl_3$) and ferrous sulfate ($Fe_2(SO_4)_3$) are commonly used coagulants (Kamaruddin et al., 2017). The optimum dose of these coagulants depends on the characteristics of the leachate. Generally, a coagulant/leachate ratio of around 15% has been found to give good results (Djeffal et al., 2021). Iron salts are more effective than aluminium salts. Because iron salts are insoluble over a more comprehensive pH range. Thus, they provide coagulation (Moradi ve Ghanbari, 2014). High molecular weight organics with a high hydrophobicity can be removed more successfully thanks to coagulation (He et al., 2006). When coagulants were applied to treat landfill leachate, 43.1% COD removal was observed when poly-aluminium chloride was applied and 62.8% COD removal was observed when alum was applied (Ghafari et al., 2009). Combining the coagulation/flocculation process and powdered activated carbon adsorption, 86% of the COD can be removed (Li et al., 2010).

The pH value of the leachate is also essential in the coagulation/flocculation processes. Because pH value is effective on the hydrolysis of coagulant and floc formation (Abbas et al., 2009). Leachate is usually acidic or neutral. The pH value should be adjusted between 4 and 5 for ferric chloride and 6 and 7 for aluminium sulfate and ordinary alum (Djeffal et al., 2021).

Mixing speed and time also affect floc formation and size. Too high or too low a mixing speed may disrupt the floc structure. The stirring time must ensure the coagulant is completely hydrolyzed (Abbas et al., 2009). A study by Djeffal et al. (2021), determined that the mixing speed for ferric chloride was 250 rpm and the mixing time was 15 minutes, while the mixing speed for aluminium sulfate and ordinary alum was 250 rpm and the mixing time was 5 minutes.

It has been reported that pollutants such as BOD, COD, Total Suspended Solids (TSS), heavy metals, colour and nitrogen compounds can be removed between 80-99% from leachate by coagulation/flocculation process (Kamaruddin et al., 2017). It has also been shown that bacterial contamination in leachate can be reduced by this method (Djeffal et al., 2021). The coagulation/flocculation process is often combined with other treatment methods. For example, biological treatment, chemical oxidation, adsorption, or filtration can be applied before or after the coagulation/flocculation process (Kamaruddin et al., 2017).

However, the coagulation/flocculation process has some disadvantages. For example, conventional coagulation systems produce excessive sludge and increase soluble iron and aluminium concentrations. Therefore, improved coagulation/flocculation methods have been developed. The Fenton-like oxidation method uses hydrogen peroxide (H_2O_2) and zero valence iron (ZVI) to generate hydroxyl radicals ($OH^\bullet$) and oxidise organic substances in water (Ertugay and Acar, 2014; Ertugay et al., 2017; Atmaca & Beyazit, 2022). This method has some advantages over the classical Fenton method. For example, using ZVI does not require pH adjustment, prevents the increase of metal ions, and provides higher OH● production with a lower H_2O_2 dose (Atmaca & Beyazit, 2022). High levels of suspended solids, colour, turbidity, and chemical oxygen demand (COD) removal can be achieved by this method (De et al., 2019; Atmaca & Beyazit, 2022). In electrocoagulation, metal ions dissolve in water and neutralize colloidal particles by applying an electric current between electrodes. This method allows coagulation without metal salts and produces less sludge. In addition, the oxidation of organic substances in water is also supported by producing hydrogen and oxygen gases by electrolysis. High removal rates of suspended solids, colour, turbidity, and COD can be achieved by this method (Mollah et al., 2004; Fernandes et al., 2015; Xu et al., 2020). In the photo electrocoagulation method, ultraviolet (UV) rays are used together with the electrocoagulation method. UV radiation increases the coagulation efficiency by increasing the activity of metal ions and accelerates the oxidation of organic substances in water. This method can achieve high suspended solids, colour, turbidity, and COD removal with lower electric current and metal ion dose (Ghernaout et al., 2011).

4.2.2. Treatment of Leachate by Adsorption

Adsorption is the attraction of a multicomponent fluid (gas or liquid) mixture to the surface of a solid adsorbent and binding by physical or chemical bonds (Reshadi et al., 2020). The advantages of the adsorption process include simplicity, low cost, high efficiency and selectivity (Foo & Hameed, 2010). Activated carbon is one of the most common adsorbents used in leachate treatment. Activated carbon is a solid material with high surface area and porosity and uses physical or chemical forces to retain organic pollutants (Gao et al., 2015). Plant or animal-origin materials can be used as the source of activated carbon. The adsorption capacity of activated carbon depends on leachate composition, pH, temperature, contact time and activated carbon dose (Foo & Hameed, 2009). The adsorption mechanism of activated carbon can be described by mathematical models such as Langmuir or Freundlich isotherms. These models are related to the number and energy of vacant sites on the surface of the adsorbent. Kinetic models can also be used to evaluate the adsorption performance of activated carbon. These models include mass transfer resistance and chemical reaction rate, which determine the adsorption rate (Foo & Hameed, 2009).

The disadvantages of the adsorption process of activated carbon include the presence of pollutants with low adsorption capacity, difficulty in reuse and waste generation when the saturation point is reached (Gao et al., 2015). Therefore, the adsorption process of activated carbon alone may not be sufficient for leachate treatment. Combining activated carbon with other methods may be more effective in this case. For example, the use of activated carbon as a pre-or post-treatment with biological or coagulation-flocculation methods; methods such as combining activated carbon with an electrocoagulation process have been reported in the literature (Cherni et al., 2021). The optimum conditions and removal efficiency of activated carbon may vary according to the characteristics of the leachate and the targeted pollutants. Different studies reported different optimum conditions in the literature.

Magnetic adsorbents are another group of adsorbents used in leachate treatment. Magnetic adsorbents are adsorbents with magnetic properties or modified with magnetic materials (Reshadi et al., 2020). The advantages of magnetic adsorbents include high adsorption capacity, selectivity, reusability, and easy separability in a magnetic field (Reshadi et al., 2020). Natural or synthetic materials can be used as the source of magnetic adsorbents.

The optimum conditions and removal efficiency of magnetic adsorbents may vary according to the characteristics of the leachate and the targeted pollutants. Different studies reported different optimum conditions in the literature. When utilized as magnetic adsorbents, nanomaterials in various forms, such as tubes, wires, and rods, offer a number of benefits. For instance, a magnetic adsorbent with a specific surface area of 160 m^2/g was produced in one study when carbon nanotubes were magnetized with iron oxide and functionalized with calcium. This material demonstrated excellent efficiency in effectively removing humic acid as well as other pollutants like heavy metals, dyes, organic pollutants, radioactive elements, and pesticides (Wang et al., 2014). This adsorbent may also be recovered and used again.

Cucurbituril's rigid structure, chemical stability, insolubility in most organic solvents, and relatively low toxicity are some of its main benefits (Yang et al., 2014). It is a useful substance that may be used in a number of procedures, including the treatment of water. Cucurbituril's key benefits are its stiff structure, chemical stability, insolubility in most organic solvents, and comparatively low toxicity (Wheate, 2008). Cucurbituril was demonstrated to have the capacity to trap many ions in very acidic solutions in one study (Yang et al., 2014). This shows that it could be useful in removing leachate from young landfills.

Magnetic adsorbents' removal effectiveness can change depending on the target pollutants and the materials used in their construction. Other factors that significantly affect adsorption include the process temperature, pH, ionic strength, other pollutants or chemicals, and the isoelectric point of the adsorbent. In addition to providing examples and more information on landfill leachate, this section emphasizes many magnetic adsorbents. The use of magnetic adsorbents to treat real landfill leachate has only been the subject of a relatively small number of research (Zhang et al., 2016; Zhang et al., 2018a; Zhang et al., 2018b). For instance, around 30% of the COD in the landfill filtrate was removed by adsorption on magnetite (Augusto et al., 2019).

Additionally, a magnetic $CuFe_2O_4$/reduced Graphene oxide nanocatalyst combined the oxidation and adsorption of mature landfill leachate from Shiraz, Iran (Karimipourfard et al., 2019). Magnetic chitosan nanoparticles were created and utilized to remove HA in research (Dong et al., 2014b). The findings demonstrate that adsorption is weakened by solution pH. The HA adsorption capacity falls from 29.3 mg/g to 7.4 mg/g when the solution pH rises from 4 to 10. Ionic strength and adsorption capacity were shown to have a comparable connection, with lower ionic strength being better for adsorption effectiveness. According to the study, the highest adsorption capacity was 32.56 mg/g under conditions of 25 °C, pH = 7, and low ionic strength. According to the researchers, compared to freshly cut adsorbent pieces, the adsorbent preserved 90% of its adsorption ability after numerous desorption/adsorption cycles.

Zhang et al. (2016) investigated using magnetic graphene oxide to extract HA, FA, and Pb(II) from landfill leachate. The results showed that the maximum adsorption capacity was 98.82 mg/g for HA, 75.38 mg/g for FA and 58.43 mg/g for lead.

Other adsorbents used in leachate treatment include natural or synthetic materials such as zeolite, clay, perlite, bentonite, alumina, and silica gel (Reshadi et al., 2020). The advantages of these materials include low cost, high selectivity and reusability (Reshadi et al., 2020). However, the disadvantages of these materials include low adsorption capacity, difficulty scaling, and the need for more information (Reshadi et al., 2020).

Erabee et al. (2018) investigated the adsorption treatment of landfill leachate using modified activated carbons with three different methods. The modified activated carbons were tested with raw landfill leachate samples. At optimum conditions of 0.5 g/L adsorbent dose, pH 7, temperature 25°C, and contact time 120 min, the removal efficiency was above 90% for TSS, ammonia-nitrogen and some heavy metals. They also found that activated carbon prepared with $KMnO_4$ had the highest removal efficiency.

San-Pedro et al. (2020) investigated the choice of activated carbon type for the Fenton-adsorption process. Two types of activated carbon, granular and powdered, were analysed for adsorption capacity. Furthermore, three isotherm models (Langmuir, Freundlich and Temkin) investigated the behaviour of the carbons on raw and Fenton-treated leachate samples. Adsorption data showed better agreement with Freundlich and Temkin models. This indicated that multilayer physical adsorption took place on the carbon surface. The results statistically showed that granular-activated carbon was more efficient in COD removal, and powder-activated carbon was more efficient in colour removal. Finally, an adsorption column was designed for the Fenton-adsorption process, and a removal capacity of 21.68 kgCOD/kg carbon was achieved. Removal efficiencies for colour and COD were more than 99%.

Ferraz and Yuan (2020) investigated the removal of organic matter from landfill leachate using spent coffee pulp-activated carbon. The authors converted spent coffee grounds (SCG) into activated carbon by impregnation with phosphoric acid (H_3PO_4), followed by pyrolysis in an inert atmosphere (N_2). The surface areas of SCG activated carbon ranged from 188 to 2118 m^2/g. SCG-activated carbon was tested in both synthetic and raw leachate treatment. Under optimum conditions (adsorbent dose 10 g/L, pH 3, temperature 25 °C and contact time 120 min), SCG activated carbon removed more than 90% of colour and COD from synthetic leachate. Similar results were obtained in real leachate treatment. The maximum adsorption capacity of SCG activated carbon was found to be 40 mg COD/g carbon.

Zeng et al. (2019) investigated removing dissolved organic matter from landfill leachate using $ZnCl_2$-activated sewage sludge and activated carbon from cabbage (Brassica oleracea). In their study, they analyzed the physicochemical properties of activated carbon and investigated the effects of different parameters such as adsorbent dose, adsorption time and solution pH on COD removal from leachate. Optimum parameters for adsorption were determined as an adsorbent dose 3%, adsorption time 60 minutes and pH=8. Under these conditions, the COD removal rate reached 85.61%. The adsorption of COD on activated carbon had the best fit with the Freundlich model. In addition, activated carbon was found to highly remove humic acid-like substances, such as persistent organic matter and short-chain alkanes in leachate, but not effective for long-chain alkanes.

Poblete et al. (2019) investigated advanced oxidation techniques based on ozonation, UV solar radiation, hydrogen peroxide, and persulfate for the total purification of a landfill permeate. Following the enhanced oxidation procedure, natural zeolite was used in a subsequent adsorption procedure. Implementing the UV sun/O_3/H_2O_2 process required an irradiation time of 140 minutes and consumption of 0.67 g/L H_2O_2 for 56% colour and 17% COD removal. In the case of adding persulfate to the system (UVsun/O_3/H_2O_2/$S_2O_8^{-2}$), colour and COD were reduced by 29% and 77%, respectively, and 250 minutes of irradiation time is required for 0.2 g/L $S_2O_8^{-2}$ concentration. In an experimental study with landfill leachate, post-adsorption treatment with natural zeolite resulted in an overall reduction of 36% in COD, 99% in ammonium and 18% in chloride. In another experimental study, adsorption with zeolite was used as a pretreatment for the advanced oxidation process (UVsun/O_3/H_2O_2 and UVsun/O_3/H_2O_2/$S_2O_8^{-2}$). Results are similar to post-adsorption treatment; A total reduction of 30% in COD, 90% in ammonium and 20% in chloride was observed.

In the study of Luo et al. (2019), phosphoric acid activated biochars prepared from rice husk were successfully used for filtrate purification, and color (100%), pollutants (>90%), COD (~80%) and NH_4^+ -N (100%) achieved a high level of removal.

As a result, the adsorption process in leachate treatment has advantages such as simplicity, low cost, high efficiency and selectivity. Different adsorbents can be used to remove organic matter, heavy metals and other contaminants from leachate. These adsorbents include activated carbon, magnetic adsorbents and other materials. The optimum conditions and removal efficiency of these adsorbents may vary depending on the characteristics of the leachate and the targeted pollutants. Different studies in the literature have reported different optimum conditions and removal percentages. For this reason, it is necessary to carry out experimental studies to select the most suitable adsorbent for leachate treatment. In addition, when the adsorption process alone is insufficient, its combination with other methods should also be investigated.

4.2.3. Treatment of Leachate by Air Stripping

Air stripping is commonly used as a pretreatment to remove NH_4^+-N by transferring NH_4^+-N from the aqueous phase to air as NH_3 is absorbed into H_2SO_4 or HCl (Renou et al., 2008; Abood et al., 2013). The principle of the air stripping method is to increase the contact surface between the leachate and the air, thus ensuring the gas-liquid balance. Various types of reactors can be used for air stripping. The most common are packed bed, propeller, and spray tower reactors (Abood et al., 2013; De et al., 2019a). In these reactors, the air contacts the leachate as counter-flow or co-flow. Factors affecting the efficiency of the air stripping process include the pH value, temperature, flow rate, ammonia concentration, air-liquid ratio, and reactor type of the leachate (Abood et al., 2013; De et al., 2019b). Air stripping can accomplish 85-95% NH_4^+-N removal at starting concentrations ranging from 220 to 3260 mg/L (Bonmati & Flotats, 2003) by air stripping within 36 hours of the optimal retention duration, followed by Fenton oxidation and increased coagulation processes (De et al., 2019a).

The advantages of the air stripping method include low operating cost, simple design and easy controllability. However, this method also has some disadvantages. The most important is that the ammonia emission from the air-stripping process harms the environment. Therefore, proper treatment or disposal of ammonia air is required after air stripping (Abood et al., 2013). In their study, Santos et al. (2020) tested ammonia removal by air stripping of leachate from the landfill and ammonia recovery by chemical absorption, and up to 98% ammonia removal and up to 92% ammonia recovery were achieved. In addition, more than the air stripping method is required for sufficient purification. Therefore, this method should often be used with other physical, chemical or biological treatment methods (De et al., 2019a; De et al., 2019b; Santos et al., 2020).

4.2.4. Membrane Treatment of Leachates

Membrane treatment separates contaminants in leachate by size using porous materials called membranes. Membrane techniques that can selectively separate by size using semi-permeable membranes include different types, such as microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF), and reverse osmosis (RO). Membrane-based methods have outstanding features, such as a small footprint, high volume loading, good wastewater quality and strong disinfection capacity. Therefore, in recent years, membrane-based methods have been seen as promising in treating landfill leachate. Figure 3 shows each membrane treatment's filtration spectrum and appropriate range (Abdel-Fatah 2018).

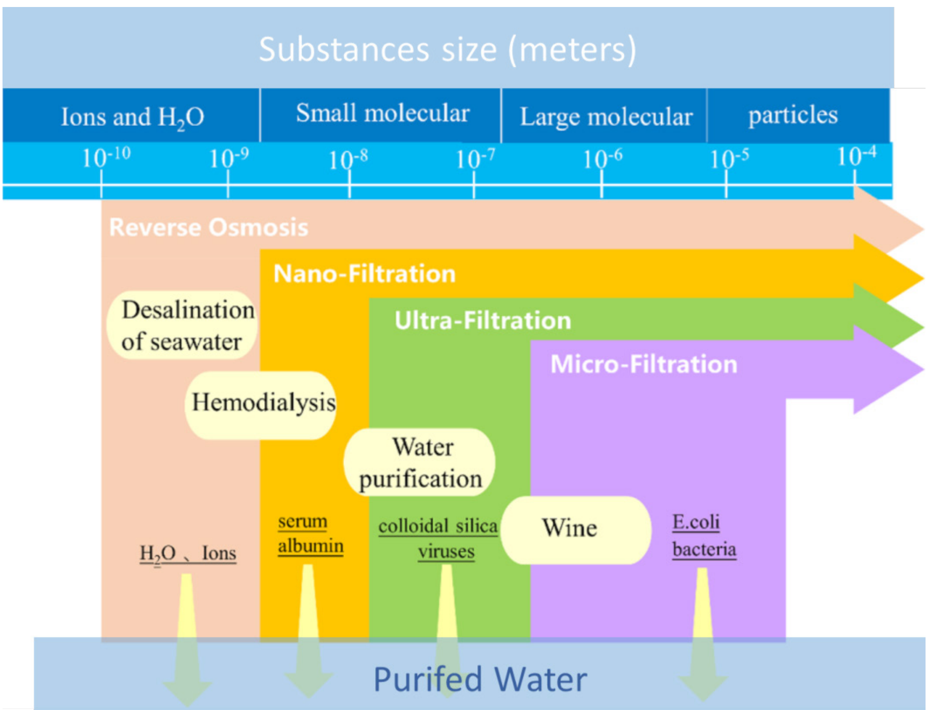

Figure 3. Filtration spectrum of membrane technologies (Abdel-Fatah 2018)

MF is frequently employed as a pretreatment unit to get rid of colloids and suspended materials ranging in size from 0.1 to 1 m in landfill leachate treatment. UF efficiently eliminates macromolecules and particles 2 nm to 0.1 m in size. According to Renou et al. (2008), COD removal rates with this technology range between 10% and 75%. UF is frequently used as a pretreatment to eliminate high molecular weight components from landfill leachate that can result in membrane fouling during RO treatment. With a molecular shear between 200 to 2000 Da, NF treatment may successfully remove organic, inorganic, and microbiological pollutants (Amaral et al. 2016). The retention rates for anions are listed as follows: $NO_3^- < Cl^- < OH^- < SO_4^{2-} < CO_3^{2-}$ and for cations: $H^+ < Na^+ < Ca^{2+} < Mg^{2+}$ (Lin et al. 2020). NF is more energy efficient to apply after RO as its processes can be operated under lower pressure conditions (Ramaswami et al., 2018). The most promising treatment technique is thus reverse osmosis. Because of their potent blocking properties, which only allow water molecules to pass through membranes, heavy metals, suspended particles, dissolved solids, organic debris, and dissolved inorganic species may all be effectively removed from landfills (Chen et al. 2020b).

The large variety of applications for membrane treatments is constrained by two intrinsic disadvantages, even though they have produced high-quality waste. The accumulation of organic, inorganic, or biological species on the membrane surface or inside its pores is the initial cause of membrane fouling. According to Chen et al. (2016), this procedure may reduce the lifespan of the membrane modules and raise operational costs. The creation of membrane-concentrated solid waste leachate is the second. Membrane methods can only concentrate pollutants in landfill leachate in lower amounts (20–30% of the original volume), not eliminate them. Leachate from landfills concentrated using membranes is more complicated and challenging to handle. There are pretreatment methods that help lessen membrane fouling. For instance, eliminating suspended materials, stopping the precipitation of insoluble salts, avoiding calcification, and eliminating organic debris, bacteria, and other microbes. The yield of membrane-concentrated storage leachate reduces when membrane permeability is increased.

In recent years, there has been much research towards fusing membrane activities with other processes. Heavy metal and organic matter concentrations in landfill leachate were treated using the Membrane Bioreactor (MBR). According to various circumstances, the MBR's effectiveness varies greatly (between 23% and 98%) (Jakopovic et al. 2008). There are several benefits to combining chemical and membrane therapies. Fenton oxidation, for instance, causes colloidal particle coagulation during the oxidation process, which can prevent colloidal particles from entering the membrane and significantly reduce membrane fouling (Chiu & James, 2006). For the most effective removal of COD (63%), colour (76%) and humic compounds (50%) from landfill leachate, the combined Fenton-MF-NF process was adopted (Moravia et al. 2013).

4.3. Biological Treatment of Leachate

Biological treatment converts colloidal and dissolved organic substances and inorganic elements (such as N, P, S, K, Ca and Mg) into cell tissue (sludge) and/or gases under suitable ambient conditions for optimum growth of microorganisms (Wiszniowski et al., 2006). Biological treatment enables the removal of pollutants with the cooperation of complex biological populations. These methods can be classified as oxygenated (aerobic), nitrate/nitrite (anoxic) and anaerobic (anaerobic) according to the electron acceptor sources in the environment. Organic compounds are reduced to CO_2 and sludge in aerobic conditions and biogas (CO_2 and CH_4) under anaerobic conditions (Luo et al., 2020). Biological treatment is widely used in treating landfill leachate containing high concentrations of BOD because this method is low-cost, reliable, and simple (Renou et al., 2008). Biological treatment techniques are very effective for young leachate with a high BOD/COD ratio (>0.5). However, biological treatment efficiencies decrease as the landfill age increases (Setiadi and Fairus, 2003). This is due to pollutants that reduce biomass activity or are resistant to biological processes (Renou et al., 2008). Old leachate also contains organic compounds that are difficult to remove by biological treatment. Therefore, a combination of biological, physical, and other treatment methods must be applied for leachate to meet the discharge standards to the receiving environment (Tauchert et al., 2006). Aerobic, anaerobic, and anoxic processes are among the biological methods to remove organic matter and ammonium nitrogen from landfill leachate (Canziani et al., 2006; Bohdziewicz et al., 2008; Trabelsi et al., 2009). In a recent study, electrocoagulation-biofiltration hybrid techniques were used to treat landfill leachate, and post-electrocoagulation biofiltration provided 37 ± 2% COD removal, primarily in the form of insoluble COD and HA, followed by 42 ± 7% COD removal (Dia et al., 2018). Integrating air stripping, MBR and NF processes reduces approximately 88%, 95%, 100% and over 100% in COD, ammonia, colour and toxicity, respectively, resulting in highly efficient landfill leachate treatment (Amaral et al. 2016).

MBR technology has recently become an intriguing procedure for treating landfill leachate. This technique combines biodegradation and membrane separation procedures. Treatment of landfill leachate with MBR has various benefits. These benefits include high process stability, minimal environmental impact, enhanced mixed liquid suspended solids biomass retention, and reduced sludge generation. They also feature good waste quality absorption. For the treatment of landfill leachate, MBR can be used. However, depending on landfill age and operating conditions, COD removal efficiencies can vary between 23-90% (Ahmed & Lan, 2012). MBR needs less hydraulic retention time than traditional activated sludge processes but has a greater loading rate and COD removal effectiveness.

4.3.1. Aerobic Treatment of Leachate

Aerobic treatment of leachate is decomposing biodegradable organic compounds by microorganisms in the presence of oxygen in the air. This method is carried out by suspending and clinging biomass growth. These methods are widely used to treat wastewater and environmental fluids (Renou et al., 2008; Abbas et al., 2009). With these methods, nitrification converts ammonium nitrogen to nitrite/nitrate nitrogen, and some of the biodegradable organic pollutants are removed (Luo et al., 2020). Aerated Lagoons (AL), Aerobic Activated Sludge (AS), Sequencing Batch Reactor (SBR), Rotating Biological Contactors (RBC), Trickling Filters, Moving Bed Bioreactor (MBBR), Fluidized Bed Bioreactors (FBBR), Membrane Bioreactor (MBR) and Various aerobic biological processes such as) and wetlands have been used successfully for organic matter and ammonium removal (Kamaruddin et al., 2017; Torretta et al., 2017).

AAS processes are widely used in treating domestic wastewater or the combined treatment of leachate and domestic wastewater. This system is a mixture of microorganisms that can convert organic matter partly into new microbial biomass and partly into CO_2, water, and minerals while consuming organic matter under aerobic conditions (Luo et al., 2014). However, alternative techniques are used to achieve high COD and nitrogen removal due to the disadvantages of AS systems, such as excess sludge production, low sludge settleability, high energy requirements, long hydraulic retention time, and microbial inhibition at high ammonium nitrogen concentrations (Renou et al., 2008; Torretta et al., 2017).

The data in Table 6 show the effectiveness of different aerobic biological processes in removing different pollutants. According to these data, SBR, MBR, MBBR and FBBR systems are very effective in terms of COD removal efficiency in the treatment of landfill leachate and have a removal efficiency of over 70%. Regarding NH_4^+-N removal efficiency, AL, AS, RBC, MBBR, and FBBR systems perform more effectively than others.

Table 6. Removal of pollutants in leachate by aerobic biological treatment (Luo et al., 2020)

Reactor Type	Pollutant Removal (%)		
	COD	**BOD**	**NH_4^+-N**
Aerated Lagoons	40	64	77
AS	50	61	75
SBR	76	84	65
RBC	38	80	98
Trickling Filters	49	77	59.5
MBBR	60-81	-	92-95
FBBR	85	-	80
MBR	79	99	60
Wetlands	50	59	51

As indicated in the table, aerobic biological treatment methods give effective results in the removal of various organic pollutants and nitrogen compounds. Each process has advantages and disadvantages, and the wastewater's characteristics should be considered when choosing.

4.3.2. Anaerobic and Anoxic Treatment of Leachate Water

Leachate waters are wastewater formed in landfills with a high organic matter concentration (Renou et al., 2008). Anaerobic and anoxic processes can be used for the treatment of leachate. The anaerobic treatment turns organic substances into products such as CO_2, CH_4, H_2S and NH_3 by decomposing microorganisms without oxygen (Tchobanoglous et al., 2003). In this process, organic substances are broken down into smaller components by hydrolysis and acid fermentation (Torretta et al., 2017). These components are then converted to methane, CO_2 and water by methanogenic bacteria during the methane formation stage (Wiszniowsk et al., 2006). Anoxic treatment, on the other hand, is a process in which nitrate is used as an electron acceptor and organic materials are used as electron donors. In this process, nitrate is reduced to elemental nitrogen and is called denitrification. The denitrification process occurs heterotrophically in conventional nitrogen removal. So, it needs organic carbon sources (Schlegel, 1988).

The advantages of anaerobic and anoxic treatment processes are:

- They require less energy and even recover energy by converting methane gas into energy. Methane gas can be collected as biogas to generate heat or electricity (Tchobanoglous et al., 2003).
- A more stable sludge is obtained and reduced (Tchobanoglous et al., 2003). Anaerobic sludge contains less water, and it can be dewatered more easily. It also contains fewer pathogens and can be used as a fertilizer.
- Nitrogen removal is ensured, and contamination of the receiving environment is prevented (Rodríguez et al., 2011). With the conversion of nitrogen to its elemental form, the risk of eutrophication in aquatic ecosystems is reduced (Renou et al., 2008).
- Bad odour formation is reduced (Wiszniowsk et al., 2006). Odour-causing compounds such as H_2S formed by anaerobic treatment are removed by oxidation with anoxic treatment (Rodríguez et al., 2011).

The disadvantages of anaerobic and anoxic treatment processes are:

- They have a low reaction rate and require a long hydraulic holding time. This means a larger reactor volume (Tchobanoglous et al., 2003).
- They are sensitive to environmental conditions, and it is important to control parameters such as pH, temperature, and nutrient ratio (Rodríguez et al., 2011). Especially since the optimum pH range of anaerobic microorganisms is narrow, acid-base balance must be provided (Wiszniowsk et al., 2006).
- They cannot provide effective NH4+-N removal (Wiszniowsk et al., 2006). An aerobic step is required to convert the nitrogen remaining from ammonia by anaerobic treatment to nitrate form by nitrification (Rodríguez et al., 2011).
- They cannot provide phosphorus removal. Bioremoval of phosphorus requires aerobic-anoxic cycles (Metcalf & Eddy, 2003).

Anaerobic and anoxic treatment processes can be applied together. A/O (pre-anoxic) or Modified Ludzack-Ettinger (MLE) processes are usually used. In these processes, an anoxic reactor is placed after the anaerobic reactor. Denitrification takes place in the anoxic reactor. For this, nitrate formed by nitrification in the aerobic reactor must be returned to the anoxic reactor. Thus, both organic matter and nitrogen removal are achieved. It is also possible to remove phosphorus in the aerobic reactor (Metcalf & Eddy, 2003). Anaerobic and anoxic treatment methods and yields are given in Table 7.

Table 7. Anaerobic and anoxic treatment methods and yields (Tchobanoglous vd., 2003; Metcalf & Eddy, 2003).

Method	Description	Treatment Efficiency
Upflow anaerobic sludge blanket (UAnSB)	It converts organic materials into methane gas in an oxygen-free environment. A granular sludge bed is formed in the reactor, and an upstream flow is maintained.	COD removal %80-90, BOD removal %70-80, Nitrogen removal %10-20
Anaerobic fixed film fixed bed reactor (AnFFFBR)	It converts organic materials into methane gas in an oxygen-free environment. A biofilm forms on the fill material in the reactor, and a downstream or upstream flow is maintained.	COD removal %70-80, BOD removal %60-70, Nitrogen removal %10-20
Anaerobic treatment of leachate with returning	It is the process of providing anaerobic treatment by pumping back the leachate within the storage area. The landfill functions like an anaerobic reactor.	COD removal %50-70, BOD removal %40-60, Nitrogen removal %10-20
Pre-anoxic treatment (A/O)	It is an anoxic treatment applied after anaerobic treatment. It converts nitrate to elemental nitrogen by reducing it with organic substances in an anoxic reactor. internal recycling between the aerobic and anoxic reactors.	COD removal %90-95, BOD removal %85-90, Nitrogen removal %70-80
Modified Ludzack-Ettinger (MLE) process	It is an anoxic treatment applied after anaerobic treatment. It converts nitrate to elemental nitrogen by reducing it with organic substances in an anoxic reactor. Internal recycle from the aerobic reactor to the anoxic reactor. In addition, the effluent from the aerobic reactor is recycled externally to the anoxic reactor.	COD removal %90-95, BOD removal %85-90, Nitrogen removal %80-90

4.4. Chemical Treatment of Leachate

Chemical treatment is an effective method of removing contaminants from leachate. Various chemical treatment methods are available, each with its advantages and disadvantages. Chemical treatment methods can be divided into chemical precipitation, chemical oxidation, coagulation-flocculation and advanced oxidation processes (AOPs) (Teng et al., 2021). *Chemical precipitation* is a process that involves adding chemicals to leachate to form insoluble precipitates that can be separated by precipitation or filtration. Commonly used chemicals for precipitation are lime, alum, iron salts and magnesium salts. Chemical precipitation can effectively remove heavy metals, phosphorus, sulfate and some organic compounds from leachate (Amr and Zainol, 2016).

Chemical oxidation is a process that involves the use of oxidizing agents to break down or convert organic matter and ammonia nitrogen into leachate. Common oxidizing agents used for oxidation are chlorine, ozone, hydrogen peroxide and persulfate. Chemical oxidation can improve the biodegradability and decolourization of leachate, but it can also produce toxic byproducts such as chlorinated and brominated organics (Teng et al., 2021).

Coagulation-flocculation is a process that involves adding coagulants and flocculants to leachate to form agglomerates that can be separated by precipitation or flotation. Common coagulants and flocculants used for coagulation-flocculation are aluminium salts, iron salts, poly aluminium chloride, polyacrylamide and chitosan. Coagulation-flocculation can effectively remove suspended solids, turbidity, colour and some organic compounds from leachate (Rathnayake and Herath, 2018).

AOPs are a group of processes involving highly reactive hydroxyl radicals (OH) that can oxidize various organic pollutants in leachate. Commonly used AOPs for leachate treatment are Fenton, electro-Fenton, photo-Fenton, ozonation, photocatalysis and sonolysis. AOPs can highly remove COD, BOD, colour, and persistent organic matter from leachate. However, they can also require high energy input and produce secondary pollutants such as sludge and metal ions (Teng et al., 2021).

In conclusion, chemical treatment methods are effective and viable options for leachate treatment. However, it has some limitations, such as high cost, low selectivity and potential environmental risks. Therefore, combining chemical treatment methods with other methods, such as biological treatment or membrane filtration, is recommended to achieve optimum results (Siddiqi et al., 2022). The chemical methods used to treat pollutants and their removal efficiencies are given in Table 8.

Table 8. Chemical methods and removal efficiencies

Chemical Method	Pollutant Removal Efficiency	Reference
Chemical precipitation	Heavy metals: %80-99, NH_4^+-N: %50-90, COD: %40-70, Colour: %60-100	Teng et al. (2021)
Advanced oxidation processes	COD: %30-90, NH_4^+-N: %20-80, Colour: %60-100, phenol: %50-100, Haloacetic acids: %40-100	Fang et al. (2021)
Electrocoagulation	COD: %17-70, NH_4^+-N: %20-90, Heavy metals: %50-99, Colour: %50-90	Fang et al. (2021)
Adsorption	COD: %10-80, NH_4^+-N: %10-70, Heavy metals: %20-90, Colour: %20-80	Teng et al. (2021)
Coagulation / flocculation	COD: %30-60, NH_4^+-N: %10-40, Heavy metals: %40-80, Colour: %40-70	Teng et al. (2021)
Air stripping	NH_4^+-N: %10-50, volatile organic compounds: %50-90	Fang et al. (2021)
Filtration	COD: %10-40, NH_4^+-N: %10-30, Heavy metals: %20-60, Colour: %20-60	Teng et al. (2021)
Evaporation	COD: %90-99, NH_4^+-N: %90-99, Heavy metals: %90-99, Colour: %90-99	Fang et al. (2021)

4.4.1. Chemical Precipitation

Chemical precipitation is a commonly used pretreatment method to remove heavy metals and substances that adversely affect biological treatment, such as NH_4^+-N. In chemical precipitation, NH_3-N and heavy metals from garbage leaching can be converted through chemical reactions to precipitate, separated by simple sedimentation or filtration (Kurniawan et al., 2006). For NH_4^+-N precipitation, precipitants such as struvite, i.e., magnesium ammonium phosphate (MAP) and lime, are typically used. Struvite precipitation can provide approximately 80% NH_4^+-N removal, depending on operating conditions such as pH, dosage, and order of addition of magnesium, ammonium, and phosphate (Kim et al., 2007; Teng et al., 2021). It remains a challenge unless methods are developed to dispose of or utilize sludge generated by the chemical precipitation process (Kundu et al., 2023).

