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PREPARATION OF NOVEL BIO-BASED ADSORBENT FOR FAST AND SELECTIVE ADSORPTION OF VARIOUS DYES

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ÇEŞITLI BOYALARIN HIZLI VE SEÇICI ADSORPSIYONU IÇIN YENI BIYO-BAZLI ADSORBANIN HAZIRLANMASI

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Dedicated to my beloved mother.

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LIST OF SYMBOLS

N	Adsorption intensity
q_e	Amount of substance adsorbed per unit weight of adsorbent at equilibrium
d	Average diameter of interconnecting windows
D	Average diameter of voids
C_e	Concentration of material in solution after adsorption
d/D	Degree of interconnectivity
K_F	Freundlich's constant
g	Gram
K_L	Langmuir's constant
L	Liter
mL	Milliliter
nm	Nanometer
ε	Polanyi potential
q_m	Quantity of substance adsorbed per unit weight of sorbent
Φ	Volume ratio

LIST OF ABBREVIATIONS

NH_4OH	Ammonium hydroxide
BOD	Biochemical Oxygen Demand
BET	Brunauer-Emmett-Teller
COD	Chemical Oxygen Demand
CR	Congo Red
EA	Eggshell-Algae biosorbent
ES	Eggshell
FTIR	Fourier Transform Infrared Spectroscopy
HCl	Hydrochloric acid
MB	Methylene Blue
MO	Methyl Orange
NOM	Natural Organic Matter
HNO_3	Nitric acid
PPM	Parts Per Million
H_3PO_4	Phosphoric acid
P1	Pseudo first-order
P2	Pseudo second-order
R-B	Rhodamine B
SEM	Scanning Electron Microscope
NaCl	Sodium chloride
$NaNO_3$	Sodium nitrate
NaOH	Sodium hydroxide
H_2SO_4	Sulphuric acid
TGA	Thermogravimetric Analysis

LIST OF ABBREVIATIONS

TEM	Transmission Electron Microscope
UV	Ultra-violet
WTP	Water Treatment Plant
XRD	X-Ray Diffraction

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ABSTRACT

Preparation of Novel Bio-Based Adsorbent for Fast and Selective Adsorption of Various Dyes

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Master of Science Thesis

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The removal of various industrial dyes being a severe problem on the planet has always taken a prominent role in maintaining a better environment throughout the globe. With the technological advances, increased public awareness of the problem has resulted in responding to the challenge of pollution, especially from the studies of new biobased materials as selective adsorbent sources. Currently, despite the effectiveness of algae nanoparticle (NPs) composite adsorbents in the adsorption of various pollutants, there are no reports of algae treated with eggshells for adsorption. Furthermore, there is a scarcity of data on biosorption of Congo Red (CR) and Methylene Blue (MB), dyes used mostly in the textile sector. In this thesis, Ulva lactuca (U. lactuca) green macroalgae were chemically treated with calcined eggshell (EA) and it is used for selective adsorption of various dyes for the first time. In addition, the individual adsorption capacity of MB and CR dyes onto EA was investigated. Moreover, the influence of parameters on MB and CR adsorption were investigated in detail. The adsorption capacity of treated macroalgae was enhanced since it is treated with calcined eggshell. The maximum

adsorption capacity of EA was 2000 $mg.g^{-1}$. The adsorption process was so fast that it reached equilibrium within 15 min. The mechanism of MB adsorption can be associated to $CaCO_3$ mineral phase in the structure of biosorbent, electrostatic interaction and hydrogen bonding between EA and MB. The findings indicate that the new developed low-cost biosorbent is a promising and effective adsorbent for dye adsorption.

Keywords: Selective adsorption, Algae, Eggshell, Low-cost adsorbent, Dye removal.

ÖZET

Çeşıtlı Boyaların Hızlı ve Seçıcı Adsorpsıyonu için Yenı Bıyo-Bazlı Adsorbanın Hazırlanması

Hussein Ahmad QULATEIN

Kimya Mühendisliği Anabilim Dalı

Yüksek Lisans Tezi

Danışman: Doç.Dr. Müge SARI YILMAZ

Gezegende ciddi bir sorun olan çeşitli endüstriyel boyaların giderimi, dünya genelinde daha iyi bir çevrenin korunmasında her zaman önemli bir rol oynamıştır. Teknolojik gelişmelerle birlikte, sorunla ilgili artan kamu bilinci, özellikle seçici adsorban kaynakları olarak yeni biyo-bazlı materyallerin çalışmalarından kaynaklanan kirlilik sorununa yanıt verilmesiyle sonuçlanmıştır. Şu anda, çeşitli kirleticilerin adsorpsiyonunda alg nanopartikül (NP'ler) kompozit adsorbanlarının etkinliğine rağmen, adsorpsiyon için yumurta kabukları ile muamele edilmiş alglere ilişkin herhangi bir rapor bulunmamaktadır. Ayrıca, çoğunlukla tekstil sektöründe kullanılan Kongo Kırmızısı (CR) ve Metilen Mavisi (MB) boyalarının biyosorpsiyonuna ilişkin veri azlığı bulunmaktadır. Bu tezde Ulva lactuca (U. lactuca) yeşil makroalgleri, kalsine yumurta kabuğu (EA) ile kimyasal olarak muamele edilmiş ve ilk kez çeşitli boyaların seçici adsorpsiyonu için kullanılmıştır. Ayrıca MB ve CR boyalarının EA üzerine ayrı ayrı adsorpsiyon kapasitesi araştırılmıştır. Ayrıca parametrelerin MB ve CR adsorpsiyonuna etkisi

detaylı olarak incelenmiştir. İşlenmiş makroalglerin adsorpsiyon kapasitesi, kalsine yumurta kabuğu ile işlemden geçirildiği için arttırılmıştır. EA'nın maksimum adsorpsiyon kapasitesi 2000 $mg.g^{-1}$ idi. Adsorpsiyon işlemi o kadar hızlıydı ki 15 dakika içinde dengeye ulaştı. MB adsorpsiyonunun mekanizması, biyosorbent yapısındaki $CaCO_3$ mineral fazı, elektrostatik etkileşim ve EA ile MB arasındaki hidrojen bağı ile ilişkilendirilebilir. Bulgular, yeni geliştirilen düşük maliyetli biyosorbentin boya adsorpsiyonu için umut verici ve etkili bir adsorban olduğunu göstermektedir.

Anahtar Kelimeler: Seçici adsorpsiyon, Alg, Yumurta kabuğu, Düşük maliyetli adsorban, Boya giderme.

1
INTRODUCTION

One of the biggest problems affecting human health is pollution. Water is without a doubt the essential requirement and source of life for all living things. Due to rapid population growth, industrialization and unplanned urban growth, the natural resources that meet the basic life needs are decreasing to the extent that they cannot be renewed and bring environmental problems. One of these problems is water pollution and constitutes an important part of environmental problems. During the last few decades, the direct discharge of industrial wastes into water bodies has caused major concerns. This leads to a rise in the discharge of so-called pollutants, which are usually unregulated toxins whose effects on the environment and living creatures are still unknown. Wastewater from industrial activities sometimes contains trace amounts of pollutants, sometimes in high concentrations. Surfactants, pharmaceuticals, personal care products, gasoline additives, fire retardants, antiseptics, industrial additives, heavy metals, and dyes are only a few examples of the most relevant chemicals that have recently emerged [1, 2].

Textile dyeing has a history of more than 4,000 years. Fabric dyeing and sugar fermentation are two specialized fields that can be traced back to ancient times in Egypt. Until the middle of the last century, these and some materials from insects and tropical rain forests were the only sources of dyes. In primeval times, dyes were acquired from natural sources, and was not possible for everyone to have colored materials. William E. Perkin created the first synthetic dye in 1856 and gave it the name "purple red." This dye is obtained by oxidation of contaminated aniline. A few years later, the structures of the natural dyes indigo and alizarin were determined, and these compounds were synthesized. However, the greatest development in synthetic dye chemistry is the discovery of diazotization and azo

coupling. Since 1856, a lot of dyes have been produced. There are more than one thousand dyes currently on the market. Dyes are an important part of material coloring [3].

Organic dyes are one of the biggest contributors to water pollution in a variety of industries, including textile, plastics, printing, photography, pulping, paint, and leather. Thousands of dyes are used for various purposes every year around the world, mainly for textiles. About 10% to 15% of these dyes are found in tap water and wastewater after use. The lives of aquatic animals will be impacted by even a tiny amount of dye (10–50 mg/l) in the water, which will restrict light penetration into bodies of water like the sea, rivers, or oceans. In addition, synthetic dyes can also cause allergic eczema, skin irritation, mutations and cancer. Certain chemicals used in the manufacture of dyes have highly toxic, carcinogenic and even hormone effects. As mentioned earlier, synthetic chemicals not only harm the environment, but can also cause the death of organisms in the ecosystem. Reported studies have shown that indirect or direct consumption of water containing synthetic dyes can cause attention disorders, allergies, asthma, behavioral disorders, hyperactivity, gastric and skin disorders, and sleep disorders, especially in children. Removal of dyes from water is one of the important research topics, because the values determined in consideration of human health, especially drinking water, must be observed. [4]

Treatment technologies to be applied are determined based on the qualitative and quantitative characteristics of wastewater. Chemical precipitation, ion exchange, reverse osmosis, membrane filtration, flotation, chemical oxidation, filtration, membrane separation, adsorption, and ultrafiltration are just a few of the wastewater treatment processes available. Because of its high efficiency, low energy consumption, and low cost, adsorption is said to be the most practical and effective of the many approaches outlined [5]. Adsorption is also used in areas such as removal of impurities and coloring matter in drinking water and purification of multi-component mixtures. More comprehensive and cheaper adsorbents are currently being developed from different scientific studies being

carried out to increase their usage. Cheap adsorbents can generally be obtained by using some industrial and agricultural wastes as adsorbents [4].

In this thesis, we tried to optimize the efficiency of U.Lactuca green algae as a dye adsorbent in aqueous solution by developing a new biobased adsorbent from the combination of inactive eggshell with U.Lactuca algae for selective adsorption of the commonly used Methylene Blue and Congo Red dyes from industrial wastewater, thereby contributing to environmental and natural water resource protection while using a simple, easy-to-apply, and time-saving process. For this purpose, U.Lactuca was chemically treated with low-cost calcined eggshell with high CaO content. Then, CR adsorption of treated U.Lactuca and selective dye adsorption in binary solutions obtained from different dyes were investigated.

1.1 Literature Review

There are many studies in the literature on the removal of various dyes from eggshell waste and their number is increasing day by day. Tsai et al. calcined the waste eggshells and used them in the adsorption of Basic Blue 9, a cationic dye, and Acid Orange 51, an anionic dye, from aqueous solution. As a result of the study, it was observed that the adsorption potential of the Basic Blue 9 dye on the eggshell was much lower than that of Acid Orange 51, and it was determined that the adsorption capacity increased with increasing the calcination temperature [6].

Elkady et al. investigated the adsorption of Remazol reactive red 198 on eggshells prepared as adsorbent by mixing with 5% polyvinyl alcohol solution. They found the maximum adsorption capacity as 46.9 mg/g [7].

Ehrampoush et al., in their study, aimed to determine the optimum conditions for the adsorption of chicken eggshell as an adsorbent and Reactive Red 123 dyestuff from aqueous solution. In the results obtained, it was observed that the amount of dye removed decreased as the amount of adsorbent increased, while the dye removal increased as the contact time increased, the working pH between 5 and 9 increased, and the higher the working temperature from 15°C to 45°C. It has been concluded that eggshell and this dye can be removed from the solution with 99% efficiency when optimum conditions are provided [8].

In the study of Kobiraj et al., the adsorption study for the removal of Brilliant Green dyestuff with eggshell, which is abundant and waste in the environment, was investigated under various experimental conditions such as the adsorbent dosage, temperature, contact time, initial dye concentration and pH. The results of the study show that eggshell powder is a good adsorbent for removing Brilliant Green cationic dyestuff from aqueous solution [9].

Abdel-Khalek et al. investigated the feasibility of using eggshell membrane as a potential and low-cost biosorbent for color removal from methylene blue and Congo red dyes. In the studies, it was observed that the adsorption of both dyes occurs spontaneously at low temperatures, and the pH influences the adsorption

capacity. The present results obtained in the study show the suitability of using eggshell waste as an adsorbent for the removal of dyestuffs [10].