Biosorption can also be applied after chemical precipitation. Biosorption is the retention of pollutants through active groups on the surface of living or dead biological materials (Fu and Wang, 2011). Different biosorbents can be used for biosorption, but waste biomass is economically and ecologically advantageous. For example, biosorbents such as activated sludge, algae, fungi, bacteria, and vegetable waste can effectively remove heavy metals from garbage seepage (Charerntanyarak, 1999). The efficiency of the biosorption process depends on factors such as pH, contact time, biosorbent dose, initial concentration, and temperature. (Mirbagheri and Hosseini, 2005).

The advantages of treating garbage leachate by chemical precipitation and biosorption are simple operating conditions, low cost, high efficiency, and reduced secondary pollution. However, these methods also have disadvantages: chemical consumption, sludge production, biosorbent regeneration, and a lack of selectivity. Therefore, these methods must be optimized or combined with other purification techniques. (Liu et al., 2015).

The chemical precipitation technique has some disadvantages that limit its practical application: (1) low COD removal efficiency; (2) high pH dependence; (3) the requirement of large volumes of precipitator; and (4) excessive sludge formation. However, sludge reuse and developing new precipitating agents are valuable research areas that could address these limitations. (Luo et al., 2020).

4.4.2. Advanced Oxidation Processes

Conventional methods used in leachate treatment often need to be revised or become more costly (Ameta and Ameta, 2018). Therefore, there is a need for alternative methods, such as advanced oxidation processes in leachate treatment. Advanced oxidation processes (AOPs) are processes used to decompose a wide range of organic pollutants in water and gas wastes using strong oxidizing agents such as hydroxyl radicals, superoxide radicals, and sulfate radicals. (Ameta and Ameta, 2018). Advanced oxidation processes include different methods such as Fenton, electro-Fenton, and photo-electro-Fenton.

With highly reactive hydroxyl radicals (OH·) and sulfate radicals ($SO_4^{-}\cdot$) formed using strong oxidants such as ozone (O_3), hydrogen peroxide (H_2O_2) and persulfate, targeting the complete mineralization of biologically resistant organic pollutants and converting them into biodegradable forms AOPs developed for chemical and organic drugs are widely used as a pretreatment stage (Chong et al., 2010; Neyens and Baeyens, 2003).

AOPs are considered a promising method of treating wastewater and are widely used. AOPs can mineralize different organic compounds in landfills into carbon dioxide and inorganic molecules or convert them into immediate biodegradable substances (Sruthi et al., 2018). Generating highly reactive hydroxyl (OH·) and sulfate radicals ($SO_4^{-}\cdot$) is a critical step with strong oxidants such as ozone (O_3), hydrogen peroxide (H_2O_2), and persulfate and determines the degradation efficiency of organic compounds (Chen et al., 2018; Zhong et al., 2017). Activating or catalysing oxidants is a critical step. Major approaches include transition metal catalysis, photolysis (UV), sonolysis, microwave and radiolytic activation. (Jung et al., 2017; Xu et al., 2017; Ye et al., 2016). Among these AOPs, O_3 can be activated to initiate the formation of OH· by combining increased pH, the presence of H_2O_2 (Equation 1), UV and various catalysts (Co (II), TiO_2, MnO_2 etc.) (Abu Amr and Aziz, 2012; Abu Amr et al., 2013). Activation of H_2O_2 can be accomplished using various transition metal catalysts, UV, sonolysis and microwave. Fe^{2+}/H_2O_2 (Equation 2) based activation methods are known as the Fenton process and are widely used for wastewater treatment (Chou et al., 2015; Gupta et al., 2014; Zhang et al., 2014). Persulfate-based AOPs occupy an important place among AOPs. Persulfate is a strong oxidant with a chemical formula $(S_2O_8)^{2-}$. Highly reactive oxidation products such as persulfate, hydroxyl radicals (OH·) and sulfate radicals ($SO_4^{-}\cdot$) can be formed. Persulfate-based AOPs include different compounds such as peroxydisulfate (PDS) and peroxymonosulfate (PMS). These compounds can be activated by various methods such as UV, heat, alkaline pH, transition metals, nanomaterials, radiolysis and generate hydroxyl radicals (OH·) and sulfate radicals ($SO_4^{-}\cdot$) (Equation 3). Persulfate-based AOPs are widely used to treat industrial wastewater, surface water, and other leachate treatments. These methods are designed to convert organic pollutants into biodegradable forms by targeting their complete mineralization. Persulfate-based AOPs can be used with ozone (O_3), hydrogen peroxide (H_2O_2) and other oxidants, or they can be used effectively alone (Chou et al., 2015; Chen et al., 2020b; Yi et al., 2021). Conditions such as pH, temperature, initial concentration of organic pollutants, and ionic strength can affect the performance of AOPs.

$$H_2O_2 + 2O_2 \rightarrow 3O_2 + 2OH\cdot \quad (1)$$
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{-} + OH\cdot \quad (2)$$
$$S_2O^{2-}{}_8 + hv \rightarrow S^{-}{}_4 \cdot + S^{-}{}_4 \quad (3)$$

4.4.2.1. Treatment of Leachate by Fenton and Fenton-like Processes

The Fenton process is a widely used method in the treatment of landfills. Landfill waters can be raw, mature, or biologically pre-treated. The Fenton process effectively removes COD, TOC, colour, and other contaminants from landfills. On average, the Fenton process provides a removal efficiency of 35-90% for COD. In addition, the Fenton process increases landfills' biodegradability (BOD_5/COD), making them suitable for further biological treatment. In this way, the organic load of the wastewater is reduced, and thus its environmental impact is reduced (Jung et al., 2017).

Fenton and Fenton-like processes are advanced oxidation processes (AOPs) that oxidize or mineralize organic matter by generating hydroxyl radicals (OH•). Hydroxyl radicals are free radicals. These radicals are a very strong oxidizers and give rapid and non-selective reactions with organic substances. (Wang et al., 2016; Zhang et al. 2016). In the Fenton process, Fe^{2+} ion is used as the catalyst, and H_2O_2 is used as the oxidizer (Kang and Hwang, 2000; Brillas et al. 2009).

The advantages of the Fenton process include high oxidation efficiency, simple operating conditions (it can operate at room temperature and atmospheric pressure), and environmental friendliness (H_2O_2 can be decomposed into harmless products) (Wang et al., 2009). The disadvantages of the Fenton process include high operating cost, narrow optimum pH range (usually works best around pH 3), large amounts of iron sludge formation, and difficulty in recovering the homogeneous catalyst (Fe^{2+}) (Umar et al., 2010; Chen et al., 2018). Xu et al. (2017) used a Box-Behnken design flank method to optimize pH and other parameters for Fenton oxidation of litter waters. The results showed that the maximum removal rates for TOC, COD and colour under optimum conditions were $\leq$ 68.9%, 69.6% and 100%, respectively.

In Fenton-like processes, other heterogeneous or homogeneous catalysts are used instead of Fe^{2+} ions. These catalysts include metal ions or minerals such as Fe^{3+}, Cu^{2+}/Cu^{+}, pyrite, and nano-zerovalent iron (Wang et al., 2016). The advantages of Fenton-like processes include a wider pH range, less iron sludge formation, and easier catalyst recovery (Hilles et al., 2016). The disadvantages of Fenton-like processes include lower oxidation efficiency and higher catalyst dose requirement (Sruthi et al., 2018).

Some improvement methods are also applied to increase the performance of Fenton and Fenton-like processes. These include methods such as UV radiation (photo-Fenton), electric field application (electro-Fenton), microwave radiation (microwave-Fenton), and ultrasound application (ultrasound Fenton).

These methods accelerate or improve organic matter oxidation by increasing hydroxyl radical production (Hilles et al., 2016; Ye et al., 2016; Chen et al., 2018; Sruthi et al., 2018).

In the Photo-Fenton process, the Fe^{3+} ion is reduced to the Fe^{2+} ion under the influence of UV radiation, thus increasing the production of hydroxyl radicals. In addition, UV radiation can directly decompose H_2O_2 to form hydroxyl radicals. The advantages of the Photo-Fenton process include higher oxidation efficiency and a lower reagent dosage requirement. The disadvantages of the Photo-Fenton process include the cost and maintenance of the UV lamp and the inability of UV radiation to penetrate deep water layers (Zazouli et al., 2012; Sruthi et al., 2018; Brillas and Garcia-Segura, 2020). In her study, Özçelik (2022) tried different Fe^{+2} and H_2O_2 doses, reaction times, and light intensities on samples taken from the leachate of a solid waste facility in Sivas. As a result, it was found that the photo-Fenton process provided higher COD (chemical oxygen demand) removal than the classical Fenton process, and the best treatment was obtained with 89% COD removal at 300 mg/L Fe^{+2}/1000 mg/L H_2O_2.

In the Electro-Fenton process, Fe^{3+} ions are reduced to Fe^{2+} ions by applying an electric field, or Fe^{2+} ions are released directly from the electrode surface. Thus, hydroxyl radical production increases. In addition, with an electric field, H_2O_2 can be produced at the electrodes, or the stability of the added H_2O_2 increases. The advantages of the Electro-Fenton process include higher oxidation efficiency and a wider pH range. The disadvantages of the Electro-Fenton process include high energy consumption, corrosion, or corrosion of the electrodes (Wang et al., 2019; Brillas and Garcia-Segura, 2020). In the study of Atmaca & Beyazıt (2021), different current densities (10-50 A/m^2) and pH values (2.5-5.0) were tested on samples taken from leachate. As a result, they stated that the best treatment was pH 3, current density was 10 A/m^2, COD removal was 79.75%, and colour removal was 80.57%.

In the microwave-Fenton process, water molecules are heated rapidly by the effect of microwave radiation, thus increasing the production of hydroxyl radicals. In addition, microwave radiation can directly decompose H_2O_2 to form hydroxyl radicals. The advantages of the microwave-Fenton process include higher oxidation efficiency and shorter reaction time. The disadvantages of the microwave-Fenton process include high energy consumption, microwave generator cost and maintenance (Chen et al., 2018). Maheswari et al. (2022) investigated the effects of microwave power, ozonation and Fenton reagent on the degradation of COD in leachate in the microwave-combined ozonation and Fenton oxidation process. As experimental parameters, pH, COD, temperature, oxidizer dose, microwave power and reaction time were changed. The results showed that 70% COD removal efficiency was achieved in the microwave process at 450 W in 10 minutes intervals, and 57.4% COD removal efficiency was obtained in the ozonation process at 159 mg/L ozone dose in 60 minutes and pH 11. In the Fenton process, on the other hand, COD removal efficiency of 52.91% was achieved with H_2O_2 66.47 mμ/L and Fe2+ 80 mμ/L in 60 minutes. Individual processes require long reaction times. When the three processes were compared, microwaves provided higher COD removal in a shorter reaction time. In the O_3^+ Fe process, 83% COD removal was achieved in 75 minutes. The experiment revealed that M^+ O_3^+ Fe enabled the decomposition of COD in leachate in a shorter reaction time.

In the ultrasound Fenton process, water molecules form small bubbles called cavitation under the influence of the ultrasound application, and they burst and produce hydroxyl radicals. In addition, ultrasound applications can directly decompose H_2O_2 to form hydroxyl radicals. The advantages of the ultrasound Fenton process include higher oxidation efficiency and lower reagent dosage requirement. The disadvantages of the ultrasound Fenton process include high energy consumption, ultrasound generator cost and maintenance (Brillas and Garcia-Segura, 2020).

4.4.2.2. O_3-Based AOPs

Compared to Fenton processes, O_3-based processes cause lower levels of sludge formation and have higher oxidative power (E0 = 2.08 V) to treat landfill leachate. O_3 can convert durable macromolecular substances into biodegradable compounds. In this case, too, it leads to an increase in biodegradability (de Brito et al., 2019).

O_3-based AOPs decompose organic materials by forming strong oxidizing free radicals (hydroxyl radicals) by contacting ozone gas with water. In O_3-based AOPs, ozone gas increases hydroxyl radical production at high pH (O_3 /OH −) or when used with hydrogen peroxide (O_3 /H_2O_2) (Rekhate and Srivastava, 2020). The hydroxyl radical reacts quickly and effectively with organic substances, as it is a non-selective and very short-lived oxidizer. Hydroxyl radical formation in O_3-based AOPs occurs as follows (Wardenier et al., 2019):

$$O_3+OH^- \rightarrow HO_2^- + O_2 \quad (4)$$
$$HO_2^- + O_3 \rightarrow \bullet OH + O_2^- + O_2 \quad (5)$$
$$O_3+H_2O_2 \rightarrow \bullet OH + HO_2^- + O_2 \quad (6)$$
$$HO_2^- + O_3 \rightarrow \bullet OH + O_2^- + O_2 \quad (7)$$

As seen in these reactions, ozone gas plays a role both as a source of hydroxyl radicals and as a consumer. Therefore, parameters such as ozone dose, pH value and hydrogen peroxide dose should be adjusted optimally. In addition, factors such as temperature, reaction time, organic matter concentration and composition also affect the performance of O_3-based AOPs.

The advantages of using O_3-based AOPs in the treatment of landfill leachate are:

- O_3-based AOPs can effectively remove colour, odour, organic matter, and heavy metals in landfill leachate (Chen and Li, 2020a).
- O_3-based AOPs can convert resistant macromolecular substances into biodegradable compounds. This leads to an increase in biodegradability (Chen and Li, 2020a).
- O_3-based AOPs result in lower sludge formation levels than the Fenton processes. In this case, too, it has higher oxidative power to treat the landfill leachate (Wu et al., 2004).

The disadvantages of using O_3-based AOPs in the treatment of landfill leachate are as follows:

- O_3-based AOPs have high operating costs and energy consumption (Gripa et al., 2023).
- Optimum operating conditions (pH, ozone dose, hydrogen peroxide dose, etc.) of O_3-based AOPs vary according to the characteristics of the landfill leachate (Wu et al., 2004).
- O_3-based AOPs alone cannot provide sufficient treatment efficiency. Therefore, it is generally required to be used with other purification methods (Gripa et al., 2023).

Catalytic ozonation, combining ozone with solid catalysts, is an effective way to remove dissolved organic matter (DOM) from landfill leachate and increase the efficiency of DOM removal by controlling radical formation. Catalytic ozonation can be classified as homogeneous catalytic ozonation or heterogeneous catalytic ozonation, depending on the form of the catalyst used (Nawrocki & Kasprzyk-Hordern, 2010). However, homogeneous catalytic ozonation can cause secondary pollution and require further separation before disposal. While heterogeneous catalytic ozonation can be improved using metal oxides, its low mass transfer efficiency limits its practical application (He et al., 2018).

Ozonation is often combined with other AOP techniques such as electrochemistry /O_3, O_3/H_2O_2, O_3/UV and $O_3/S_2O_8^{2-}$ to improve landfill leachate treatment performance (Ghahrchi and Rezaee, 2020). These techniques aim to break down or mineralize organic pollutants in landfill leachate by exploiting the strong oxidation property of ozone. Electrochemistry/O_3 process uses hydrogen peroxide and hydroxyl radicals formed by electrolysis in combination with ozone. The O_3/H_2O_2 process is based on the reaction of ozone with hydrogen peroxide to produce hydroxyl radicals. The O_3/UV process allows ozone to photolysis under UV rays to form hydroxyl radicals. The $O_3/S_2O_8^{2-}$ process is based on the reaction of ozone with persulfate ions to produce sulfate radicals. Each of these techniques has advantages and disadvantages, and the landfill should be selected according to the characteristics of the leachate (Gorito et al., 2021; Polatidou et al., 2022).

The integrated Fe0-O_3/H_2O_2 process was used for semi-aerobic treatment of aged waste biofilter pretreated landfill leachate under conditions of 0.6 g/L Fe0, 26.80 mg/min O_3 and 1 mL/L H_2O_2 formation, resulting in 43% COD removal (Wang et al., 2020b). In this process, FeO reacts with hydrogen peroxide and ozone to produce the hydroxyl radical. In addition, Fe0 electrochemically dissolves to form Fe^{2+} and Fe^{3+} ions. These ions also participate in Fenton or photo-Fenton reactions. Thus, the integrated Fe0-O_3/H_2O_2 treatment offers multiple oxidation mechanisms, increasing the removal of organic contaminants from landfill leachate (Gorito et al., 2021).

Ozonation remains a viable option for treating landfill leachate, enabling measures to increase ozone efficiency (Wang et al., 2020b). Ozone efficiency depends on factors that affect the transfer of ozone gas to water. These factors include the concentration of ozone gas, flow rate, pressure, temperature, pH value of water, alkalinity, pollution level and reactor type. New technologies like the microballoon reactor are being developed to increase ozone efficiency. Microballoon reactor has small bubble size and high bubble surface area. In this way, the transfer of ozone gas to water and contact time is increased (Gorito et al., 2021; Polatidou et al., 2022).

4.4.2.3. UV-Based AOPs

By producing strong oxidizers such as hydroxyl radicals (•OH) or sulfate radicals ($SO_4{\bullet}^-$), pollutants can be broken down and mineralized. UV-based

AOPs include different processes such as UV/H_2O_2, UV-Fenton, UV/persulfate, UV/peroxomonosulphate and TiO_2 photocatalysis.

In the UV/H_2O_2 process, •OH is produced as a result of the decomposition of H_2O_2 with UV light. This process has advantages such as high oxidation rates, simple operational procedures, and no sludge formation (Rehman et al., 2018). However, disadvantages of this process include the low UV absorbance of H_2O_2, and the high energy inputs required to produce sufficient OH due to the high OH scavenging rate of water and DOM (Zhao et al., 2020). Therefore, the UV-H_2O_2 or UV-Fenton process combined with Fe^{2+} can be used to improve the performance of this process. The UV-Fenton process allows the Fe^{2+} catalyst to react with H_2O_2 and O_2 to produce •OH. This process makes obtaining higher treatment efficiency with lower H_2O_2 doses possible compared to the UV- H_2O_2 process (Deng and Zhao, 2015). However, the disadvantages of this process include the need for pH adjustment, the formation of Fe sludge and the difficulty of recovering the Fe catalyst.

Sulfate radical (SO_4•$^-$) - based techniques such as UV/persulfate ($S_2O_8^{2-}$) and UV/peroxomonosulphate (HSO_5^-) have also attracted wide attention. SO_4•$^-$ has a high standard redox potential ranging from 2.5 to 3.1 V and can react with organic matter with rate constants of 10^5 to 10^9 1/M s (Lin and Wu, 2014). In addition, SO_4•$^-$ is converted to non-toxic sulfate after oxidation reactions, which does not require additional treatment and disposal (Gao et al., 2012). In addition, $S_2O_8^{2-}$ and HSO_5^- are more stable and economical than H_2O_2. However, the disadvantages of these techniques include that SO_4•$^-$ is affected by the staining composition due to its selectivity, and SO_4•$^-$ has a slower reaction rate than •OH.

TiO_2 photocatalysis produces radicals such as •OH and • O_2^- as a result of activating the TiO_2 photocatalyst with UV light. This technique has received great attention due to its non-toxicity, low cost, high chemical stability, and environmental friendliness for landfill leachate treatment (Deng and Zhao, 2015). However, disadvantages of TiO_2 photocatalysis include low quantum efficiency, the inability of unadulterated TiO_2 to absorb visible light, and difficulty separating the photocatalyst.

The application of UV-based AOPs in the treatment of landfill leachate has been reported in many studies in the literature. For example, Parthenidis et al. (2023) compared the performance of UV/Fe^{2+}/H_2O_2 ve UV/Fe^{2+}/$S_2O_8^{2-}$ processes on biologically pre-treated landfill leachate. The results showed that both processes were effective in COD, TOC, colour index and ammonia removal, but the sulfate radical-based process varied depending on the staining composition.

Oxidant dosing and coagulation/flocculation have also been found to increase the efficiency of photocatalytic applications.

In another study, Ghanbari et al. (2020) purified litter leachate using a sequential electrocoagulation + electrooxidation + SR-AOP process. The results showed that the sequential process achieved 95.6% COD and 99.8% ammonia removal. In addition, it was determined that the phytotoxicity decreased after each treatment, and the biodegradability of the final effluent was significantly improved.

AOPs have emerged as powerful tools for treating landfill leachate (Rizzo et al., 2020). However, AOPs have inherent limitations, such as high sludge formation, high chemical dosages, and narrow operating pH ranges (Babuponnusami & Muthukumar, 2014). Although energy-enriched AOPs can increase the removal efficiency of conventional methods, energy consumption increases the overall operating cost (Gogate & Pandit, 2004). Despite these problems, despite the relatively good waste quality, most AOPs still need to be expanded to laboratory-scale studies. Finding a tradeoff between energy consumption and operating efficiency is crucial for achieving environmental benefits at the lowest possible cost.

The basic principle of AOPs is to generate strong oxidizers, such as hydroxyl radicals, to break down organic pollutants in water (Babuponnusami & Muthukumar, 2014). Hydroxyl radicals react with organic pollutants, converting them into smaller, harmless compounds (Rizzo et al., 2019). The advantages of AOPs include being effective against a wide range of pollutants, not producing sludge and requiring low chemical dosage (Gogate & Pandit, 2004). The disadvantages of AOPs include high energy consumption, narrow operating pH range and formation of some by-products (Babuponnusami & Muthukumar, 2014).

The energy consumption of AOPs is a major component of operating costs. Energy consumption depends on the type of AOP, reactor design and operating parameters (Gogate & Pandit, 2004). Some strategies that can be used to reduce energy consumption include catalysts, reactor optimization and hybrid systems (Babuponnusami & Muthukumar, 2014). Using catalysts can increase the reaction rate and efficiency by increasing the production of hydroxyl radicals. Reactor optimization can improve energy efficiency by improving geometry, fluid dynamics, and distribution. On the other hand, hybrid systems can create synergistic effects by combining AOPs with other treatment methods (Rizzo et al., 2019).

In conclusion, AOPs are effective for treating landfill leachate but require high energy. Finding a tradeoff between energy consumption and processing efficiency is critical to the viability of AOPs. Strategies such as catalyst use, reactor optimization and hybrid systems can be used to increase energy efficiency.

5. Conclusion

This study investigated landfill leachate properties, environmental effects and treatment methods. Studies show that the fate of pollutants such as endocrine-disrupting compounds in leachate is not fully known and requires further research. Landfill cannot fully prevent the effects of leachate on soil and water resources, and existing practices need to be improved. The performance of commonly used materials such as geotextile should be further improved. In addition, more data should be collected on the analysis of leachate samples from landfills and the amount and spread of contaminants.

Landfilling can only partially prevent the effects of leachate on soil and water resources. Therefore, improving the existing practices used in leachate management is necessary and finding more effective solutions is necessary. Using geotextiles and similar materials is common, but it is important to improve their performance further. The efficiency and durability of these materials in leachate management should be increased.

More research needs to be done on the environmental impacts of municipal solid waste incineration residues. Disposing combustion residues raises concerns about releasing pollutants into the atmosphere and storing residues. More work should be done to improve this process's environmental impacts and disposal methods. More sustainable waste management solutions should focus on energy generation and recycling alternatives.

New methods and materials created to treat municipal wastewater can also be utilized to treat landfill leachate since wastewater and leachate both contain comparable contaminants. However, leachate contains pollutants in concentrations that increase over time. Therefore, selecting advanced technologies and materials must be carefully and strategically applied at each stage. The efficiency of the treatment systems should be increased and aimed to purify the leachate completely.

Treatment methods include leachate treatment, conventional adsorbents, coagulation/flocculation processes, membrane technologies and biodegradation. However, more than these methods is required. Therefore, it is important to combine and integrate different methods. Innovative technologies such as advanced oxidation processes also need to be explored. Enhancing the physicochemical characteristics of traditional adsorbents may enable effective leachate treatment performance. The regeneration capacity of adsorbents is an important factor for successful application. In addition, developing conventional coagulation/flocculation processes and membrane technologies may enable alternative methods in leachate treatment.

Current biodegradation approaches alone do not offer an adequate solution. For this reason, different technologies need to be used together and integrated. Combining different treatment methods should establish a more effective and efficient leachate treatment process. This will result in more effective removal of pollutants, thereby reducing environmental impacts.

Consequently, more research and development work on landfill leachate management and treatment is required. This will reduce environmental impacts, create a sustainable waste management system, and protect human health. Researchers, governments, and industry stakeholders should collaborate on this issue to develop more effective solutions and take steps for a sustainable future.

References

Abbas, A. A., Jingsong, G., Ping, L. Z., Ya, P. Y., & Al-Rekabi, W. S. (2009). Review on LandWll leachate treatments. *Journal of Applied Sciences Research*, 5(5), 534-545.

Abd El-Salam, M. M., & Abu-Zuid, G. I. (2015). Impact of landfill leachate on the groundwater quality: A case study in Egypt. *Journal Of Advanced Research*, 6(4), 579-586.

Abdel-Fatah, M. A. (2018). Nanofiltration systems and applications in wastewater treatment. *Ain Shams Engineering Journal*, 9(4), 3077-3092.

Abdel-Shafy, H. I., & Mansour, M. S. (2018). Solid waste issue: Sources, composition, disposal, recycling, and valorization. *Egyptian Journal of Petroleum*, 27(4), 1275-1290.

Abood, A. R., Bao, J., Abudi, Z. N., Zheng, D., & Gao, C. (2013). Pretreatment of nonbiodegradable landfill leachate by air stripping coupled with agitation as ammonia stripping and coagulation–flocculation processes. *Clean Technologies and Environmental Policy*, 15(6), 1069-1076. https://link.springer.com/article/10.1007/s10098-012-0575-1

Abu Amr, S.S., Aziz, H.A. (2012). New treatment of stabilized leachate by ozone/Fenton in the advanced oxidation process. *Waste Management*, 32(9):1693–1698. https://doi. org/ 10. 1016/j. wasman. 2012. 04. 009

Abu Amr, S.S., Aziz, H.A., Adlan, M.N. (2013). Optimization of stabilized leachate treatment using ozone/persulfate in the advanced oxidation process. *Waste Management*, 33(6):1434–1441. https:// doi. org/ 10. 1016/j. wasman. 2013. 01. 039

Ahmed, F.N., Lan, C.Q., (2012). Treatment of landfill leachate using membrane bioreactors: A review. Desalination 287, 41–54.

Alemayehu, T., Mebrahtu, G., Hadera, A., & Bekele, D. N. (2019). Assessment of the impact of landfill leachate on groundwater and surrounding surface water: a case study of Mekelle city, Northern Ethiopia. *Sustainable Water Resources Management*, 5, 1641-1649.

Amaral, M. C., Moravia, W. G., Lange, L. C., Zico, M. R., Magalhães, N. C., Ricci, B. C., & Reis, B. G. (2016). Pilot aerobic membrane bioreactor and nanofiltration for municipal landfill leachate treatment. *Journal of Environmental Science and Health, Part A*, 51(8), 640-649.

Ameta, S. C., & Ameta, R. (Eds.). (2018). Advanced oxidation processes for wastewater treatment: emerging green chemical technology. *Academic press*.

Amr, S. S. A., & Zainol, N. A. B. (2016). Chemical Treatment Technologies for Landfill Leachate. In Control and Treatment of Landfill Leachate for Sanitary Waste Disposal (pp. 286-314). IGI Global.

Anqi, T., Zhang, Z., Suhua, H., & Xia, L. (2020, September). Review on landfill leachate treatment methods. In IOP Conference Series: Earth and Environmental Science (Vol. 565, No. 1, p. 012038). IOP Publishing.

Ateş, H., & Argun, M. E. (2021). Advanced oxidation of landfill leachate: removal of micropollutants and identification of by-products. *Journal of Hazardous Materials*, 413, 125326.

Atmaca K., & Beyazit N. (2022). İleri oksidasyon proseslerinin sızıntı sularının arıtımında kullanımı. *Sinop Üniversitesi Fen Bilimleri Dergisi*, 7(2), 173-187. https://doi.org/10.33484/sinopfbd.11621453

Atmaca, K., & Beyazıt, N. (2021). Sızıntı suyundan foto-elektro-Fenton yöntemi ile KOİ ve Renk giderimi üzerine akım yoğunluğu ve pH etkisi. *Niğde Ömer Halisdemir Üniversitesi Mühendislik Bilimleri Dergisi*, 10(1), 33-37.

Augusto, P. A., Castelo-Grande, T., Merchan, L., Estevez, A. M., Quintero, X., & Barbosa, D. (2019). Landfill leachate treatment by sorption in magnetic particles: preliminary study. *Science of the Total Environment*, 648, 636-668. https://doi.org/10.1016/j.scitotenv.2018.08.056.

Aziz, A., Agamuthu, P., & Fauziah, S. H. (2018). Removal of bisphenol A and 2, 4-Di-tert-butylphenol from landfill leachate using plant-based coagulant. *Waste Management & Research*, 36(10), 975-984.

Babuponnusami, A., & Muthukumar, K. (2014). A review on Fenton and improvements to the Fenton process for wastewater treatment. *Journal of Environmental Chemical Engineering*, 2(1), 557–572. https://doi.org/10.1016/j.jece.2013.10.011

Baderna, D., Caloni, F., & Benfenati, E. (2019). Investigating landfill leachate toxicity in vitro: A review of cell models and endpoints. *Environment International*, 122, 21-30.

Bandala, E. R., Liu, A., Wijesiri, B., Zeidman, A. B., & Goonetilleke, A. (2021). Emerging materials and technologies for landfill leachate treatment: A critical review. *Environmental Pollution*, 291, 118133.

Bhalla, B., Saini, M. S., & Jha, M. K. (2013). Effect of age and seasonal variations on leachate characteristics of municipal solid waste landfill. *International Journal of Research in Engineering and Technology*, 2(8), 223-232.

Bohdziewicz, J., Neczaj, E., Kwarciak, A. (2008). Landfill leachate treatment by means of anaerobic membrane bioreactor. *Desalination*, 221(1-3), 559-565.

Bonmati, A. & Flotats, X. (2003). Air stripping of ammonia from pig slurry: characterisation and feasibility as a pre- or post-treatment to mesophilic anaerobic digestion. *Waste Management,* 23, 261–272.

Boonyaroj, V., Chiemchaisri, C., Chiemchaisri, W., & Yamamoto, K. (2017). Enhanced biodegradation of phenolic compounds in landfill leachate by enriched nitrifying membrane bioreactor sludge. *Journal of Hazardous Materials*, 323, 311-318.

Bove, D., Merello, S., Frumento, D., Arni, S. A., Aliakbarian, B., & Converti, A. (2015). A critical review of biological processes and technologies for landfill leachate treatment. *Chemical Engineering & Technology*, 38(12), 2115-2126.

Brillas, E., & Garcia-Segura, S. (2020). Benchmarking recent advances and innovative technology approaches of Fenton, photo-Fenton, electro-Fenton, and related processes: A review on the relevance of phenol as model molecule. *Separation and Purification Technology*, 237, 116337. https:// doi.org/ 10. 1016/j.seppur.2019.116337

Brillas, E., Sirés, I., & Oturan, M. A. (2009). Electro-Fenton process and related electrochemical technologies based on Fenton's reaction chemistry. *Chemical Reviews*, 109(12), 6570-6631.

Canziani, R., Emondi, V., Garavaglia, M., Malpei, F., Pasinetti, E., Buttiglieri, G. (2006). Effect of oxygen concentration on biological nitrification and microbial kinetics in a cross-flow membrane bioreactor (MBR) and moving-bed biofilm reactor (MBBR) treating old landfill leachate. *Journal of Membrane Science*, 286(1-2), 202-212.

Charerntanyarak, L. (1999). Heavy metals removal by chemical coagulation and precipitation. *Water Science and Technology*, 39(10-11), 135-138.

Chen, W., Wang, F., He, C., & Li, Q. (2020b). Molecular-level comparison study on microwave irradiation-activated persulfate and hydrogen peroxide processes for the treatment of refractory organics in mature landfill leachate. *Journal of Hazardous Materials*, 397, 122785. https:// doi. org/ 10. 1016/j. jhazm at. 2020. 122785

Chen, G., Wu, G., Li, N., Lu, X., Zhao, J., He, M., ... & Wang, S. (2021). Landfill leachate treatment by persulphate related advanced oxidation technologies. *Journal of Hazardous Materials*, 418, 126355.

Chen, W. & Li, Q. (2020a). Elimination of UV-quenching substances from MBR- and SAARB treated mature landfill leachates in an ozonation process: a comparative study. *Chemosphere,* 242, 125256.

Chen, W., Liu, X.Y., Huang, B.C., Wang, L.F., Yu, H.Q., Mizaikoff, B. (2016). Probing membrane fouling via infrared attenuated total reflection mapping coupled with multivariate curve resolution. *Chemphyschem*, 17, 358–363.

Chen, W., Zhang, A., Gu, Z., & Li, Q. (2018). Enhanced degradation of refractory organics in concentrated landfill leachate by Fe0/H2O2 coupled with microwave irradiation. *Chemical Engineering Journal*, 354, 680-691. https://doi.org/10.1016/j.cej.2018.08.012.

Chen, W., Zhuo, X., He, C., Shi, Q., & Li, Q. (2020b). Molecular investigation into the transformation of dissolved organic matter in mature landfill leachate during treatment in a combined membrane bioreactor-reverse osmosis process. *Journal of Hazardous Materials*, 397, 122759.

Cherni Y., Elleuch L., Messaoud M., Kasmi M., Chatti A., Trabelsi I. (2021). Recent technologies for leachate treatment: a review. *Euro-Mediterranean Journal for Environmental Integration*, 6:79, (1-20).

Chiu, T.Y., James, A.E. (2006). Sustainable flux enhancement in non-circular ceramic membranes on wastewater using the Fenton process. *Journal of Membrane Science*, 279(1-2), 347-353.

Chong, M. N., Jin, B., Chow, C. W., & Saint, C. (2010). Recent developments in photocatalytic water treatment technology: a review. *Water Research*, 44(10), 2997-3027. https://doi.org/10.1016/j.watres.2010.02.039.