In the study conducted by Dinçer et al., the adsorption of reactive red 195 (RR195) and reactive black 5 (RB5) dyes in the azo dye class on the eggshell membrane from aqueous solution was investigated. The maximum adsorption capacity was determined as 76.9 mg/g and 333.33 mg/g for RR195 and RB5, respectively [11].

In a study by Rápó et al., the capacity and mechanism of adsorbing the Remazol Brilliant Violet 5R dyestuff in aqueous solution with eggshell, which is a biological waste, was investigated. In the results obtained, it was observed that the adsorption capacity increased, but the efficiency decreased when the initial dye concentration was increased. It has been observed that the increase in the amount of eggshell also increases the adsorption efficiency until the saturation level [12].

In the adsorption study conducted by Belibağlı and Uysal, the effects of hydroxyapatite (YKHAp) particles synthesized from waste eggshells on the removal of Malachite Green (MG) from aqueous media were investigated. It has been determined that MG removal is 93% under optimum conditions [13].

Alkalinic (Djilali; Stawiski; Zarina et al.) or acidic activation (Stawiski et al.) have been observed to improve the efficiency of low-cost adsorbents. Stawiski et al. (2017) found that adding citric acid or NaOH to vermiculite increased the adsorption ability for dye elimination [14,15,16].

Furthermore, Nasuha and Hameed discovered that sodium hydroxide improves the tea's adsorption capability by increasing the negative charge of the adsorbent [17]. Furthermore, Djilali et al. discovered that adding sodium hydroxide to timber sawdust significantly improved the density of sorption sites, improving the cationic dyes removal efficiency by adsorbent [16]. $Ca(OH)_2$, is an additional suitable alkali treatment material for improving the natural adsorption capability of cellulosic materials [18]. However, in order to reduce the cost of the treatment process, it would be beneficial to examine the use of wastes to be low-cost substitutes for commercial Calcium Hydroxide.

Due to the high CaO concentration of the calcined bivalve shell, which resulted in MB having a similar adsorption capacity as commercial $Ca(OH)_2$ in a previous study by Jalil et al., bivalve shells were used for alkali treatment of Zea mays L. (maize) husk leaves. [19].

Rais Ahmad et al, studied the adsorption properties of eggshell powder coated with iron oxide (IOESP) in aqueous solution to Cu^{2+}. Adsorption experiments were performed to investigate different parameters. It was found that the adsorption kinetics follows the pseudo second-order rate equation. In the presence of anionic surfactants (SDS), the adsorption of Cu^{2+} increased, while the adsorption capacity of cationic surfactants (CTAB) did not change significantly. The thermodynamic parameters indicated that the adsorption of Cu^{2+} IOESP is possible, spontaneous and exothermic [20].

S. J. Chen et al, investigated the possibility of using eggshell residue (ES) as an adsorbent to sequentially remove microbial products that are soluble, heavy metals, and dye residues. Chicken egg white protein (CEW) was selected as a simulated pollutant from soluble microbial products. Eggshell residue was used to trap metal ions (such as Cu^{2+} and Zn^{2+}), and the produced eggshell metal complex was used to pick up microbial products (such as soluble protein), and then subsequently removing the dye from the aqueous solution. The experimental conditions for ES-M adsorption of CEW protein include stirring speed, adsorption isothermal and kinetic studies together with the pH. The best adsorption capacities of ES-Zinc and ES-Copper were 175.67 and 153.65 mg/g, respectively. The pH values of ES-M-CEW particles used for toluidine blue and acid orange dyes are 12 and 2, and the yields are 114.18 and 75.38 mg/g, respectively. The ES-M-CEW adsorbent's capacity to remove TBO dye reached equilibrium after 5 minutes. The outcomes demonstrated that customized ES particles for various wastewater treatments may be made easily and cheaply. [21].

1.2 Objective of the Thesis

Considering the environmental degradation, the health of living beings, and the technological relevance they have, it is vital to remove or recover dyes from wastewater to reduce their impacts. Although there are a variety of methods for removing dyes from wastewater, adsorption utilizing natural substances is one of the most effective and cost-effective [22].

The goal of this research is to develop a new biobased adsorbent from U.Lactuca treated with eggshell for selective adsorption of the commonly used MB and CR dyes from aqueous solutions, thereby contributing to environmental and natural water resource protection while using a simple, cheap, easy-to-apply, and time-saving process.

Initially, the U.Lactuca treated with eggshell (EA) adsorbent will be prepared, and the two selected dyes (MB and CR) will be used to determine the adsorption capabilities of the adsorbent. In addition to the adsorption performance and mechanism to be found, regeneration studies in this dye adsorption will be examined through experimenting on the various potential compounds found from literature.

As a result of the thesis completion, the advantages of the adsorbent to be produced from cheap sources, its high adsorption capacity and rapid procurement feasibility will lead to a great promise for cleaning MB and CR color dyes from aqueous solutions, and the information obtained can be used to provide contributions that can be made to scientific knowledge, the national economy, and social welfare around the globe.

1.3 Hypothesis

Although this new developed biosorbent material will be used for the selective adsorption of various textile dyes for the first time, a biosorbent with high performance is expected due the high potential of the individual materials to be used.

According to the literature review and the previous works of various researchers, the uptake of CR and MB is expected to be enhanced by the U.Lactuca green algae when it treated eggshell waste. The treatment of algae is also expected to enhance the spontaneity of the process and display regeneration characteristics.

After determining the isotherm model, the maximum adsorption capacity is expected to be of a high value since both adsorbents to be used have been reported to have a high performance on various dyes.

After performing the cyclic adsorption/desorption test, good reuse performance of up to the fifth cycle is expected to be obtained since the regeneration/desorption process is crucial for determining the cost and recovery rate after concentration and adsorption. High CR and MB adsorption from the dye loaded EA as well as efficient reusability should show the efficacy of the prepared adsorbent for CR and MB desorption.

2
GENERAL THEORETICAL INFORMATION

2.1 Wastewater and Treatment Methods

Due to the position of humanity, industrialization has become widespread, and the increase in the world population has gained a great momentum. With the increase in consumption, many resources have started to decrease and become unusable by getting dirty. One of the most vital of these resources is water. The rapidly developing and changing needs cause the rapid development and change of technology, as well as an increase in industrialization. In addition to the industrial facilities that are constantly operating to meet the changing needs, the increase in settlements has also increased the amount of wastewater considerably. In addition, environmental awareness is developing at the same pace and sensitivity towards the environment has developed considerably. With the development of environmental awareness, it has made it possible to realize the damage caused to the environment by the wastewater given to different environments. Damages to the environment greatly affect the lives of humans and other living things, and nowadays they have reached almost life-threatening dimensions. Water pollution is the leading cause of environmental damage [23]. Since water is indispensable for living things, living things are affected the most by it. If the water used in the settlements and various establishments is left to the nature without treatment, the damage to the environment is multiplied. Purification of the water to be released into the environment as wastewater ensures that the damage to the environment and water is minimized. Therefore, the number of treatment plants around the world is increasing day by day. The increase in awareness in the world, the increasing number of environmental organizations, the implementation of the legislation created to prevent environmental pollution and the supervision of relevant institutions are becoming more stringent. With increasing sensitivity, it makes it necessary to improve the operating quality of treatment plants depending on the developing technology.

The quality of operation in the treatment plants is very important in order to prevent the damage to the nature. Because knowing the purpose for which the water to be treated is being treated and ensuring that the treatment processes are carried out by using the right methods is a very important issue for the treatment plants. The increase in wastewater treatment plants in the world has considerably reduced the amount of wastewater released to nature without treatment [23].

2.1.1 Wastewater

Wastewater is water that has been contaminated by organic and inorganic toxic compounds as a result of household, industrial, agricultural, and other activities and then being released into nearby water resources such as streams, lakes, and seas. Wastewater can be divided into two main groups namely as “domestic wastewater” and “industrial wastewater”. Domestic wastewater is sewage water that has been contaminated by its use in residential units such as houses, construction sites, dwellings, motels, and hotels. The most polluting contaminants in these waters include detergents, organic compounds, and oils. Industrial wastewater characteristics vary greatly from industry to industry. Even in industries of the same branch, the differences in the raw materials used and the processes applied, together with many other factors, create differences in the structure of their wastewater. The chemical composition of industrial wastewater contains more toxic substances than the chemical composition of domestic wastewater. The flow rate of industrial wastewater is more emitted than that of domestic wastewater [24].

The discharge of wastewater to the surrounding water resources without any treatment process causes damage to the living life in natural waters and causes the extinction of some living species in a short time. Even if the components present in the wastewater are not high enough to kill the living life, they accumulate in the water and become involved in the food chain from there, thus disrupting the balance of the ecosystem. Recently, along with industrial developments, there has been a great increase in the effects of polluting the environment due to factors such as population growth and industrialization. Many

waterbodies (rivers, lakes etc.) in various countries have been heavily polluted due to performing various industrial activities [25,26].

2.1.2 Wastewater Pollution

The pollution of wastewater can be basically examined under three headings as physical, chemical and biological pollution [27].

2.1.2.1 Physical Pollution

Physical pollution results from coloration, odor, increase in the temperature of water sources due to hot wastes, turbidity, suspended total solids and foaming. The physical parameters to be determined in such waters are color, temperature, odor and taste, turbidity and electrical conductivity of water. Water is colorless in its pure form, but the presence of some metal compounds such as iron, manganese and chromium in water or the presence of water-soluble, colloidally suspended organic substances in water also gives color to the water [28].

2.1.2.2 Chemical Pollution

The chemical properties of wastewater can be explained by dissolved organic substances, toxic, nitrogenous, and phosphorous substances. On the other hand, organic-inorganic wastes and gases cause chemical pollution. Heavy metals are considered as the main chemical pollutants in inorganic wastes. In wastewater, pH, alkalinity, acidity, chloride, sulfate, nitrogen, COD (Chemical Oxygen Demand), BOD (Biochemical Oxygen Demand), heavy metals and toxic substances (phenol, cyanide, pesticides) are the chemical parameters to be determined. Chemical pollutants can be grouped into three groups according to their persistence [29].

i) Non-Degradable Chemical Pollutants - Chloride and similar inorganic compounds that do not undergo chemical and biological degradation over time.

Their concentrations increase over time due to accumulation and decrease with rainwater.

ii) Degradable Chemical Pollutants - Degradable chemical pollutants are organic substances that can be biodegraded. These pollutants decompose through microorganisms and turn into inorganic substances.

iii) Persistent - Metals such as mercury, arsenic, cadmium, chromium, lead, copper and organic substances such as pesticides lead to bioaccumulation over time.

2.1.2.3 Biological Pollution

Biological pollution in wastewater, on the other hand, can be considered the most important pollution in terms of public health, and it is the type of pollution caused by pathogenic microorganisms in the wastes poured into the receiving environment. Until the microorganisms causing biological pollution are destroyed, they pose a danger to the health of the receiving environment. Determination of microbiological contamination caused by pathogenic microorganisms in the receiving environment is made with the help of certain microorganisms called indicators, and coliform bacteria group is generally used for this work [30].

2.1.3 Wastewater Treatment

The process of treating wastewater entails eliminating contaminants and turning it into effluent, which may then be recycled back into the water cycle. The effluent can be reused for a variety of purposes or has a low environmental impact once it is returned to the water cycle (called water reclamation). The treatment happens at a wastewater treatment facility. Wastewater treatment facilities of the right kind treat a variety of wastewaters. Sewage treatment plants are used to treat household wastewater, sometimes referred to as municipal wastewater or sewage. The treatment of industrial wastewater takes occur in either a separate industrial wastewater treatment plant or a sewage treatment facility (usually after some

form of pre-treatment). Agricultural wastewater treatment facilities and leachate treatment plants are two more types of wastewater treatment plants [31,32].

According to the Turkish Constitution's Environmental Law, it is illegal to deliver, store, transport, remove, and carry out similar actions that harm the environment, either directly or indirectly, in violation of the criteria and methods established in the applicable regulations. When there is a risk of contamination, the parties involved take steps to avoid it; when pollution occurs, the polluter is required to take the appropriate steps to stop it, as well as to eradicate or lessen the pollution's effects. The output values of water used in residences or industries are regulated by the receiving environment's standards. After the operations to be carried out in the wastewater treatment facilities, the discharge values of those who do not comply with the limit values should be decreased below these limits. The term ‘receiving environment' refers to near or far ecosystems such as lakes, rivers, coastal and sea waters, and subsurface waters where waste waters are discharged or mixed indirectly [33].

Any water treatment is carried out as part of a treatment train, which is a series of unit processes. Screening, sedimentation, flotation, coagulation, filtration, adsorption, ion exchange, gas transfer, oxidation, biological reactions, and disinfection are examples of unit processes [34]. The selected aggregate, i.e., the treatment train, is a water treatment plant (WTP) if it is implemented to full scale with all of the necessary appurtenances and engineering to make it operate on a continuous basis. The goal of water treatment, by this treatment train, is to achieve the desired change in water quality by reducing the amount of BOD, suspended solids, pathological organisms, toxic substances, dissolved solids and non-biodegradable compounds in the wastewater, leaving the wastewater in a cleaner and harmless environment. Wastewater treatment can be basically grouped under three main groups. A wastewater treatment plant generally includes pre-treatment, physical, chemical and biological treatment units [35].

2.1.3.1 Pretreatment

In this procedure, coarse materials including paper, textile wastes, plastic, metal, and substances like sand and oil-grease are separated from wastewater. If these compounds are not removed at this time, they can damage pumps, sludge removal equipment, valves, and pipes, causing issues in the treatment process. Suspended particles can sometimes be removed using fine screens and sieves [36].

2.1.3.1.1 Physical Treatment

In this procedure, suspended solid substances and floating particles in water are removed by physical treatment methods. During these processes, solid particles with a slight decrease in the value of biochemical oxygen demand were observable. Solid suspended substances carried by wastewater are mainly screening, grit retention, settling, treatment with balancing pools, flotation and removed by oil separation processes [37].

2.1.3.1.2 Chemical Treatment

Chemical treatment is used to transform pollutants dissolved in water into low-solubility chemicals by chemical processes, or to eliminate colloidal and suspended particles by clumping them together. Neutralization, coagulation, and flocculation are some of the processes involved [38].

2.1.3.1.3 Biological Treatment

The biological treatment process is essentially the conversion of organic compounds and suspended solids dissolved in wastewater into substances that can be broken down by bacteria and precipitated. This purification method is actually an accelerated form of the decay events that take place in the ongoing carbon cycle in nature. During biological treatment, microorganisms use nitrogen and carbon-containing organic compounds as nutrients and convert them into stable compounds. Decomposition reactions of organic pollutants are carried out by

many and different microorganisms. These microorganisms can be classified as aerobic, anaerobic and facultative [39].

2.1.4 Wastewater from Textile industry

The main problems in the textile industry are color in the dye part, high pH and sudden changes due to NaOH during processing. Machine oils, high BOD, sulfites and heavy metals are other polluting parameters according to the sector type. Chemical industry wastewater may contain oil emissions, sulfites and phenols, machine oils, solids, high pH, phosphates and non-reducible organics. Typical effects are taste and smell problems. It can also cause thermal contamination. Chromium, cadmium, cyanide and zinc metal impurities can be seen in the wastewater from metal production while some metals remain in the food chain [40,41].

2.2 Dyes

The substances used to protect the surfaces of objects from external effects or to provide a better appearance by coloring them in accordance with the purpose of use are called Colorants. Today, the colorant industry constitutes an important part of modern chemistry. They are used in many industries: clothing, paint, photography, printing, and ceramics for various purposes. They are also widely used in a variety of industries, including construction, automotive, and plastics [43].

Depending on the usage, the colorant can either be a dye or a pigment. Dyes, unlike pigments, are colored organic compounds that are soluble in various solvents such as water and are often applied to textiles as an aqueous solution [44,45]. They are designed to bind tightly to the polymer molecules that make up textile fibers. Mineral and organic dyes are used in the textile industry. Organic

dyes vary as natural and synthetic dyes. In the main paint industry, paints are produced as water-based and solvent-based [47,48].

Dyes are a mixture of unsaturated aromatic chemicals with properties such as strong color, solubility, substantiveness, and speed [49]. Each dye class has its own unique chemistry, structure, and bonding method. Some dyes react chemically with substrates to produce strong links, while others are held in place by physical forces [50]. Although dyes contain different chemical structures, they usually consist of compounds such as chromophores and functional groups. Chromophore is an essential compound that contributes to the color of paint and is used to create color. One or more bonds can be found in chromophore groupings. The bonds in the chromophore structure are variable, and by their absorption of light, they make the dye appear brightly colored. The azo group is generally used as the chromophore group in paints. Other important groups include indigo and sulfur. These groups in the structure of the paint give color to the aromatic structure and cause the appearance of adsorbent bands in the visible spectrum [52].

2.2.1 Textile Dyeing

Textile dyeing is one of the most serious pollution factors in the global fashion industry, destroying the environment and threatening human health.

Some examples of commonly used dyes are methylene blue, janciana purple, fuchsin dye, malachite green, safranin dye, bismarck brown, brilliant green,chrysoidin dye, methyl violet - 6b, and nigrosin. Some of the dye structures are seen in the figure below [55].

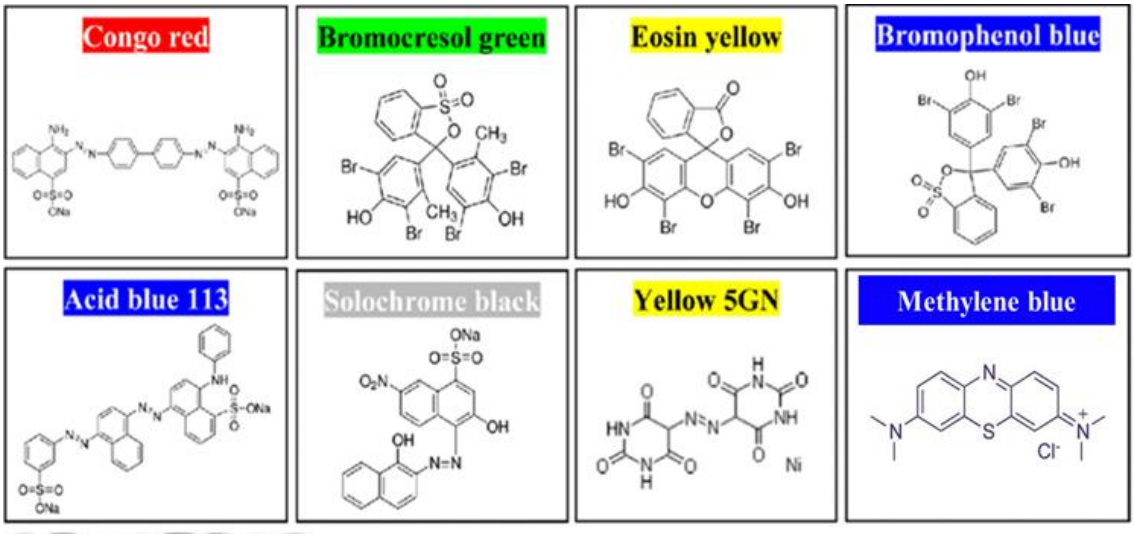


Figure 2.1 Examples of commonly used dyes

2.2.2 Types And Classification Of Dyes

There are several ways to classify dyes. Dyes are complexes of unsaturated aromatic compounds with strong color, solubility, substance and hardness. Each type of dye has a different chemical composition, structure and shape. Some dyes chemically react with the substrate to form a strong bond, while others can maintain physical strength. The following are some of the more popular classification forms [58].

2.2.2.1 Classification by Material Source

A very common classification of colorants is based on their source of material. Most dyes are organic molecules with complex properties. The synthesis of organic dyes begins with the synthesis of fluorene; in the past, dyes were made from

pigments, so dyes can be divided into natural dyes and synthetic dyes according to their source. There are generally more synthetic dyes than natural dyes [58,59].

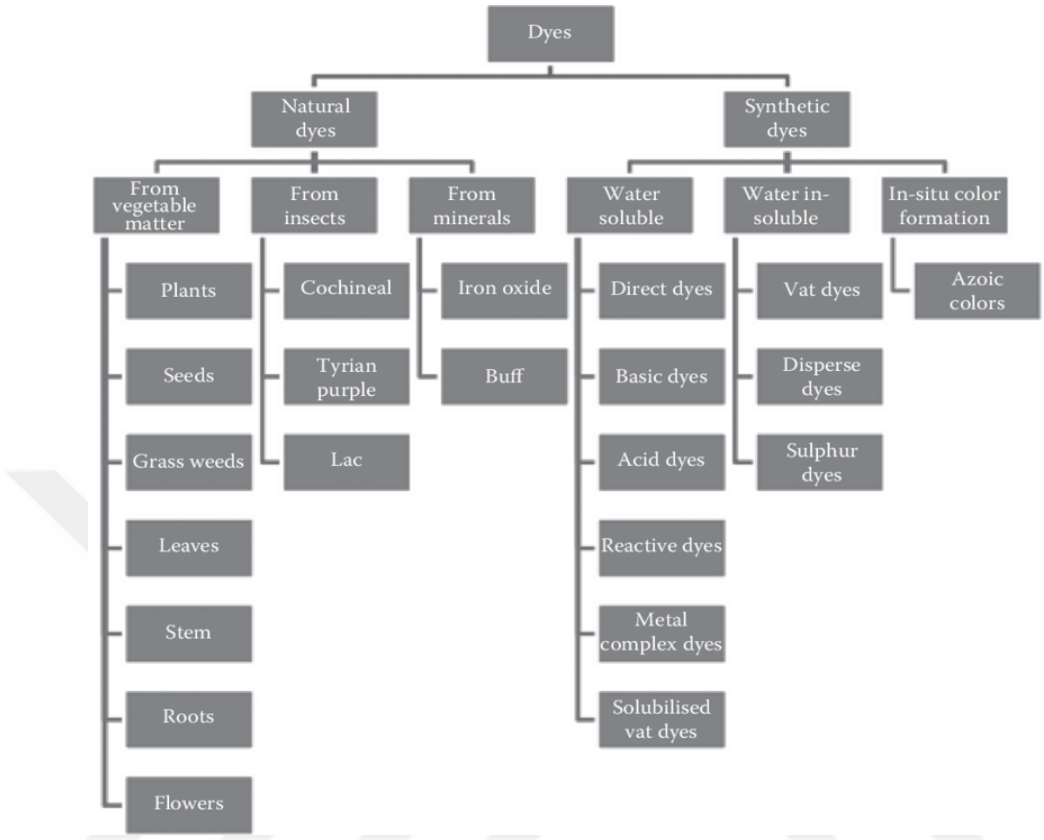


Figure 2.2 Classification of dyes based on their material sources [59].

I) Natural Dyes

For thousands of years, dyes have been used and modified in textiles, food, ceramics, leather and households. Painting and dyeing are two ancient methods of coloring materials that use pigments from colored rocks and minerals. Plants and animals are used to make or extract natural colors. Some of the most common dyes obtained from natural sources are called natural dyes. The color index used in the dye classification and naming system corresponds to the sample (Natural + base color + number). This classification is based on the source and color of the dye but does not include chemical information or information about the dye mechanism. Natural dyes are usually negatively charged, that is, the colored part of the molecule is usually negatively charged. The dyes used since ancient times

include kermes (natural red 3), carmine (natural red 4) and lacquer (natural red 25). All three dyes are obtained from insects of the genus Cocci [58,59].

II) **Synthetic Dyes**

Artificial dyes made from organic and inorganic compounds are usually called synthetic dyes and are usually made from petroleum by-products or synthetic resource types of natural minerals. As William Henry Perkin's attempt to synthesize quinine failed in 1856, Movein was the first man-made organic aniline dye to be discovered by accident. Since then, thousands of synthetic dyes such as magenta, safranin and indole have been manufactured. Synthetic dyes have been divided into many other categories such as acid (anionic), basic (cationic), mordant, vat, reactive, disperse, azoic and Sulphur dyes based on their source and properties as shown in table 2.1 [58,59].