Chou, Y. C., Lo, S. L., Kuo, J., & Yeh, C. J. (2015). Microwave-enhanced persulfate oxidation to treat mature landfill leachate. *Journal of Hazardous Materials*, 284, 83-91. https:// doi. org/ 10. 1016/j. jhazm at. 2014. 10. 043

Chugh, S., Clarke, W., Pullammanappallil, P., & Rudolph, V. (1998). Effect of recirculated leachate volume on MSW degradation. *Waste Management & Research*, 16(6), 564-573.

Coffin, E. S., Reeves, D. M., & Cassidy, D. P. (2022). PFAS in Municipal Solid Waste Landfills: Sources, Leachate Composition, Chemical Transformations, and Future Challenges. *Current Opinion in Environmental Science & Health*, 100418.

Costa, A. M., Alfaia, R. G. D. S. M., & Campos, J. C. (2019). Landfill leachate treatment in Brazil–An overview. *Journal of Environmental Management*, 232, 110-116.

Dabaghian, Z., Peyravi, M., Jahanshahi, M., & Rad, A. S. (2018). Potential of advanced nano-structured membranes for landfill leachate treatment: a review. *ChemBioEng Reviews*, 5(2), 119-138.

De Almeida, R., Porto, R. F., Quintaes, B. R., Bila, D. M., Lavagnolo, M. C., & Campos, J. C. (2023). A review on membrane concentrate management from landfill leachate treatment plants: The relevance of resource recovery to close the leachate treatment loop. *Waste Management & Research,* 41(2), 264-284.

De Brito, R. A., Filho, H. J. I., Aguiar, L. G., de Alcântara, M. A. K., Siqueira, A. F., & da Rós, P. C. M. (2019). Degradation kinetics of landfill leachate by continuous-flow catalytic ozonation. *Industrial & Engineering Chemistry Research*, 58(23), 9855-9863.

De Oliveira, M. S., da Silva, L. F., Barbosa, A. D., Romualdo, L. L., Sadoyama, G., & Andrade, L. S. (2019). Landfill leachate treatment by combining coagulation and advanced electrochemical oxidation techniques. *ChemElectroChem*, 6(5), 1427-1433.

De, S., Hazra, T., & Dutta, A. (2019a). Sustainable treatment of municipal landfill leachate by combined association of air stripping, Fenton oxidation, and enhanced coagulation. *Environmental Monitoring and Assessment*, 191, 1-14.

De, S., Hazra, T., & Dutta, A. (2019b). Treatment of landfill leachate by integrated sequence of air stripping, coagulation–flocculation and adsorption. Environment, *Development and Sustainability*, 21, 657-677.

Deng Y. & Zhao R. (2015). Advanced oxidation processes (AOPs) in wastewater treatment. *Current Pollution Reports*, 1: 167–176.

Deng, Y., Jung, C., Zhao, R., Torrens, K., & Wu, L. (2018). Adsorption of UV-quenching substances (UVQS) from landfill leachate with activated carbon. *Chemical Engineering Journal*, 350, 739-746.

Dia, O., Drogui, P., Buelna, G., & Dubé, R. (2018). Hybrid process, electrocoagulation-biofiltration for landfill leachate treatment. *Waste Management*, 75, 391-399.

Djeffal, K., Bouranene, S., Fievet, P., Déon, S., & Gheid, A. (2021). Treatment of controlled discharge leachate by coagulation-flocculation: influence of operational conditions. *Separation Science and Technology*, 56(1), 168-183.

Dong, C., Chen, W., Liu, C., Liu, Y., & Liu, H. (2014b). Synthesis of magnetic chitosan nanoparticle and its adsorption property for humic acid from aqueous solution. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 446, 179-189.

Duran, E. B., & Cuci Y. (2016). Katı atık düzenli depolama sahası sızıntı suyunun Kimyasal ve Elektrokimyasal Arıtım Yöntemlerle Arıtılabilirliğinin araştırılması. *Kahramanmaraş Sütçü İmam Üniversitesi Mühendislik Bilimleri Dergisi*, 19(2), 104-110.

Erabee, I. K., Ahsan, A., Jose, B., Aziz, M. M. A., Ng, A.W. M., Idrus, S., & Daud, N. N. N. (2018). Adsorptive treatment of landfill leachate using activated carbon modified with three different methods. *KSCE Journal of Civil Engineering*, 22, 1083-1095.

Ertugay, N. & Acar, F.N. (2014). Sıfır Değerlikli Demir Kullanılarak Fenton Benzeri Oksidasyon Yöntemi İle Azo Boyar Madde Giderimi. *DEÜ Mühendislik Fakültesi Mühendislik Bilimleri Dergisi*, 16 (1):1-9.

Ertugay, N., Malkoç, E., & Kocakaplan, N. (2017). Sızıntı Suyundan Fenton-Benzeri Prosesi İle Kimyasal Oksijen İhtiyacı ve Renk Giderimine ZVI ve H2O2 Konsantrasyonlarının Etkisi. *KSÜ Doğa Bilimleri Dergisi*, 20(4), 320-325.

Esfahani, A. R., Zhai, L., & Sadmani, A. A. (2021). Removing heavy metals from landfill leachate using electrospun polyelectrolyte fiber mat-laminated ultrafiltration membrane. *Journal of Environmental Chemical Engineering*, 9(4), 105355.

Fang, D., Wang, J., Cui, D., Dong, X., Tang, C., Zhang, L., & Yue, D. (2021). Recent advances of landfill leachate treatment. *Journal of the Indian Institute of Science*, 101(3), 685–724

Fernandes, A., Pacheco, M. J., Ciríaco, L., & Lopes, A. J. A. C. B. E. (2015). Review on the electrochemical processes for the treatment of sanitary landfill leachates: present and future. *Applied Catalysis B: Environmental*, 176, 183-200.

Ferraz, F. M., & Yuan, Q. (2020). Organic matter removal from landfill leachate by adsorption using spent coffee grounds activated carbon. *Sustainable Materials and Technologies*, 23, e00141.

Foo, K. Y., & Hameed, B. H. (2009). An overview of landfill leachate treatment via activated carbon adsorption process. *Journal of Hazardous Materials*, 171(1-3), 54-60.

Foo, K. Y., & Hameed, B. H. (2010). Insights into the modeling of adsorption isotherm systems. *Chemical Engineering Journal*, 156(1), 2-10.

Fu, F., & Wang, Q. (2011). Removal of Heavy Metal Ions from Wastewaters: A Review. *Journal of Environmental Management*, 92(3), 407-418.

Gao, J., Oloibiri, V., Chys, M., Audenaert, W., Decostere, B., He, Y., Van Langenhove, H., Demeestere, K., Van Hulle, S.W. (2015). The present status of landfill leachate treatment and its development trend from a technological point of view. *Reviews in Environmental Science and Bio/Technology*, 14, 93–122.

Gao, Y. Q., Gao, N. Y., Deng, Y., Yang, Y. Q., & Ma, Y. (2012). Ultraviolet (UV) light-activated persulfate oxidation of sulfamethazine in water. *Chemical Engineering Journal*, 195, 248-253.

Ghafari, S., Aziz, H. A., Isa, M. H., & Zinatizadeh, A. A. (2009). Application of response surface methodology (RSM) to optimize coagulation–flocculation treatment of leachate using poly-aluminum chloride (PAC) and alum. *Journal of Hazardous Materials*, 163(2-3), 650-656.

Ghahrchi, M., & Rezaee, A. (2020). Electro-catalytic ozonation for improving the biodegradability of mature landfill leachate. *Journal of Environmental Management*, 254, 109811.

Ghanbari, F., Wu, J., Khatebasreh, M., Ding, D., & Lin, K. Y. A. (2020). Efficient treatment for landfill leachate through sequential electrocoagulation, electrooxidation and PMS/UV/CuFe2O4 process. *Separation and Purification Technology*, 242, 116828.

Ghernaout, D., Naceur, M. W., & Aouabed, A. (2011). On the dependence of chlorine by-products generated species formation of the electrode material and applied charge during electrochemical water treatment. *Desalination*, 270(1-3), 9-22.

Gogate, P. R., & Pandit, A. B. (2004). A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions. *Advances in Environmental Research*, 8(3–4), 501–551. https://doi.org/10.1016/S1093-0191(03)00032-7

Gorito, A. M., Pesqueira, J. F., Moreira, N. F., Ribeiro, A. R., Pereira, M. F. R., Nunes, O. C., ... & Silva, A. M. (2021). Ozone-based water treatment (O3, O3/UV, O3/H2O2) for removal of organic micropollutants, bacteria inactivation and regrowth prevention. *Journal of Environmental Chemical Engineering*, 9(4), 105315.

Gripa, E., Daflon, S. D. A., de Almeida, R., da Fonseca, F. V., & Campos, J. C. (2023). Landfill Leachate Treatment by Membrane-based and Advanced Oxidation Techniques with a focus on Ecotoxicity and By-products Management: A Review. *Process Safety and Environmental Protection*.

Guo, J. S., Abbas, A. A., Chen, Y. P., Liu, Z. P., Fang, F., & Chen, P. (2010) Treatment of landfill leachate using a combined stripping, Fenton, SBR, and coagulation process. *Journal of Hazardous Materials*, 178(1-3), 699-705. https:// doi. org/ 10. 1016/j.jhazm at. 2010. 01. 144

Gupta, A., Zhao, R., Novak, J.T., Douglas Goldsmith, C. (2014). Application of Fenton's reagent as a polishing step for removal of UV quenching organic constituents in biologically treated landfill leachates. *Chemosphere*, 105, 82–86. https:// doi. org/ 10. 1016/j. chemo sphere. 2013. 12. 066

He, P., Chen, L., Shao, L., Zhang, H., & Lü, F. (2019). Municipal solid waste (MSW) landfill: A source of microplastics?-Evidence of microplastics in landfill leachate. *Water Research*, 159, 38-45.

He, P. J., Xue, J. F., Shao, L. M., Li, G. J., & Lee, D. J. (2006). Dissolved organic matter (DOM) in recycled leachate of bioreactor landfill. *Water Research*, 40(7), 1465-1473.

He, Y., Zhang, H., Li, J., Zhang, Y., Lai, B., & Pan, Z. (2018). Treatment of landfill leachate reverse osmosis concentrate from by catalytic ozonation with γ-Al2O3. *Environmental Engineering Science*, 35(5), 501-511.

Hilles, A. H., Amr, S. S. A., Hussein, R. A., El-Sebaie, O. D., & Arafa, A. I. (2016). Performance of combined sodium persulfate/H2O2 based advanced oxidation process in stabilized landfill leachate treatment. *Journal of Environmental Management*, 166, 493-498.

Jung, C., Deng, Y., Zhao, R., & Torrens, K. (2017). Chemical oxidation for mitigation of UV-quenching substances (UVQS) from municipal landfill leachate: Fenton process versus ozonation. *Water Research*, 108, 260-270. https://doi. org/ 10. 1016/j. watres. 2016. 11. 005

Kamaruddin, M. A., Abdullah, M. M. A., Yusoff, M. S., Alrozi, R., & Neculai, O. (2017, June). Coagulation-flocculation process in landfill leachate treatment: focus on coagulants and coagulants aid. In IOP conference series: materials science and engineering (Vol. 209, No. 1, p. 012083). IOP Publishing.

Kang, Y. W., & Hwang, K. Y. (2000). Effects of reaction conditions on the oxidation efficiency in the Fenton process. *Water Research*, 34(10), 2786-2790. https:// doi. org/ 10. 1016/S0043- 1354(99) 00388-7

Karimipourfard, D., Eslamloueyan, R., & Mehranbod, N. (2019). Novel heterogeneous degradation of mature landfill leachate using persulfate and magnetic CuFe2O4/RGO nanocatalyst. *Process Safety and Environmental Protection*, 131, 212-222. https://doi.org/10.1016/j.psep.2019.09.009.

Kim, D., Ryu, H. D., Kim, M. S., Kim, J., & Lee, S. I. (2007). Enhancing struvite precipitation potential for ammonia nitrogen removal in municipal landfill leachate. *Journal of Hazardous Materials*, 146(1-2), 81-85.

Kjeldsen, P., Barlaz, M., Rooker, A., Baun, A., Ledin, A. and Christensen, T. (2002). Present and long-term composition of MSW landfill leachate: a review. *Critical Reviews in Environmental Science and Technology*, 32(4), pp.297-336.

Ko, J. H., Wang, Q., Yuan, T., Wu, H., & Xu, Q. (2019). Geotextile clogging at different stages of municipal solid waste landfills co-disposed with bottom ash. *Science of the Total Environment*, 687, 161-167.

Jakopovic, H. K., Matosic, M., Muftic, M., Curlin, M., & Mijatovic, I. (2008). Treatment of landfill leachate by ozonation, ultrafiltration, nano-filtration and membrane bioreactor. *Fresenius Environmental Bulletin*, 17(6), 687-695.

Kundu, A., Reddy, C. V., Singh, R. K., & Kalamdhad, A. S. (2023). Critical review with science mapping on the latest pre-treatment technologies of landfill leachate. *Journal of Environmental Management,* 336, 117727.

Kurniawan, T. A., Lo, W. H., & Chan, G. Y. (2006). Physico-chemical treatments for removal of recalcitrant contaminants from landfill leachate. *Journal of Hazardous Materials*, 129(1-3), 80-100.

Li, W., Hua, T., Zhou, Q., Zhang, S. & Li, F. (2010). Treatment of stabilized landfill leachate by the combined process of coagulation/flocculation and powder activated carbon adsorption. *Desalination*, 264, 56–62.

Li, Y., Park, S. Y., & Zhu, J. (2011). Solid-state anaerobic digestion for methane production from organic waste. *Renewable and Sustainable Energy Reviews*, 15(1), 821-826.

Lim, E. W. (1999). Effect of Landfill Leachate on Groundwater Quality (Doctoral dissertation, Universiti Putra Malaysia).

Lin, C. C., & Wu, M. S. (2014). Degradation of ciprofloxacin by UV/ S2O82− process in a large photoreactor. *Journal of Photochemistry and Photobiology A: Chemistry*, 285, 1-6.

Lin, D., Bai, L., Gan, Z., Zhao, J., Li, G., Aminabhavi, T. M., & Liang, H. (2020). The role of ferric coagulant on gypsum scaling and ion interception efficiency in nanofiltration at different pH values: performance and mechanism. *Water Research*, 175, 115695.

Lindamulla, L., Nanayakkara, N., Othman, M., Jinadasa, S., Herath, G., & Jegatheesan, V. (2022). Municipal Solid Waste Landfill Leachate Characteristics and Their Treatment Options in Tropical Countries. *Current Pollution Reports*, 8(3), 273-287.

Liu, Z., Wu, W., Shi, P., Guo, J., & Cheng, J. (2015). Characterization of dissolved organic matter in landfill leachate during the combined treatment process of air stripping, Fenton, SBR and coagulation. *Waste Management*, 41, 111-118.

Lu, M. C., Chen, Y. Y., Chiou, M. R., Chen, M. Y., & Fan, H. J. (2016). Occurrence and treatment efficiency of pharmaceuticals in landfill leachates. *Waste Management*, 55, 257-264.

Luo, H., Zeng, Y., Cheng, Y., He, D., & Pan, X. (2020). Recent advances in municipal landfill leachate: A review focusing on its characteristics, treatment, and toxicity assessment. *Science of the Total Environment*, 703, 135468.

Luo, H. W., Chen, J. J., Sheng, G. P., Su, J. H., Wei, S. Q., & Yu, H. Q. (2014). Experimental and theoretical approaches for the surface interaction between copper and activated sludge microorganisms at molecular scale. *Scientific Reports*, 4(1), 7078.

Luo, Y., Li, R., Sun, X., Liu, X., Li, D. (2019). The roles of phosphorus species formed in activated biochar from rice husk in the treatment of landfill leachate. *Bioresource Technol*. 288, 121533.

Ma, S., Zhou, C., Pan, J., Yang, G., Sun, C., Liu, Y., ... & Zhao, Z. (2022). Leachate from municipal solid waste landfills in a global perspective: Characteristics, influential factors and environmental risks. *Journal of Cleaner Production*, 333, 130234.

Maheswari, V. G., Ajisha, M. A. T., & Christopher, J. J. (2022). Municipal solid waste leachate treatment using ultrasonication microwave & Ozonation combined Fenton process. *Australian Journal of Civil Engineering*, 20(1), 147-155.

Metcalf, L., Eddy, H.P. (2003) Wastewater engineering treatment and reuse. McGraw-Hill, New York

Miao, L., Yang, G., Tao, T., & Peng, Y. (2019). Recent advances in nitrogen removal from landfill leachate using biological treatments–A review. *Journal of Environmental Management*, 235, 178-185.

Mirbagheri, S. A., & Hosseini, S. N. (2005). Pilot plant investigation on petrochemical wastewater treatmentfor the removal of copper and chromium with the objective of reuse. *Desalination*, 171(1), 85-93.

Mollah, M. Y., Morkovsky, P., Gomes, J. A., Kesmez, M., Parga, J., & Cocke, D. L. (2004). Fundamentals, present and future perspectives of electrocoagulation. *Journal of Hazardous Materials*, 114(1-3), 199-210.

Moradi, M. & Ghanbari, F. (2014). Application of response surface method for coagulation process in leachate treatment as pretreatment for Fenton process: Biodegradability improvement. *Journal of Water Process Engineering*, 4, 67–73.

Moravia, W. G., Amaral, M. C., & Lange, L. C. (2013). Evaluation of landfill leachate treatment by advanced oxidative process by Fenton's reagent combined with membrane separation system. *Waste Management*, 33(1), 89-101.

Nawrocki, J., & Kasprzyk-Hordern, B. (2010). The efficiency and mechanisms of catalytic ozonation. *Applied Catalysis B: Environmental,* 99(1-2), 27-42.

Neyens, E., & Baeyens, J. (2003). A review of classic Fenton's peroxidation as an advanced oxidation technique. *Journal of Hazardous Materials,* 98(1-3), 33-50. https://doi.org/10.1016/S0304-3894(02)00282-0.

Nika, M. C., Ntaiou, K., Elytis, K., Thomaidi, V. S., Gatidou, G., Kalantzi, O. I., ... & Stasinakis, A. S. (2020). Wide-scope target analysis of emerging contaminants in landfill leachates and risk assessment using Risk Quotient methodology. *Journal of Hazardous Materials*, 394, 122493. https://doi.org/10.1016/j.jazmat.2020.122493.

Özçelik, D. (2022). Katı atık düzenli depolama tesisi sızıntı sularının foto-fenton prosesiyle arıtılabilirliğinin araştırılması (Master›s thesis, Nevşehir Hacı Bektaş Veli Üniversitesi).

Parthenidis P., Evgenidou E., Lambropoulou D. (2023). Landfill leachate treatment by hydroxyl and sulfate radical-based advanced oxidation processes (AOPs). *Journal of Water Process Engineering*, 53: 103768

Poblete, R., Oller, I., Maldonado, M. I., & Cortes, E. (2019). Improved landfill leachate quality using ozone, UV solar radiation, hydrogen peroxide, persulfate and adsorption processes. *Journal of Environmental Management*, 232, 45-51.

Polatidou, E., Azis, K., Polatides, C., Remmas, N., Ntougias, S., & Melidis, P. (2022). Evaluation of electrochemical and O3/UV/H2O2 methods at various combinations during treatment of mature landfill leachate. *Journal of Environmental Science and Health, Part A*, 57(4), 298-305.

Ramaswami, S., Behrendt, J. & Otterpohl, R. (2018). Comparison of NF-RO and RO-NF for the treatment of mature landfill leachates: a guide for landfill operators. *Membranes,* 8, 17.

Rathnayake, P., & Herath, G. B. (2018, December). A review of leachate treatment techniques. In The 9th International Conference on Sustainable Built Environment (pp. 7-106).

Rehman, F., Sayed, M., Khan, J. A., Shah, N. S., Khan, H. M., & Dionysiou, D. D. (2018). Oxidative removal of brilliant green by UV/S2O82–, UV/HSO5– and UV/H2O2 processes in aqueous media: a comparative study. *Journal of Hazardous Materials*, 357, 506-514.

Rekhate, C. V., & Srivastava, J. K. (2020). Recent advances in ozone-based advanced oxidation processes for treatment of wastewater-A review. *Chemical Engineering Journal Advances*, 3, 100031.

Renou, S., Givaudan, J.G., Poulain, S., Dirassouyan, F., Moulin, P. (2008). Landfill leachate treatment: Review and opportunity. *Journal of Hazardous Materials*, 150(3), 468-493.

Reshadi M.A.M., Bazargan A., McKay G. (2020). A review of the application of adsorbents for landfill leachate treatment: focus on magnetic adsorption. *Science of The Total Environment,* 731:138863.

Rezapour, S., Samadi, A., Kalavrouziotis, I. K., & Ghaemian, N. (2018). Impact of the uncontrolled leakage of leachate from a municipal solid waste landfill on soil in a cultivated-calcareous environment. *Waste Management*, 82, 51-61.

Rizzo, L., Gernjak, W., Krzeminski, P., Malato, S., McArdell, C. S., Perez, J. A. S., ... & Fatta-Kassinos, D. (2020). Best available technologies and treatment trains to address current challenges in urban wastewater reuse for irrigation of crops in EU countries. *Science of the Total Environment*, 710, 136312. https://doi.org/10.1016/j.scitotenv.2019.136312

Rodríguez, D. C., Pino, N., & Peñuela, G. (2011). Monitoring the removal of nitrogen by applying a nitrification–denitrification process in a Sequencing Batch Reactor (SBR). *Bioresource Technology*, 102(3), 2316-2321.

Rodriguez-Narvaez, O. M., Goonetilleke, A., Perez, L., & Bandala, E. R. (2021). Engineered technologies for the separation and degradation of microplastics in water: A review. *Chemical Engineering Journal*, 414, 128692.

Salam, M., & Nilza, N. (2021). Hazardous components of landfill leachates and its bioremediation. In Soil Contamination-Threats and Sustainable Solutions. IntechOpen.

San-Pedro, L., Méndez-Novelo, R., Hernández-Núñez, E.,Flota-Bañuelos, M., Medina, J., & Giacomán-Vallejos, G. (2020). Selection of the activated carbon type for the treatment of landfill leachate by fenton-adsorption process. *Molecules*, 25(13), 3023.

Santos, H. A. P., Castilhos Júnior, A. B., Nadaleti, W. C., & Lourenço, V. A. (2020). Ammonia recovery from air stripping process applied to landfill leachate treatment. *Environmental Science and Pollution Research*, 27(36), 45108-45120. https://link.springer.com/article/10.1007/s11356-020-10397-9

Sauve, G., & Van Acker, K. (2020). The environmental impacts of municipal solid waste landfills in Europe: A life cycle assessment of proper reference cases to support decision making. *Journal of Environmental Management*, 261, 110216.

Schlegel, S. (1988). The use of submerged biological filters for nitrification. *Water Science and Technology*, 20(4-5), 177-187.

Setiadi, T., & Fairus, S. (2003). Hazardous waste landfill leachate treatment using an activated sludge-membrane system. *Water Science and Technology*, 48(8), 111-117.

Sewwandi, B. G. N., Takahiro, K., Kawamoto, K., Hamamoto, S., Asamoto, S., & Sato, H. (2012). Characterization of landfill leach ate from municipal solid wastes landfills in Sri Lanka.

Sharma, V., & Gupta, R. (2022). Biomass Digestion for Production of Electrical Energy. In Sustainable and Clean Energy Production Technologies (pp. 151-178). Singapore: Springer Nature Singapore.

Siddiqi, S. A., Al-Mamun, A., Baawain, M. S., & Sana, A. (2022). A critical review of the recently developed laboratory-scale municipal solid waste landfill leachate treatment technologies. *Sustainable Energy Technologies and Assessments*, 52, 102011.

Sruthi, T., Gandhimathi, R., Ramesh, S.T., Nidheesh, P.V. (2018) Stabilized landfill leachate treatment using heterogeneous Fenton and electro-Fenton processes. *Chemosphere*, 210:38–43. https:// doi. org/ 10. 1016/j. chemosphere. 2018. 06. 172

Tauchert, E., Schneider, S., de Morais, J.L., Peralta-Zamora, P. (2006). Photochemically-assisted electrochemical degradation of landfill leachate. *Chemosphere*, 64(9), 1458-1463.

Tchobanoglous, G., Burton, F.L., Stensel, H.D. (2003) Wastewater engineering: treatment and reuse, 4th edn. Metcalf and Eddy, Inc, McGraw-Hill, Boston

Tee, P. F., Abdullah, M. O., Tan, I. A. W., Rashid, N. K. A., Amin, M. A. M., Nolasco-Hipolito, C., & Bujang, K. (2016). Review on hybrid energy systems for wastewater treatment and bio-energy production. *Renewable and Sustainable Energy Reviews*, 54, 235-246.

Teng, C., Zhou, K., Peng, C., ve Chen, W. (2021). Characterization and treatment of landfill leachate: A review. *Water Research*, 117525.

Top, S., Akkaya, G. K., Demir, A., Yıldız, Ş., Balahorli, V., & Bilgili, M. S. (2019). Investigation of leachate characteristics in field-scale landfill test cells. *International Journal of Environmental Research*, 13, 829-842.

Torretta, V., Ferronato, N., Katsoyiannis, I. A., Tolkou, A. K., & Airoldi, M. (2017). Novel and conventional technologies for landfill leachates treatment: A review. *Sustainability*, 9(1), 9.

Trabelsi, I., Sellami, I., Dhifallah, T., Medhioub, K., Bousselmi, L., Ghrabi, A. (2009). Coupling of anoxic and aerobic biological treatment of landfill leachate. *Desalination*, 246(1-3), 506-513.

Umar, M., Aziz, H. A., & Yusoff, M. S. (2010). Trends in the use of Fenton, electro-Fenton and photo-Fenton for the treatment of landfill leachate. *Waste Management*, 30(11), 2113-2121.

Viegas, C., Nobre, C., Mota, A., Vilarinho, C., Gouveia, L., & Gonçalves, M. (2021). A circular approach for landfill leachate treatment: Chemical precipitation with biomass ash followed by bioremediation through microalgae. *Journal of Environmental Chemical Engineering*, 9(3), 105187. https://doi.org/10.1016/j.jece.2021.105187.

Wang, F., Luo, Y., Ran, G., & Li, Q. (2020b). Sequential coagulation and Fe0-O3/H2O2 process for removing recalcitrant organics from semi-aerobic aged refuse biofilter leachate: Treatment efficiency and degradation mechanism. *Science of the Total Environment*, 699, 134371.

Wang, H., Wang, Y. N., Li, X., Sun, Y., Wu, H., & Chen, D. (2016). Removal of humic substances from reverse osmosis (RO) and nanofiltration (NF) concentrated leachate using continuously ozone generation-reaction treatment equipment. *Waste Management*, 56, 271-279.

Wang, J., Bi, L., Ji, Y., Ma, H., & Yin, X. (2014). Removal of humic acid from aqueous solution by magnetically separable polyaniline: Adsorption behavior and mechanism. *Journal of Colloid and Interface Science*, 430, 140-146.

Wang, H., Cheng, Z., Yuan, H., Zhu, N., Lou, Z., & Otieno, P. (2020a). Occurrence of banned and commonly used pesticide residues in concentrated leachate: Implications for ecological risk assessment. *Science of The Total Environment*, 710, 136287.

Wang, X., Chen, S., Gu, X., & Wang, K. (2009). Pilot study on the advanced treatment of landfill leachate using a combined coagulation, fenton oxidation and biological aerated filter process. *Waste Management*, 29(4), 1354-1358. https:// doi. org/ 10. 1016/j. wasman. 2008. 10. 006

Wang, Z., Li, J., Tan, W., Wu, X., Lin, H., & Zhang, H. (2019). Removal of COD from landfill leachate by advanced Fenton process combined with electrolysis. *Separation and Purification Technology*, 208, 3-11.

Wardenier, N., Liu, Z., Nikiforov, A., Van Hulle, S. W., & Leys, C. (2019). Micropollutant elimination by O3, UV and plasma-based AOPs: An evaluation of treatment and energy costs. *Chemosphere*, 234, 715-724.

Wheate, N. J. (2008). Improving platinum (II)-based anticancer drug delivery using cucurbit [n] urils. *Journal of Inorganic Biochemistry*, 102(12), 2060-2066.

Wiszniowski, J., Robert, D., Surmacz-Gorska, J., Miksch, K., & Weber, J. V. (2006). Landfill leachate treatment methods: A review. *Environmental Chemistry Letters*, 4, 51-61.

Wu, H., Wang, Q., Ko, J. H., & Xu, Q. (2018). Characteristics of geotextile clogging in MSW landfills co-disposed with MSWI bottom ash. *Waste Management*, 78, 164-172.

Wu, J.J., Wu C.C., Ma H.W., Chang C.C., (2004). Treatment of landfill leachate by ozone-based advanced oxidation processes, *Chemosphere,* 54, 997–1003.

Xu, J., Long, Y., Shen, D., Feng, H., & Chen, T. (2017). Optimization of Fenton treatment process for degradation of refractory organics in pre-coagulated leachate membrane concentrates. *Journal of Hazardous Materials*, 323, 674-680. https:// doi. org/ 10. 1016/j. jhazm at. 2016. 10. 031

Xu, B., Iskander, S. M., & He, Z. (2020). Dominant formation of unregulated disinfection by-products during electrocoagulation treatment of landfill leachate. *Environmental Research*, 182, 109006.

Yang, Q., Jiang, Y., Li, X., Yang, Y., & Hu, L. (2014). Magnetic-supported cucurbituril: A recyclable adsorbent for the removal of humic acid from simulated water. *Bulletin of Materials Science*, 37, 1167-1174.

Yang, X., Meng, L., & Meng, F. (2019). Combination of self-organizing map and parallel factor analysis to characterize the evolution of fluorescent dissolved organic matter in a full-scale landfill leachate treatment plant. *Science of the Total Environment*, 654, 1187-1195.

Ye, L., Chai, L., Li, Q., Yan, X., Wang, Q., & Liu, H. (2016). Chemical precipitation granular sludge (CPGS) formation for copper removal from wastewater. *RSC advances*, 6(115), 114405-114411.

Ye, Z., Zhang, H., Yang, L., Wu, L., Qian, Y., Geng, J., & Chen, M. (2016). Effect of a solar Fered-Fenton system using a recirculation reactor on biologically treated landfill leachate. *Journal of Hazardous Materials*, 319, 51-60.

Ye, M., Sun, M., Chen, X., Feng, Y., Wan, J., Liu, K., ... & Jiang, X. (2017). Feasibility of sulfate-calcined eggshells for removing pathogenic bacteria and antibiotic resistance genes from landfill leachates. *Waste Management*, 63, 275-283.

Yi, C., He, Z., Hu, Y., Liang, D., Zhang, Y., & Chen, Y. (2021). FeOOH@ MoS2 as a highly effective and stable activator of peroxymonosulfate-based advanced oxidation processes for pollutant degradation. *Surfaces and Interfaces*, 27, 101465.

Yu, X., Sui, Q., Lyu, S., Zhao, W., Liu, J., Cai, Z., ... & Barcelo, D. (2020). Municipal solid waste landfills: an underestimated source of pharmaceutical and personal care products in the water environment. *Environmental Science & Technology*, 54(16), 9757-9768.

Zazouli, M. A., Yousefi, Z., Eslami, A., & Ardebilian, M. B. (2012). Municipal solid waste landfill leachate treatment by fenton, photo-fenton and fenton-like processes: Effect of some variables. *Iranian Journal of Environmental Health Science & Engineering*, 9, 1-9.

Zeng, F., Liao, X., Pan, D., & Shi, H. (2019). Adsorption of dissolved organic matter from landfill leachate using activated carbon prepared from sewage sludge and cabbage by ZnCl2. *Environmental Science and Pollution Research*, 27(5), 4891-4904.

Zhang, H., Wang, Z., Liu, C., Guo, Y., Shan, N., Meng, C., & Sun, L. (2014). Removal of COD from landfill leachate by an electro/Fe2+/peroxydisulfate process. *Chemical Engineering Journal*, 250, 76-82. https:// doi. org/ 10. 1016/j. cej. 2014. 03. 114

Zhang, C., Jiang, S., Tang, J., Zhang, Y., Cui, Y., Su, C., Qu, Y., Wei, L., Cao, H., Quan, J. (2018a). Adsorptive performance of coal based magnetic activated carbon for perfluorinated compounds from treated landfill leachate effluents. *Process Safety and Environmental Protection*, 117, 383–389. https://doi.org/10.1016/j.psep.2018.05.016.

Zhang, C., Jiang, S., Zhang, W. (2018b). Adsorptive performance of coalbased magnetic activated carbon for cyclic volatile methylsiloxanes from landfill leachate. *Environmental Science and Pollution Research*, 25, 4803–4810. https://doi. org/10.1007/s11356-017-0812-6.

Zhang, J., Gong, J. L., Zenga, G. M., Ou, X. M., Jiang, Y., Chang, Y. N., ... & Liu, H. Y. (2016). Simultaneous removal of humic acid/fulvic acid and lead from landfill leachate using magnetic graphene oxide. *Applied Surface Science*, 370, 335-350.

Zhao, J., Lu, X. Q., Luo, J. H., Liu, J. Y., Xu, Y. F., Zhao, A. H., ... & Peng, B. (2013). Characterization of fresh leachate from a refuse transfer station under different seasons. *International Biodeterioration & Biodegradation*, 85, 631-637.

Zhao, J., Ouyang, F., Yang, Y., & Tang, W. (2020). Degradation of recalcitrant organics in nanofiltration concentrate from biologically pretreated landfill leachate by ultraviolet-Fenton method. *Separation and Purification Technology*, 235, 116076.

Zhao, R., Novak, J. T., & Goldsmith, C. D. (2012). Evaluation of on-site biological treatment for landfill leachates and its impact: a size distribution study. *Water Research*, 46(12), 3837-3848.

Zhao, R., Wang, X., Chen, X., & Liu, Y. (2019). Impacts of different aged landfill leachate on PVC corrosion. *Environmental Science and Pollution Research,* 26, 18256-18266.

Zhong, H., Tian, Y., Yang, Q., Brusseau, M. L., Yang, L., & Zeng, G. (2017). Degradation of landfill leachate compounds by persulfate for groundwater remediation. *Chemical Engineering Journal*, 307, 399-407. https:// doi. org/ 10. 1016/j. cej. 2016. 08. 069

CHAPTER IV

PROSPECTS OF BIODIESEL PRODUCTION WITH IMMOBILIZED LIPASES

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1. Introduction

Energy is among the most basic elements of human life. Without sustainable energy sources, the continuation of modern human life is improbable. There are two fundamental reasons for humanity's search for sustainable energy sources. The first is the decreasing amount of petroleum reserves in the world, and the second is the environmental consequences of these fuels (Crookes, Kiannejad, & Nazha, 1997; Roberts, 2004). World petroleum reserves have been declining at accelerated rates due to greater use and the increasing demand for oil in the world (Roberts, 2004; Z. Tan et al., 2022). Therefore, the development of energy efficient systems enabling conservation of existing resources and the use of renewable clean fuel resources are in great need (Crookes et al., 1997).

Alleviating the demand for petroleum based liquid fuels, biomass based fuels such as ethanol, butanol, and biodiesel are most probable alternative liquid fuels obtained from agricultural raw materials by biotechnological transformations (Kaygusuz, 2002). Since biomass based fuels contain various carbon compounds formed by photosynthesis, they are reproducible (renewable) compounds that indirectly contain solar energy (Nigam & Singh, 2011). Various forms of these fuels can be burned directly as liquid fuels or as fuel additives in diesel or gasoline engines (Ali, Hanna, & Leviticus, 1995). Biodiesel fuel is easily obtained from agricultural oils, burns cleaner than petroleum diesel, and does not result in extra carbon dioxide to the environment (Mekala, Potumarthi, Baadhe, & Gupta, 2014). Compared to petroleum based diesel, direct use of biodiesel releases 100% less sulfur, 80% less hydrocarbons, 60% less carbon monoxide and 50% less solid particles and 20% less carbon dioxide to the environment (Aljaafari et al., 2022). Biodiesel with a standard fuel purity does not contain carcinogenic compounds such as carcinogenic benzene derivatives and polycyclic aromatic hydrocarbons with or without nitrogen in fossil diesel exhaust fumes, so biodiesel exhaust gas is less harmful to human health (Sher, 1998; Graboski & McCormick, 1998; Pham, Aljaafari et al., 2022; Nguyen, Imamura, Furuta, & Maeda, 2022). Biodiesel is produced industrially, especially in Europe and North America, and is the most important biofuel with a share of 82% in the European Union (Iso, Chen, Eguchi, Kudo, & Shrestha, 2001; Lai, Zullaikah, Vali, & Ju, 2005). In Brazil, 4.6 million metric tons of biodiesel is produced in 2020 from soybean oil (Parmegiani Marcucci, Zunta Raia, Zanin, & Arroyo, 2023). Biodiesel has the most advantageous position among alternative liquid fuels because it can be easily obtained from the oil in agricultural raw materials, mixed with petroleum diesel at any ratio (Lotero et al., 2005), and used directly as a fuel in diesel engines without requiring any modification (Lin & Lin, 2006; Tesser, Di Serio, Guida, Nastasi, & Santacesaria, 2005). Biodiesel fuel is often attained from the renewable natural resources including plant oils, animal fats, or recycled cooking oil (da Cunha et al., 2009).

2. Biodiesel Production Methods

Renewable biological resources such as vegetable or animal fats and oils can be used as the basic raw material in biodiesel production (Vasistha, Khanra, Clifford, & Rai, 2021). Not to compete for food sources, the majority of biodiesel is made from waste plant oils delivered by stores, restaurants, and industrial food processors. Biodiesel production based on ester exchange (transesterification) of fatty acids on glycerol in triglyceride form with a mono alkyl (alcohol) can be catalyzed by chemical catalysts such as acid, alkali or by biochemical methods with lipase enzymes (Lotero et al., 2005). A typical transesterification reaction of triglyceride with methanol is shown in Fig 1 but the actual reaction takes place in three separate steps. Although it has been stated that the transesterification reaction can occur as a result of the degradation of esters at high temperatures such as 400 °C without a catalyst (Ranganathan, Narasimhan, & Muthukumar, 2008), most of the industrial biodiesel production, nearly 90% efficiency transesterification reaction is achieved by using chemical catalysts.

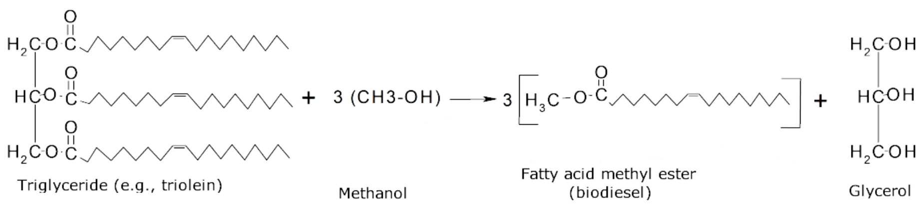

Figure 1. Formation of fatty acid methyl esters (biodiesel) by transesterification reaction of triolein with methanol (methanolysis).

2.1. Alkaline Catalyzed Biodiesel Production

In standard biodiesel production, oils (triglycerides) and methanol enter into an alkali-catalyzed transesterification reaction to form methyl esters of fatty acids (biodiesel). Alkaline catalysts includes NaOH, KOH, carbonates, sodium and potassium alkoxides such as sodium methoxide, sodium ethoxide, sodium butoxide (Ganesan, Rajendran, & Thangavelu, 2009). Polar and short-chain alcohols such as methanol and ethanol are commonly used. While NaOH catalyst can easily dissolve in these alcohols, the activated alcohols can react with triglycerides. Biodiesel production with alkaline catalysis is widely used due to its simplicity, despite some drawbacks (F. Ma & Hanna, 1999). Nevertheless, the rate of transesterification with alkali catalysis is low due to limited by the interface between oil and alcohol phases (Pham et al., 2022). In the alkali-catalyzed reaction; a mixture of free fatty acids, water and alkali salts occurs inevitably as by-products besides glycerol as outlines in Fig 2 (Chiu, Dasari, Sutterlin, & Suppes, 2006). The presence of free fatty acids and water in the oil source react with the alkaline catalyst, causing the catalyst to become dysfunctional. Large clump of soap masses formed with water and free fatty acids not only decrease the reaction performance and efficiency but increase the cost of the product as well (Tesser et al., 2005). Therefore, with alkali catalysis, extensive purification for biodiesel and glycerol are generally needed (Lai et al., 2005; Yagiz, Kazan, & Akin, 2007). Alkali catalysis is not suitable for oil substrates with higher content of water and/or free fatty acid such as recycle oil, which are the two main factors limiting the transesterification reaction in alkali-catalyzed biodiesel production (Enweremadu & Mbarawa, 2009). Using isopropanol as a co-solvent in KOH catalyzed biodiesel production was resulted in a distinct separations of FAME and glycerol as greener production (Pham et al., 2022). However, it was necessary that the solvent (*ca.*, 10%) needed to be distilled from mixture. In general, the biodiesel plant operating with the chemical method is generally associated with not only high costs for the initial setup and operation, but the use of water, steam and electricity as well (Xu, Du, Liu, & Zeng, 2003; Yagiz et al., 2007). Table 1 summarized critical aspects of different methods of biodiesel productions. In order to overcome these drawbacks observed in chemical catalysis, there has been an increasing interest in lipase catalyzed biodiesel production (Shahedi, Habibi, Yousefi, Brask, & Mohammadi, 2021; Xu, Du, & Liu, 2005)

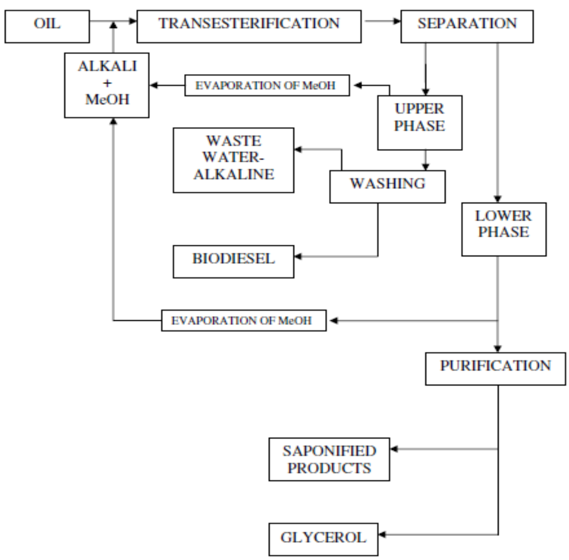

Figure 2. Alkaline catalyzed production of biodiesel (Ranganathan et al., 2008).

2.2. Acid Catalyzed Biodiesel Production

Acid-catalyzed biodiesel production is occasionally used in industry. Technically any mineral acid can be used to catalyze the transesterification reaction, mostly sulfuric and sulfonic acids are preferred in this process (Canakci

& Van Gerpen, 1999; Ganesan et al., 2009). Despite higher yields achieved in acid-catalyzed biodiesel production, it has also well-known disadvantage due to the corrosive nature of the acids damaging the equipment. Also, the reaction occurs at a slower rate and requires greater (e.g., 30:1) molar equivalent of alcohol to oil (Canakci & Van Gerpen, 1999) which needs additional evaporation process. Compared with the acid-catalyzed reaction, the alkali-catalyzed transesterification reaction is considerably faster which constitutes one of the reason for industrial preference (Ganesan et al., 2009; Ranganathan et al., 2008). As opposed to limited applicability of alkaline catalyst for the oil with high free fatty acid or water, acid catalysts are not sensitive to free fatty acids, in fact, it is more suitable for the transesterification reaction for vegetable oils with more than 1% free fatty acids (Canakci & Van Gerpen, 1999) (Enweremadu & Mbarawa, 2009).

2.3. Biodiesel Production by Enzymatic Method

In recent years, the use of lipases in biodiesel production has gained significant attention, especially with lipases immobilized on suitable supports. Compared with the alkaline catalyzed biodiesel production associated with the above-mentioned drawbacks, the enzyme catalyzed transesterification offers clean and environmentally friendly processing (Z. Tan et al., 2022). Enzymes, on the other hand, have their own limitations such as the high costs and their instability against alcohols. Table 1 compares critical aspects of different production methods for catalysis (Ganesan et al., 2009). In recent years, there have been increasing number of studies in the literature for enzymes use in biodiesel production (Ranganathan et al., 2008).

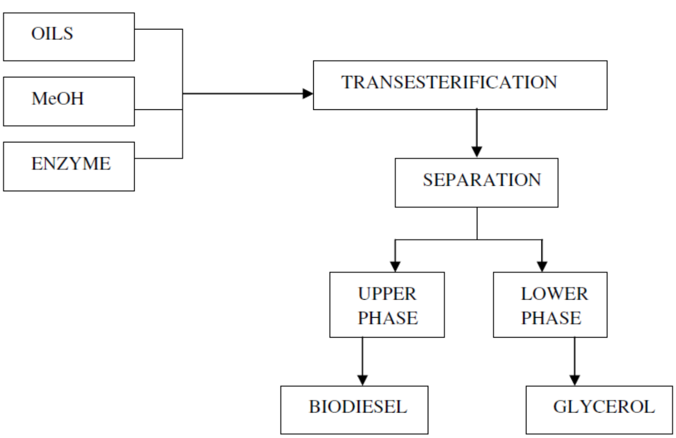

Figure 3. Enzymatic production of biodiesel (Ranganathan et al., 2008).

In enzymatic transesterification reaction, mainly glycerol is produced as a clean by-product that can easily be separated from biodiesel with a separator as seen in Figure 3. Compared to the chemical catalysis, with the use of enzyme catalyzed biodiesel production, alkaline cost, the need for acid neutralization, the soaps formation with alkali salts can be avoided (Fukuda, Kond, Noda, Kondo, & Noda, 2001) (see Fig 1 and Table 1). Therefore, the enzymatic conversion does not generate waste under ideal conditions, which results in clean products very little or no need for purification and relatively inexpensive processing (Nelson, Foglia, & Marmer, 1996; Shimada, Watanabe, Sugihara, & Tominaga, 2002; Yagiz et al., 2007). Similar to normal natural oils, waste frying oils can also be used as substrates in the production of biodiesel by enzymatic reaction because lipases are more insensitive to water and free fatty acids in the oil composition (Enweremadu & Mbarawa, 2009). In addition, mild reaction conditions (35-45 ^{o}C) and probable reuse of catalyst are other advantages of this method (Ganesan et al., 2009). Also, the initial investment and energy input of enzymatic biodiesel production is very low compared to chemical catalysis (Shieh, Liao, & Lee, 2003; Yagiz et al., 2007).

Table 1 Comparison Of Different Methods For Biodiesel Production

Variable	Acid catalysis	Alkali catalysis	Lipase catalysis
Reaction temperature (^{o}C)	50-80	60-70	30-40
FFA in raw material	Esters	Saponified products	Methyl esters
Water in raw material	Interfere with reaction	Interfere with reaction	No interference
Yield of methyl esters	Normal	Normal	Higher
Recovery of glycerol	Difficult	Difficult	Easy
Purification	Repeated washing	Repeated washing	None
Cost of catalyst	Cheap	Cheap	Expensive

In the production of enzymatic biodiesel, lipases are used (Ranganathan et al., 2008). Lipases (triacyl glycerol acylhydrolases EC 3.1.1.3) normally catalyze the hydrolysis of fatty acid ester bonds in the presence of water (X. J. Zhang et al., 2022). However, given the reaction constrains changed towards limiting water, lipases are able catalyze esterification, inter- and trans-esterification type synthesis reactions (Causevic, Olofsson, Adlercreutz, & Grey, 2023; Paiva, Balca, & Malcata, 2000; Shimada et al., 2002). Apart from biodiesel production, lipases are industrially significant enzymes used in detergents, leather and paper industries and in the synthesis of pharmaceuticals and food ingredients (Dimitrijević et al., 2012; R. Sharma, Chisti, & Banerjee, 2001). Lipases are also widely used in organic synthesis with their high stability in organic solvents (X. J. Zhang et al., 2022). Lipases are generally obtained from fungi and bacteria with high efficiencies (Tüter, Aksoy, Gılbaz, & Kurşun, 2004). The lipases frequently evaluated for the production of biodiesel are from *Candida antarctica* (Shimada et al., 1999; Watanabe et al., 2000); *Candida rugose* (Zhu, Wu, & Yu, 2005), *Pseudomonas cepacia*, *Pseudomonas fluorescens, Rhizomucor miehei* (Salis, Pinna, Monduzzi, & Solinas, 2005) *and Thermomyces lanuginosa* (Hsu, Jones, Foglia, & Marmer, 2004). In general, lipase production from fungi have well recognized benefits such as, ease of mass production from inexpensive biomass, extracellular and soluble properties of lipases allowing ease extraction, good thermal and pH stabilities and specificity for wide substrates (Mahfoudhi, Benmabrouk, Fendri, & Sayari, 2022).

3. Biodiesel Production with Lipases

3.1. Enzyme Specificity

Enzymes are biological catalysts with known characteristics for high activity, selectivity under mild operation conditions (Gurgel et al., 2022). One of the well-known characteristics of biological catalysts is their specificity, and lipases are no exception. As listed previously, many lipases studied for their ability to catalyze the alcoholysis of fats and oils to simple alkyl esters differ from each other. All lipase have certain characteristic such as the position and types of fatty acids including chain length, degree of unsaturation, the number and position of double bonds (Causevic et al., 2023). For example, lipases from *Rhizomucor miehei* and *Thermomyces lanuginose* are known as Sn-1,-3 regioselective lipases (Causevic et al., 2023) yet they catalyzes alkyl ester yields of 70 to 100% from natural oils irrespective of chain length or degree of unsaturation of the acyl groups due to acyl migration to either position (Fernandez-Lafuente, 2010). Nevertheless, a combination of immobilized lipases from *T. lanuginosus* and *R. miehei* resulted in significantly greater yield of transesterification of soybean oil (Rodrigues & Ayub, 2011). Accordingly, enzyme specificity matters. For example a very specific enzyme from *C. antarctica* lipase Cal A accepts tertiary and sterically hindered alcohols (Palomo et al., 2002), recognizes the Sn-2 recognition in triglycerides, therefore produces approximately at most 30% yield of alcoholysis or transesterifications of oils and fats (Ondul, Dizge, & Albayrak, 2012) and is selective towards trans-fatty acids (Kirk & Christensen, 2002). Thus, it is important to obtain most suitable lipase catalyst for the fatty acid characteristics of fats and oils for alcoholysis (Ganesan et al., 2009).

3.2. Methods of Immobilization

As a water soluble hydrolyze, lipases normally catalyzes reactions at the oil-water interface (Sarmah et al., 2018; T. Tan, Lu, Nie, Deng, & Wang, 2010). The rate of catalysis is largely dependent on the available area of the interphase (Foresti, Alimenti, & Ferreira, 2005). One way to increase interphase is to distribute lipases throughout medium or the support matrices by means of immobilization (Causevic et al., 2023). It is commonly known that immobilization of the lipase on a support prevents the lipase from aggregating due to spreading the enzyme on the surface of the supports (Girelli & Chiappini, 2023). In biodiesel production, the use of immobilized lipases is generally studied, with the exception of a few studies (Kaieda et al., 2001; Kojima, Du, Sato, & Park, 2004; Nelson et al., 1996), due to the fact that not only the commonly known drawbacks for the use of free enzyme in catalysis such as loss enzyme (Andersch et al., 1997; Iso et al., 2001), but also the reaction conditions of biodiesel production in particular (Kaieda, Samukawa, Kondo, & Fukuda, 2001; Kaieda et al., 1999) including various lipase-specific limitations, (Al-Zuhair, 2007; Brzozowski et al., 1991; Giorno & Drioli, 2000; Soumanou & Bornscheuer, 2003a). With the use of immobilized enzyme, well recognized advantages are expected such as the possibility of reuse of the enzyme, the reduction in the cost of purification due to the absence of enzyme, continuous transformation for production, the realization of product formation under more controlled conditions, the relatively simple and efficient conversion processes (Antczak, Kubiak, Antczak, & Bielecki, 2009; Maghraby, El-Shabasy, Ibrahim, & Azzazy, 2023) and up to 50% reduction in the cost of the process (Gurgel et al., 2022).

Enzyme immobilization simply means to restrict the movement of enzyme protein by means of fixation to a permanent support material in the reaction medium (Homaei, Sariri, Vianello, & Stevanato, 2013). Therefore, various support materials and enzyme immobilization methods have been used for enzyme fixation. For biodiesel productions, it is observed that ion exchange resins, diatomaceous earth and porous silica gels are frequently chosen supports materials for the immobilization of lipases while simple adsorption is frequently used as the fixing method (de Fuentes, Viseras, Ubiali, Terreni, & Alcántara, 2001; Parmegiani Marcucci et al., 2023; Salis, Sanjust, Solinas, & Monduzzi, 2003; H. Wang, Wu, Ho, & Weng, 2006) Most of the studies investigating biodiesel production with immobilized lipases have used commercial enzyme preparations. One of the most commonly used commercial enzyme preparation for biodiesel production is Novozyme 435 lipase from Novo Nordisk (Balcão, Vieira, & Malcata, 1996; Bélafi-Bakó, Kovács, Gubicza, & Hancsók, 2002; de Oliveira et al., 2004; Fukuda et al., 2001; Köse, Tüter, & Ayşe Aksoy, 2002; Lai et al., 2005; Samukawa et al., 2000; Shimada et al., 1999; Tüter et al., 2004; Watanabe et al., 2000; Xu et al., 2005, 2003). Novozyme 435 (*C. antarctica* lipase B) was entrapped in coarse porous polyacrylic resin particles while Lipozyme IM 20 (Yadav & Trivedi, 2003), IM 60 and IM 77 (*R. miehei*) lipases trapped in weakly acidic resin in macroporous form are frequently used enzymes (de Fuentes et al., 2001; Fukuda et al., 2001; Lai et al., 2005; Shieh et al., 2003; Xu et al., 2003; Yadav & Trivedi, 2003). Another frequently used lipase from *Pseudomonas cepacia* marketed by Amano is sold in diatomaceous earth (PS-D) and ceramic (PS-C) forms (Salis et al., 2005). In addition to the lipase listed, similarly prepared other lipases were commonly evaluated for biodiesel productions.

It was noted that adsorption was the most common immobilization methods applied to lipase enzymes in not only the commercial enzyme preparations mentioned above but also the techniques developed by various researcher (Balcão, Paiva, & Malcata, 1996; Balcão, Vieira, et al., 1996; de Fuentes et al., 2001). Enzyme immobilization by adsorption consists of contacting the enzyme solution and the support material for a certain period. Although it is a simple and easy, the method mostly relies on formation of weak bonding between the enzyme and the support material (Balcão, Vieira, et al., 1996; de Fuentes et al., 2001; Paiva et al., 2000). Enzyme immobilization by adsorption has also widely known disadvantages such as detachment and therefore the loss of enzyme. Due to the weakness of the bonds between the support and the enzyme, the immobilized enzyme is separated from the support material during its use and leaches to the reaction medium, so not only the product is contaminated with the enzyme but also the catalytic activity is lost over time (Gaur, Pant, Jain, & Khare, 2006; Sardar, Agarwal, Kumar, & Gupta, 1997; Torres et al., 2002; Weaver & Carta, 1996).

Biodiesel production with various immobilized lipase systems has been investigated in the literature. Although lipase-catalyzed biodiesel production predicts the above-mentioned advantages, there is no commercially significant lipases catalyzed biodiesel production (Al-Zuhair, 2007; Shimada et al., 1999;

X. Wang et al., 2009). It has been stated that the cost of biodiesel production with lipases is higher than that of alkaline catalyst (de Fuentes et al., 2001). Some of the noted difficulties associated with the use of lipases in industrial biodiesel applications include high cost of immobilized enzymes (de Fuentes et al., 2001; Du, Xu, Liu, & Zeng, 2004; Shimada et al., 1999), low activity and instability under processing conditions (Gaur et al., 2006; Iso et al., 2001; Shimada et al., 2002; Watanabe et al., 2000; Watanabe, Shimada, Sugihara, & Tominaga, 1999, 2001; Xu et al., 2003). For biodiesel production, some of the commercial preparation of immobilized lipases were evaluated (Lai et al., 2005; Shieh et al., 2003; Xu et al., 2003). The common types of supports often used for lipase immobilization were porous or particulate in nature including ion exchange resins, diatomaceous earth and porous silica gels along with adsorption method for immobilization (Balcão, Paiva, et al., 1996; de Fuentes et al., 2001; Dizge, Keskinler, & Tanriseven, 2008; Salis et al., 2003; H. Wang et al., 2006). Some of these commercially available supports are both expensive (Mateo, Abian, Fernandez-Lafuente, & Guisan, 2000; Würtz Christensen et al., 2003) and difficult to use in packed-bed column type industrial reactors (Anspach, Huckel, Brunke, SChÜTte, & Deckwer, 1994; de Castro, de Lima, & Roberto, 2001). It is essential to contain high load of enzyme with catalytic functionality for the potential applicability of the immobilized lipases (Guldhe, Singh, Mutanda, Permaul, & Bux, 2015; Velasco-Lozano et al., 2014). For example, epoxy functionalized silica gel with good properties of lipase activity was used for simultaneous immobilization lipases from *C. antarctica* B and *R. miehei* or *T. lanuginose* at the amount of 4 and 15 or 10 mg/g, respectively, which is relatively insufficient for productive application (Shahedi et al., 2021; Shahedi, Yousefi, Habibi, Mohammadi, & As'habi, 2019). Mainly due to frequently noted shortcomings such as high costs not only for the enzyme and some of the support materials (Fernández-Lorente et al., 2006), but also for the chemicals used in support activation and immobilization, both the cost and performance of the immobilized lipase systems (Ranganathan et al., 2008) for biodiesel production are insufficient to meet industrial expectations (Würtz Christensen et al., 2003).

In recent years, the development of immobilized lipases on nano-sized materials has offered for transesterification type reactions. Among nano-sized materials including carbon nanotubes, Fe_2O_3, Fe_3O_4, magnetic or non-magnetic nano-particles, graphene/graphene oxide, etc. were reviewed recently (Z. Tan et al., 2022) with some renewable materials such as non-woven nanofibers made from poly (lactic acid)/chitosan blends fiber mats (Siqueira et al., 2015). Because of the minimized size of supports, greater number of enzyme can be immobilized per weight of nanomaterials that promises the high loading of the catalyst (X. Wang et al., 2009). It was noted that these type of supports appear to possess very good catalytic characteristics such as high catalytic efficacy, high catalytic turnover, great stabilities and low diffusional resistance (Aggarwal & Ikram, 2023; Ansari & Husain, 2012; Bilal et al., 2021). For example, the magnetic materials offer facilitation of ease of separation after catalysis (J. Wang et al., 2012). However, most of these supports needed to be chemically activated before or after immobilization similar to other types of supports (Garmroodi et al., 2016). Moreover, highly engineered types of these supports tend to be expensive and involve tedious methods for their preparation and enzyme immobilization. For example, amino functionalized and then glutaraldehyde activated magnetic nanoparticle immobilized lipase was used for biodiesel production in a packed-bed reactor, where it was observed that the shear stress of the fluid flow damaged the lipase nanoparticle leading to the loss of lipase activity at the flow rates above 0.25 mL/min in 160 ml reactor volume (X. Wang, Liu, Zhao, Ding, & Xu, 2011). In terms of industrial application, the criteria such as low cost, long half-life, high stability and smooth continuous production in the packed column may not be anticipated with the current immobilized lipase systems (X. Wang et al., 2011). These aspects pose difficulty for implementing in industrial size applications especially for high volume of operation vs low value products such as biodiesel.

Effectively catalyzed biodiesel production with a robust immobilized lipase, the main desirable attributes include (1) sufficient stability for mono alkyl short chain alcohols, (2) high mechanical / thermal stability for higher operation temperatures potentially allowing higher reaction rates through the effect of low viscosity or increased rate of mass transfer (J. Zhang et al., 2022), (3) simple, rapid and cost effective or inexpensive support as well as the method for immobilization, (4) hydrophobic functional groups on the support for possibly open-lid lipase conformation (Dizge et al., 2008; Garmroodi et al., 2016; Salis et al., 2005) and repellence of glycerol, (5) minimal regioselectivity towards fats and oils for general applicability. These characteristics can be significantly modified with immobilization procedures (Causevic et al., 2023; Gurgel et al., 2022).

3.3. Reactor Type

Stirred tank and plug-flow (packed-bed) type reactors are the two well-known type reactors where the catalysis reaction takes place in batch or continuous modes (Poppe, Fernandez-Lafuente, Rodrigues, & Ayub, 2015). When the enzyme is immobilized on or in the micro particulate type supports such as granular resins or porous spheres, which are frequently encountered for the biodiesel production, a stirred tank reactor was generally used with dispersed immobilized enzyme in the reaction mixture (Al-Zuhair, 2007). The immobilized enzyme can be retained within the reactor by a filter or membrane. Low cost of construction and well-mixed reaction medium are normally associated with these reactors (Al-Zuhair, 2007). However, a mechanical disruption the support from the propeller speed and an enzyme leach often encountered. Compared with stirred tanks, plug-flow type reactors holds immobilized enzyme in a fixed place while allowing the reaction mixture to pass through therefore offering probable high volumetric productivity with ease of operation and maintenance (J. Wang et al., 2012). Most of biodiesel productions with immobilized lipases listed in the section of the immobilization method were carried in stirred tank type reactors. With this type of reactor, it was note that as the reaction proceeds, the generated glycerol physically mixes well with the alcohol tend to form a separate liquid phase mentioned before (Ganesan et al., 2009). Use of immobilized enzyme in a plug-flow type reactor preferably in continuous mode allows operational ease for introduction of a separator to remove glycerol due to its higher density (1.2 g/mL) from the other components (0.8 - 0.9 g/mL). In addition, the residual glycerol on the immobilized enzyme in plug-flow type reactor can be washed with appropriate solvent and the glycerol in the washing solution can be excluded from the heavy glycerol by the separator as well (Ondul et al., 2012). It was noted that the enzymatic alcoholysis of natural oils can be carried out considerably faster and more economically in continuous reactors. (Dalla Rosa et al., 2009; Komers, Skopal, & Čegan, 2010; Lee et al., 2010). Use of continuous mode suits well for automation and saves considerable cost, labor and time for the production (Halim, Kamaruddin, & Fernando, 2009).

Especially suited well for plug-flow type reactors, fibrous materials offer important advantages as an industrial-scale immobilized enzyme support with notable features such as good flow properties, limited back pressure and negligible diffusion resistance of the substrates or products (T. Tan et al., 2010). Fibrous type materials generally offering superior mechanical strength, chemical stability, high surface area, open-form of structure for flow (H. Chen & Hsieh, 2005; Ichijo et al., 1990; Li et al., 2015; S. Sharma & Yamazaki, 1984; X. Wang et al., 2011). The fibrous materials used include polydimethylsiloxane modified nonwoven fabrics (Li et al., 2015) polyethylene terephthalate fibers

(Elçin & Saçak, 1996), cotton terry cloths (Albayrak & Yang, 2002; Nie, Xie, Wang, & Tan, 2006; S. Sharma & Yamazaki, 1984) nylon fibers (Braun, Klein, & López, 1996; Seng, Rhee, Cho, & Ryu, 1980), silk fabrics (Furuhata, Deno, & Sakamoto, 1996). In order to take advantage of packed-bed reactor in biodiesel production in n-hexane, cotton fiber was used as a support not only to hold the nanoparticles in place with even distribution and adjustable loading but also to provide good flow characteristics (X. Wang et al., 2011). However, it was noted that the shear stress of the fluid flow at the highest flow rates damaged the lipases–nanoparticle biocomposite, leading to the loss of lipase activity (X. Wang et al., 2011). The effect of shear stress was also noted other studies using microporous particle or membrane (Poppe et al., 2015). A stirred tank was used with lipases adsorbed on fibrous support treated with relatively hydrophobic molecules, very good stability during long-term reuse and high catalytic activity was obtained (Li et al., 2015).

Despite increasing academic interest for lipase catalyzed biodiesel production, the enzymatic production of biodiesel has not been applied commercially, greatly due to the high cost of lipase enzyme and the insufficient rate of catalysis (Robles-Medina, González-Moreno, Esteban-Cerdán, & Molina-Grima, 2009). Loss of enzyme efficiency due to deactivation and/or inhibition with glycerol over time was observed in many of the biodiesel productions with the immobilized lipases on variety of supports or immobilization techniques (Li et al., 2015; Parmegiani Marcucci et al., 2023). Reduction in the cost of lipase and therefore of catalysis can be realized by containing a high load of enzyme immobilized with extended lifetime, employing suitable immobilized enzyme technology and inexpensive support in an effective type of reactor (Nie et al., 2006).

3.4. Alcohols

In the production of biodiesel, the use of alcohol is required, as the fatty acids in the triglyceride will be subjected to transesterification with monohydric alcohols (Du, Li, Sun, Chen, & Liu, 2008). Theoretically, all alcohols can be used in biodiesel production, nevertheless there are crucial differences among alcohols for biodiesel production including solubility in oils, efficiency and effects on the enzymes stability (Ranganathan et al., 2008). Furthermore, methanol is more suitable and the most commonly used alcohol for biodiesel production because of the high reactivity, cost-effectiveness, and low boiling point (Pham et al., 2022; Salis et al., 2005). For this reason, biodiesel is referred to as fatty acid methyl esters. In order to achieve a complete conversion in biodiesel production, theoretically, 3 moles of alcohol should be used for 1 mole of triacylglycerol (oil). It has been reported that a positive result in terms of biodiesel yield and efficiency was not obtained with the use of alcohol in more than the molar equivalent of fatty acids in the oil (Salis et al., 2005). For a complete transesterification, a stoichiometric ratio of one mole of triglyceride to three moles of alcohol is necessary to yield three moles of fatty acid alkyl esters. However, a large excess of alcohol is required to drive the reaction to the forward direction (especially with acid and alkaline types of catalysts) because transesterification is an equilibrium reaction (Ganesan et al., 2009; Pham et al., 2022). It has been stated that many lipases are denatured, especially with methanol and ethanol, at the minimum molar equivalent alcohol ratio (oil:alcohol, 1:3) (Nelson et al., 1996). In this sense, the most important selection and application criteria for lipases to be used in biodiesel production is the stability of enzymes against alcohols (Matassoli, Corrêa, Portilho, Veloso, & Langone, 2009). High alcohol concentrations denature every enzyme, but the alcohol stability at the minimum molar equivalent level is important (Noureddini, Gao, & Philkana, 2005). Significant variations in terms of alcohol stabilities were found among lipases used in investigations for alcoholysis. Several studies have reported that *P. cepacia* lipase is resistant to higher methanol concentrations compared to *P. fluorescens, C. rugosa* or *C. antarctica* lipases (Fukuda et al., 2001; Kaieda et al., 2001). It has been reported that *C. antarctica* lipase (Novozyme 435) begins to denature from methanol above 0.66 molar equivalents (Samukawa et al., 2000) while *P. cepacia* lipase is not affected by 2-3 molar equivalents of methanol (Fukuda et al., 2001). It was found that the methanol stability of *C. antarctica* lipase B (Novozyme 435) pretreated in oil soaking was reduced. While the normal enzyme begins to denature from methanol above 0.66 molar equivalents, the oil pretreated enzyme begins to denature at alcohol concentrations above 0.33 molar equivalents (Samukawa et al., 2000). When a different acyl acceptor for example methyl acetate or ethyl acetate was used for transesterification instead of methanol, the lipase inactivation by alcohol is largely avoided (T. Tan et al., 2010). However, higher molar ratio was needed with the esters and they considerably costs high (Du et al., 2004).

In general, transesterification demands thorough miscibility of alcohol with the oil. It is important to note that the enzyme stability against alcohol is directly related to their immiscibility with oils with long chain fatty acids (Ganesan et al., 2009). Such alcohols as methanol and ethanol, which are frequently used in biodiesel production, are not sufficiently miscible with the oil medium at the required equivalent molar ratio, and the insoluble part denatures the enzyme. Thus, the gradual inclusion of alcohol were adopted in most studies for biodiesel production. In the gradual addition of alcohol, the alcohol (in molar equivalents) required to be added to the medium is added in parts and after the majority of the previous part is used, the other part is added (Shimada et al., 1999). While some researchers use a two-stage (1+2) system in which the production starts with a ratio of methanol in one molar equivalent and the remaining two molar equivalents of alcohol are added in the later stage of the reaction (Shimada et al., 2002; Watanabe et al., 1999), more often methanol is used in three equal stages (1+1+1) (Du et al., 2004; Kaieda et al., 2001, 1999; Shimada et al., 1999; Watanabe et al., 1999). In an experiment investigating the methanol resistance of *C. antarctica* lipase (Novozym 435), it was stated that the enzyme was denatured from 0.66 mol and above methanol, and the reaction was carried out with the addition of methanol in 5 stages (Samukawa et al., 2000). In the ethanolysis study of tuna oil with *C. antarctica* (Novozym 435) enzyme, ethanol stability of lipase was found to be higher than methanol (Watanabe et al., 1999). While the enzyme was denatured from methanol above 0.66 moles, it was stated that it was denatured from ethanol above 1 mole and three-stage ethanol addition was performed (Watanabe et al., 1999).