Table 2.1 Categories of synthetic dyes [60]

Category	Description
Acid dyes	These are colored anions that are applied to wool, silk, and nylon at a low pH.
Azoic dyes	These are insoluble azo dyes created by reacting a diazonium salt (azoicdiazo component) with a naphthol within the substrate (azoic coupling component).
Basic dyes	These are colored cations that are employed on acid-side-chained polyacrylonitrile (acrylic) textiles, as well as proteinaceous rubbers and tannic acid-treated cotton.
Direct dyes	These are dyes used to color fabrics that can form hydrogen bonds with the dye molecule. Acid dyes with big molecules that attach directly to cellulose fibers are known as direct dyes. Preparing an aqueous solution and immersing the fabric in it is how these dyes are applied to the fabric. With the introduction of this method for cotton dyeing, the use of

	mordants or other binders became superfluous. Direct dyes are more fastidious than other dyes, but they lack the color brilliance of other dyes. The diazotization treatment compensates for this. Direct dyes are used to dye fabrics such as cotton, linen, rayon, wool, silk, and nylon.
Disperse dyes	They are made by grinding dye into small particles and dissolving it in a solution with the help of dispersing agents. These dyes were created to color secondary cellular acetate fibers and are relatively water insoluble. When fiber is submerged in the solution, it absorbs the color. Disperse dyes are used to color polyester, nylon, acetate, and triacetate fibers. When sprayed with a "plasticizer," disperse dyes are insoluble colored chemicals in fine suspension that permeate hydrophobic materials (cellulose acetate, polyester).
Fluorescent brighteners	They absorb ultraviolet light and emit blue light, which is used to prevent white textiles from fading.
Ingrain dyes	These are soluble colorants that alter chemically and become insoluble after being applied to the dyed substrate.
Mordant dyes	These are dyes that have been combined with metals. The metal can be used before, during, or after the dyeing process.
Oxidation bases	They are colorless amines and aminophenols that, when oxidized (typically by hydrogen peroxide), polymerize to brown or black insoluble compounds; they are used on fur and hair.
Vat dyes	These are applied to cotton as a soluble compound that is later oxidized to the insoluble, fully colored form of the dye.
Sulfur dyes	Heating aromatic amines and phenols with sulfur or sodium polysulfide produces sulfur dyes, which are inexpensive polymeric pigments. The cloth is treated with a soluble

	(reduced) form, and the insoluble polymer is then oxidized to renew it.
Solvent dyes	These are colored chemicals that are only soluble in hydrophobic solvents and are used to color liquids and polymers in large quantities. Alcohol, chlorinated hydrocarbons, and liquid ammonia can all dissolve these dyes, but not water. These dyes are widely used in the petroleum sector. The dye's colors are created by dissolving it in a target, which is usually lipids or non-polar solvents. Plastics, synthetics, gasoline, oil, and waxes are all colored with them.
Reactive dyes	These are colorful chemicals with side chains that react with the substrate to generate covalent bonds; they're used to dye cellulose and other materials very quickly (and resistantly). Covalent bonds are created with cellulose fibers in reactive dyes. Such connections have a high degree of fastness. It happens because strong molecular connections are difficult to break. As a result, they have a higher comparative resistance to light and washing. Reactive dyes have numerous advantages that include its ease of cleaning and fast wet speed, which is achieved by a quick and easy coloring procedure.
Pigments	These are finely split white, black, or colorful materials that are insoluble in water and organic solvents.In addition, they are used in paints and plastic mass coloring. Pigments, unlike dye, do not have an affinity for textile fibers or other surfaces. Pigments are insoluble and applied to the surface as oily suspensions.

2.2.2.2 Classification by Chemical Structure

According to the chemical classification system, dyes can be classified according to the type of chromophore and industry as seen in the Table 2.2 below.

Table 2.2 Classification of dyes based on chromophore groups and industrial applications [61]

Chromophoric Group	Industries
Acridine dyes, derivatives of acridine >C=N & >C=C Texties, Anthraquinone dyes, derivatives of anthraquinone >C=O and >C=C, Arylmethane dyes; Diarylmethane dyes, based on diphenyl methane, Triarylmethane dyes, based on triphenyl methane, Azo dyes, based on a -N=N- azo structure, Cyanine dyes, derivatives of phthalocyanine, Diazonium dyes, based on diazonium salts, Nitro dyes, based on the NO2 nitro functional group and Nitroso dyes, are based on a –N=O nitroso functional group	Textiles
Phthalocyanine dyes, derivatives of phthalocyanine >C=N	Paper
Azin dyes; -Eurhodin dyes, -Safranin dyes, derivatives of safranin -C-N=C-	Leather and Textile
Xanthene dyes, derived from xanthene -O-C6H4-0	Cotton, silk & Wood
Quinone-imine dyes, derivatives of quinine	Wood & Paper
Indophenol dyes, derivatives of indophenol >C=N-and >C=O	Color photography
Oxazin dyes, derivatives of oxazin -C-N=C =C-O-C=, Thiazin dyes, derivatives of thiazin	Calico printing

2.3 Dye Removal

The qualitative and quantitative characteristics of the wastewater determine the types of treatment that should be used. There are numerous methods for treating wastewater, including ion exchange, chemical precipitation, reverse osmosis, membrane filtration, flotation, chemical oxidation, filtration, membrane separation, adsorption, and ultrafiltration. Some of the advantages and disadvantages of various dye removal technologies are explained in Table 2.3. Because of its high adsorption efficiency, cheap cost, and low energy consumption, adsorption is the most practical and effective approach among the numerous approaches outlined.

Table 2.3 Dye removal technology; a brief description of the advantages and disadvantages [62]

Technology	Strengths	Drawbacks
Chemical treatment		
Chlorine oxidation	Simplicity of application, and low cost	Unavoidable negative effects and harmful byproducts
Hydrogen peroxide (H_2O_2) oxidation	Simplicity of application	pH dependency, and sludge production
Ozonation	Gaseous state of ozone reagent, no increase in water volume, and no sludge production	Short half-life (20 min)
Fenton`s reagent	Effective decrease of COD (chemical oxygen demand), total organic carbon, and toxicity, and applicable even with high-suspended solid concentration. Efficient decolorization of soluble/insoluble colors.	formation of sludge, efficiency within a limited pH range, and slower reaction time
Coagulation/flocculation	Economically feasible, and satisfactory removal of	Acid, basic, reactive, and azo dyes that are extremely soluble are not

	disperse, sulfur, and vat dyes	satisfactorily removed due to the large amounts of concentrated sludge, the pH dependence, and other factors.
Physical treatment		
Adsorption with activated carbon	High quality treated water, effective for variety of dyes	Costly, requires regeneration or disposal of the concentrates must be taken into account, and performs poorly after regeneration or re-use
Membrane filtration	Effective for all dye kinds, temperature resistance, microbial assault resistance, and high-quality treated effluent	High cost, lengthy membrane life, large energy use, high operating pressure, and frequent clogging
Ion-exchange resin	After use, regeneration of the solvent doesn't result in any weight loss, and it works well for soluble colors.	Not effective for all colours, including disperse dyes, costly organic solvents, and high costs.
Biological treatment		
Aerobic	Low running costs, and non-toxic end products of complete mineralization	Many synthetic colors are resistant to biological degradation and nontransferable under aerobic conditions, and synthetic dyes are not uniformly decolored.
Anaerobic	Inexpensive, well-established degradation of variety of synthetic dyes, no foaming problems with surfactants, and cheap removal of biochemical oxygen demand (BOD)	Insufficient BOD removal, dyes and other refractory organics are not mineralized, nutrients (N, P) are not removed, and transformation of sulfates to sulfide

2.4 Adsorption

Adsorption is the most commonly used physical and chemical balance method in wastewater treatment. It is a process based on two phases. Ions or molecules present in one phase (gas or liquid) tend to accumulate and concentrate on the surface of the other phase (usually solid). When there is a weak bond between the adsorbate and the adsorbent, the physical adsorption process will occur, and when the substance forms a strong bond due to the exchange of electrons, chemical adsorption will occur. It can remove certain types of chemical pollutants that traditional biological agents cannot handle. Activated carbon is a common adsorbent used to clean industrial dyes before they are released into the environment. The use of powdered activated carbon to remove chemically reactive dyes from textiles from aqueous solutions has been studied. However, activated carbon also has some shortcomings, such as its high cost, the regeneration ability, carbon loss and decreased efficiency after regeneration. These limitations have stimulated researchers' interest in finding new alternatives to traditional adsorbents. Because of their ability to remove inorganic and organic pollutants, people are now paying more and more attention to the use of biobased adsorbents to remove various cationic and anionic dyes from water. The process of pollutant sequestration by non-living biomass from algae, lichens, mushrooms, mosses, bacteria, and biomass waste is known as biosorption. This treatment method is modernized by development of several new adsorbents such as eggshells, sugarcane bagasse, hen feathers, almond peel and algae [63,64,66].

2.4.1 Types of Adsorptions

There are generally three types of adsorptions which are physical adsorption (Van der Waals adsorption), chemical adsorption (activated adsorption) and Ionic adsorption (electrostatic adsorption). Although these three types of adsorptions differ in certain ways, in most adsorption events, the three types of adsorptions

indicated above occur simultaneously or in succession, making it impossible to determine which type of adsorption is dominant [63].

2.4.1.1 Physical Adsorption (Physisorption)

Physisorption is a type of adsorption in which the adsorbate sticks to the surface only as a result of weak intermolecular interactions. It is understood that the weak Van-der Waal's forces attach the adsorbent and adsorbate. There is no transfer or exchange of electrons, although the balance is re-established without losing the original connection between the electrons and the corresponding interacting particles. It is distinguished by its low heat of adsorption, which is typically less than 10 kcal/mol [63-84 kJ/mol]. This type of adsorption is only evident at temperatures below the adsorbate's boiling point. It is reversible and has no specificity. According to the theory that physical adsorption might result in the production of several layers, the type of adsorbent matters more than the kind of solid adsorbent [63,64].

2.4.1.2 Chemical Adsorption (Chemisorption)

Chemisorption is a type of adsorption whereby a molecule adheres to a surface through the formation of a chemical bond. When a substance is adsorbed on a surface, a chemical bond is often formed between the adsorbate and the adsorbent through electron transfer or exchange, and it is usually caused by high adsorption heat, that is, more than 20-150 Kcal/mol and can occur at high temperatures. This is usually irreversible and non-specific for adsorbates and adsorbents. Due to the high initial heat, there is too much adsorption, which is a sign of chemical adsorption, forming a multilayer material that is held in place by physical force. The table 2.4 below shows some major comparisons between behaviors of chemical adsorption (chemisorption) and physical adsorption (physiosorption) [66].

Table 2.4 Comparison between physisorption and chemisorption [65]

Physical adsorption	Chemical adsorption
It is due to intermolecular Van der waal's force.	It is due to chemical bond formation.
Depends on the nature of gas. Easily liquefiable gases are adsorbed readily.	More specific than the physical adsorption.
Heat of adsorption is small.	Heat of adsorption is large.
Reversible.	Irreversible.
It occurs rapidly at low temperature and decreases with increase of temperature.	Increases with increase of temperature.
Increase of pressure increases adsorption.	Change of pressure has no effect.
Forms multimolecular layers on adsorbent surface.	Forms unimolecular layer

2.4.1.3 Ionic Adsorption

Electrostatic attraction forces play a major role in this type of adsorption. It is the process of using electrostatic forces on charged spots on the surfaces to keep ionic adsorbates in the solution. The distinction between ionic and physical adsorption is that the ionic interaction, or bonding force, is stronger in ionic adsorption. The environment's ionic strength and pH level have a direct impact on such adsorption [66].

2.4.2 Factors Influencing Adsorption

There are many factors that affect the adsorption, including the characteristics of the adsorbate and the adsorption material together with the process parameters. The impact criteria related to the adsorbate include polarity, molecular structure, stability, and concentration. Equilibrium capacity and kinetics are the main determinants of adsorption. They are affected by the surface affinity of different species, physical, chemical, and morphological characteristics, surface area, surface charge and porosity of the adsorbent material. The adsorption performance of the system is also affected by operating parameters such as pH value of the solution, temperature, and coexisting particles in the solution. Before using the complete system, it is crucial to investigate and optimize the factors that affect the adsorption system [67]

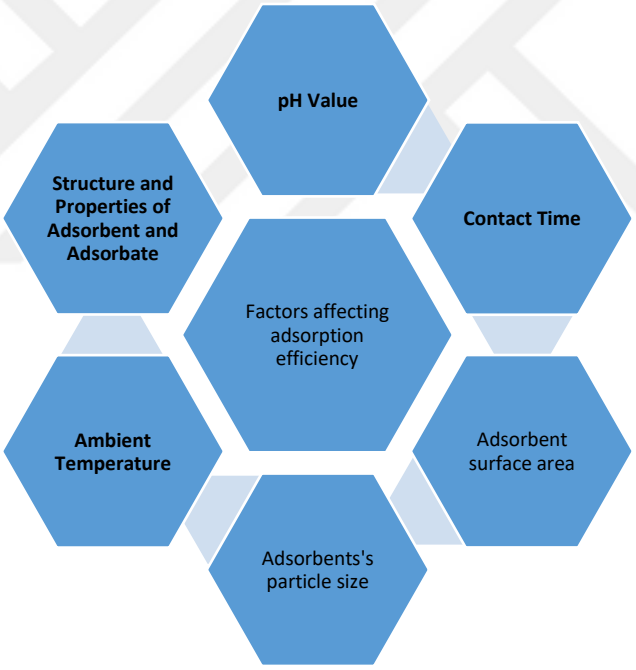


Figure 2.3 Factors affecting adsorption efficiency.

2.4.2.1 pH Value

One of the most important parameters affecting adsorption is the pH value of the medium. Since hydroxyl (OH^-) and hydronium ions can be adsorbed very strongly, the adsorption of other ions is directly affected by the pH of the solution. In

adsorption, ions with different charges can be adsorbed at different pH values. Compounds with simple structure are adsorbed at the lowest rates at pH 7 and around. The increase in positive ions on the adsorbent surface at low pH values increases the adsorption of negatively charged adsorbates, while the opposite occurs in solutions with high pH values. For example, cationic ions adsorb better at high pH, while anionic ions adsorb better at low pH [68].

2.4.2.2 Structure and Properties of Adsorbent and Adsorbate

The specific surface area of the adsorbent to be used in the adsorption process directly affects the adsorption efficiency. The part of the total surface area of the adsorbent that can be used for adsorption is called the "specific surface area". Since adsorption is an event that takes place on the particle surface, the adsorption efficiency is directly proportional to the specific surface area. The adsorption efficiency of a solid adsorbent in a given mass increases with the unit surface weight and porous structure of this material. For this reason, the use of solid adsorbents with a large pore volume and more granular structure increases the adsorption capacity [69].

Although there are a wide variety of adsorbent types that can be used in adsorption, the pore structures of these materials show differences. Different adsorbents can have different sizes of micro, meso and macro pore structures. When the pore diameter is less than 2 nm, the adsorbent is micropore, when the pore diameter varies between 2-50 nm, it is mesoporous, and adsorbents with a pore diameter larger than 50 nm are macroporous. The more micropores there are in the adsorbent, the larger the surface area of the adsorbent [69].

The solubility of the adsorbate is also one of the important parameters that affect the adsorption and control the adsorption balance. The adsorption of a substance depends on its solubility in the environment. Usually, there is an inverse proportion between the adsorbed amount of a substance and its solubility in the medium in which its adsorption occurs. In other words, high solubility increases

the interaction between adsorbate and solution and causes the amount of adsorbed substance to be low.

The concentration of the adsorbate in the solution has an effect on the rate and amount of adsorption. Since the amount of adsorbate per unit volume changes at different concentrations, the amount that the adsorbent will adsorb changes [70,71].

2.4.2.3 Ambient Temperature

Since adsorption reactions are generally exothermic, adsorption efficiency increases with decreasing temperature. If the adsorption reaction is endothermic, the adsorption efficiency increases with increasing temperature. Small changes in temperature do not significantly change the adsorption intensity. On the other hand, as the solubility of the substances in the solution increases with the increase in temperature, the adsorption efficiency may decrease. Temperature is an important parameter that also affects the reaction rate.

2.4.2.4 Contact Time

One of the important factors affecting the rate and efficiency of adsorption is the contact time. According to the interaction between adsorption and contact time, there is an increase in the amount of adsorption due to the presence of high surface area of the adsorbent in the initial stage. However, as the adsorption process continues, it is expected that the adsorption rate will start to decrease due to the decrease in the amount of adsorbate. After the saturation value is reached, the adsorption process takes place in the adsorbent pores rather than the outer surface of the adsorbent, and with the increase of the contact time, the adsorption amount decreases [72].

2.4.3 Adsorbents Used in Adsorption

Many adsorbents can be used in the adsorption process. Studies are still ongoing to develop adsorbents that can be used efficiently and economically. Among these, activated carbon is the most commonly used adsorbent in the world for the removal of chemical pollutants from wastewater. However, the high cost of activated carbon causes restrictions in its use and limits the use of activated carbon in small-scale industries.

Depending on these disadvantages, adsorbents, which can be alternatives to activated carbon, have been used in recent years. Because of their efficiency, low cost, and environmental protection, biosorbents have been drawing much attention. Agricultural wastes (sugarcane pulp, eggshells, corn cob, rice paddy, coconut shell), industrial wastes (waste sludge, metal hydroxide sludges) are few of the many materials being utilized in many adsorbent studies [73,74].

2.4.3.1 Eggshells

Eggshells from the poultry industry is a by-product (mostly referred to as waste-product) that is currently being neglected. Eggshells compose of about 97% calcium carbonate and the ability of this to be obtained as pure Calcium Oxide (CaO) and used as an adsorbent has been scientifically proven [75].

2.4.3.2 Algae

Algal biomass is a highly effective adsorbent for heavy metals and organic dyes in aqueous waste. Because of its great efficiency and wide variety of uses, the adsorption of dyes in polluted water by aquatic plants and algae has attracted a lot of study attention. U.Lactuca is a tiny genus of sea algae that is widely available around the world. This marine alga, sometimes known as sea lettuce, is an edible green alga. The use of U. Lactuca as a biomaterial for biological treatment of dye effluent and toxic heavy metal from the solution has been recently permitted [76].

2.4.4 Regenerating Ability of Adsorbents (Desorption And Recovery)

The adsorption material is no longer effective after saturation and needs to be regenerated/desorbed. Desorption is effective for both chemically and physically adsorbed compounds. The state of releasing a material or the energy that a substance has adsorbed is known as desorption. Desorption, in other terms, is the separation of particles adhered to a solid surface from the adsorbate surface. Desorption actually occurs at the same time as adsorption. A substance adsorbed more strongly than itself replaces the substance adsorbed on the adsorbent. The regeneration of used adsorption media provides the advantages of reusing the media, recovering adsorbents, discovering adsorption mechanisms, and reducing costs. The adsorption capacity is close to the original characteristics of several regeneration cycles. Regeneration can be done thermally or physically and chemically. For example, activated carbon is thermally regenerated under the action of hot air or steam, and chemically regenerated with acidic and alkaline solutions. The goal of the recovery process is to restore the adsorbent's effective adsorption property. As a result, powerful acid or base solutions are frequently used. Acids such as HCl, H_2SO_4, H_3PO_4, alkalis, NaOH and electrolytes, $NaNO_3$ and NaCl are commonly used as regenerators to desorb various adsorbents from adsorbed waste. The adsorbent material loses volume and hence its adsorptive ability at the end of each adsorption operation. The degree of adsorbent regeneration is one of the elements that determines the adsorption process' economic viability. NaOH is an effective dye desorption eluent used a desorption process to regenerate the adsorbent and confirmed the electrostatic attraction between the positively charged surface of the adsorbent material and the dye. Mesoporous materials with excellent adsorption and regeneration capabilities have been studied to improve the removal and recovery of phosphate. For instance, mesoporous waste can be recycled with chemicals such as NaOH, KOH, NaCl or Na_2SO_4 without affecting the adsorption capacity. The regeneration/desorption process is crucial for determining the cost and recovery rate after concentration and adsorption. Mainly non-recyclable adsorbents can also be used in sewage treatment plants [77].

3
EXPERIMENTAL SYSTEM MATHEMATICAL DESCRIPTION

Multiplying the adsorbed substance concentration (C_{ads}) by the solution volume and dividing by the amount of adsorbent present in the adsorption medium yields the amount of adsorbed substance q (mg/g) per unit weight of adsorbent [78].

$$q = \frac{(C_0 - C_e) \times V}{m} = \frac{C_{ads} \times V}{m} \quad (3.1)$$

Where,

C_0 = Initial dye concentration (mg/L)

C_e = Equilibrium dye concentration (mg/L)

V = Solution volume (L)

C_{ads} = Concentration of adsorbed substance (mg/L)

m = The amount of biosorbent

The adsorption efficiency (%) is computed by dividing the adsorbed substance concentration C_{ads} by the initial concentration once the adsorption equilibrium has been established in the system [78].

$$Adsorption\ Efficiency\ (\%) = \frac{C_{ads}}{C_0} \times 100 \quad (3.2)$$

3.1 Adsorption Isotherms and Adsorption Equilibrium

Adsorption isotherms can be used to explain the adsorption equilibrium. The adsorption isotherm is the relationship between Ce, the concentration of the substance remaining unadsorbed in the solution, and qe, the amount of substance adsorbed per unit weight of the adsorbent. Adsorption isotherms are mathematical expressions that depict the interaction between the adsorbed substance and the adsorbent. These expressions also reveal the adsorbent's capacity, the adsorption energy, and the kind of adsorption. Adsorption is a response that is in a state of equilibrium. The concentration of the adsorbed substance in the solution reduces as it comes into contact with a given amount of adsorbent until it reaches equilibrium with that on the adsorbent surface. The concentration of the adsorbed substance in the solution becomes fixed once the adsorption equilibrium is attained [79,82].

At constant temperature, the amount of adsorbed material is usually calculated as a function of concentration. Many isotherm models have been devised to mathematically express adsorption isotherms. Langmuir, Freundlich, Redlich-Peterson, BET, Tempkin, and Koble-Corrigan are some of the existing isotherm models for single-component systems. The data collected for this thesis was applied to the Langmuir and Freundlich isotherm models. The following sections contain all of the relevant information regarding these isotherms [79,82].

3.1.1 Langmuir Model

Langmuir developed the isotherm equation in 1916. Langmuir equation is a viable equation for monolayer physical adsorption and adsorption from solution. The

Langmuir model is a technique that is used to model adsorption on homogenous surfaces based on a set of assumptions [80]. These assumptions may include:

- On the whole surface of the adsorbent, there are a defined number of active sites with consistent energies.
- There is no contact between the molecules that have been adsorbed.
- Adsorption happens in a monolayer because each active site on the adsorbent adsorbs only one molecule.

The adsorption increases linearly with the starting concentration of the adsorbate in the Langmuir isotherm, and when the saturation point is achieved, the adsorbent's surface is coated in a monolayer, and the amount of adsorbate adsorbed on the surface remains constant. The equation for the Langmuir model is as follows:

$$q_e = \frac{a\, C_e}{1 + bC_e} \tag{3.3}$$

$$a = q_m \times b \tag{3.4}$$

$$b = A \times e^{\frac{-\Delta H}{RT}} \tag{3.5}$$

Where, C_e represents the concentration of the chemical remaining in the solution at equilibrium without being adsorbed in milligrams per liter (mg/L), q_e is the amount of substance adsorbed per unit weight of adsorbent at equilibrium (mg/g), K_L is a Langmuir's constant that is related to adsorption's net enthalpy and q_m is the quantity of substance adsorbed per unit weight of sorbent (adsorbent's maximum adsorption capacity) to form a full layer on the surface (mg/g).

Langmuir models in various linear forms can be created by linearizing the model. As seen below:

$$\frac{1}{q_e} = \left(\frac{1}{K_L . q_m}\right)\frac{1}{C_e} + \frac{1}{q_m} \qquad (3.6)$$

Following the plotting of the $1/q_e$ and $1/C_e$ values, q_m is computed from the line's y-axis intersection point, and the Langmuir constant K_L is calculated from the slope. The dimensionless equilibrium parameter, the equilibrium factor R_L, can then be used to convey the main characteristic of the Langmuir isotherm [80,83].

$$R_L = \frac{1}{1 + K_L(C_0)} \qquad (3.7)$$

Where, R_L is the dimensionless separation factor constant, K_L is the Langmuir constant (L/mg), which represents the adsorption energy and C_0 is the initial concentration (mg/L).

The R_L constant values and isotherm types based on availability condition that is satisfied if the R_L constant takes values between 0 and 1 is listed in the Table 3.1 below [81].

Table 3.1 R_l constant values and isotherm types.

R_L value	**Isotherm Type**
$R_L = 0$	Irreversible
$0 < R_L < 1$	Appropriate
$R_L = 1$	Linear
$R_L > 1$	Inappropriate

3.1.2 Freundlich Model

The Freundlich isotherm is a model based on some assumptions in the Langmuir isotherm that describes adsorption as reversible and non-ideal adsorption rather than monolayer formation. Active sites for adsorption on the adsorbent surface have heterogeneous features, according to the Freundlich model [82].