The most important problem related to the effects of alcohols on the enzyme in biodiesel production conditions is that small alcohols such as methanol and to some extent ethanol do not dissolve sufficiently in the reaction medium, so they come to the enzyme surface and disrupts the enzyme. In order for alcohols to enter into the enzymatic reaction, the alcohol must be completely dissolved (Shimada et al., 1999). It was stated the enzyme denaturation was due to insoluble portion of alcohols in the oil (Watanabe et al., 1999). In general, the longer the carbon chain, the more hydrophobic alcohols, and thus they reach the greater miscibility in oil at higher ratios. Unfortunately, methanol with the shortest alkyl alcohol with highest reactivity (Pham et al., 2022) has the lowest solubility in oil and causes the highest rate of denaturation, followed by ethanol (Shimada et al., 2002). At molar equivalent ratios of alcohols containing three or more carbons, the problems of immiscibility in oil and instability of lipases were not noted (Parmegiani Marcucci et al., 2023; Shimada et al., 2002), and better alcohollysis yields and efficiencies are obtained with these alcohols compared to methanol and ethanol (Fukuda et al., 2001; Linko, Lamsa, Wu, & Uosukainen, 1998; Nelson et al., 1996; Salis et al., 2005; Shimada et al., 2002; Soumanou & Bornscheuer, 2003a; Stevenson, Stanley, & Furneaux, 1994).

3.5. Oils

All organic renewable oils contain triglycerides with varying types of fatty acid compositions while they can be grouped by their chain length (short, medium, long), the degree of unsaturation or *sn* position on triglyceride. In terms of agricultural production, oils from palm and soybean constitutes nearly 90% while the rest consists of oils from sunflower, rapeseed (canola), olive and corn (Kuhnt, Degen, Jaudszus, & Jahreis, 2012). Refines, recycled or waste oils from these sources have been used in various investigations for biodiesel production. Also, some alternative renewable sources such as animal waste (Cavali et al., 2020) or fish waste oils (Marín-Suárez, Méndez-Mateos, Guadix, & Guadix, 2019), microalgae (Ferreira Mota et al., 2022), yeasts (Selvakumar & Sivashanmugam, 2019) etc., have also been proposed or used for transesterifications (Marín-Suárez et al., 2019). To mention some of a few common sources used for feed stock, sunflower oil (Mittelbach, 1990; Soumanou & Bornscheuer, 2003a), canola oil (Jeong et al., 2004; Uosukainen, Lämsä, Linko, Linko, & Leisola, 1999) animal tallow or lard (Lu, Nie, Xie, Wang, & Tan, 2007) (Nelson et al., 1996), soybean oil (Du et al., 2004; Parmegiani Marcucci et al., 2023; Shieh et al., 2003), rice bran oil (Lai et al., 2005), coconut, peanut, palm kernel (Soumanou & Bornscheuer, 2003a), microbial oils and including frying waste oils (Antczak et al., 2009) as such, almost all types of oil have been used with lipase for biodiesel production.

Lipases generally act well on oils consisting of long chain (16-18 carbon) fatty acids, although their rate of action varies slightly on different oils used. The fatty acids in the triglycerides of most oils are long-chain carboxylic acids and, lipase enzymes have high rates on these fatty acids (Paiva et al., 2000; T. Tan et al., 2010) It has been stated that the effects of lipases on polyunsaturated fatty acids are generally weak (Shimada et al., 1998, 1997, 2002). Studies on the effects of various enzymes on different oils have not found significant differences in their effects on oils with similar fatty acid composition. For example, there was no significant difference between *C. antarctica* and *P. cepacia* lipases in biodiesel production from triolein and sunflower oil (Iso et al., 2001; Soumanou & Bornscheuer, 2003a)

3.6. Glycerol

The glycerol formed in the biodiesel production process adversely affects the reaction due to its physicochemical properties, including polarity, high density and viscosity (Soumanou & Bornscheuer, 2003b). First of all, glycerol reversibly inhibits lipases because it is insoluble in the medium consisting of biodiesel - oil mixture, and also, it significantly prevents substrate and/or product diffusion by coating the enzyme polar surface (Watanabe et al., 2000). Due to these interference, glycerol reversibly stops enzymatic catalysis (Soumanou & Bornscheuer, 2003b). The negative effect of glycerol has been reported in almost all investigations (Bélafi-Bakó et al., 2002; Dossat, Combes, & Marty, 1999; Du et al., 2004; Kojima et al., 2004; Parmegiani Marcucci et al., 2023; Shimada et al., 2002; Soumanou & Bornscheuer, 2003b; Watanabe et al., 1999). In fact, a protocol for the preparation of a new biodiesel that keeps glycerol into their composition as monoacylglycerols was developed by using 1,3-regiospecific lipase from *Rhizomucor miehei* through selective ethanolysis of sunflower oil (Calero et al., 2014). In a few studies, hydrophilic alcohols tert-butanol was used to regenerate the enzyme (J. Chen & Wu, 2003). However, it is cumbersome to desorb glycerol from the immobilized lipase especially in large-scale productions. For example, using fibrous support immobilized lipase in packed-bed reactor for methanolysis of pure or waste oil in petroleum ether (3/2, v/v of oil), a hydrocyclone separator was used for removal of glycerol from the reaction mixture after completion every 1/3 molar equivalent of methanol (Nie et al., 2006).

Challenging nature of glycerol was noted with the lipase catalyzed alcoholysis reactions from natural oils. The glycerol generated tend to mix the alcohol and form a polar phase, which is not completely miscible with the oil, in turn drawing alcohol from the oil phase (Ganesan et al., 2009). Therefore, decreasing alcohol concentration in oil phase decreases the rate of the alcoholysis reaction (Al-Zuhair, 2007). The conversions toward transesterification will be greatly enhanced if the free glycerol is removed from the substrate mixture as the reaction proceeds. A suitable solvent such as isopropanol may be evaluated in lipase catalyzed biodiesel production for separation of glycerol (Pham et al., 2022).

3.7. Water

Since the production of enzymatic biodiesel is a transesterification reaction, the water proportion in the medium must be precisely controlled. As a substrate, water determines the dominant direction of the lipase-catalyzed reaction (Balcão, Paiva, et al., 1996). Lipases perform different reactions depending on the water activity in the medium (Wehtje & Adlercreutz, 1997a). In general, in the reaction medium consisting of an oil-alcohol mixture, the hydrolytic reaction of lipases increases proportionally with increasing water content in the medium, while the transesterification reaction increases as the water activity decreases. However, regardless of this general manifestation, it is also known that the enzyme protein needs a certain amount of water to maintain its native stable structure (L. Ma, Persson, & Adlercreutz, 2002). In case of excessive drying of the medium or removing water from the enzyme with various solvents or adsorbents, the enzyme loses its activity (Stevenson et al., 1994). Depending on the lipase, it is stated that lipases are active in a wide range of water activity and maintain their activity even at very low water activity values (Koller, Aris, Ujang, & Vaidya, 2001; Valivety, Halling, & Macrae, 1992; Wehtje & Adlercreutz, 1997b). The minimum level of water required for lipase activity should be used in biodiesel production. In the alcoholysis reaction, the water level in the environment will disrupt the competition between the transesterification and hydrolysis reactions towards the direction of hydrolysis. Optimal proportion of the water level varies among enzymes. While some lipases require high water for optimal transesterification activity, or even in the presence of water, the transesterification reaction of some enzymes comes to a halt even at low water levels (Meher, Vidyasagar, & Naik, 2006; Wehtje & Adlercreutz, 1997a).

3.8. Solvents

In various studies for lipase-catalyzed biodiesel production, the alcoholysis reaction was carried out in the presence of solvent. Solvent has conventionally been used to solubilize the hydrophobic substrates in aqueous media for lipases reactions (Lara & Park, 2004). The presence of solvent in the medium for alcoholysis reaction are expected primarily to dissolve immiscibility problem among the substrates (alcohol and oils), decrease the viscosity especially in saturated oils, thus increase the biodiesel yield and efficiency. Depending on the solvent used, it is observed that the use of the solvent aimed at increasing the alcohol solubility in the oil and/or protecting the enzyme from alcohol denaturation (Iso et al., 2001; Soumanou & Bornscheuer, 2003a). With the use of appropriate solvents, higher biodiesel yields and efficiencies are obtained (Nelson et al., 1996; Shimada et al., 2002; Soumanou & Bornscheuer, 2003a). The presence of solvent in the environment in the alcoholysis reaction with methanol and ethanol, which denatures the enzyme above a certain ratio, increases the alcoholysis efficiency (Fukuda et al., 2001; Shimada et al., 2002). Especially in systems where there is high viscosity such as animal tallow and waste oils, high viscosity causes a decrease in efficiency (Nelson et al., 1996) and requires the use of solvents. Among the solvents investigated, n-hexane is the most frequently used solvent within the ratios between 70% (Nelson et al., 1996) and 95% (Kojima et al., 2004; Shieh et al., 2003; Soumanou & Bornscheuer, 2003a; X. Wang et al., 2009). Depending on the type of enzyme, the highest biodiesel efficiency is obtained with hydrophobic solvents such as n-hexane (X. Wang et al., 2011), n-heptane and isooctane, while lower yields are obtained with hydrophilic solvents such as acetone (Nelson et al., 1996). Lipases are known to vary in their sensitivity to miscible organic solvent, but they tend to be inactivated by water miscible organic solvents due to exclusion of the bound water from the enzyme (Yu, Qin, & Tan, 2007). Although biodiesel can be obtained in high yields with the use of solvents, the use of solvent causes a decrease in space-time efficiency in biodiesel production, requires additional evaporation costs and increases the safety risks related to explosion and environmental health (Penzol, Armisén, Fernández-Lafuente, Rodés, & Guisán, 1998).

4. Conclusions

Production of biodiesel relies on transesterification of naturally existing organic fats and oils with small alcohols catalyzed by various methods. The primary burden associated with biodiesel production is limited availability of fat and oil resources without competing natural resources for food commodities. To overcome the problem, studies are needed to focus on nonedible sources such as recycled cooking oils, oils with high free fatty acid contents, microbial sources grown in organic waste and finally photosynthetic oil rich algae to make biodiesel fuel. Inexpensive catalysts but high cost of downstream processing associated with chemical catalysts for biodiesel production have led to the investigations for alternative catalysts. Due to the fact of efficient productions of lipase catalysts not only decreased the cost of catalysis but also aids the recovery of high quality glycerol, both of which lowers the cost of bioconversion for transesterifications. Combination of bioethanol production derived from renewable biomass, alcoholysis with bioethanol may aid for generation of diesel fuel. However, lipase stability against ethanol or methanol as the acyl acceptor appears one of the main hurdle for lipase catalysis resulting in short lifetimes. Although stepwise addition of alcohols appears to ease the problem, it lowers the rate of transesterification. In addition to undissolved alcohol causing serious inactivation, the persistence presence of glycerol smeared on enzyme inhibits the forward alcoholysis reaction. As with the inclusion of sonication, more effective glycerol separation approaches need to be integrated in reactor design. Finally, for economically viable lipase catalyzed biodiesel production, better enzyme immobilization techniques achieving not only a high load of enzyme but also sufficiently stable and active lipase need to developed and evaluated for industrially applicable type reactors so that the shorter reaction times and greater production capacity may be realized.

References

Aggarwal, S., & Ikram, S. (2023). A comprehensive review on bio-mimicked multimolecular frameworks and supramolecules as scaffolds for enzyme immobilization. *Biotechnology and Bioengineering*, *120*(2), 352–398.

Al-Zuhair, S. (2007). Production of biodiesel: possibilities and challenges. *Biofuels, Bioproducts and Biorefining*, *1*(1), 57–66.

Albayrak, N., & Yang, S. T. (2002). Immobilization of β-galactosidase on fibrous matrix by polyethyleneimine for production of galacto-oligosaccharides from lactose. *Biotechnology Progress*, *18*(2), 240–251.

Ali, Y., Hanna, M. a., & Leviticus, L. I. (1995). Emissions and power characteristics of diesel engines on methyl soyate and diesel fuel blends. *Bioresource Technology*, *52*(2), 185–195.

Aljaafari, A., Fattah, I. M. R., Jahirul, M. I., Gu, Y., Mahlia, T. M. I., Islam, M. A., & Islam, M. S. (2022). Biodiesel Emissions: A State-of-the-Art Review on Health and Environmental Impacts. *Energies*, *15*(18), 1–24.

Andersch, P., Berger, M., Hermann, J., Laumen, K., Lobell, M., Seemayer, R., … Schneider, M. P. (1997). [19] Ester Synthesis via Acyl Transfer (Transesterification). *Methods in Enzymology*, *286*, 406–443.

Ansari, S. A., & Husain, Q. (2012). Potential applications of enzymes immobilized on/in nano materials: A review. *Biotechnology Advances*, *30*(3), 512–523.

Anspach, F. B., Huckel, M., Brunke, M., SChÜTte, H., & Deckwer, W. D. (1994). Immobilization of Mercuric reductase from a Pseudomonas putida strain on different activated carriers. *Applied Biochemistry and Biotechnology*, *44*(2), 135–150.

Antczak, S. M., Kubiak, A., Antczak, T., & Bielecki, S. (2009). Enzymatic biodiesel synthesis – Key factors affecting efficiency of the process. *Renewable Energy*, *34*(5), 1185–1194.

Balcão, V. M., Paiva, a L., & Malcata, F. X. (1996). Bioreactors with immobilized lipases: state of the art. *Enzyme and Microbial Technology*, *18*(6), 392–416.

Balcão, V. M., Vieira, M. C., & Malcata, F. X. (1996). Adsorption of Protein from Several Commercial Lipase Preparations onto a Hollow-Fiber Membrane Module. *Biotechnology Progress*, *12*(2), 164–172.

Bélafi-Bakó, K., Kovács, F., Gubicza, L., & Hancsók, J. (2002). Enzymatic Biodiesel Production from Sunflower Oil by Candida antarctica Lipase in a Solvent-free System. *Biocatalysis and Biotransformation*, *20*(6), 437–439.

Bilal, M., Fernandes, C. D., Mehmood, T., Nadeem, F., Tabassam, Q., & Ferreira, L. F. R. (2021). Immobilized lipases-based nano-biocatalytic systems — A versatile platform with incredible biotechnological potential. *International Journal of Biological Macromolecules*, *175*, 108–122.

Braun, B., Klein, E., & López, J. L. (1996). Immobilization of Candida rugosa lipase to nylon fibers using its carbohydrate groups as the chemical link. *Biotechnology and Bioengineering*, *51*(3), 327–341.

Brzozowski, A. M., Derewenda, U., Derewenda, Z. S., Dodson, G. G., Lawson, D. M., Turkenburg, J. P., … Thim, L. (1991). A model for interfacial activation in lipases from the structure of a fungal lipase-inhibitor complex. *Nature*, *351*(6326), 491–494.

Cadena, P. G., Jeronimo, R. a S., Melo, J. M., Silva, R. a, Lima Filho, J. L., & Pimentel, M. C. B. (2010). Covalent immobilization of invertase on polyurethane, plast-film and ferromagnetic Dacron. *Bioresource Technology*, *101*(6), 1595–1602.

Calero, J., Verdugo, C., Luna, D., Sancho, E. D., Luna, C., Posadillo, A., … Romero, A. A. (2014). Selective ethanolysis of sunflower oil with Lipozyme RM IM, an immobilized Rhizomucor miehei lipase, to obtain a biodiesel-like biofuel, which avoids glycerol production through the monoglyceride formation. *New Biotechnology*, *31*(6), 596–601.

Canakci, M., & Van Gerpen, J. (1999). Biodiesel production via acid catalysis. *Transactions of the American Society of Agricultural Engineers*, *42*(5), 1203–1210.

Causevic, A., Olofsson, K., Adlercreutz, P., & Grey, C. (2023). Effects of Lipase Immobilization Conditions and Support Materials for the Production of Structured Triacylglycerols. *European Journal of Lipid Science and Technology*, *125*(2), 1–11.

Cavali, M., Bueno, A., Fagundes, A. P., Priamo, W. L., Bilibio, D., Mibielli, G. M., … Oliveira, J. V. (2020). Liquid lipase-mediated production of biodiesel from agroindustrial waste. *Biocatalysis and Agricultural Biotechnology*, *30*(101864), 1–7.

Chen, H., & Hsieh, Y.-L. (2005). Enzyme immobilization on ultrafine cellulose fibers via poly(acrylic acid) electrolyte grafts. *Biotechnology and Bioengineering*, *90*(4), 405–413.

Chen, J., & Wu, W.-T. (2003). Regeneration of immobilized Candida antarctica lipase for transesterification. *Journal of Bioscience and Bioengineering*, *95*(5), 466–469.

Chiu, C.-W., Dasari, M. a., Sutterlin, W. R., & Suppes, G. J. (2006). Removal of Residual Catalyst from Simulated Biodiesel's Crude Glycerol for Glycerol Hydrogenolysis to Propylene Glycol. *Industrial & Engineering Chemistry Research*, *45*(2), 791–795. h

Crookes, R., Kiannejad, F., & Nazha, M. (1997). Systematic assessment of combustion characteristics of biofuels and emulsions with water for use as diesel engine fuels. *Energy Conversion and Management*, *38*(15–17), 1785–1795.

da Cunha, M. E., Krause, L. C., Moraes, M. S. A., Faccini, C. S., Jacques, R. A., Almeida, S. R., … Caramão, E. B. (2009). Beef tallow biodiesel produced in a pilot scale. *Fuel Processing Technology*, *90*(4), 570–575.

Dalla Rosa, C., Morandim, M. B., Ninow, J. L., Oliveira, D., Treichel, H., & Oliveira, J. V. (2009). Continuous lipase-catalyzed production of fatty acid ethyl esters from soybean oil in compressed fluids. *Bioresource Technology*, *100*(23), 5818–5826.

de Castro, H. F., de Lima, R., & Roberto, I. C. (2001). Rice straw as a support for immobilization of microbial lipase. *Biotechnology Progress*, *17*(6), 1061–1064.

de Fuentes, I. E., Viseras, C. A., Ubiali, D., Terreni, M., & Alcántara, A. R. (2001). Different phyllosilicates as supports for lipase immobilisation. *Journal of Molecular Catalysis B: Enzymatic*, *11*(4–6), 657–663.

de Oliveira, D., Di Luccio, M., Faccio, C., Rosa, C. D., Bender, J. P., Lipke, N., … de Oliveira, J. V. (2004). Optimization of enzymatic production of biodiesel from castor oil in organic solvent medium. *Applied Biochemistry and Biotechnology*, *115*(1), 771–780.

Dimitrijević, A., Veličković, D., Bihelović, F., Bezbradica, D., Jankov, R., & Milosavić, N. (2012). One-step, inexpensive high yield strategy for Candida antarctica lipase A isolation using hydroxyapatite. *Bioresource Technology*, *107*, 358–362.

Dizge, N., Keskinler, B., & Tanriseven, A. (2008). Covalent attachment of microbial lipase onto microporous styrene-divinylbenzene copolymer by means of polyglutaraldehyde. *Colloids and Surfaces B: Biointerfaces*, *66*(1), 34–38.

Dossat, V., Combes, D., & Marty, A. (1999). Continuous enzymatic transesterification of high oleic sunflower oil in a packed bed reactor: influence of the glycerol production. *Enzyme and Microbial Technology*, *25*(3–5), 194–200.

Du, W., Li, W., Sun, T., Chen, X., & Liu, D. (2008). Perspectives for biotechnological production of biodiesel and impacts. *Applied Microbiology and Biotechnology*, *79*(3), 331–337.

Du, W., Xu, Y., Liu, D., & Zeng, J. (2004). Comparative study on lipase-catalyzed transformation of soybean oil for biodiesel production with different acyl acceptors. *Journal of Molecular Catalysis B: Enzymatic*, *30*(3–4), 125–129.

Elçin, Y. M., & Saçak, M. (1996). Acrylamide grafted poly(ethylene terephthalate) fibers activated by glutaraldehyde as support for urease. *Applied Biochemistry and Biotechnology - Part A Enzyme Engineering and Biotechnology*, *60*(1), 19–32.

Enweremadu, C. C., & Mbarawa, M. M. (2009). Technical aspects of production and analysis of biodiesel from used cooking oil—A review. *Renewable and Sustainable Energy Reviews*, *13*(9), 2205–2224.

Fernandez-Lafuente, R. (2010). Lipase from Thermomyces lanuginosus: Uses and prospects as an industrial biocatalyst. *Journal of Molecular Catalysis B: Enzymatic*, *62*(3–4), 197–212.

Fernández-Lorente, G., Palomo, J. M., Mateo, C., Munilla, R., Ortiz, C., Cabrera, Z., … Fernandez-Lafuente, R. (2006). Glutaraldehyde cross-linking of lipases adsorbed on aminated supports in the presence of detergents leads to improved performance. *Biomacromolecules*, *7*(9), 2610–2615.

Ferreira Mota, G., Germano de Sousa, I., Luiz Barros de Oliveira, A., Luthierre Gama Cavalcante, A., da Silva Moreira, K., Thálysson Tavares Cavalcante, F., … dos Santos, J. C. S. (2022). Biodiesel production from microalgae using lipase-based catalysts: Current challenges and prospects. *Algal Research*, *62*(July 2021).

Foresti, M. L., Alimenti, G. A., & Ferreira, M. L. (2005). Interfacial activation and bioimprinting of Candida rugosa lipase immobilized on polypropylene: effect on the enzymatic activity in solvent-free ethyl oleate synthesis. *Enzyme and Microbial Technology*, *36*(2–3), 338–349.

Fukuda, H. H., Kond, A., Noda, H., Kondo, A., & Noda, H. (2001). Biodiesel Fuel Production by Transesterification. *Journal of Bioscience and Bioengineering*, *92*(5), 405–416.

Furuhata, K. I., Deno, S., & Sakamoto, M. (1996). Immobilization of invertase onto silk fabrics enriched in amino groups. *Journal of Sericultural Science of Japan*, *65*(5), 378–384.

Ganesan, D., Rajendran, A., & Thangavelu, V. (2009). An overview on the recent advances in the transesterification of vegetable oils for biodiesel production using chemical and biocatalysts. *Reviews in Environmental Science and Biotechnology*, *8*(4), 367–394.

Garmroodi, M., Mohammadi, M., Ramazani, A., Ashjari, M., Mohammadi, J., Sabour, B., & Yousefi, M. (2016). Covalent binding of hyper-activated Rhizomucor miehei lipase (RML) on hetero-functionalized siliceous supports. *International Journal of Biological Macromolecules*, *86*, 208–215.

Gaur, R., Pant, H., Jain, R., & Khare, S. (2006). Galacto-oligosaccharide synthesis by immobilized Aspergillus oryzae β-galactosidase. *Food Chemistry*, *97*(3), 426–430.

Giorno, L., & Drioli, E. (2000). Biocatalytic membrane reactors: applications and perspectives. *Trends in Biotechnology*, *18*(August), 339–349.

Girelli, A. M., & Chiappini, V. (2023). Renewable, sustainable, and natural lignocellulosic carriers for lipase immobilization: A review. *Journal of Biotechnology*, *365*(February), 29–47.

Graboski, M. S., & McCormick, R. L. (1998). Combustion of fat and vegetable oil derived fuels in diesel engines. *Progress in Energy and Combustion Science*, *24*(2), 125–164.

Guldhe, A., Singh, B., Mutanda, T., Permaul, K., & Bux, F. (2015). Advances in synthesis of biodiesel via enzyme catalysis: Novel and sustainable approaches. *Renewable and Sustainable Energy Reviews*, *41*, 1447–1464.

Gurgel, D., Vieira, Y. A., Henriques, R. O., Machado, R., Oechsler, B. F., Junior, A. F., & de Oliveira, D. (2022). A Comprehensive Review on Core-Shell Polymeric Particles for Enzyme Immobilization. *ChemistrySelect*, *7*(46).

Halim, S. F. A., Kamaruddin, A. H., & Fernando, W. J. N. (2009). Continuous biosynthesis of biodiesel from waste cooking palm oil in a packed bed reactor: optimization using response surface methodology (RSM) and mass transfer studies. *Bioresource Technology*, *100*(2), 710–716.

Homaei, A. A., Sariri, R., Vianello, F., & Stevanato, R. (2013). Enzyme immobilization: An update. *Journal of Chemical Biology*, *6*(4), 185–205.

Hsu, A.-F., Jones, K. C., Foglia, T. a, & Marmer, W. N. (2004). Transesterification activity of lipases immobilized in a phyllosilicate sol-gel matrix. *Biotechnology Letters*, *26*(11), 917–921.

Ichijo, H., Suehiro, T., Nagasawa, J., Honda, S., Uedaira, H., Yamauchi, A., … Sagesaka, M. (1990). Fibrous Support Module Composed of Braided Poly(Vinyl Alcohol) Superfine Fibers. *Annals of the New York Academy of Sciences*, *613*(1), 858–862.

Iso, M., Chen, B., Eguchi, M., Kudo, T., & Shrestha, S. (2001). Production of biodiesel fuel from triglycerides and alcohol using immobilized lipase. *Journal of Molecular Catalysis B: Enzymatic*, *16*(1), 53–58. Jeong, G.-T., Park, D.-H., Kang, C.-H., Lee, W.-T., Sunwoo, C.-S., Yoon, C.-H., … Lee, U.-T. (2004). Production of biodiesel fuel by transesterification of rapeseed oil. *Applied Biochemistry and Biotechnology*, *113–116*, 747–758.

Kaieda, M., Samukawa, T., Kondo, a, & Fukuda, H. (2001). Effect of methanol and water contents on production of biodiesel fuel from plant oil catalyzed by various lipases in a solvent-free system. *Journal of Bioscience and Bioengineering*, *91*(1), 12–15.

Kaieda, M., Samukawa, T., Matsumoto, T., Ban, K., Kondo, A., Shimada, Y., … others. (1999). Biodiesel fuel production from plant oil catalyzed by Rhizopus oryzae lipase in a water-containing system without an organic solvent. *Journal of Bioscience and Bioengineering*, *88*(6), 627–631.

Kaygusuz, K. (2002). Renewable energy sources: The key to a better future. *Energy Sources*, *24*, 787–799.

Kirk, O., & Christensen, M. W. (2002). Lipases from Candida a ntarctica : Unique Biocatalysts from a Unique Origin. *Organic Process Research & Development*, *6*(4), 446–451.

Kojima, S., Du, D., Sato, M., & Park, E. Y. (2004). Efficient production of fatty acid methyl ester from waste activated bleaching earth using diesel oil as organic solvent. *Journal of Bioscience and Bioengineering*, *98*(6), 420–424.

Koller, G., Aris, M. J., Ujang, Z., & Vaidya, A. M. (2001). Dependence of the synthetic activity of nine immobilized lipases on water activity. *Biocatalysis and Biotransformation*, *19*(1), 37–49.

Komers, K., Skopal, F., & Čegan, A. (2010). Continuous biodiesel production in a cascade of flow ideally stirred reactors. *Bioresource Technology*, *101*(10), 3772–3775.

Köse, O., Tüter, M., & Ayşe Aksoy, H. (2002). Immobilized Candida antarctica lipase-catalyzed alcoholysis of cotton seed oil in a solvent-free medium. *Bioresource Technology*, *83*(2), 125–129.

Kuhnt, K., Degen, C., Jaudszus, A., & Jahreis, G. (2012). Searching for health beneficial n-3 and n-6 fatty acids in plant seeds. *European Journal of Lipid Science and Technology*, *114*(2), 153–160.

Lai, C.-C., Zullaikah, S., Vali, S. R., & Ju, Y.-H. (2005). Lipase-catalyzed production of biodiesel from rice bran oil. *Journal of Chemical Technology & Biotechnology*, *80*(3), 331–337.

Lara, P., & Park, E. Y. (2004). Potential application of waste activated bleaching earth on the production of fatty acid alkyl esters using Candida cylindracea lipase in organic solvent system. *Enzyme and Microbial Technology*, *34*(3–4), 270–277.

Lee, J. H., Kim, S. B., Park, C., Tae, B., Han, S. O., & Kim, S. W. (2010). Development of batch and continuous processes on biodiesel production in a packed-bed reactor by a mixture of immobilized Candida rugosa and Rhizopus oryzae lipases. *Applied Biochemistry and Biotechnology*, *161*(1–8), 365–371.

Li, W., Shen, H., Ma, M., Liu, L., Cui, C., Chen, B., … Tan, T. (2015). Synthesis of ethyl oleate by esterification in a solvent-free system using lipase immobilized on PDMS-modified nonwoven viscose fabrics. *Process Biochemistry*, *50*(11), 1859–1869.

Lin, C.-Y. Y., & Lin, H.-A. A. (2006). Diesel engine performance and emission characteristics of biodiesel produced by the peroxidation process. *Fuel*, *85*(3), 298–305.

Linko, Y., Lamsa, M., Wu, X., & Uosukainen, E. (1998). Biodegradable products by lipase biocatalysis. *Journal Of*, *66*(1), 41–50.

Lotero, E., Liu, Y., Lopez, D. E., Suwannakarn, K., Bruce, D. A., & Goodwin, J. G. (2005). Synthesis of biodiesel via acid catalysis. *Industrial and Engineering Chemistry Research*, *44*(14), 5353–5363.

Lu, J., Nie, K., Xie, F., Wang, F., & Tan, T. (2007). Enzymatic synthesis of fatty acid methyl esters from lard with immobilized Candida sp. 99-125. *Process Biochemistry*, *42*(9), 1367–1370.

Ma, F., & Hanna, M. a. (1999). Biodiesel production: a review. *Bioresource Technology*, *70*(1), 1–15.

Ma, L., Persson, M., & Adlercreutz, P. (2002). Water activity dependence of lipase catalysis in organic media explains successful transesterification reactions. *Enzyme and Microbial Technology*, *31*(7), 1024–1029.

Maghraby, Y. R., El-Shabasy, R. M., Ibrahim, A. H., & Azzazy, H. M. E. S. (2023). Enzyme Immobilization Technologies and Industrial Applications. *ACS Omega*, *8*(6), 5184–5196.

Mahfoudhi, A., Benmabrouk, S., Fendri, A., & Sayari, A. (2022). Fungal lipases as biocatalysts: A promising platform in several industrial biotechnology applications. *Biotechnology and Bioengineering*, *119*(12), 3370–3392.

Marín-Suárez, M., Méndez-Mateos, D., Guadix, A., & Guadix, E. M. (2019). Reuse of immobilized lipases in the transesterification of waste fish oil for the production of biodiesel. *Renewable Energy*, *140*, 1–8.

Matassoli, A. L. F., Corrêa, I. N. S., Portilho, M. F., Veloso, C. O., & Langone, M. a P. (2009). Enzymatic synthesis of biodiesel via alcoholysis of palm oil. *Applied Biochemistry and Biotechnology*, *155*(1–3), 347–355.

Mateo, C., Abian, O., Fernandez-Lafuente, R., & Guisan, J. M. J. M. (2000). Reversible enzyme immobilization via a very strong and nondistorting ionic adsorption on support–polyethylenimine composites. *Biotechnology and Bioengineering*, *68*(1), 98–105.

Meher, L., Vidyasagar, D., & Naik, S. (2006). Technical aspects of biodiesel production by transesterification—a review. *Renewable and Sustainable Energy Reviews*, *10*(3), 248–268.

Mekala, N. K., Potumarthi, R., Baadhe, R. R., & Gupta, V. K. (2014). *Chapter 1- Current Bioenergy Researches: Strengths and Future Challenges*. (V. K. Gupta, M. G. Tuohy, C. P. Kubicek, J. Saddler, F. Xu, B. R. A. and Applications, … P. 1-21, Eds.), *Bioenergy Research: Advances and Applications*.

Mittelbach, M. (1990). Lipase catalyzed alcoholysis of sunflower oil. *Journal of the American Oil Chemists' Society*, *67*(3), 168–170.

Nelson, L. A., Foglia, T. A., & Marmer, W. N. (1996). Lipase-catalyzed production of biodiesel. *Journal of the American Oil Chemists' Society*, *73*(8), 1191–1195.

Nie, K., Xie, F., Wang, F., & Tan, T. (2006). Lipase catalyzed methanolysis to produce biodiesel: Optimization of the biodiesel production. *Journal of Molecular Catalysis B: Enzymatic*, *43*(1–4), 142–147.

Nigam, P. S., & Singh, A. (2011). Production of liquid biofuels from renewable resources. *Progress in Energy and Combustion Science*, *37*(1), 52–68.

Noureddini, H., Gao, X., & Philkana, R. S. (2005). Immobilized Pseudomonas cepacia lipase for biodiesel fuel production from soybean oil. *Bioresource Technology*, *96*(7), 769–777.

Ondul, E., Dizge, N., & Albayrak, N. (2012). Immobilization of Candida antarctica A and Thermomyces lanuginosus lipases on cotton terry cloth fibrils using polyethyleneimine. *Colloids and Surfaces B: Biointerfaces*, *95*(0), 109–114.

Paiva, A. L., Balca, V. M., & Malcata, F. X. (2000). Kinetics and mechanisms of reactions catalysed by immobilized lipases. *Enzyme and Microbial Technology*, *27*(6), 426–446.

Palomo, J. M., Fernández-Lorente, G., Mateo, C., Fuentes, M., Guisan, J. M., & Fernández-Lafuente, R. (2002). Enzymatic production of (3S,4R)-(−)-4-(4′-fluorophenyl)-6-oxo-piperidin-3-carboxylic acid using a commercial preparation from Candida antarctica A: the role of a contaminant esterase. *Tetrahedron: Asymmetry*, *13*(24), 2653–2659.

Parmegiani Marcucci, S. M., Zunta Raia, R., Zanin, G. M., & Arroyo, P. A. (2023). Ethyl ester production with immobilized lipase in tin modified SBA -15: Effect of the support characteristic and reaction conditions . *The Canadian Journal of Chemical Engineering*, (February), 1–11.