The Freundlich model is utilized in multilayer adsorption when the adsorption heat and behavior are not uniformly distributed on the heterogeneous surface of the adsorbent [26,29]. The equation of Freundlich isotherm model is expressed in equation 3.8

$$q_e = K_F \times C_e^{\frac{1}{n}} \qquad (3.8)$$

Where, C_e is the concentration of material in solution after adsorption (mg/L), q_e is the amount of material adsorbed per unit weight of adsorbent at equilibrium (mg/g), K_F is the Freundlich's adsorption constant. The adsorption constant represents the magnitude of the adsorption capacity as a function of the adsorbent-adsorbed material interaction. High K_F values suggest that there is sufficient contact between the adsorbent and the adsorbed substance.

The adsorption intensity is represented by n. If n is bigger than 1, adsorption is likely to be favorable. The heterogeneity factor, 1/n, is a number that ranges from 0 to 1. The fact that this value (1/n) is so near to zero shows that the surface is heterogeneous. For heterogeneous systems, the Freundlich isotherm is more accurate than the Langmuir model [82].

By linearizing the isotherm equation with the logarithms of both sides of the Freundlich equation:

$$ln(q_e) = ln(K_F) + \left(\frac{1}{n}\right) lnC_e \qquad (3.9)$$

To calculate K_F and n constant, the change of $\ln(q_e)$ versus $\ln C_e$ is plotted. The value where the drawn line intersects the y-axis gives $\ln(K_F)$, and the line's slope gives 1/n.

In wastewater research, Langmuir and Freundlich isotherms can be utilized to analyze and evaluate adsorption data. For mixed or dilute solutions, the Langmuir equation does not work as well as the Freundlich equation. In practice, when determining which isotherm to use, the equation that yields a linear line is used.

3.1.3 Redlich Peterson Model

Redlich Peterson produced a more advanced empirical isotherm by merging the three factors to represent a wider range of equilibrium data. The Langmuir and Freundlich isotherms' qualities are combined in the Redlich Peterson model as expressed below [83]:

$$q_e = \frac{K_R C_e}{1 + a_R {C_e}^{\beta}} \qquad (3.10)$$

The Redlich Peterson equation is simplified to the Langmuir model when is β equal to 1. If $a_R C_e^{\beta}$ is substantially more than 1, the Freundlich equation is formed. The equation becomes a linear isotherm equation when $a_R C_e^{\beta}$ is substantially less than 1, which occurs at low concentrations.

3.2 Adsorption Kinetics

Different kinetic models that characterize the adsorption process have been presented to establish what kind of mechanism is involved during the adsorbed substance's adsorption onto the adsorbent. Kinetic studies are critical for determining the steps that influence adsorption rate. Adsorbing a material in a solution by an adsorbent involves four main steps [84,85]:

I. A material in the gas or liquid phase diffuses toward the edge of a film layer that covers the adsorbent. Because there is some mobility (mixing) in the adsorption assembly, this step is frequently overlooked.

II. When the substance reaches the film layer, it passes through the sluggish area and begins to travel toward the adsorbent pores.

III. The adsorbent then proceeds to migrate through the pore spaces, eventually reaching the surface, where the adsorption event will occur.

IV. The attachment of the substance to be removed to the pore surface of the adsorbent happens in the final phase.

3.2.1 Pseudo 1st order kinetic model

The reaction rates of adsorption systems are calculated using a variety of kinetic models. The Pseudo first-order (P1) kinetic model created by Lagergren is the most widely used kinetic model. The pseudo-kinetic model can be obtained using the following formula [84]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (3.11)$$

After integration with the initial conditions, $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, the equation becomes:

$$q_t = q_e(1 - e^{-k_1 t}) \qquad (3.12)$$

where, q_e is the amount of material adsorbed per unit adsorbent at equilibrium (mg/g), q_t is the quantity of material absorbed per unit of adsorbent at any given time (mg/g), k_1 is the P1 adsorption rate constant of Lagergren (min^{-1}) and t is the contact time (min).

The theoretical q_e value is obtained from the point where the graph meets the y-axis, and the rate constant k_1 is calculated from the slope, after plotting the change of $\log(q_e - q_t)$ versus t.

3.2.2 Pseudo 2nd order kinetic model

Y.S. Ho created the pseudo-second-order (P2) kinetic model. The model's chemical adsorption rate is explained by the following equation [85]:

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \frac{1}{q_e} t \qquad (3.13)$$

where, q_e is the amount of substance adsorbed per unit adsorbent at equilibrium (mg/g), q_t is the amount of substance adsorbed per unit adsorbent at any one time (mg/g), k_2 is the P2 adsorption rate constant (g/mg.min), and t is the contact time (min).

The k_2 value is obtained from the point where the graph intersects the y-axis, and the theoretical qe value is calculated from the slope, after plotting the change of t/q_t against t on the graph [85].

In dual system adsorption experiments, the error of the adsorption isotherm models was calculated using the equation below.

$$Average\ Relative\ Error\ (\%) = \frac{100}{N} \sum_{i=1}^{N} \left| \frac{q_{e_{Experimental}} - q_{e_{calculated}}}{q_{e_{Experimental}}} \right| \qquad (3.14)$$

4
MATERIALS AND METHODOLOGY

4.1 Tools and Equipment Used

A summary of the various devices used in this research are represented in the Table 4.1 below. The descriptions of the devices and equipment can also be observed from Table 4.1 to give a better understanding on the purpose and usage of each device in the experiments.

Table 4.1 Experimental tools and equipment used

Name	Brand	Description
Glass Apparatus	Isolab	Includes flask, funnels and other apparatus used to carry out experiments.
Magnetic Stirring Heater	Ika-Werke	Used stir and heat chemical substances at the same time to make a homogenous mixture.
Furnace	Protherm	Used in the calcination of eggshells.
Oven	Binder	Used to heat up samples in the experiments
Shaking Incubator	Zhicheng	Designed to incubate and shake or agitate samples at the same time to ensure optimal mixing.
Ultraviolet-Visible (UV-Vis) spectrophotometer	Perkin Elmer	Used for absorption measurements by measuring the intensity of light that passes through a sample with respect to the intensity of light through a reference sample or blank

X-ray diffraction (XRD)	PANalytical	Used for the characterisation of the samples to obtain their crystal structure analysis.
BET (Brunauer, Emmett and Teller) Adsorption Analyzer	Micromeritics ASAP2020	Used to determine the specific surface areas, pore volumes and sizes of the samples.
ZetaSizer	Malwern	Measurement of Biosorbent isoelectric point
Thermogravimetry/Differential Thermal Analysis (TG/DTA)	Perkin-Elmer Pyris Diamond	Used to determine the thermal stability of the samples.
Fourier Transform Infrared Spectrometer (FTIR)	Perkin-Elmer Spectrun One	Used to reveal the chemical structure, composition and bond determination of the samples
Scanning Electron Microscope (SEM)	Zeiss EVO®LS 10	Used to obtain information about the EA surface's topography and composition.
X-ray photoelectron spectroscopy (XPS)	Thermo Scientific K-Alpha	Used to investigate the change in the chemical structure of the biosorbent surface before and after adsorption.

4.2 Chemicals Used

The experiments performed in this research were undertaken through the usage of the mentioned chemicals in Table 4.2. Analytical standards were employed for all reagents and chemicals used. Water that had been distilled was used in all of the trials.

Table 4.2 Experimental materials used

Chemical	Brand	Usage Stage
Methylene Blue (MB)	Merck	It was used in dye adsorption and selective adsorption experiments
Congo Red (CR)	Sigma-Aldrich	It was used in dye adsorption and selective adsorption experiments
Rhodamine B (R-B)	Sigma-Aldrich	It was used in the selective dye adsorption experiments
Methyl Orange (MO)	Merck	It was used in the selective dye adsorption experiments
Hydrochloric Acid (HCl)	Merck	It was used in the regeneration and desorption experiments
Nitric Acid (HNO_3)	Merck	It was used in the regeneration and desorption experiments
Sodium Hydroxide (NaOH)	Merck	It was used in the regeneration and desorption experiments
Ammonium Hydroxide (NH_4OH)	Merck	It was used in the regeneration and desorption experiments

4.3 Materials

4.3.1 Dyes

For adsorption investigations, two distinct dyes namely methylene blue and congo red was chosen based on the availability and common usage in various industries. First, a 100 ppm (mg/L) stock solution was made by dissolving 100mg of dye powder with distilled water filling up a 1000 mL flask. The dye solutions were then diluted from stock solutions to achieve the necessary concentrations (10, 20, 30, 40, and 50 mg/L).

4.3.2 Eggshells

Eggshells were collected from domestic household waste to be used in biosorbent preparation. To begin, the eggshells were brushed under running water to remove any dirt or dust. Then, the membranes in the eggshells were cleaned with tweezers. The eggshells were then ground to fine particles using a mortar and a pestle before being put to dry in an oven. Finally, the ground eggshells powder was then calcined for 3 hours at 600°C and the thermally treated eggshell powder was then sent for characterization. The experimental procedure is given in Figure 4.2. The XRD and FTIR analysis of the calcined eggshells were carried out.

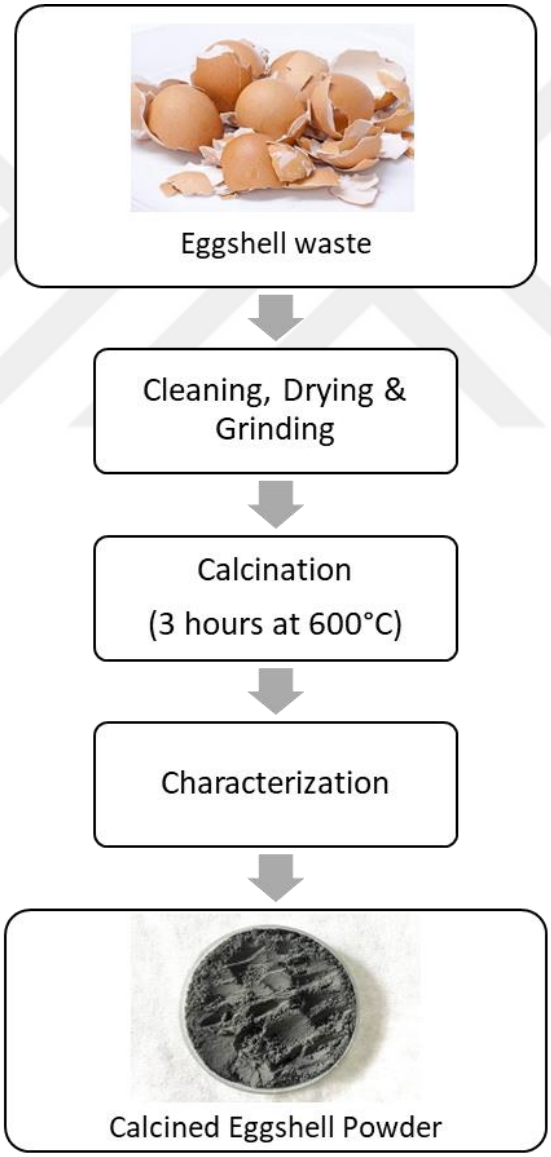


Figure 4.1 Treatment flow diagram for the waste eggshells.

After calcination, it is expected that some of the calcium carbonate ($CaCO_3$) in the structure of eggshell will be converted to CaO. The basic $Ca(OH)_2$ will be obtained according to the reaction given below with the obtained CaO and water (Eq. 4.1). The obtained $Ca(OH)_2$ will be used in the treatment of U.lactuca.

$$CaO + H_2O \rightarrow Ca(OH)_2 \qquad (4.1)$$

4.3.3 U.Lactuca Green Algae

Ulva, often known as sea lettuce, is another material that was utilized in the biosorbent preparation. U.Lactuca is a green algae that accumulates by hitting the coastline with currents and waves. During October 2020, U.Lactuca (green algae) was gathered from the Ağva coast, a resort destination in Istanbul's Şile district (Figure 4.3).

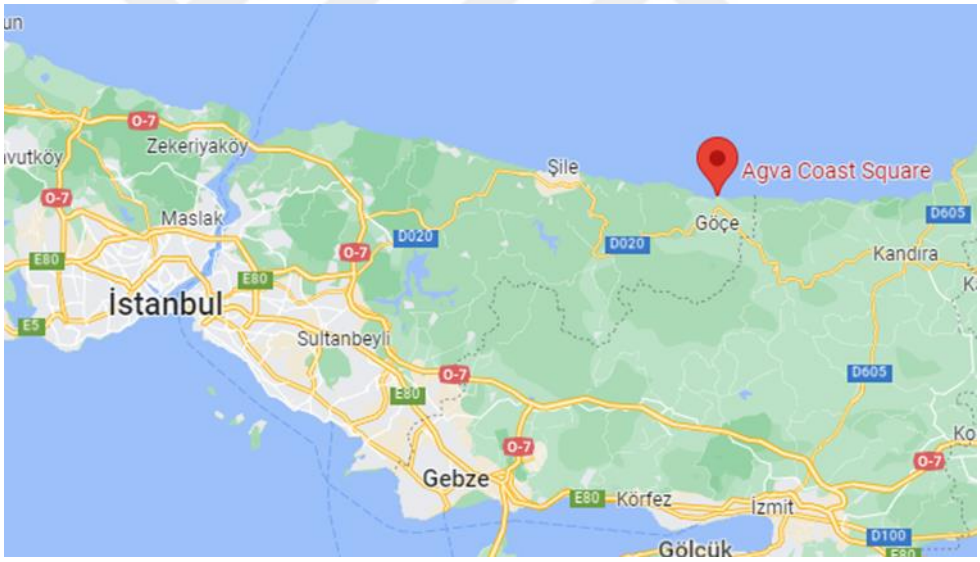


Figure 4.2 Location where the Ulva Lactuca (green algae) was gathered from.

Foreign materials, such as grass, rubbish, and sand were recovered from the algae and separated using tweezers, then washed and cleaned from the sand under running water (Figure 4.4). The cleaned algae were processed in the grinder to obtain a powder after drying at room temperature. The dried and ground algal powder was then sieved through 45-mesh sieve.

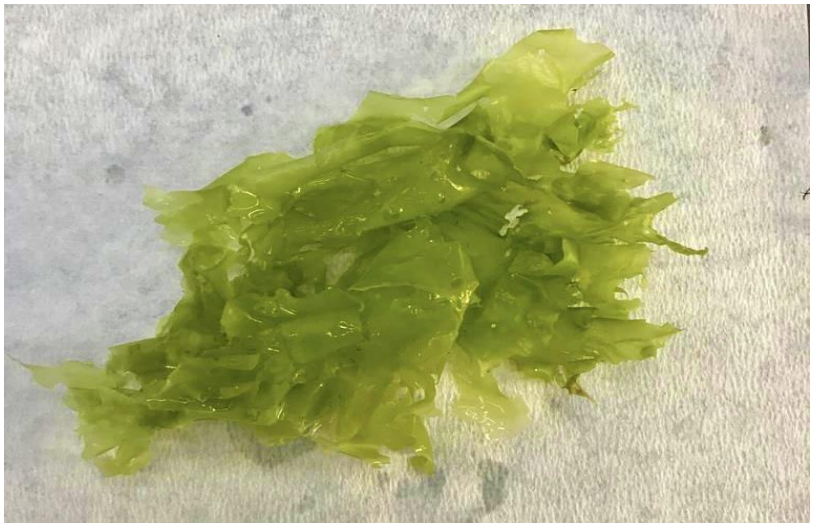


Figure 4.3 Ulva Lactuca (green algae) gathered from the Ağva coast.

4.4 Biosorbent Preparation

In the experimental studies, a blend from two different materials namely, calcinated eggshells and dried marine algae were used to remove the CR and MB dyes. To prepare the biosorbent, 8.6g of the calcined eggshell powder was mixed in 1L of distilled water for an hour. After that, a particular amount of algae powder was added to the mixture and stirred at room temperature for 4 hours. The resulting mixture was then filtered at the end of the period and the filtrate was then put in an oven to dry at 80°C for 12 hours. After the drying stage, the obtained biosorbent sample was then stored in a bottle and given the label of EA.

4.5 Selective Adsorption Experimentation

The selective dye adsorption of EA was studied for different binary mixtures of MB, CR, R-B and MO. In this experiment, 0.075 g of biosorbent was poured into 25 mL of dye solution obtained by mixing two different dyes with an initial concentration of 20 ppm in a 1: 1 ratio. The resulting solution was mixed on a shaker for 30 min. When the mixing process was finished, the obtained solutions were filtered and separated from the adsorbent. Dye concentrations in the obtained filtrates were determined by UV–Vis spectrophotometer. According to

the results of UV-vis analysis, the dyes with the best adsorbing capacity of the biosorbent were determined and the adsorption performance of the biosorbent in removing these dyes individually, and the parameters affecting the performance were investigated.

4.6 Batch Adsorption Experimentation

For batch adsorption investigations, MB and CR were chosen according to selective adsorption results and repeated three times for each experimentation. In the individual adsorption experiments, 100 ppm stock solution was prepared from both dyes. Then, the dye solutions were diluted from stock solutions to achieve the necessary concentrations (10, 20, 30, 40, and 50 mg/L).

4.7 Regeneration Studies

To analyze the regeneration capability of the prepared biosorbent, different solutions of Hydrochloric Acid (HCl), Nitric Acid (HNO_3), Sodium Hydroxide (NaOH) and Ammonium Hydroxide (NH_sOH) based on their performance in various literature studies were created for the desorption study. The solution with the best desorption efficiency was chosen, and the regeneration study on it was carried out.

4.8 Methodology

The batch adsorption experiments were performed at room temperature by different parameters such as contact time, adsorbent dosage, and initial concentration.

4.8.1 Effect of contact time

The adsorption experiment was done in a batch setting. At room temperature (25±2 °C), a set of 50 mL flasks containing 25 mL CR and MB dye solution,

respectively with a known beginning concentration of 20 ppm each were created. Each flask was filled with weighted amounts (0.075 g) of EA adsorbent then stirred continuously with a shaker and was mixed at 200 rpm for 1, 2, 3, 5, 15, 30, 90 and 120 minutes. After each batch, the solutions were then filtered out using a filter paper in a funnel and the resulting dye content in supernatants was determined by observing the absorbance variations at a wavelength of 495 and 665 nm for CR and MB, respectively with a spectrophotometer. Additionally, the adsorption experiment was also performed using the conventional eggshell adsorbent to compare the performance with the EA biosorbent. The results are presented in section 5.2.3.

4.8.2 Effect of Adsorbent Dosage

Different weights of the prepared EA biosorbent were varied to validate the effect of adsorbent amount of 0.05, 0.075, 0.1, and 0.125 g on 25 mL of MB dye solution with the concentration of 20 ppm. The mixtures were then stirred continuously with a shaker at room temperature and was mixed at 200 rpm for 30 minutes. After each batch, the solutions were then filtered out using a filter paper in a funnel and the resulting dye content in supernatants was determined by the ultraviolet-visible region (UV-Vis) spectrophotometer.

4.8.3 Effect of Initial Concentration

To evaluate the effect of concentration, change on adsorption, solutions of various concentrations were produced from the stock dye solutions of CR and MB. 0.075 grams of EA biosorbents were added to 25 mL of each dye solution. The respective dye solution initial concentrations were 10; 20; 30; 40; 50 and 100 ppm for each dye. The mixtures were then stirred continuously with a shaker at room temperature and was mixed at 200 rpm for 30 minutes. After each batch, the solutions were then filtered out using a filter paper in a funnel and by sampling samples with a micropipette and measuring using a UV-Vis spectrophotometer, the percentage dye removal was found.

Using Freundlich and Langmuir isotherms, the adsorption quantities of dyes were estimated. The isotherm constants are computed in equilibrium using straight equations and graph slopes; the quantity of dyes retained by 0.075 g of EA biosorbent is plotted against the concentration of dyes remaining in the solution phase, with the findings reported in Section 5.2.2.

4.8.4 Regeneration Study

To analyze the performance of the regeneration of the prepared EA biosorbent, four different compounds (HCl, HNO_3, NaOH and NH_4OH) were tested on 20 ppm MB dye solution and the solution with the highest desorption ability was taken for further examination. With 5 repeated adsorption/desorption cycles, the regeneration study of the dye type was done by mixing 25mL of 20 ppm MB solution with 0.075g of EA biosorbent mixed at 200 rpm for 30 minutes with a shaker at room temperature and then filtered out using a filter paper in a funnel then dried at 80°C for 4 hours to recover the remaining biosorbent to be used in the next cycle. After each cycle the adsorbed solution was then further analyzed by sampling samples with a micropipette and measuring using a UV-Vis spectrophotometer to show the corresponding adsorption and desorption efficiencies which will be reported in Section 5.4.1 and Section 5.4.2.

5
RESULTS AND DISCUSSION

5.1 Characterization Results

This section represents the results obtained after the characterizations of the prepared biosorbent before and after treatment for the analysis of the morphologies and composition of the materials.

5.1.1 The XRD Analysis

The XRD patterns of the calcined eggshell at 600°C and the obtained EA are shown in comparison in Figure 5.1. The major diffraction peak at 29.59° and the other peaks at 39.62°, 43.36°, 47.73°, and 57.61° represent $CaCO_3$ in the XRD pattern of eggshell [86]. The peaks appeared at 2θ=31.61°, 32.48°, 36.16°, 61.64°, and 64.9° indicate the presence of calcium oxide (CaO) [87,88]. It can be seen that the XRD pattern of EA is almost the same as eggshell except that the intensity of the diffraction peaks is smaller than eggshell.

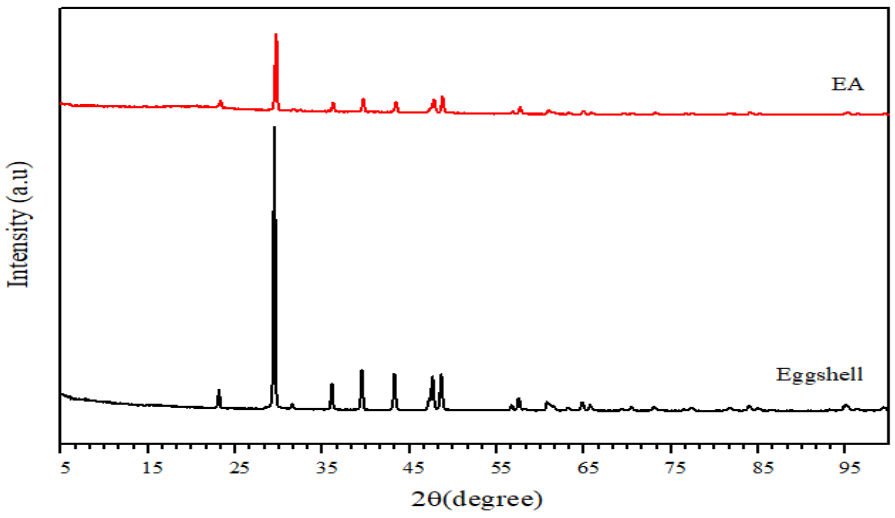


Figure 5.1 XRD pattern of the thermally treated eggshell and EA

5.1.2 The FTIR Analysis

The FTIR spectra of the calcined eggshell at 600°C and the EA produced are shown in comparison in Figure 5.2. The peak at 3420 cm^{-1} corresponded to hydroxyl group (–OH) stretching vibrations of alcohols, phenols, and carboxylic acids. The presence of carbonate ion in the eggshell matrix is shown by the peaks at 2515, 1799 and 1436 cm^{-1} [89]. Peaks at 876 cm^{-1} and 713 cm^{-1} correspond to characteristic of the C–O stretching and bending modes of $CaCO_3$ and Ca–O bonds [90,91]. Unlike calcined eggshell, the peak development between 1770 and 1575 cm^{-1} in the FTIR spectrum of the synthesized EA biosorbent is attributable to the carboxylic and amide groups in algae. Another distinction is that in the EA, the peak in the spectrum of the eggshell that occurred between 1180 cm^{-1} and 915 cm^{-1} appeared as three separate peaks. The carboxyl group in algae is assumed to be responsible for the peak at 1047 cm^{-1} [92].