Penzol, G., Armisén, P., Fernández-Lafuente, R., Rodés, L., & Guisán, J. M. (1998). Use of dextrans as long and hydrophilic spacer arms to improve the performance of immobilized proteins acting on macromolecules. *Biotechnology and Bioengineering*, *60*(4), 518–523.

Pham, T., Nguyen, U., Imamura, K., Furuta, M., & Maeda, Y. (2022). Transesterification using isopropanol as a co-solvent for the production of green biodiesel fuel. *International Journal of Energy Research*, *46*(4), 4352–4361.

Poppe, J. K., Fernandez-Lafuente, R., Rodrigues, R. C., & Ayub, M. A. Z. (2015). Enzymatic reactors for biodiesel synthesis: Present status and future prospects. *Biotechnology Advances*, *33*(5), 511–525.

Ranganathan, S. V., Narasimhan, S. L., & Muthukumar, K. (2008). An overview of enzymatic production of biodiesel. *Bioresource Technology*, *99*(10), 3975–3981.

Roberts, P. (2004). *The end of oil: on the edge of a perilous new world*. *Choice Reviews Online* (Vol. 42). New York: Houghton Mifflin Company.

Robles-Medina, a, González-Moreno, P. a, Esteban-Cerdán, L., & Molina-Grima, E. (2009). Biocatalysis: towards ever greener biodiesel production. *Biotechnology Advances*, *27*(4), 398–408.

Rodrigues, R. C., & Ayub, M. A. Z. Z. (2011). Effects of the combined use of Thermomyces lanuginosus and Rhizomucor miehei lipases for the transesterification and hydrolysis of soybean oil. *Process Biochemistry*, *46*(3), 682–688.

Salis, A., Pinna, M., Monduzzi, M., & Solinas, V. (2005). Biodiesel production from triolein and short chain alcohols through biocatalysis. *Journal of Biotechnology*, *119*(3), 291–299.

Salis, A., Sanjust, E., Solinas, V., & Monduzzi, M. (2003). Characterisation of Accurel MP1004 polypropylene powder and its use as a support for lipase immobilisation. *Journal of Molecular Catalysis B: Enzymatic*, *24–25*, 75–82.

Samukawa, T., Kaieda, M., Matsumoto, T., Ban, K., Kondo, A., Shimada, Y., … Fukuda, H. (2000). Pretreatment of immobilized Candida antarctica lipase for biodiesel fuel production from plant oil. *Journal of Bioscience and Bioengineering*, *90*(2), 180–183.

Sardar, M., Agarwal, R., Kumar, a., & Gupta, M. N. (1997). Noncovalent immobilization of enzymes on an enteric polymer Eudragit S-100. *Enzyme and Microbial Technology*, *20*(5), 361–367.

Sarmah, N., Revathi, D., Sheelu, G., Yamuna Rani, K., Sridhar, S., Mehtab, V., & Sumana, C. (2018). Recent advances on sources and industrial applications of lipases. *Biotechnology Progress*, *34*(1), 5–28.

Selvakumar, P., & Sivashanmugam, P. (2019). Ultrasound assisted oleaginous yeast lipid extraction and garbage lipase catalyzed transesterification for enhanced biodiesel production. *Energy Conversion and Management*, *179*(July 2018), 141–151.

Seng, B. L., Rhee, J. S., Cho, I., & Ryu, D. D. Y. (1980). Properties of Penicillin Amidohydrolase Immobilized on Nylon Fiber. *Bulletin of Korean Chemical Society*, *1*(1), 10–17.

Shahedi, M., Habibi, Z., Yousefi, M., Brask, J., & Mohammadi, M. (2021). Improvement of biodiesel production from palm oil by co-immobilization of Thermomyces lanuginosa lipase and Candida antarctica lipase B: Optimization using response surface methodology. *International Journal of Biological Macromolecules*, *170*, 490–502.

Shahedi, M., Yousefi, M., Habibi, Z., Mohammadi, M., & As'habi, M. A. (2019). Co-immobilization of Rhizomucor miehei lipase and Candida antarctica lipase B and optimization of biocatalytic biodiesel production from palm oil using response surface methodology. *Renewable Energy*, *141*, 847–857.

Sharma, R., Chisti, Y., & Banerjee, U. C. (2001). Production, purification, characterization, and applications of lipases. *Biotechnology Advances*, *19*(8), 627–662.

Sharma, S., & Yamazaki, H. (1984). Preparation of hydrophobic cotton cloth. *Biotechnology Letters*, *6*(5), 301–306.

Sher, E. (Ed.). (1998). Environmental aspects of air pollution. In *Handbook of air pollution from internal combustion engines—pollutant formation and control* (pp. 25–41). San Diego, California.: ACADEMIC PRESS, INC.

Shieh, C., Liao, H., & Lee, C. (2003). Optimization of lipase-catalyzed biodiesel by response surface methodology. *Bioresource Technology*, *88*, 103–106.

Shimada, Y., Sugihara, A., Minamigawa, Y., Higashiyama, K., Akimoto, K., Fujikawa, S., … Tominaga, Y. (1998). Enzymatic enrichment of arachidonic acid from Mortierella single-cell oil. *JAOCS, Journal of the American Oil Chemists' Society*, *75*(9), 1213–1217.

Shimada, Y., Sugihara, A., Nakano, H., Kuramoto, T., Nagao, T., Gemba, M., & Tominaga, Y. (1997). Purification of docosahexaenoic acid by selective esterification of fatty acids from tuna oil with rhizopus delemar lipase. *JAOCS, Journal of the American Oil Chemists' Society*, *74*(2), 97–101.

Shimada, Y., Watanabe, Y., Samukawa, T., Sugihara, A., Noda, H., Fukuda, H., & Tominaga, Y. (1999). Conversion of vegetable oil to biodiesel using immobilized Candida antarctica lipase. *Journal of the American Oil Chemists' Society*, *76*(7), 789–793.

Shimada, Y., Watanabe, Y., Sugihara, A., & Tominaga, Y. (2002). Enzymatic alcoholysis for biodiesel fuel production and application of the reaction to oil processing. *Journal of Molecular Catalysis B: Enzymatic*, *17*(3–5), 133–142.

Siqueira, N. M., Garcia, K. C., Bussamara, R., Both, F. S., Vainstein, M. H., & Soares, R. M. D. (2015). Poly (lactic acid)/chitosan fiber mats: Investigation of effects of the support on lipase immobilization. *International Journal of Biological Macromolecules*, *72*, 998–1004.

Soumanou, M. M., & Bornscheuer, U. T. (2003a). Improvement in lipase-catalyzed synthesis of fatty acid methyl esters from sunflower oil. *Enzyme and Microbial Technology*, *33*(1), 97–103.

Soumanou, M. M., & Bornscheuer, U. T. (2003b). Lipase-catalyzed alcoholysis of vegetable oils. *European Journal of Lipid Science and Technology*, *105*(11), 656–660.

Stevenson, D. E., Stanley, R. a., & Furneaux, R. H. (1994). Near-quantitative production of fatty acid alkyl esters by lipase-catalyzed alcoholysis of fats and oils with adsorption of glycerol by silica gel. *Enzyme and Microbial Technology*, *16*(6), 478–484.

Tan, T., Lu, J., Nie, K., Deng, L., & Wang, F. (2010). Biodiesel production with immobilized lipase: A review. *Biotechnology Advances*, *28*(5), 628–634.

Tan, Z., Bilal, M., Li, X., Ju, F., Teng, Y., & Iqbal, H. M. N. (2022). Nanomaterial-immobilized lipases for sustainable recovery of biodiesel – A review. *Fuel*, *316*(February), 123429.

Tesser, R., Di Serio, M., Guida, M., Nastasi, M., & Santacesaria, E. (2005). Kinetics of oleic acid esterification with methanol in the presence of triglycerides. *Industrial & Engineering Chemistry Research*, *44*(21), 7978–7982. Retrieved from

Torres, R., Mateo, C., Fuentes, M., Palomo, J. M., Ortiz, C., Fernández-Lafuente, R., … Daminati, M. (2002). Reversible immobilization of invertase on Sepabeads coated with polyethyleneimine: optimization of the biocatalyst's stability. *Biotechnology Progress*, *18*(6), 1221–1226.

Tüter, M., Aksoy, H. A., Gılbaz, E. E., & Kurşun, E. (2004). Synthesis of fatty acid esters from acid oils using lipase B fromCandida antarctica. *European Journal of Lipid Science and Technology*, *106*(8), 513–517.

Uosukainen, E., Lämsä, M., Linko, Y. Y. Y., Linko, P., & Leisola, M. (1999). Optimization of enzymatic transesterification of rapeseed oil ester using response surface and principal component methodology. *Enzyme and Microbial Technology*, *25*(3–5), 236–243.

Valivety, R. H., Halling, P. J., & Macrae, A. R. (1992). Rhizomucor miehei lipase remains highly active at water activity below 0.0001. *FEBS Letters*, *301*(3), 258–260.

Vasistha, S., Khanra, A., Clifford, M., & Rai, M. P. (2021). Current advances in microalgae harvesting and lipid extraction processes for improved biodiesel production: A review. *Renewable and Sustainable Energy Reviews*, *137*(October 2020), 110498.

Velasco-Lozano, S., López-Gallego, F., Vázquez-Duhalt, R., Mateos-Díaz, J. C., Guisán, J. M., & Favela-Torres, E. (2014). Carrier-free immobilization of lipase from Candida rugosa with polyethyleneimines by carboxyl-activated cross-linking. *Biomacromolecules*, *15*(5), 1896–1903.

Wang, H., Wu, H., Ho, C.-T., & Weng, X.-C. (2006). Cocoa butter equivalent from enzymatic interesterification of tea seed oil and fatty acid methyl esters. *Food Chemistry*, *97*(4), 661–665.

Wang, J., Meng, G., Tao, K., Feng, M., Zhao, X., Li, Z., … Lu, J. R. (2012). Immobilization of Lipases on Alkyl Silane Modified Magnetic Nanoparticles: Effect of Alkyl Chain Length on Enzyme Activity. *PLoS ONE*, *7*(8), 21–25.

Wang, X., Dou, P., Zhao, P., Zhao, C., Ding, Y., & Xu, P. (2009). Immobilization of lipases onto magnetic Fe3O4nanoparticles for application in biodiesel production. *ChemSusChem*, *2*(10), 947–950.

Wang, X., Liu, X., Zhao, C., Ding, Y., & Xu, P. (2011). Biodiesel production in packed-bed reactors using lipase-nanoparticle biocomposite. *Bioresource Technology*, *102*(10), 6352–6355.

Watanabe, Y., Shimada, Y., Sugihara, A., Noda, H., Fukuda, H., & Tominaga, Y. (2000). Continuous production of biodiesel fuel from vegetable oil using immobilized Candida antarctica lipase. *Journal of the American Oil Chemists' Society*, *77*(4), 355–360.

Watanabe, Y., Shimada, Y., Sugihara, A., & Tominaga, Y. (1999). Stepwise ethanolysis of tuna oil using immobilized Candida antarctica lipase. *Journal of Bioscience and Bioengineering*, *88*(6), 622–626.

Watanabe, Y., Shimada, Y., Sugihara, A., & Tominaga, Y. (2001). Enzymatic conversion of waste edible oil to biodiesel fuel in a fixed-bed bioreactor. *Journal of the American Oil Chemists' Society*, *78*(7), 703–707.

Weaver, L. E., & Carta, G. (1996). Protein adsorption on cation exchangers: Comparison of macroporous and gel-composite media. *Biotechnology Progress*, *12*(3), 342–355.

Wehtje, E., & Adlercreutz, P. (1997a). Lipases have similar water activity profiles in different reactions. *Biotechnology Letters*, *19*(6), 537–540.

Wehtje, E., & Adlercreutz, P. (1997b). Water activity and substrate concentration effects on lipase activity. *Biotechnology and Bioengineering*, *55*(5), 798–806.

Würtz Christensen, M., Andersen, L., Husum, T. L. T. L., Kirk, O., Christensen, M. W., Andersen, L., … Kirk, O. (2003). Industrial lipase immobilization. *European Journal of Lipid Science and Technology*, *105*(6), 318–321.

Xu, Y., Du, W., & Liu, D. (2005). Study on the kinetics of enzymatic interesterification of triglycerides for biodiesel production with methyl acetate as the acyl acceptor. *Journal of Molecular Catalysis B: Enzymatic*, *32*(5–6), 241–245.

Xu, Y., Du, W., Liu, D., & Zeng, J. (2003). A novel enzymatic route for biodiesel production from renewable oils in a solvent-free medium. *Biotechnology Letters*, *25*, 1239–1241.

Yadav, G. D., & Trivedi, A. H. (2003). Kinetic modeling of immobilized-lipase catalyzed transesterification of n-octanol with vinyl acetate in non-aqueous media. *Enzyme and Microbial Technology*, *32*(7), 783–789.

Yagiz, F., Kazan, D., & Akin, a. (2007). Biodiesel production from waste oils by using lipase immobilized on hydrotalcite and zeolites. *Chemical Engineering Journal*, *134*(1–3), 262–267.

Yu, M., Qin, S., & Tan, T. (2007). Purification and characterization of the extracellular lipase Lip2 from Yarrowia lipolytica. *Process Biochemistry*, *42*(3), 384–391.

Zhang, J., Chen, H., Wang, Z., Xu, H., Luo, W., Xu, J., & Lv, P. (2022). Heat-induced overexpression of the thermophilic lipase from Bacillus thermocatenulatus in Escherichia coli by fermentation and its application in preparation biodiesel using rapeseed oil. *Biotechnology and Applied Biochemistry*, *69*(5), 1812–1820.

Zhang, X. J., Qi, F. Y., Qi, J. M., Yang, F., Shen, J. W., Cai, X., … Zheng, Y. G. (2022). Efficient enzymatic synthesis of L-ascorbyl palmitate using Candida antarctica lipase B-embedded metal-organic framework. *Biotechnology Progress*, *38*(1), 1–11.

Zhu, S., Wu, Y., & Yu, Z. (2005). Immobilization of Candida rugosa lipase on a pH-sensitive support for enantioselective hydrolysis of ketoprofen ester. *Journal of Biotechnology*, *116*(4), 397–401.

CHAPTER V

AGENT-BASED SYSTEM DESIGN FOR MULTIPLE LOAD AUTOMATED GUIDED VEHICLE

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1. Introduction

Present market demands require that manufacturing systems develop their activities under a dynamic and uncertain production environment. In recent years, agent technology has been considered as an important approach for developing industrial distributed systems (Wooldridge and Jennings, 1995). A number of researchers have attempted to apply agent technology to manufacturing enterprise integration, supply chain management, concurrent engineering, manufacturing scheduling and control, material handling, and holonic manufacturing systems.

Agents realize to solve a problem of your own, submit bids, after the submission of bids, wait for a while, wait for an offer as a result of the evaluations and evaluate the answers from the other agents as a result of a new initiative. The criteria that the agents use when evaluating incoming responses are defined by the agent programmer. An agent obtained in a software environment waits in the system until a goal is defined for it or an event occurs that it needs to respond to (Hahn et. al 2009). The design of agent-based systems differs from classical modeling and design systems. Until now, instead of a standard design template, special designs have usually been used in agent-based systems. Prometheus is a design method used in the identification, design and application of agent-based systems. Perepletchikov et al. (2005) presented a mechanism for dividing an agent oriented application into the three scoping levels of essential, conditional and optional was applied after the initial system specification, and was then used to direct incremental development with three separate release. Fernández-Caballero and Gascueña (2009) composed an Analysis Overview Diagram to obtain an initial sketch of the application. Afterwards, the model obtained - by following the two first stages proposed by Prometheus methodology – could be integrated into INGENIAS through UML-AT language. Next, the modeling integrated on with INGENIAS. Finally, code was generated for the ICARO-T platform. Lhafiane et al. (2015) proposed multi agent system (MAS) architecture using the Prometheus methodology to efficiently manage reverse logistics processes. The proposed MAS architecture included five types of agents: Gate keeping Agent, Collection Agent, Sorting Agent, Processing Agent and Disposal Agent which act respectively during the five steps of reverse logistics Network. Ehimwenma and Krishnamoorthy (2020) presented the use of Prometheus approach for the modelling of a pre-assessment system of five interactive agents which was a multi-agent-based e-learning system was developed to support the assessment of prior learning skills in students to classify their skills and make recommendation for their learning. Larıouı and Byed (2020) designed a multi-agent architecture using Prometheus method to effectively manage the movements of travelers in a multimodal network. The proposed MAS architecture included six types of agents: Personal Travel Agent, Information Agent, Directory Selecting Agent, Sorting Agent, Calculating Agent and Decision-Making Agent. The multi-agent architecture proposed was efficient, flexible, designed to easily be adapted and to manage disturbances in the transport network.

AGVs are one or more computer-controlled, operating independently of the operator in the factory or warehouse. This definition is a general term that covers all transport systems that can work without an operator. It is a material transportation system such as wheelbarrows pallets that are programmed to move between different production and warehouse stations without an operator (Schulze and Wullner, 2006). If the AGV carries more than one load, the researchers have specified it as Multiple-load AGV (MAGV). Ho et al. (2004) identified four problems for MAGV scheduling. The first problem is the problem of task determination for loads. The second problem is the problem of delivery the load. The third and fourth problems are the problem of determining the pick-up point and load selection when the pick-up point is reached.

When looking at previous studies, there were no studies that performed MAGV and agent modeling. In Prometheus method of modeling; there are three main stages: system specifications, architectural design and detailed design by using agent interface. In this study, Prometheus agent-based design software has been applied for MAGV.

2. Method

One of the systems that differs from the classical modeling and design systems is the agent-based systems. Special design templates are used for agent-based systems. Prometheus, one of the special templates, plays an important role in the design and implementation of systems. A software with the same name has been developed to design the Prometheus methodology. In this method, there are three basic stages: system specifications, architectural design and detailed design (Padgham and Winikoff 2005).

The stage of determining the system specifications of the Prometheus method focuses on the goals and basic functions of the system. At the same time, at this stage, the communication interfaces of the agent-based system are being prepared.

At the architectural design stage, the types of agents present in the system are determined. How the agents will communicate among themselves is determined by the information from the system.

At the detailed design stage, the detail design of the agents and how to organize the work within the system are determined. At this stage, it is designed in detail which plans the agent types will execute in the face of the situations they face. The plans to be realized by the agents are implemented by triggering messages from other agents. Messages are transmitted as a result of the negotiation of the agents within themselves or with other agents.

The name of the software containing the Prometheus method, which is most commonly used in the design of agent-based systems, is the Prometheus Design Tool (PDT). (Figure 1)

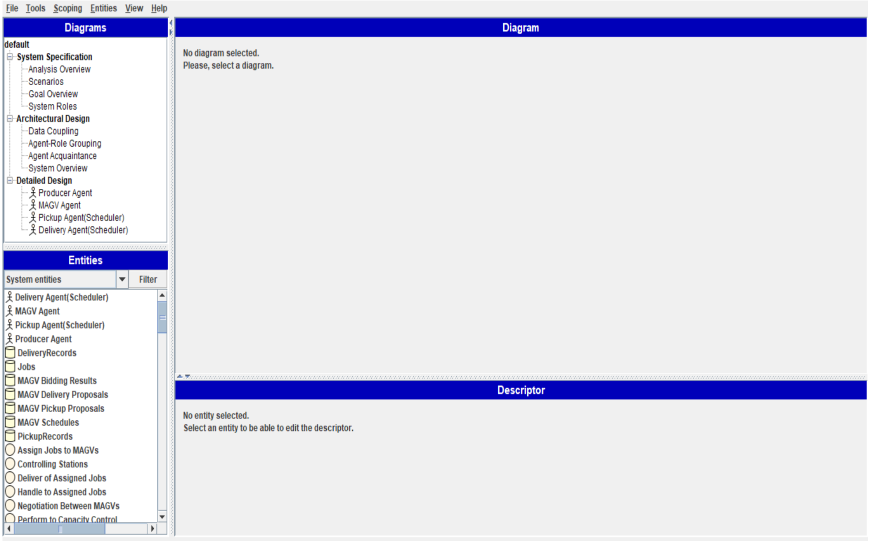

Figure 1. Prometheus Software

3. Model Design

At the first stage of the Prometheus method, at the stage of system specifications, scenarios, goals and sub-goals, as well as roles that will achieve these goals are determined. System startup information is entered using the main menu of system specifications via the "System specifications" panel.

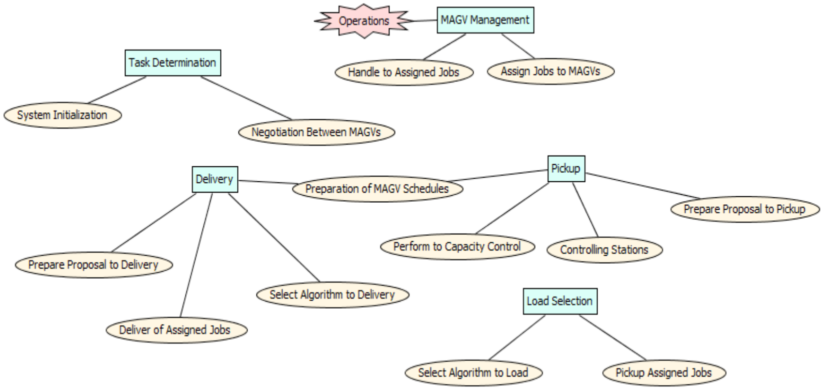

Figure 2. System roles and goals

There are five roles in the MAGV agent based system: MAGV management, task determination, pickup, delivery and load selection. The goals and roles definition for MAGVs are as follows (In Figure 2);

- MAGV Management role
  - Handle to assigned jobs
  - Assign jobs to MAGVs
- Task Determination role
  - System initializing
  - Negotiation between MAGVs
- Delivery role
  - Prepare proposal to delivery
  - Deliver of assigned jobs
  - Select algorithm to delivery
  - Preparation of MAGV Schedules
- Pickup role
  - Perform to capacity control
  - Controlling station
  - Prepare proposal to pickup
  - Preparation of MAGV Schedules
- Load selection role
  - Select algorithm to load
  - Pickup assigned jobs

This stage groups the roles determined in the system specifications stage by determining the agents. After deciphering the agents, protocols are written between the agents and a negotiation system is composed. Figure 3 shows the agent and role definitions.

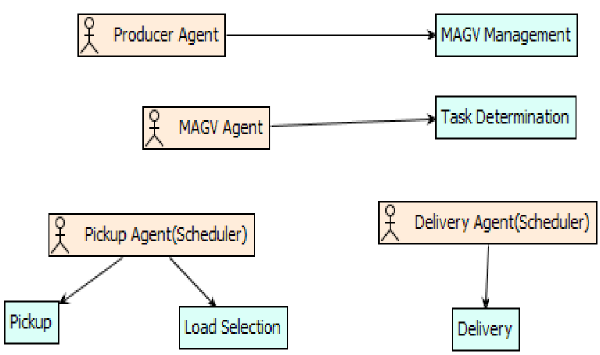

Figure 3. Agent role interaction

The MAGV management is carried out by the producer agent. In addition, the task determination role is performed by the MAGV agent, the pickup and load selection role is performed by the pickup agent (scheduler), and the delivery role is performed by the delivery agent (scheduler).

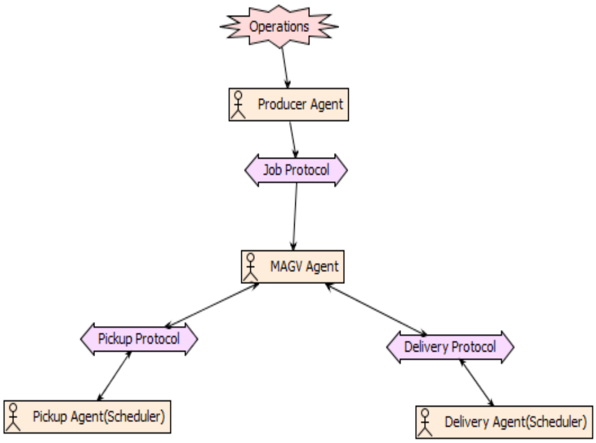

Figure 4. Agent protocol

Figure 4 shows the agents and the protocols. The job protocol is available between the producer agent and the MAGV agent, the pickup protocol is available between the MAGV agent and the pickup agent (scheduler), and the delivery protocol is available between the MAGV agent and the delivery agent (scheduler). In these protocols, there is an interaction between each other the messaging method. The perception of operations is also analyzed by the producer agent.

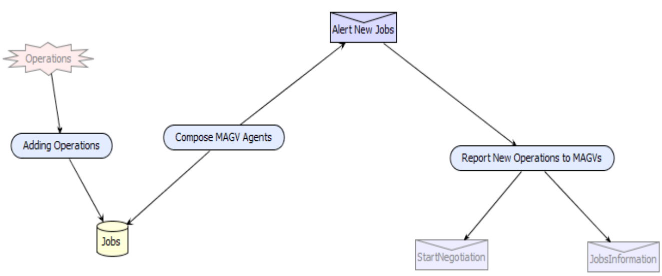

Figure 5. Producer agent –Detailed design

If the types of agents receive messages from the environment in which they are located or from other agents, it is defined which plans they will run and which database they will operate on. Messages can come from other agents, as well as from agents themselves. Figure 5 shows producer agent detailed design. The producer agent activates adding operations, compose MAGV agents and report operations to MAGVs. The agent starts negotiation and jobs information events send to the MAGV agent.

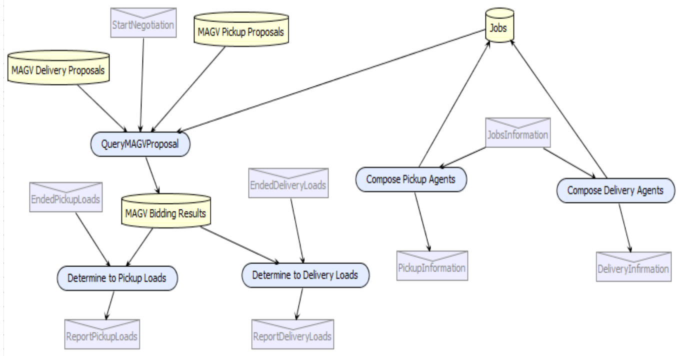

Figure 6. MAGV Agent –Detailed Design

Figure 6 shows MAGV agent detailed design. The agent starts negotiation message trigger to Query MAGV Proposal plan. Jobs information message is triggered to compose pickup agent and delivery agent's plans. And then, MAGV agent sends to pickup information message to pickup agent (scheduler). MAGV agent also sends to delivery information message to delivery agent (scheduler). The agent determine to pickup loads plan send to report pickup loads message to pickup agent (scheduler) and to delivery loads plan send to report delivery loads message to delivery agent (scheduler). Jobs, MAGV pickup proposals, MAGV delivery proposals and MAGV bidding result belief sets are recorded to data.

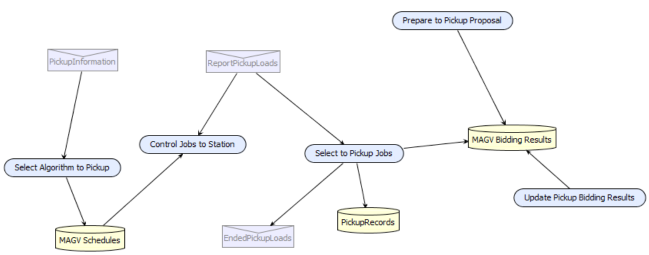

Figure 7. Pickup Agent (Scheduler)

Pickup information message is triggered the select algorithm to pickup plan for pickup agent (scheduler). Figure 7 shows pickup agent (Scheduler) detailed design. Control jobs to station, select to pickup jobs, prepare to pickup proposal and update pickup bidding results plans are performed by pickup agent (scheduler). MAGV schedules, pickup records and MAGV bidding results belief sets are used by the agents.

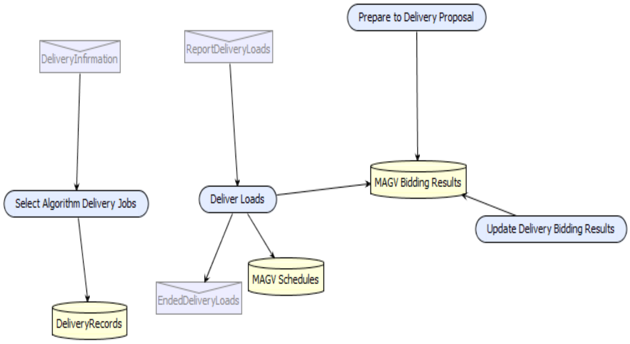

Figure 8. Delivery Agent (Scheduler)

Figure 8 shows delivery agent (Scheduler) detailed design. Select algorithm delivery jobs, deliver loads, prepare to delivery proposal, and update delivery bidding results plans are implemented by the delivery agent (scheduler). Delivery records, MAGV schedules and MAGV bidding results belief sets are conducted by the agent.

The final stage in the development of an agent-based system is the implementation of a software application. However, it was not included in the Prometheus method because it requires the use of different platforms.

4. Conclusion

In this study, the software used in the design of agent based systems is designed for the operations performed by MAGV material handling systems in enterprises. The model differs from traditional methods of modeling and designing. In agent based systems, custom designs are usually used instead of a standard design template. The three stages of the Prometheus design method have been studied and the design of the necessary works for MAGV has been provided. In future studies, it is considered to make the system more efficient by performing the coding of the software on the platforms.

References

Ehimwenma, Kennedy E., & Sujatha Krishnamoorthy (2020). Design and analysis of a multi-agent e-learning system using prometheus design tool. *arXiv preprint arXiv:2007.09645*

Fernández-Caballero, Antonio, & José M. Gascueña (2009). Developing multi-agent systems through integrating Prometheus, INGENIAS and

ICARO-T. *International Conference on Agents and Artificial Intelligence*. Springer, Berlin, Heidelberg.

Hahn, C., Madrıgal-Mora, C. & Fıscher, K., (2009). A platform-independent metamodel for multiagent systems", Autonomous Agents and Multi-Agent Systems, 18:239-66.

Ho, Y.C., Chien, S. H., and Liu, H. C., (2004). A simulation study on the performance of load-selection rules for multiple-load AGVs. The Annual Conference of Chinese Institute of Industrial Engineering,

Larioui, Jihane, & A. E. Byed (2020). Multi-agent system architecture oriented prometheus methodology design for multi-modal transportation. *International Journal* 8.5: 2118-2125.

Lhafiane, F., A. Elbyed, & M. Bouchoum (2015). Multi-agent system architecture oriented prometheus methodology design for reverse logistics. *International Journal of Computer and Information Engineering* 9.8: 1907-1913.

Padgham, L. and M. Winikoff, Developing intelligent agent systems: A practical guide. Vol. 13. 2005: John Wiley & Sons.

Perepletchikov, Mikhail, & Lin Padgham (2005). Systematic incremental development of agent systems, using Prometheus. *Fifth International Conference on Quality Software (QSIC'05)*. IEEE.

Schulze, L., & Wullner, A. (2006). The approach of automated guided vehicle systems. In Service Operations and Logistics, and Informatics, 2006. SOLI'06. IEEE, 522-527.

Wooldrıdge, M. & Jennıngs, N. R., (1995) Intelligent agents: theory and practice, The Knowledge Engineering Review, 10:115-52.

CHAPTER VI

THE EFFECTS OF USER EXPERIENCES ON PROCESSES IN THE DEVELOPMENT OF INTERFACE DESIGNS OF HYBRID SOFTWARE PROJECTS

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1. Introduction

As an effective result of the technological benefits of Web 2.0 and later Web 3.0, there are very important changes in user experiences and user habits (Kollmann vd., 2016). More accurately, developments in the light of innovative technologies force all users to change their habits. At this point, institutions or organizations should be able to design the products they will develop in order to ensure the continuity of their services, reach large masses and gain superiority over their competitors in the sector, taking into account user needs and expectations, in accordance with the user-oriented design approach and be open to innovations when necessary. In this explanation, "User Experience Design" is considered as a factor that constitutes one of the key factors of the production and development process. User experience [UX], in short (Hartson & Pyla, 2019), starts from the moment any product is put into the service of users after the development process and refers to the positive or negative experiences that users experience while using it (Anderson vd., 1988).

This process includes every stage of the user's interaction with the company and its products and services. User experience design [UXD] (Da Silva vd., 2018) refers to the impact of the user experience on the product development process to improve usability, accessibility, improvability and satisfaction resulting from the interaction between a product and its user. As can be understood, a product, system or service can only be successful if it is accepted and preferred by its users. Based on this information, the concept of user experience design enables users to focus on ease of use, meeting requirements, easily performing tasks, enjoying the product and similar issues while examining and evaluating how users feel about the product or service. Applications developed on mobile and web platforms constitute one of the most common environments where different expectations and opinions on user-oriented design understanding are seen.

The most important concept in a wide range of products developed in recent years, from IT products to industrial products, is "usability". Since usability is an element that increases productivity, it can prevent people from wasting time and resources and can lead to great economic gains. When users use a product, they should be able to perform the tasks they want to perform easily and without physical and cognitive difficulties (Greiner, 2007). Based on these, products with a high level of usability are efficient, effective and satisfying, easy to learn, contain elements that can be easily remembered during reuse even after a long break in use, do not cause the user to make mistakes, and even if mistakes are made, they offer solutions for the user to get rid of the errors encountered (Çağıltay, 2020). The developed products should be able to provide functionality with the minimum error rate within the framework of usability. In order to prevent the problems encountered, product usage should be determined and optimization should be ensured in the design process by considering different prototype studies and test phases. In addition, usability testing methods that can be applied at the point of obtaining data to increase the usability of the product should be applied and users should be included in this testing process (Riihiaho, 2018). With the tests applied, different results can be obtained in the detection of problems occurring in the interfaces of the products.

The software product on which the proposed work was tested has functionalities that enable employees in a company to track their work, plans and daily activities, and to communicate with each other. In order to obtain data on usability issues on this and similar systems and to make the system more usable and user-oriented, different test methods such as first click and tree testing were applied (Sivaji vd., 2011). The tests were carried out by involving seven to ten users in the testing process and it was aimed to analyze the design problems on different prototypes and make improvements. (Bastien, 2010). In addition, the product was also developed using the SAPUI5 application framework, as it is capable of working in conjunction with SAP (System Applications Products) and SAP applications are widely used by many corporate companies. The applications developed to communicate on mobile and web platforms were developed using ReactJs and React Native frameworks. Similarly, the hierarchical structure of both the page layouts and the hierarchical structure of the menus within the application of products with many features is a challenging situation compared to products with simpler structures. At this point, user audiences constitute the most fundamental element that will guide product design, functionality and ease of use. By evaluating the designed interfaces with usability tests, positive or negative situations encountered in the use of the product can be easily observed and changes can be made in the design structure.

This study is based on the usability evaluation of the applications of a software product on different platforms and the evaluation of the users' degree of task execution, performance and satisfaction levels. Usability evaluations were carried out on different prototypes, and the goal was to identify the problems, requirements and expectations of the users. In line with the objectives, it is aimed to offer solutions to the problems encountered.

S.Kantar, emerging usability in the interface of smart TVs problems, examining them with user experience techniques, card grouping, user testing using a number of testing methods and metrics, such as experience surveys and A/B testing and in the systematic improvement of film categories. has been found (Kantar, 2018).

In Çakmak's study on the usability of education management systems, he conducted a usability test to measure the effectiveness, efficiency and user satisfaction of social elements. In the study, collecting information about the user profile with a demographic questionnaire, observing user behaviors during the use of social elements, observing the eye movements of users with eye tracking method to determine user focal points monitoring and collecting user comments through think aloud method provided. Task completion to determine the effectiveness with the observations made status, during the performance of tasks to determine efficiency the number of errors made, during task completion to determine efficiency to determine the time spent and users' satisfaction levels The comments made by the participants were taken into consideration and evaluated (Çakmak, 2013).

In the thesis study conducted by Ş. Akın, the university library web usability evaluation on the page has been discussed. Sakarya In order to evaluate the usability of the University's web pages questionnaire, usability test, think-aloud protocol and observation. Different methods were used. Unlike the studies in the literature users' information retrieval skill levels [IARS] were also measured. In the study It was found that users with high BEBD also had high satisfaction rates (Akin, 2015).

M.Dalcı, card grouping the problems of METU's current website study and using google analytics, and the data obtained was used to develop new used in the site design. In the thesis study, students, academics, staff and different user groups, such as researchers, and the METU website, information architecture and information in terms of usability. Google analytics, users preferences, landing page optimization and disappearance factor analysis. used as a web analytics tool to obtain reports(Dalci, t.y.) (Dalcı, 2011).

In another study conducted to identify the design problems of the website of the Radar Performance and Track Analysis Center (RAPSİM), studies were carried out to evaluate the usability of the website and to update the website design in line with user-oriented design qualities with the results obtained. Participants were given a usability test and usability evaluation questionnaire was applied. Functional problems encountered on the website identified, and the results obtained in order to prevent and improve these problems findings were presented to the developers (Bati & Durdu, t.y.)

In another study conducted by Stephan, Cheng and Young in 2006 usability study was conducted at the University of Mississippi's library home page. on the site. The test was conducted with 12 participants and the satisfaction of the level as well as providing access to library resources (Stephan vd., 2006).

Fung, Chiu, Ko and Lo's study on the evaluation of the University of Hong Kong's library web page was tested according to Nielsen's ten usability methods. The study found that the mobile website had five intuitive immediate usability problems: users were not adequately informed about waiting time, some information was not logically supported, there were some compatibility problems in viewing content, error messages did not provide enough helpful information, and there was a lack of search for experts (Fung vd., 2016)more and more students use mobile devices for educational purposes. Under this circumstance libraries, especially academic libraries, should try to expand their services and design mobile websites to meet users' needs. The history of mobile library websites is relatively short, especially in Asia. Usability evaluation of mobile library websites is a new issue for study. As such, this paper evaluates the usability of the University of Hong Kong Library (HKUL.

2. Theoretical Background

The product, on which the concepts subject to the study are tested, is used for two different purposes, namely the ability to provide communication between the employees of the company and the ability to manage the work, plans and daily activities of the personnel within the company, and is developed on three different platforms: mobile, web and desktop. In order to realize the tracking of personnel, ExtJs application framework was used for the components used in the interface together with javascript language on the web platform and MVVM model was used as the design pattern (Oban, 2022). In addition, the hierarchical structure of both the page layouts and the hierarchical structure of the menus within the application of products developed for different platforms with more features in a similar structure constitutes a challenging situation compared to products with a simpler structure. At this point, user audiences constitute the most fundamental element that will guide product design, functionality and ease of use. By evaluating the designed interfaces together with usability tests, positive or negative situations encountered in the use of the product can be easily observed and changes can be made in the design structure. Since the product in question is an application used by the majority of the personnel, it has caused users to have many different types of requests for both product design and additional features. Depending on the continuous change in user needs over time, the product has gone through many stages in terms of both design and functionality, increasing the product quality and user satisfaction level.

Because of the tasks assigned to the users, usability evaluation was carried out by evaluating the relationships between task performance and satisfaction levels. Based on this information, the objectives planned to be realized are expressed as follows:

- Identifying expectations and requirements by taking into account user feedback on the application,
- To determine the level of users' ability to access information,
- Evaluate the performance of the performance of tasks,
- Realizing the detection of click maps related to the tasks given on application interfaces,
- Evaluate user satisfaction levels.

Based on the definition of usability stated in the ISO 9241-11 document in Figure 1 and the interrelationships between the concepts, usability evaluation methods such as the first click test and the tree test were applied to determine performance variables and usability metrics such as efficiency, effectiveness, satisfaction levels and the number of errors.

The number of test users applied in the study varies between seven and ten. The research was conducted on seven different tasks that were prepared by taking into account the features of the application. These tasks are defined in Table 1.

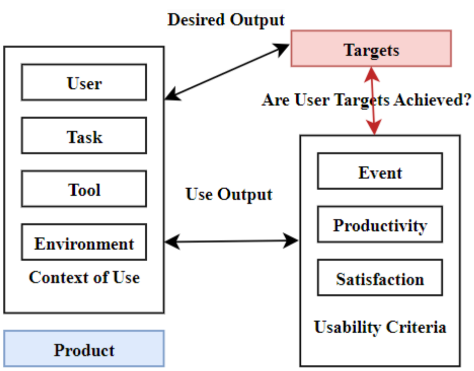


Figure 1. ISO 9241-11 Usability Scheme According to Standard

Table 1. Description of Tasks Tasks Task Description Task

Task 1	Please report problems that occur in the application
Task 2	View the tasks you have already assigned to your colleagues
Task 3	Change the application settings
Task 4	View the Reports page
Task 5	Please forward your suggestions regarding the application to the necessary units
Task 6	View jobs of company employees
Task 7	Log out of the application

One of the limitations of the study is that participants are affected by the environmental conditions (Hawthorne effect) in usability tests applied with real users and real tasks. The Hawthorne effect is defined as changes in user behavior due to the presence of the researcher or the test user's awareness of being observed by the researcher (Akin, 2015). These changes may affect usability studies by creating negative consequences for some users during the performance of tasks, both in terms of time and by causing tasks not to be completed correctly (Ritch Macefield, 2007) .

The functionality of interface designs is developed through a certain trial process before reaching the end user. For this, creating a prototype design is important to test the user experience (Türkmenoğlu & Atalar, 2020) . Before the product was presented to the employees of the company, it was prepared in line with the current needs and the competencies of the designers, inspired by the designs of different products that had been previously developed, without any prototype work. Some of the development stages representing these preparation processes can be exemplified as follows:

- Within the framework of the use of the product, color selection was one of the most demanded by the users in terms of design. The blue color intensity of the screens used for each module on the interfaces caused eye fatigue in the users and caused an effect that reduced the comprehensibility rate. In addition, the fact that the status of the records on the list was not expressed with icons, but only in the form of a description (plain text) caused users to waste time in determining which jobs were important or completed at first glance. The screen design with the records related to the jobs on the list is shown in Figure 2.

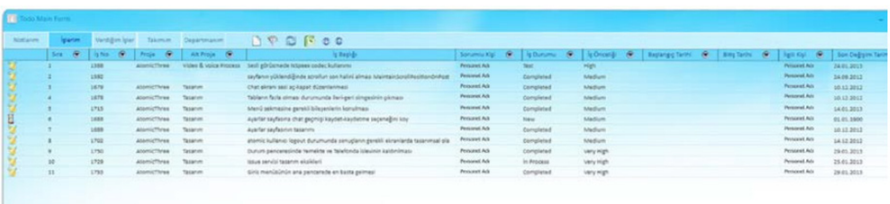


Figure 2. Screen Design Displaying Job Lists

- The development phases of interface designs are based entirely on user feedback, and thanks to the “ToDo” module of the application, users can notify the relevant people about the problems they encounter in terms of both design and functionality and the additional features they want to be included in the application. After deciding on the intensity of the requests received from the users and how necessary the requested additional features were for the system, the necessary arrangements were made on the existing application design and the update process was provided. In the first design, after logging in to the system, the user could change the session status (online, busy, away, etc.), see the number of personnel in the relevant units and whether these personnel were active or offline in the system, and make a call with any personnel selected from the list.

- Based on this information about the usage problems observed, the design of the product went through a number of design processes due to the intensity and diversity of the incoming requests and different prototype studies as shown in Figure 3, and reached its appearance in Figure 4. The product was presented to the users with its new design and after this process; usability tests and tools were utilized in order to ensure the highest level of user satisfaction. It was ensured that the problems encountered by users on application interfaces were identified in a technical context rather than observation method. In the product prototypes developed in the process, grouping work was carried out on the main screen in order to make it easier and faster for users to access the modules of the application. The user's frequent contacts are grouped under the tab "Favorite Contacts", recent contacts are grouped under the tab "Coming Soon", other personnel in the department where the user is located are grouped under the tab "My Department" and the user groups created by the user are grouped under the tab "Groups" in order to enable the personnel to communicate more quickly and to perform their tasks in a shorter time and with the least number of clicks.

- The design example in Figure 4 was re-coded using the "XAML" language, taking into account the prototype work in Figure 3 mentioned earlier. With the realization of this interface design, it was ensured that the location information of the users is displayed on the screen when they first log in, the people they frequently meet and their colleagues in the same unit are indicated on the list. In addition to these, links were included to facilitate access to other modules and shortcut menus were prepared to perform tasks faster. In order for the information in the lists to be more easily understood by the users, the content to be emphasized has been made clear by coloring and icon work.

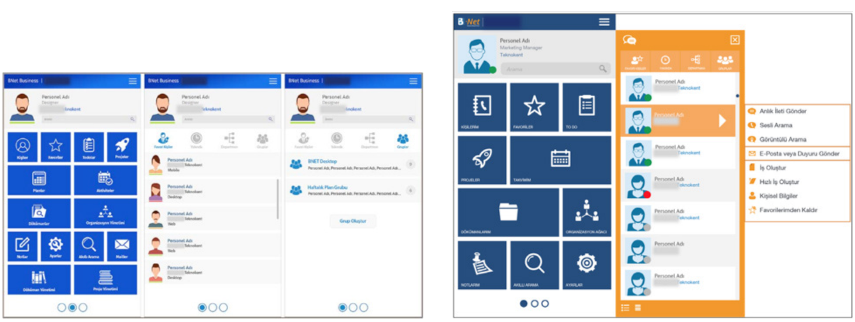


Figure 3. Examples of Prototype Work

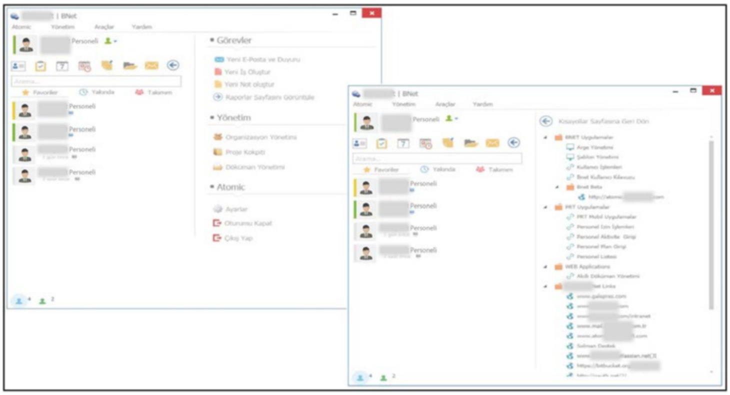


Figure 4. Design Arrangements of the Application

2.1. Usability Evaluation Approaches

Brinck et al. categorized usability methods into two different categories. In the first method, real data can be obtained by involving real users in the testing process (usability tests and interviews), while in the second method, in the absence of test users, predictions can be made about how usable the product design is based on previous experiences and design principles (Brinck vd., 2001).In usability testing methods, the usability of web or mobile products is measured according to certain criteria as a result of real users fulfilling the tasks/scenarios given to them. Usability testing methods are applied to evaluate the system in line with the opinions of real users, to develop easy-to-use system interfaces and to increase the satisfaction levels of users. In usability testing, participants are observed while performing the tasks assigned to them on a developed website, mobile application or a prototype (Battleson vd., 2001). During these tests, different types of problems can be identified and more user-friendly products can be produced as a result of continuous improvement of the problems obtained (Greiner, 2007).

2.1.1. Eye Tracking Technique

Eye tracking is a method used to obtain information about where and for how long the user looks on any system interface and at which points they concentrate (Bergstrom & Schall, 2014). The inclusion of eye tracking method in testing processes requires technological products with high costs. For this reason, when the studies in the literature were analyzed, it was seen that the usage rate of this technique was lower than other test methods. Jacob and Karn stated that the eye-tracking technique is a separate method for determining the focus points of users (Jacob & Karn, 2003). In the eye tracking method, the focus points on the screen can be detected due to the information obtained from user comments. However, automatic recording of these movements using a tool allows for more data to be obtained and analyzed, as well as identifying the places where the focal points are seen most intensely with the temperature maps obtained with mouse clicks.

2.1.2. Tree Test

Tree testing is another UX method used to measure the availability of menu items on an interface design and the appropriateness of category headings constructed with the labeling method applied in the card grouping study, and to understand how users comprehend the structure of an interface and what their expectations are (*Dancing with the Cards: Quick-and-Dirty Analysis of Card-Sorting Data :: UXmatters*, t.y.). By applying the tree test together with the test users, it can be determined which navigation maps the users use to reach any menu, and in this way, it can be ensured that the categorization structure of the system can be reconstructed repeatedly and products with more useful interfaces can be offered to users (*Tree Testing: The Complete Guide to Evaluating Findability | Maze*, t.y.).

2.1.3. A/B Test

It is ensured that the existing interface design of any developed mobile or web application is analyzed comparatively with newly developed different design studies in line with the expectations of the users. In A/B testing, an interface can be redesigned and the elements on it (menu, button, color, etc.) are designed with a different variation and presented to the users, and determinations can be made about findability and noticeability. This test is generally used in the optimization of the arrival page that users encounter when they first enter the site. A/B testing has four important benefits: measuring users' actual behavior, measuring even small changes, analyzing trade-offs, and being inexpensive to implement (Experience, t.y.).

2.1.4. First Click Test

The first click test is used to evaluate the intuitiveness of elements and clickable elements on a website in relation to the site design. It refers to the first object on the interface that the test takers focus on and click on while performing their assigned tasks (*First Click Testing | UsabilityHub*, t.y.).

2.1.5. System Usability Scale (SUS) Questionnaire

The system usability scale is a simple and reliable tool for obtaining data on usability issues of an interface. It was developed by Jon Brooke in 1986 in response to the need to measure usability. This type of questionnaire uses fewer or more measurement criteria than ten subjectively used items. The score obtained from the SUS questionnaire is used to evaluate the overall usability of the system [22](Brooke, 2013).

3. The Research Findings and Methods

Together with the test users performed on the application, a task-based usability evaluation (Table 1) was discussed. Some basic concepts need to be expressed in the results obtained as a result of the tests performed. Explanations of these concepts are given as follows:

- Correct Path: It shows whether the users act in accordance with the menu hierarchy designed by the designers.
- Incorrect Path (Invalid Path): Refers to users trying to complete the tasks they want to perform by following a path other than the menu hierarchy that was previously set up.
- Back From Here: It refers to the situation where users navigate to other menu items other than the main menu items that cover the relevant menu contents while navigating the menu items.
- Nominated Answer (Expected Answer): Indicates under which main headings the menu item that users plan to access is located.
- Skip Task: Refers to the situation where users do not fulfill the task assigned to them.

3.1. Task 1

It is the process of notifying the support team of situations that are difficult to use, difficult to access or low perceived by the users. In the tree test method performed with the test users, the navigation movements of the users between the constructed menus were observed. With the explanation of the concepts mentioned above, Figures 5-a, 5-b and 5-c below show the results obtained with the tree test method. In Figure 5-a, it was observed that five of the seven users who participated in the tree test acted in accordance with the menu steps and a success rate of 83.3% was obtained. The remaining two users followed a path other than the main heading of the “Help” menu and preferred the “Tools” menu. Figure 5-b shows which menu items the test users clicked on first and the navigation maps between the menu items. Figure 5-c shows the average task completion time of the users and the direct or indirect success or error rates. The direct success rate represents that users act in accordance with the constructed menu steps without making any mistakes, while the indirect success rate represents that users first navigate through different menu items to find the correct menu step and then perform the correct menu steps. Direct error refers to the incorrect menu steps made by the users by selecting other menu items different from the set menu steps, and indirect error refers to the users acting in accordance with the menu hierarchy determined as the correct path and then making incorrect menu selections.

Figure 5-a. Users' Preference Rates for Menu Headings

SUCCESS	PARTICIPANT	PATH
	1	› Yardım ‹ SessionView › Araçlar › Ayarlar › Uygulama Seçenekleri › Güncelleme Kontrolü - Hata Bildirme
	2	› Yardım › Güncelleme Kontrolü - Hata Bildirme
	3	› Yardım › Güncelleme Kontrolü - Hata Bildirme
	4	› Yardım › Güncelleme Kontrolü - Hata Bildirme
	5	› Yardım › Güncelleme Kontrolü - Hata Bildirme
	6	› Araçlar › Ayarlar › Uygulama Seçenekleri › Güncelleme Kontrolü - Hata Bildirme
	7	› Yardım › Güncelleme Kontrolü - Hata Bildirme

Figure 5-b. Users' Navigation Maps between Menus

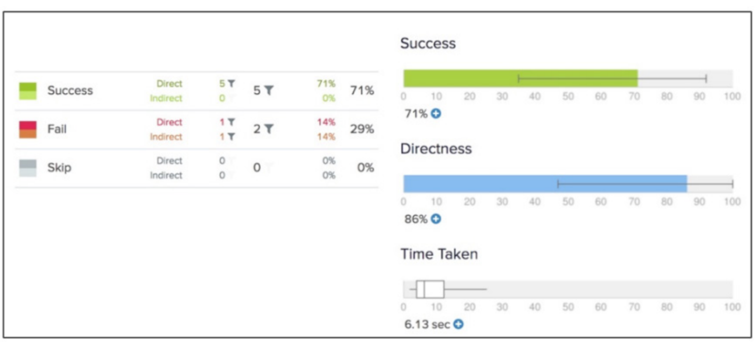


Figure 5-c. Direct or Indirect Success/Failure Rates

3.2. Task 2

It refers to the process of viewing the tasks that users have given to other personnel. The navigation maps showing the test users' access to the list, success and error rates are shown in Figure 6-a. The results of the tasks performed by the 10 users participating in the test showed a 50% success rate and a 50% error rate. It was observed that 5 of the users acted in accordance with the menu steps, while two of the remaining 5 users preferred the "Shortcuts" menu and three preferred the "Quick Access" menu. Figure 6-b shows which menu items the test users clicked on first and the navigation maps between the menu items. In this task, 5 of the test takers achieved direct success, while 2 of the other 5 made direct errors and 3 made indirect errors. The time spent by 10 participants on this task was 22.15 seconds Figure 6-c

Figure 6-a. Users' Preference Rates for Menu Headings

SUCCESS	PARTICIPANT	PATH
	1	› Kişisel › Todo › Verdiğim İşler
	3	› Kişisel › Todo › Verdiğim İşler
	4	› Kişisel › Todo › Verdiğim İşler
	5	› Kişisel › Todo › Verdiğim İşler
	6	› Kısayollar › Verdiğim İşler
	7	› Kısayollar ‹ Dashboard › Seçenekler ‹ Dashboard › Seçenekler ‹ Dashboard › Kısayollar › Verdiğim İşler
	8	› Kişisel › Todo › Verdiğim İşler
	9	› Hızlı Erişim ‹ Dashboard › Hızlı Erişim › ToDo Arama › Verdiğim İşler
	10	› Hızlı Erişim › ToDo Arama › Verdiğim İşler
	11	› Hızlı Erişim › ToDo Arama › Verdiğim İşler ‹ ToDo Arama › Verdiğim İşler

Figure 6-b. Users' Navigation Maps between Menus

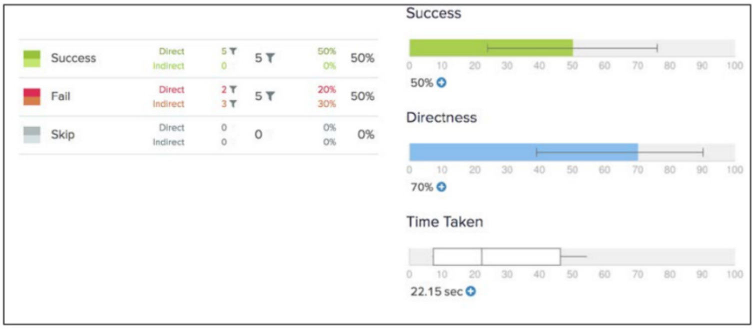
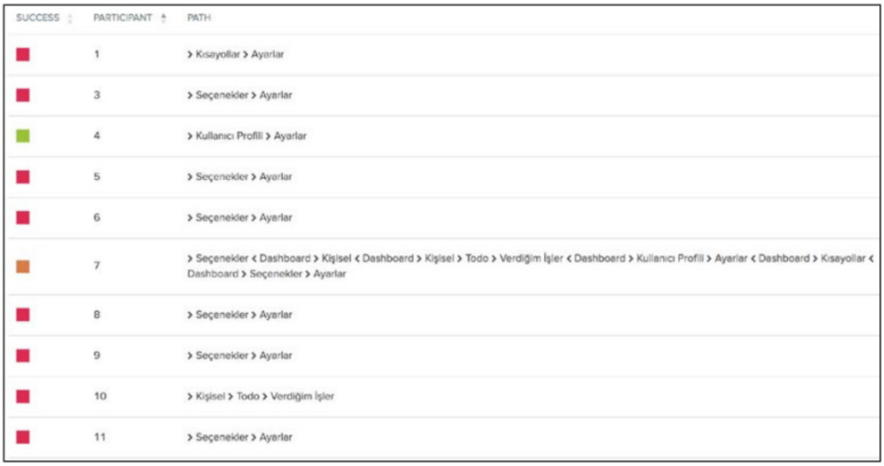


Figure 6-c. Direct or Indirect Success/Failure Rates

3.3. Task 3

In this defined task, users are asked to view the settings page of the application and make any changes. Figure 7-a shows that 7 of the 10 users who participated in the tree test tried to access the “Settings” page from the “Options” menu. While 2 of the other 3 users followed a step in accordance with the determined hierarchy, 1 user used the “Shortcuts” menu. The most important conclusion to be drawn from this test study is that the structure designed by the designer for the “Settings” page is wrong. It is seen that the majority of the test participants used different menu steps to fulfill the relevant task. At this point, the interface design should be adjusted by considering the access steps to the “Settings” page. Figure 7-b shows that the majority of the menu steps performed by the test users have direct error definitions. Figure 7-c shows that 9 out of the 10 users who participated in the test for the task performed in Figure 7-c followed menu steps with errors in direct and indirect ways. Only 1 of the participants followed the steps in accordance with the menu hierarchy designed by the designer.

Figure 7-a. Users’ Preference Rates for Menu Headings



SUCCESS	PARTICIPANT	PATH
	1	> Kısayollar > Ayarlar
	3	> Seçenekler > Ayarlar
	4	> Kullanıcı Profili > Ayarlar
	5	> Seçenekler > Ayarlar
	6	> Seçenekler > Ayarlar
	7	> Seçenekler < Dashboard > Kişisel < Dashboard > Kişisel > Todo > Verdiğim İşler < Dashboard > Kullanıcı Profili > Ayarlar < Dashboard > Kısayollar < Dashboard > Seçenekler > Ayarlar
	8	> Seçenekler > Ayarlar
	9	> Seçenekler > Ayarlar
	10	> Kişisel > Todo > Verdiğim İşler
	11	> Seçenekler > Ayarlar

Figure 7-b. Users' Navigation Maps between Menus

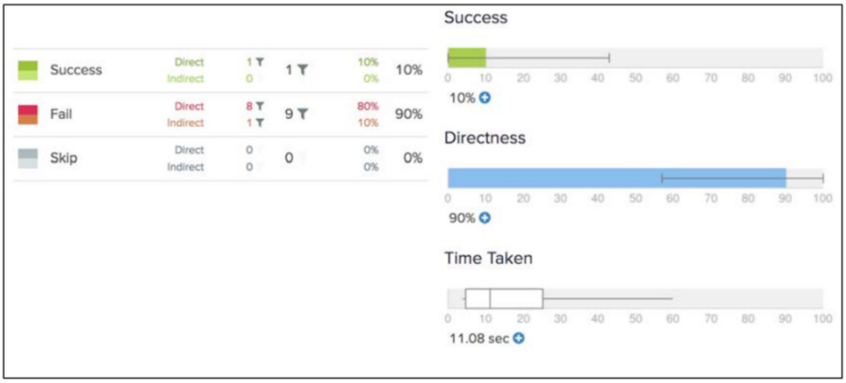


Figure 7-c. Direct or Indirect Success/Failure Rates

3.4. Task 4

This defined task includes shortcuts in the application and viewing the reports page. Figure 8-a shows that 7 of the participants in the tree test used the "Administration" menu item to view the "Reports" page. 3 of the participants tried to access it in accordance with the determined menu steps. Figure 8-b shows the menu steps performed by the test users. Figure 8-c shows that 6 of the 10 users who participated in the test regarding the task performed directly and indirectly followed the incorrect menu steps. Among the other 3 participants, 2 of them directly and 1 of them indirectly followed the menu steps.

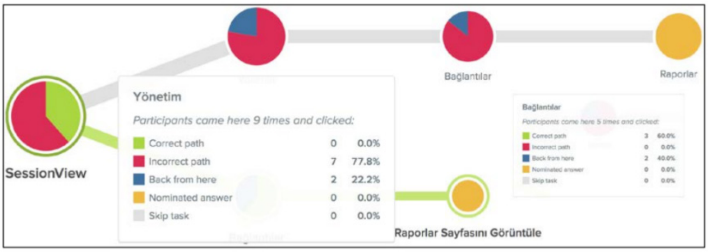


Figure 8-a. Users' Preference Rates for Menu Headings

SUCCESS	PARTICIPANT	PATH
	1	> Bağlantılar < SessionView > Yönetim > Bağlantılar > Raporlar
	2	> Yönetim > Bağlantılar > Raporlar
	3	> Yönetim > Bağlantılar < Yönetim < SessionView > Bağlantılar < SessionView > Bağlantılar > Raporlar Sayfasını Görüntüle
	4	> Bağlantılar > Raporlar Sayfasını Görüntüle
	5	> Yönetim > Bağlantılar > Raporlar
	6	> Yönetim > Bağlantılar > Raporlar
	7	> Yönetim > Bağlantılar > Raporlar
	8	> Yönetim < SessionView > Yönetim > Bağlantılar > Raporlar
	9	> Bağlantılar > Raporlar Sayfasını Görüntüle

Figure 8-b. Users' Navigation Maps between Menus

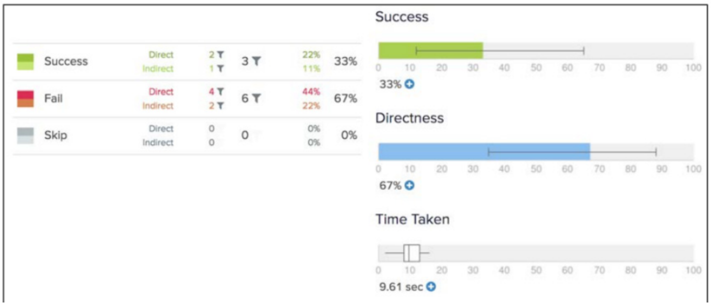


Figure 8-c. Direct or Indirect Success/Failure Rates

As a result of the information obtained from the tests, when the design problems were taken into consideration, the desktop platform of the product was improved in terms of both menu hierarchies and color scheme. Usability tests for this improved design are discussed in Task 5, Task 6, Task 7, Task 8, Task 9 and Task 10 in the next section.

3.5. Task 5

Suggestions and opinions about the application and errors encountered were requested to be reported to the support team. This task resulted in a 60% success rate and 40% error rate. Figures 9-a and 9-b and Table 2 show the distribution of the regions that users clicked on the screen and the data on the time spent.

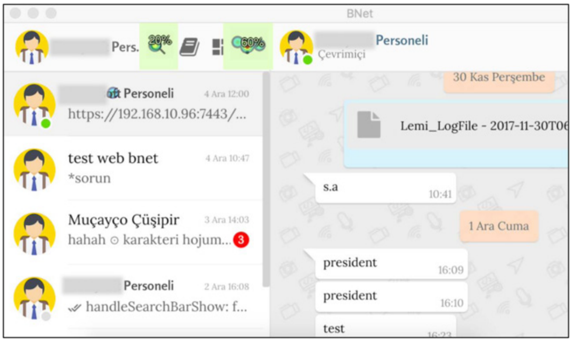


Figure 9-a. Users' Click Maps on the Screen

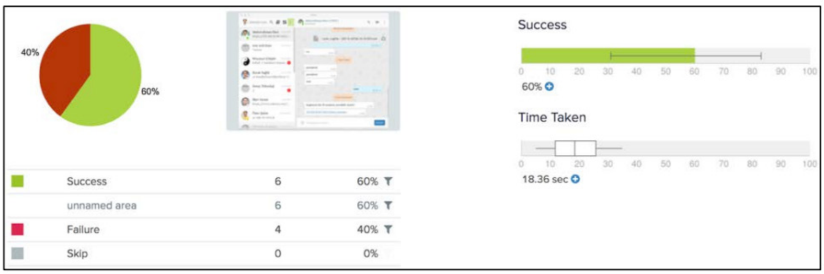


Figure 9-b. Direct or Indirect Success/Failure Rates

Table 2. Data on Members' Term of Completion of Tasks

Member ID	Task 5: Submit your suggestions regarding the implementation to the necessary units	
	Result	*Time Spent (s)*
1	Successful	5,04
2	Faulty	17,57
3	Successful	10,42
4	Successful	19,16
5	Successful	16,66
6	Faulty	35,02
7	Faulty	11,78
8	Successful	21,64
9	Successful	30,95
10	Faulty	25,71

3.6. Task 6

The task includes a request for users to create jobs for their colleagues within the company. With this task, 70% success rate and 30% error rate were achieved. While 7 of the users attempted to assign tasks to their colleagues by clicking on the user profile page and viewing the person's job list, 3 of the remaining test participants attempted to access the web interface by clicking on the "Dashboard" link. Figures 10-a and 10-b and Table 3 show the distribution of the regions that users clicked on the screen and the data on the time spent.

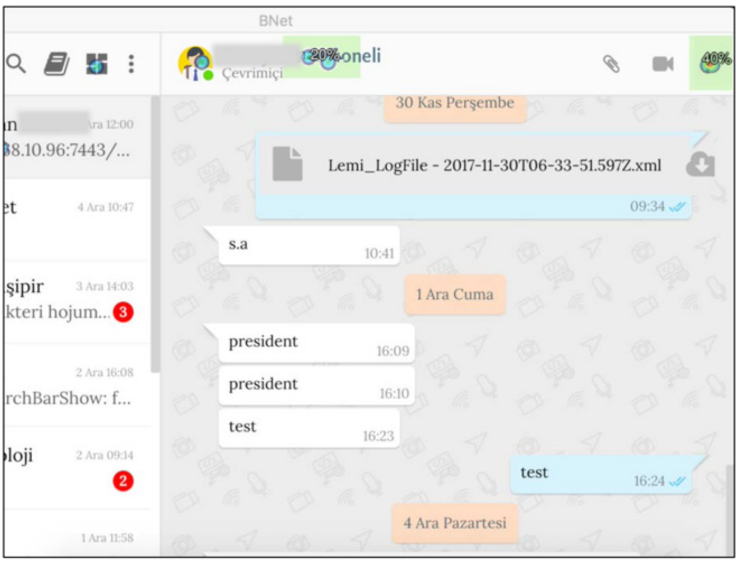


Figure 10-a. Users' Click Maps on the Screen

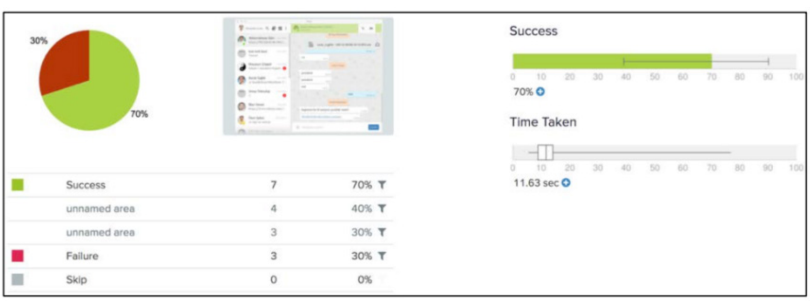


Figure 10-b. Direct or Indirect Success/Failure Rates

Table 3. Data on Members' Term of Completion of Tasks

Member ID	**Task 6: View jobs of company employees**	
	Result	*Time Spent (s)*
1	Faulty	6,98
2	Successful	11,93
3	Successful	5,5
4	Successful	76,71
5	Successful	14,03
6	Successful	9,41
7	Faulty	8,97
8	Successful	12,2
9	Faulty	11,33
10	Successful	58,08

3.7. Task 7

In the process of conducting usability tests and observing user behaviors, the last of the tasks directed to the test users was the request to log out of the application. As a result of the implementation of this task, 50% success rate and 50% failure rate were obtained from the participants. It was observed that 5 users who participated in the task clicked on the application menu option to log out of the application, while the other 5 participants clicked on the user profile or unidentified regions. Figures 11-a and 11-b and Table 4 show the distribution of the regions that users clicked on the screen and the data on the time spent.

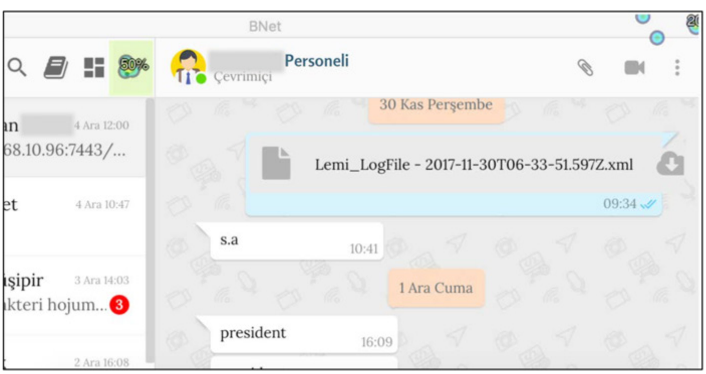


Figure 11-a. Users' Click Maps on the Screen

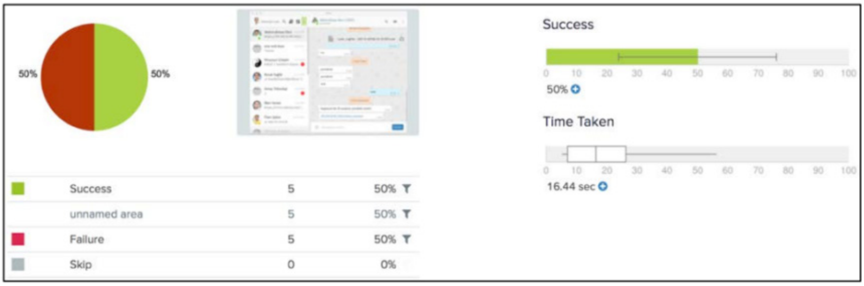


Figure 11-b. Direct or Indirect Success/Failure Rates

Table 4. Data on Members' Term of Completion of Tasks

Member ID	Task 7: Log out of the application	
	Result	*Time Spent (s)*
1	Successful	5,36
2	Successful	16,7
3	Faulty	7,14
4	Successful	5,15
5	Faulty	29,55
6	Faulty	16,44
7	Successful	13,67
8	Successful	16,44
9	Faulty	26,43
10	Faulty	56,19

3.8. Task-Based Comparative Analysis of Click Percentages of Menu Headings in Applied Test Methods

Table 5, Table 6, Table 7, Table 8, Table 9, Table 10 and Table 11 show the percentage of clicks on the menus in the tasks given to the users as a result of the usability tests performed in the application that is the source of the proposed study. The first 4 of the tasks implemented with real users reflect the results of the tree test and the remaining 3 reflect the results of the first click test.

Table 5. Menu click percentages for Task 1

Job Description Task 1	Please report any problems in implementation?	
Menu Label	Percentage of First Clicked Menu	Percent Visited
Personal	10%	10%
Help	60%	60%
User Profile	0%	0%
Options	10%	20%
Shortcuts	10%	10%
Quick Access	10%	10%

Table 6. Percentage of menu clicks for Task 2

Job Description Task 2	View the tasks you have already assigned to your colleagues	
Menu Label	Percentage of First Clicked Menu	Percent Visited
Personal	50%	50%
Help	0%	0%
User Profile	0%	0%
Options	0%	10%
Shortcuts	20%	20%
Quick Access	30%	30%

Table 7. Percentage of menu clicks for Task 3

Job Description Task 3	Change the application settings	
Menu Label	Percentage of First Clicked Menu	Percent Visited
Personal	10%	20%
Help	0%	0%
User Profile	10%	20%
Options	70%	70%
Shortcuts	10%	20%
Quick Access	0%	0%

Table 8. Percentage of menu clicks for Task 4

Job Description Task 4	View the Reports page	
Menu Label	Percentage of First Clicked Menu	Percent Visited
Governance	67%	78%
Connections	33%	44%

Table 9. Percentage of menu clicks for Task 5

Job Description Task 5	Please forward your suggestions regarding the application to the necessary units
Menu Label	Click Percentage
User Profile Menu	60%
Other (Objects clicked outside the specified region on the screen)	40%

Table 10. Percentage of menu clicks for Task 6

Job Description Task 6	View jobs of company employees
Menu Label	Click Percentage
User Profile and User Details Menu	70%
Other (Objects clicked outside the specified region on the screen)	30%

Table 11. Percentage of menu clicks for Task 7

Job Description Task 7	Log out of the application
Menu Label	Click Percentage
User Profile and User Avatar	50%
Other (Objects clicked outside the specified region on the screen)	50%

3.9. System Usability Measure (SUS) Results of the Application

The SUS (System Usability Scale) [14] questionnaire is used to find out whether a product is usable and learnable. The result of applying this questionnaire with the test users does not provide information about the source of the problems encountered in the interface. In order to determine how useful, the product is in the eyes of the users, a usability survey was conducted with 12 employees. Based on the SUS survey questions and evaluation criteria, the data shown in Table 12 were obtained.

	Question 1	Question 2	Question 3	Question 4	Question 5	Question 6	Question 7	Question 8	Question 9	Question 10	Overall
Person 1	2	4	4	4	3	3	3	3	1	3	30x2.5=75
Person 2	2	3	3	2	2	1	3	3	2	3	24x2.5=60
Person 3	3	3	3	3	3	2	3	4	2	4	30x2.5=75
Person 4	4	1	4	4	4	1	4	4	4	4	34x2.5=85
Person 5	4	4	3	4	3	4	4	4	4	4	38x2.5=95
Person 6	4	4	4	3	3	2	4	4	3	3	34x2.5=85
Person 7	3	3	3	3	3	3	3	4	3	3	31x2.5=77.5
Person 8	2	4	3	3	3	4	4	4	4	4	34x2.5=85
Person 9	2	2	2	1	3	3	4	3	4	2	26x2.5=65
Person 10	4	1	3	0	0	0	2	2	0	2	14x2.5=35
Person 11	2	4	0	4	1	4	4	4	3	4	30x2.5=75
Person 12	4	4	4	3	3	3	4	4	4	3	36x2.5=90
Total Result: 902.5 Average usefulness of the product:902.5/12=75											

The total result of the survey conducted with twelve test users was 902.5, which was divided by the total number of users to obtain a score of 75. The fact that the product has a usability level of 75 points reveals the fact that this product offers a medium level of use and that there are some aspects of the product that need to be improved.

4. Conclusion and Discussions

As a result of the increasing variety of software products, the impact of usability on product quality is of great importance. Software usability testing is a methodology that ensures the easy usability of products by target user groups and is a process in which the deficiencies that exist or may arise in the system are identified by measuring the human-computer interaction features of a system. Products with high usability provide great benefits to both users and developers. In this direction, when the studies conducted in the field of usability in both academic and internet environments are examined, it is mentioned that usability is a key factor in obtaining a Successful product and the necessity of conducting tests with real users is emphasized.

Based on these, the quality and acceptability of a product depends not only on its technical features but also, and more importantly, on its ease of use and its compatibility with the physical, mental and psychological characteristics of the users. For this reason, the impact of user experiences on product design in the product development process is quite high. Having a good user experience is extremely important for a software product because there are applications or websites on the internet that are very similar to each other in terms of their functionality.

This study focuses on the basics of usability and user testing of desktop and web applications of a software product under development. In order to increase the usability and user satisfaction level of the product, the first-click tree test, which is one of the usability testing methods, was selected and the SUS questionnaire was applied to measure the usability level of the system. In the process of determining these test methods, the methods applied in the studies in the literature were examined. In addition to the test methods used in the study, the basic concepts of many test methods that can be applied in the design process were mentioned and a task-based scenario was prepared in the testing process to be carried out with the users. Based on the features of the product, usability tests were applied with seven different tasks that were predetermined based on the features of the product, and statistical data were obtained on the time spent by the users while performing the tasks assigned to them and the “Faulty” or “Successful” performance of the tasks.

Before starting the realization of the study, the contents of domestic and foreign sources related to usability studies in the literature were examined and the qualities of the results obtained together with the test methods used in the relevant studies were also taken into consideration. As a result of the literature review, it was observed that usability tests conducted with real users in some of the studies examined in some of the studies were mostly carried out with the results obtained from the survey types on the sites on the web platform, while it was found that there was not much room for scenario-based testing processes. In this study, since the tested product has many categories, options and a complex structure like e-commerce sites, in addition to the application of the SUS questionnaire, testing methods such as tree test and first click test were also included. In this way, the menu steps followed by the users while performing the relevant tasks were obtained in real time and graphically. With the results obtained, statistical data on which task users spend too much time while performing the task on the application subject to this study, and whether they perform the tasks as Successful or Faulty have been obtained, and arrangements have been made on new interfaces supported by prototype studies so that users do not experience the same questions over and over again.

The results of the SUS questionnaire with the test users revealed that there are aspects of the application that need to be improved. The score of 75, which was calculated as a result of the questionnaire, showed that the product provides a moderate level of user experience and usability to its users. This study was carried out in order to help the personnel who will work on the usability of software products and aims to shed light on software product developers with the methods applied in the study and the usability testing tools used in the study.

Suggestions for Implementation;

- Within the scope of this study, a short, concise and understandable language was used for the definition of the tasks in the usability tests and it was ensured that questions such as misunderstanding that may arise during the test were prevented.
- The number of participants in the tests varies between seven and ten, and the results that can be obtained with a larger number of participants should be evaluated. The generally accepted opinion in the literature regarding the number of test users is that it is sufficient to choose the number of participants between five and fifteen.
- Considering that usability studies are a process that should be applied repeatedly in product development stages, usability studies should be carried out periodically on the relevant application subject to this study.
- The users included in the test process in the study were selected among the personnel working within the company.
- It is recommended to conduct studies on how experienced and inexperienced users affect the results obtained from usability tests during the testing process.
- Whether the product to be developed is a software or an industrial product, user experiences and usability tests conducted with users should be prioritized. The importance given to usability studies should be increased in presenting more usable and user-friendly products to the target audience.

References

Akin, Ş. (2015). Kütüphane Web Sayfalarinin Öğrenciler Tarafindan Kullanilabilirliğinin Değerlendirilmesi: Sakarya Üniversitesi Kütüphanesi Uygulama Çalişmasi [Master Thesis, Sakarya Üniversitesi]. https://acikerisim.sakarya.edu.tr/handle/20.500.12619/91102

Anderson, N. S., Norman, D. A., & Draper, S. W. (1988). User Centered System Design: New Perspectives on Human-Computer Interaction. The American Journal of Psychology, 101(1), 148. https://doi.org/10.2307/1422802

Bastien, J. M. C. (2010). Usability testing: A review of some methodological and technical aspects of the method. International Journal of Medical Informatics, 79(4), e18-e23. https://doi.org/10.1016/j.ijmedinf.2008.12.004

Bati, B., & Durdu, P. O. (t.y.). Rapsim Web Sitesi Kullanılabilirlik Araútırması: Bir Durum Çalıúması.

Battleson, B., Booth, A., & Weintrop, J. (2001). Usability testing of an academic library Web site: A case study. The Journal of Academic Librarianship, 27(3), 188-198. https://doi.org/10.1016/S0099-1333(01)00180-X

Bergstrom, J. R., & Schall, A. (2014). Eye Tracking in User Experience Design. Elsevier.

Brinck, T., Gergle, D., & Wood, S. (2001). Usability for the Web: Designing Web Sites that Work. Morgan Kaufmann Publishers.

Brooke, J. (2013). SUS: A retrospective. Journal of Usability Studies, 8, 29-40.

Çağıltay, K. (2020). İnsan Bilgisayar Etkileşimi ve Öğretim Teknolojileri. İçinde K. Çağıltay (Ed.), Öğretim Teknolojilerinin Temelleri Teoriler, Araştırmalar, Eğilimler (3. bs, ss. 297-314). Ankara Pegem Akademi Yayıncılık. https://doi.org/10.14527/9786053644576.18

Çakmak, Ş. (2013). Bir Eğitim Yönetim Sisteminin Sosyal Ağ Bağlaminda Kullanilabilirlik Analizi [Master Thesis, Gazi Üniversitesi]. https://avesis.gazi.edu.tr/yonetilen-tez/fab6e727-cb2a-469d-bef5-1ff9faf8b1c5/bir-egitim-yonetim-sisteminin-sosyal-ag-baglaminda-kullanilabilirlik-analizi

Da Silva, T. S., Silveira, M. S., Maurer, F., & Silveira, F. F. (2018). The evolution of agile UXD. Information and Software Technology, 102, 1-5. https://doi.org/10.1016/j.infsof.2018.04.008

Dalcı, M. (2011). Using Google analytics, card sorting and search statistics for getting insights about metu website's new design: A case study [Master Thesis, Middle East Technical University]. https://open.metu.edu.tr/handle/11511/20399

Dancing with the Cards: Quick-and-Dirty Analysis of Card-Sorting Data: UXmatters. (t.y.). (2023), https://www.uxmatters.com/mt/archives/2010/09/dancing-with-the-cards-quick-and-dirty-analysis-of-card-sorting-data.php

Experience, W. L. in R.-B. U. (t.y.). Putting A/B Testing in Its Place. Nielsen Norman Group. Geliş tarihi 01 Ekim 2023, gönderen https://www.nngroup.com/articles/putting-ab-testing-in-its-place/

First Click Testing | UsabilityHub. (t.y.). Geliş tarihi 01 Ekim 2023, gönderen https://usabilityhub.com/guides/first-click-testing

Fung, R. H. Y., Chiu, D. K. W., Ko, E. H. T., Ho, K. K. W., & Lo, P. (2016). Heuristic Usability Evaluation of University of Hong Kong Libraries' Mobile Website. The Journal of Academic Librarianship, 42(5), 581-594. https://doi.org/10.1016/j.acalib.2016.06.004

Greiner, L. (2007). Usability 101. netWorker, 11(2), 11-13. https://doi.org/10.1145/1268577.1268585

Hartson, H. R., & Pyla, P. S. (2019). The UX book: Agile UX design for a quality user experience (Second edition). Morgan Kaufmann.

Jacob, R. J. K., & Karn, K. S. (2003). Commentary on Section 4 - Eye Tracking in Human-Computer Interaction and Usability Research: Ready to Deliver the Promises. İçinde J. Hyönä, R. Radach, & H. Deubel (Ed.), The Mind's Eye (ss. 573-605). North-Holland. https://doi.org/10.1016/B978-044451020-4/50031-1

Kantar, S. (2018). User experience design: Optimization of video on demand interface [masterThesis, Fen Bilimleri Enstitüsü]. https://acikbilim.yok.gov.tr/handle/20.500.12812/615609

Kollmann, T., Lomberg, C., & Peschl, A. (2016). Web 1.0, Web 2.0, and Web 3.0: The Development of E-Business. Içinde Encyclopedia of E-Commerce Development, Implementation, and Management (ss. 1139-1148). IGI Global. https://doi.org/10.4018/978-1-4666-9787-4.ch081

Oban, H. (2022, Kasım 21). MVVM architecture, ViewModel and LiveData. Medium. https://blog.devgenius.io/mvvm-architecture-viewmodel-and-livedata-d6c74ef45728

Riihiaho, S. (2018). Usability Testing. Içinde K. L. Norman & J. Kirakowski (Ed.), The Wiley Handbook of Human Computer Interaction (1. bs, ss. 255-275). Wiley. https://doi.org/10.1002/9781118976005.ch14

Ritch Macefield. (2007, Mayıs 7). Usability studies and the Hawthorne Effect—JUX. JUX - The Journal of User Experience. http://uxpajournal.org/usability-studies-and-the-hawthorne-effect/

Sivaji, A., Abdullah, A., & Downe, A. G. (2011). Usability Testing Methodology: Effectiveness of Heuristic Evaluation in E-Government Website Development. 2011 Fifth Asia Modelling Symposium, 68-72. https://doi.org/10.1109/AMS.2011.24

Stephan, E., Cheng, D. T., & Young, L. M. (2006). A Usability Survey at the University of Mississippi Libraries for the Improvement of the Library Home Page. The Journal of Academic Librarianship, 32(1), 35-51. https://doi.org/10.1016/j.acalib.2005.10.011

Tree Testing: The Complete Guide to Evaluating Findability | Maze. (t.y.). Geliş tarihi 01 Ekim 2023, gönderen https://maze.co/guides/ux-research/tree-testing/

Türkmenoğlu, H., & Atalar, D. (2020). User Experience In Interface Design Prototype Design. Idil Journal of Art and Language, 9(70). https://doi.org/10.7816/idil-09-70-10

CHAPTER VII

CLASSIFICATION OF LUNG CANCER WITH DEEP LEARNING METHODS USING HISTOPATHOLOGY IMAGES

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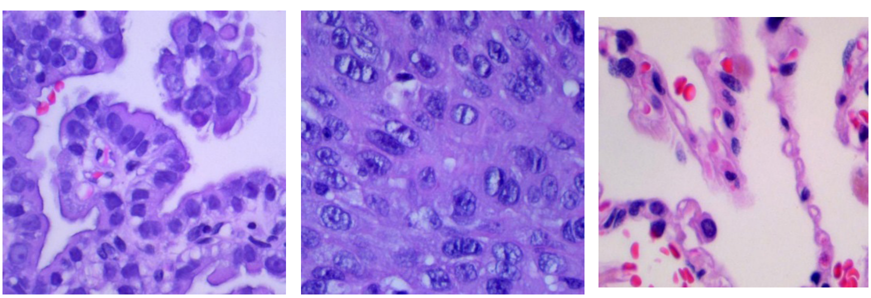
1. Introduction

Malignant tumors that occur as a result of unbalanced proliferation of cells in the lung are called lung cancer. Cancer cells first multiply in their location and form a mass structure. When it reaches advanced stages, it spreads to surrounding tissues and organs. The most common type of cancer in the world in recent years is lung cancer. (Schabath and Cote, 2019). According to recent research, the reasons for the spread of lung cancer can be listed as air pollution, smoking, genetic susceptibility, inhalation of radon gas, occupational deformation and malnutrition. (Mao et al., 2016). Lung cancer is the most-deadly type of cancer in men worldwide. In women, it ranks second after breast cancer (Gültekin et al., 2008). As with other types of cancer, early diagnosis of lung cancer is of vital importance (Sebik and Bülbül, 2018). Therefore, many countries are developing strategies for the early detection of lung cancer. With the expected increase in the number of preventive/early detection measures, scientists are working on computerized solutions that help ease the work of doctors, increase the accuracy of diagnosis by reducing the factor of subjectivity, speed analysis and reduce medical costs (Çifçi, 2022). The use of deep learning methods in the health sector has increased considerably in recent years (Kaya et.al, 2019) because these methods give effective results in the field of medical image processing. Deep learning methods usually work on computer scanning images. One of these types of images is the histopathological image, and it is the most important factor in the diagnosis of cancer. Histopathology is the examination of changes in organs, tissues and cells under a microscope using various methods. It is used in diagnosis by making use of different pathological features of various diseases in tissues (Wikipedia, 2023). This study aims to achieve a more sensitive and accurate classification by using previously trained machine learning and deep learning methods for classification of normal tissue, adenocarcinoma and squamous cell carcinoma tissues in lung histopathology images. In this study, the dataset named "Lung and Colon Cancer Histopathological Image Dataset (LC25000)" created by Borkowski et al. was used (Figure 1). The dataset contains a total of 25,000 color digital images. These images are divided into 5 equal numbers of classes and compressed with the jpeg algorithm. These classes include images about lung benign tissue, lung adenocarcinoma, lung squamous cell carcinoma, colon adenocarcinoma, and colon benign tissue. The images are tissue images taken by biopsy from individuals in the sample. The resolution of the images in the dataset is 768x768 pixels (Borkowski et al., 2019). A total of 15000 images were selected from the data set, 5000 images of squamous cell carcinoma, 5000 images of adenocarcinoma and 5000 images of normal tissue.



(a) (b) (c)

Figure 1. Samples of Three Tissues in the LC2500 Dataset
(a) Adenocarcinoma (b) Squamous Cell Carcinoma (c) Normal Tissue

2. Method

InceptionV3, Xception, DenseNet121, ResNet50, ResNet101, ResNet101v2, VGG16, VGG19 and MobileNet architectures were used to extract the attributes of the dataset. These are deep convolutional neural network architectures and they involve depthwise separable convolutions. Random Forest, KNN, and Support Vector Machine algorithms were used for classification in this study (Figure 2).

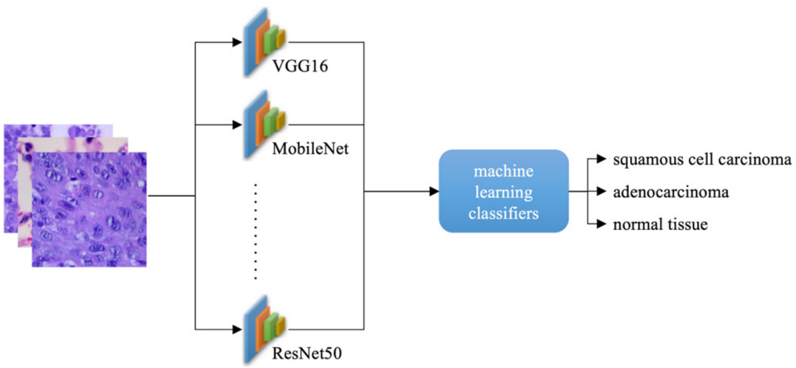


Figure2. Working Principle of the Model

Deep learning is a machine learning technique that finds patterns and generates outputs and answers using algorithms and large data sets, without requiring any human intervention. Deep learning methods teach devices to filter, classify, and make predictions about input in the form of images, text, or audio. Deep-learningz methods are multi-level representation-learning (LeCun et.al., 2015). Today's popular deep learning techniques associate input data with target outputs using flexible artificial neural networks (Kleppe et.al., 2021). In the context of deep learning, transfer learning algorithms allow the information acquired in a model or task to be used to perform another task. Thus, the pre-trained model is enabled to learn effectively and quickly in the new task. It can take advantage of previously trained algorithm models to show high performance in the new task by reducing the computational resource.

Support Vector Machines (SVM) is one of the supervised learning methods often used in classification problems. SVM simply draws two boundary lines close to and parallel to both groups. These boundary lines are brought closer together, producing a common boundary line. In other words, a feature extraction is made for each input entering the system and a different point representing each input is obtained on the two-dimensional plane. It is suitable for complex but small and medium-sized data sets. SVM is effectively used to solve classification and regression problems based on statistical learning theory (Yakut et.al., 2014). A SVM creates an n-dimensional hyperplane. This nD hyperplane divides the data into categories optimally (Figure 3). SVM models are closely related to artificial neural networks. (Haykin, 1999).

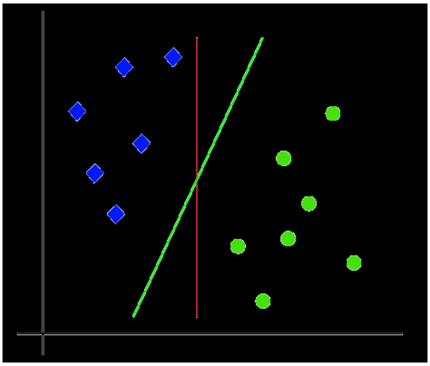


Figure 3. A sample of the SVM Algorithm hyperplane

SVM is based on the theory of Vladimir Vapnik and Alexey Chervonenkis (Vapnika and Izmailov, 2021). After successful applications in the 90s, it attracted the attention of scientists working in the field of artificial intelligence. The transformation that takes place in the SVM algorithm is performed by the nonlinear movement of vectors from a low-dimensional input space to a high-dimensional space. SVM can classify or perform regression by taking advantage of the gaps between the data. A kernel that determines this transformation is specified for the system that performs the transformation. During classification, vectors are transferred to high-dimensional space and made linearly separable. The vector with the maximum distance to the classes within the separation planes is determined as the most suitable linear separator. (Hsu and Lin, 2002)

Random Forest is one of the supervised learning algorithms. It is used in both regression and classification problems. Random Forest increases the classification value by producing several decision trees. It is suitable for use in classification and prediction models and is considered one of the basic algorithms (Pal, 2005). Common machine learning methods are distinguished by high predictive accuracy and model interpretability. (Suchetana, et al. 2017) Random Forest, on the other hand, can be applied to missing data or unstable datasets. It aims to increase the accuracy rate by producing more than one decision tree during the implementation phase. It creates a decision forest using decision trees (Figure 4). The reason why the Random Forest algorithm has a high success rate is the low bias rate and low tree correlation. The low drift rate is achieved by creating fairly large trees.

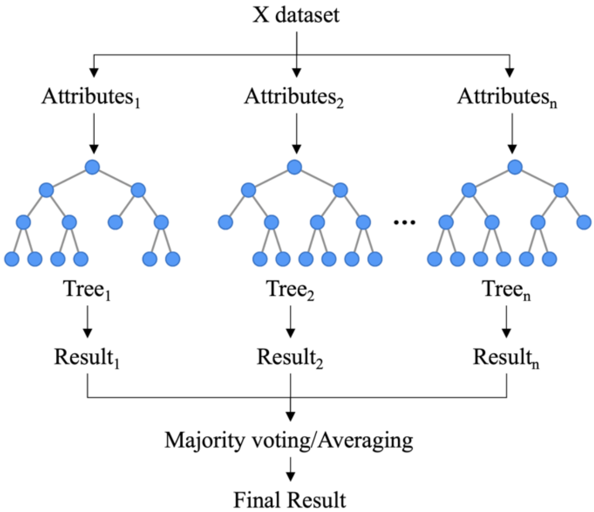


Figure 4. Random Forest Classifier

K-Nearest Neighbor (KNN) Algorithm is a basic non-parametric classification algorithm. The algorithm is proposed by T. M. Cover and P. E. Hart. It is a classification method in which the class in which the sample data point is located and the nearest neighbor are determined according to the k value (Cover and Hart, 1967). The distance between the classes is calculated by the Euclidean distance (Agrawal, 2014). KNN is an old but simple algorithm. It is widely used because it is easy to use and produces effective results (Qiu et.al., 2008).

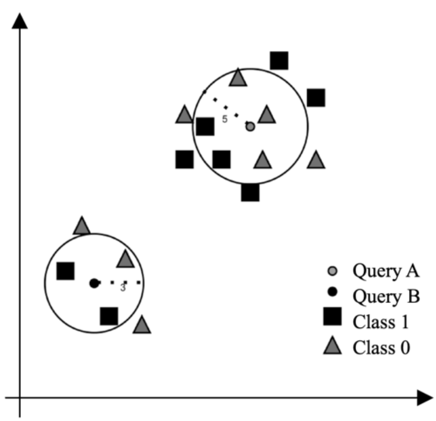


Figure 5. Visual illustration of the KNN algorithm (Uddin et.al., 2022)

In this study, InceptionV3, Xception, DenseNet121, ResNet50, ResNet101, ResNet101v2, VGG16, VGG19 and MobileNet architectures were used for feature extraction. In this study, SVM, Random Forest and KNN Algorithm were used to classify feature vectors of lung histopathology images. The confusion matrix was used as a benchmark to calculate the performance of the Classifiers. (Figure 6).

	Actual values	
	Positive (+)	Negative (-)
Positive (+)	TP	FP
Negative (-)	FN	TN

Figure 6. Confusion Matrix

The confusion matrix is used to solve classification problems. It can be applied to binary classification as well as multi-class classification problems. It is a very popular measurement. It is generally used for measuring Recall, Precision, Specificity, Accuracy, and most importantly Area Under the Curve (AUC) and Receiver Operating Characteristics Curve (ROC), which are one of the most important evaluation metrics for checking any classification model's performance. AUC can be calculated by antiderivative area finding method or by knowing the curve equation, the area under it and its boundaries. There is no exact formula to calculate AUC. The ROC curve compares TP and FP values. The aim is to reduce the classification threshold. This way more objects stay on the positive side. There are 4 terms in the matrix (Table 1) which are True Positive (TP), False Positive (FP), False Negative (FN), and True Negative (TN) (Ünal and Dudak, 2020).

Table 1. Terms of Confusion Matrix

Term	Observation	Prediction
TP	+	+
FP	-	-
FN	+	-
TN	-	+

Specificity, Accuracy, precision, sensitivity, and F-measurements can be made using these 4 terms.

$$Accuracy = \frac{(\mathrm{TP} + \mathrm{TN})}{(\mathrm{TP} + \mathrm{FP} + \mathrm{TN} + \mathrm{FN})}$$

$$Sensitivity = \frac{(\mathrm{TP})}{(\mathrm{TP} + \mathrm{TN})}$$

$$Specificity = \frac{(\mathrm{TN})}{(\mathrm{TP} + \mathrm{FN})}$$

$$Precision = \frac{(\mathrm{TP})}{(\mathrm{TP} + \mathrm{FN})}$$

$$f - measurement = \frac{(2\mathrm{TP})}{(2\mathrm{TP} + \mathrm{FP} + \mathrm{FN})}$$

3. Results

Data is the raw material of deep learning. Although deep learning models can theoretically be applied with a small amount of data, accuracy increases as the amount of data approaches infinity. The number of data used in this study is 15000 and it is divided into two parts as 80% training and 20% testing. Nine different deep learning architectures, namely DenseNet121, InceptionV3, MobileNet, ResNet50, ResNet101, ResNet101v2, VGG16, VGG19 and Xception, were used for feature extraction. Features were extracted for more successful classification of tumor types in the histopathological images in the data set. Extracted features are classified with machine learning models of SVM, Random Forest and KNN Algorithm. The results for the first level are given in Table 2.

Table 2. Machine Learning Models Success

Feature Extracted Networks	K-NN	SVM	Random Forest	Average Success
ResNet50	95.933	99.867	97.533	97.778
DenseNet121	94.356	96.356	93.867	94.860
VGG16	86.889	97.442	95.467	93.266
VGG19	83.467	96.967	94.044	91.393
MobileNet	85.800	95.667	87.400	89.622
ResNet101	84.978	92.854	89.400	89.077
ResNet101v2	82.089	92.711	91.862	88.887
InceptionV3	83.289	91.733	88.400	87.807
Xception	89.511	80.533	92.562	87.565

Pre-trained machine learning and deep learning methods were used together for classification of squamous carcinoma, adenocarcinoma and healthy tissues obtained from lung histopathology images. The features extracted using nine different deep learning architectures were classified by three different machine learning algorithms. According to the classification results, it was seen that the ResNet50 model, with average 97.778 percent success, could be more useful than other models in the early diagnosis of lung cancer.

References

Schabath, M.B., Cote, M.L. (2019). Cancer Progress and Priorities: Lung Cancer, Cancer Epidemiology Biomarkers Prevention, 28(10): 1563–1579.

Mao, Y., Yang, D., He, J., Krasna, M.J. (2016). Epidemiology of Lung Cancer, Surg Oncol Clin N Am, 25(3):439-45. doi: 10.1016/j.soc.2016.02.001.

Gültekin, Z., Pınar, G., Pınar, T., Kızıltan, G., Doğan, N., Algıer, L., Bulut, I., Özyılkan, Ö. (2008). Akciğer Kanserli Hastaların Yaşam Kaliteleri ve Sağlık Bakım Hizmet Beklentileri, International Journal of Hematology and Oncology, 2(18): 99-106.

Sebik, N.B., Bülbül, H.İ, (2018), Veri Madenciliği Modellerinin Akciğer Kanseri Veri Seti Üzerinde Başarilarinin İncelenmesi, TÜBAV Bilim, 11(3): 1-7

Çifçi, M.A. (2022). Derin Öğrenme Metodu ve Ayrık Dalgacık Dönüşümü Kullanarak BT Görüntülerinden Akciğer Kanseri Teşhisi, Mühendislik Bilimleri ve Araştırmaları Dergisi, 4(2): 141-154.

Kaya, U., Yılmaz, A., Dikmen, Y. (2019). Sağlık Alanında Kullanılan Derin Öğrenme Yöntemleri. Avrupa Bilim ve Teknoloji Dergisi, (16), 792-808.

https://en.wikipedia.org/wiki/Histopathology

Borkowski, A.A., Bui, M.M., Thomas, L.B., Wilson, C.P., DeLand, L.A., Mastorides, S.M. (2019). arXivLabs, https://doi.org/10.48550/arXiv.1912.12142

LeCun, Y., Bengio, Y. & Hinton, G. Deep learning. Nature 521, 436–444 (2015). https://doi.org/10.1038/nature14539

Kleppe, A., Skrede, OJ., De Raedt, S. et al. Designing deep learning studies in cancer diagnostics. Nat Rev Cancer 21, 199–211 (2021). https://doi.org/10.1038/s41568-020-00327-9

Yakut, E., Elmas, B., Yavuz, S. (2014). Yapay Sinir Ağları ve Destek Vektör Makineleri Yöntemleriyle Borsa Endeksi Tahmini, Süleyman Demirel Üniversitesi İktisadi ve İdari Bilimler Fakültesi Dergisi, (19)1: 139-157.

Haykin, S. (1999). Neural Networks: A Comprehensive Foundation [Electronic Version], Prentice Hall Inc, New Jersey.

Vapnika, V., Izmailov, R. (2021). Reinforced SVM Method and Memorization Mechanisms, Journal of Pattern Recognition, (19), ISSN: 0031-3203, https://doi.org/10.1016/j.patcog.2021.108018.

Hsu, C. W., Lin, C. (2002). A comparison of methods for multiclass support vector machines. IEEE Transactions on Neural Networks, 13(2):415-425. DOI: 10.1109/72.991427.

Pal, M. (2005). Random forest classifier for remote sensing classification, International Journal of Remote Sensing, 26:1, 217-222, DOI: 10.1080/01431160412331269698

Suchetana, B., Rajagopalan, B., Silverstein, J. (2017). Assessment of wastewater treatment facility compliance with decreasing ammonia discharge limits using a regression tree model,

Science of The Total Environment, (598): 249-257, ISSN 0048-9697, https://doi.org/10.1016/j.scitotenv.2017.03.236.

Cover, T.M., Hart, P.E. (1967) Nearest neighbor pattern classification". IEEE Transactions on Information Theory, IT-13(1): 21–27.

Agrawal, R. (2014). K-Nearest Neighbor for Uncertain Data. International Journal of Computer Applications, (105)11: 13-16, DOI: 10.5120/18420-9714.

Qiu, X.Y., Kang, K., Zhang, H.X. (2008). Selection of kernel parameters for K-NN", IEEE International Joint Conference on Neural Networks (IJCNN), 61-65.

Uddin, S., Haque, I., Lu, H., Moni, M.A., Gide, E. (2022). Comparative performance analysis of K-nearest neighbour (KNN) algorithm and its different variants for disease prediction. Scientific Reports (12), https://doi.org/10.1038/s41598-022-10358-x

Ünal Y., Dudak M.N., (2020). Classification of Covid-19 Dataset with Some Machine Learning Methods, Journal of Amasya University the Institute of Sciences and Technology, 1(1), 36-44