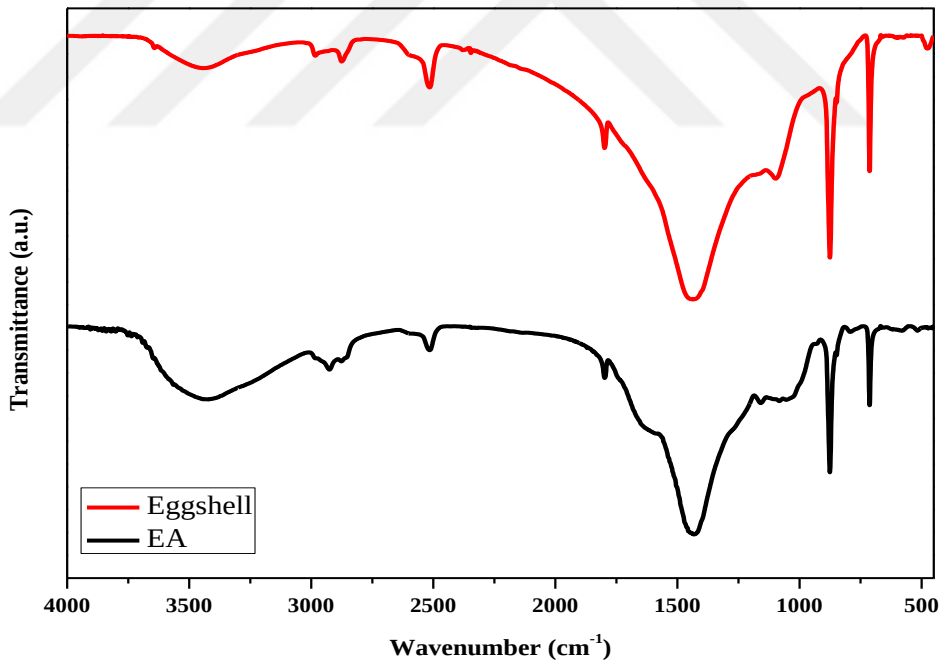


Figure 5.2 FTIR spectrum of the thermally treated eggshell and EA

5.1.3 The BET Analysis

Multipoint BET analysis is used to study the biosorbent's textural features. The biosorbent's specific surface area, total pore volume, and average pore width were found to be 0.02 m^2/g, 0.0001 cm^3/g, and 1.17 nm, respectively.

5.1.4 Zeta Potential Analysis

The technique of detecting the surface charge of the adsorbent in a solution is known as zeta potential analysis. The zeta potential is a useful tool for determining the condition of the adsorbent surface, as well as forecasting the adsorbent's long-term stability and interactions with other substrates. Fig.5.3 demonstrates the zeta potential distribution graph of EA. The zeta potential value of EA was found as -27.7 mV. The presence of negative zeta potential of EA suggesting that there were attractive electrostatic forces between EA and cationic dye molecules, which led to the remarkable adsorption process.

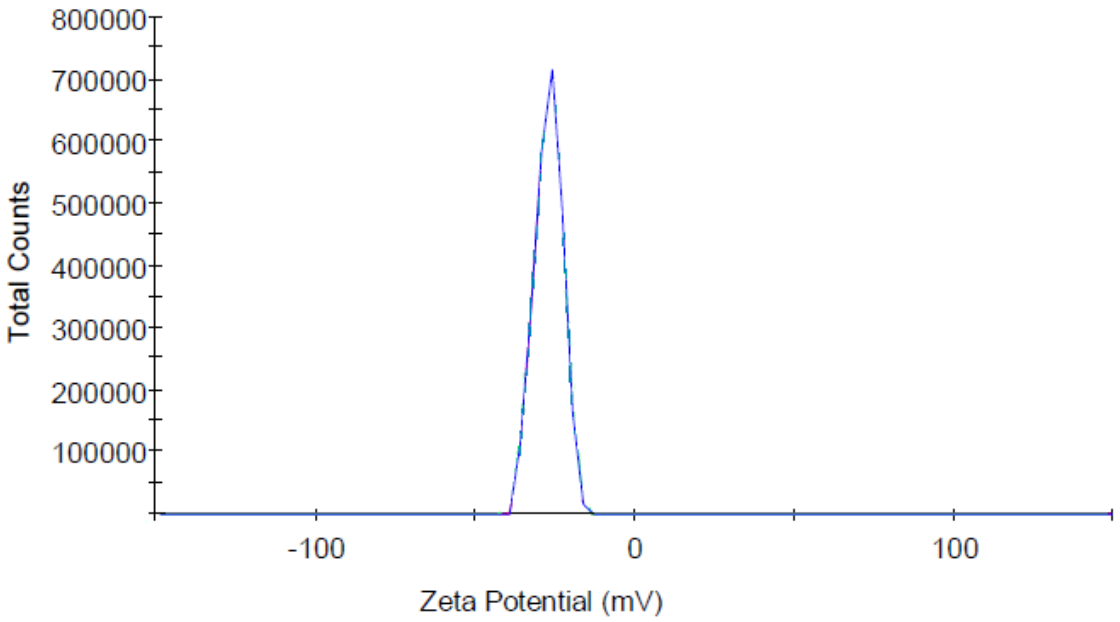


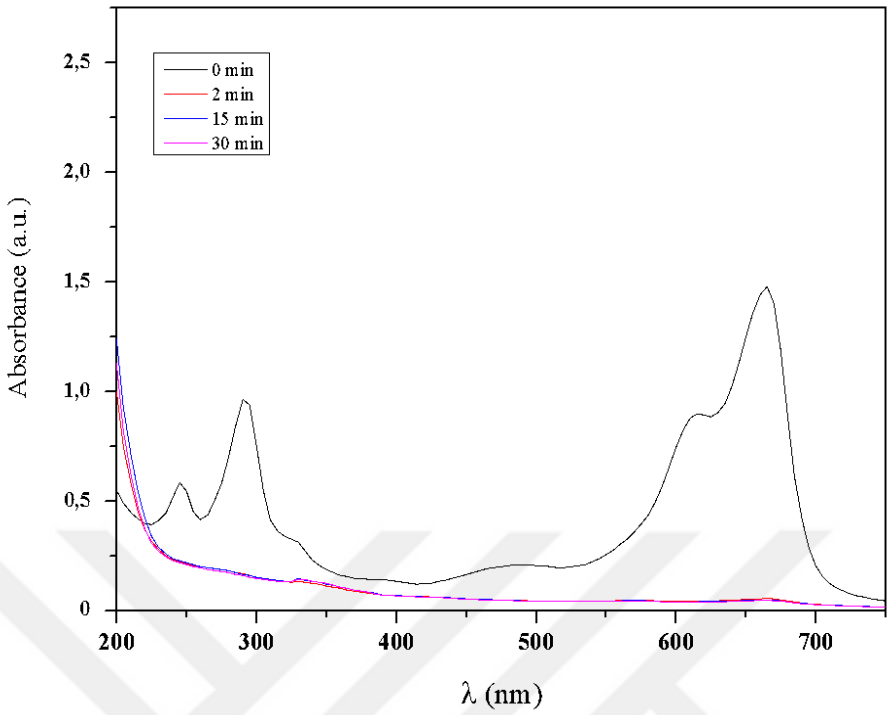
Figure 5.3 The zeta potential distribution graph of EA

5.2 Selective Dye Adsorption Results

The binary mixtures of MB, CR, R-B, and MO dyes were used in the selective dye adsorption experiments. Firstly, 20 ppm of CR and 20 ppm of MB solutions were mixed to obtain the binary mixture (Fig. 5.4a). Then, 0.075 g of biosorbent was added to the binary mixture and stirred for 2, 15, and 30 min. After each batch, the solutions were then filtered out using a filter paper in a funnel and the resulting dye content in supernatants was determined by UV-Vis spectrophotometer. The UV-Vis analysis results were given in (Fig. 5.4b). In the first 2 minutes, it is seen that MB and CR remove from the binary mixture very quickly and the percentages of removal of MB and CR were found to be 98% and 96%, respectively. After 30 minutes, the percentages of removal of MB and CR were found to be 99% and 98%, respectively. This is supported with the corresponding photograph (Fig. 5.4a) that the binary solution is almost colorless after adsorption.



a)



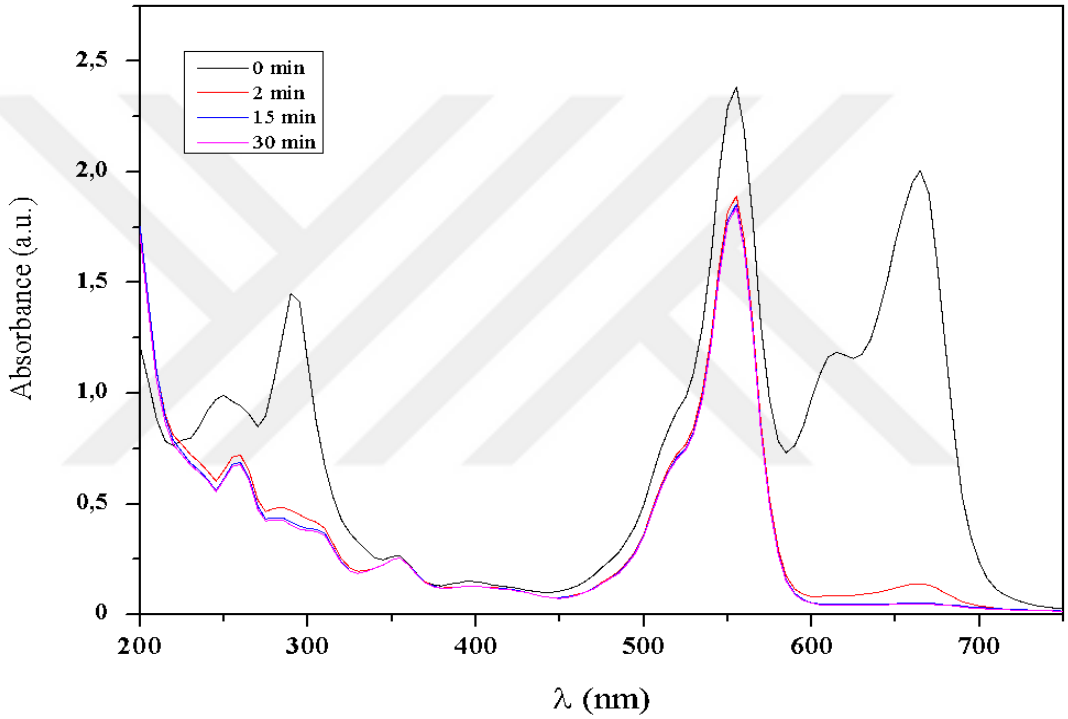
b)

Figure 5.4 a) The color change of the CR-MB solutions and b) UV-Vis spectra of CR and MB binary solution with increasing time.

In the continuation of the selective dye adsorption experiments, 20 ppm of MB and 20 ppm of R-B solutions were mixed to obtain the binary mixture (Fig. 5.5a). Then, 0.075 g of biosorbent was added to the binary mixture and stirred for 2, 15, and 30 min. After each batch, the solutions were then filtered out using a filter paper in a funnel and the resulting dye content in supernatants was determined by UV-Vis spectrophotometer. The UV-Vis analysis results were given in (Fig. 5.5b). In the first 2 minutes, it is seen that the removal of MB from the binary mixture very quickly and the percentages of removal of MB was found to be 94%. After 30 minutes, the percentages of removal of MB and R-B from the binary dye mixture were found to be 99% and 23%, respectively attributed by hindrance from higher particle size of R-B. This is supported with the corresponding photograph (Fig. 5.5a) that the binary solution is almost pinky after adsorption.



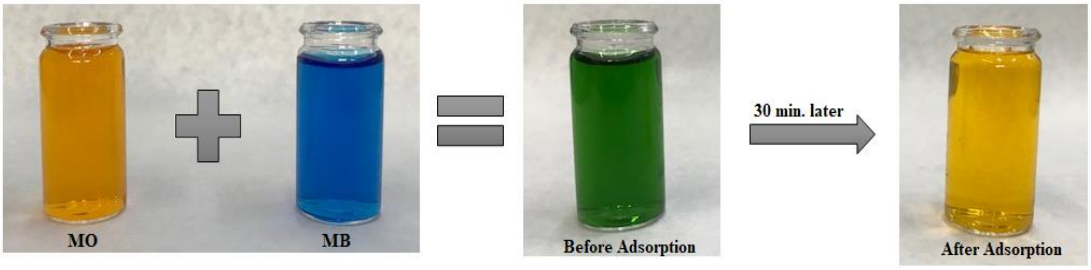
a)



b)

Figure 5.5 a) The color change of the MB and R-B solutions and b) UV-Vis spectra of MB and R-B binary solution with increasing time.

To continue the selective dye adsorption experiments, 20 ppm of MO and 20 ppm of MB solutions were mixed to obtain the binary mixture (Fig. 5.6a). Then, 0.075 g of biosorbent was added to the binary mixture and stirred for 2, 15, and 30 min. After each batch, the solutions were then filtered out using a filter paper in a funnel and the resulting dye content in supernatants was determined by UV-Vis spectrophotometer. The UV-Vis analysis results were given in (Fig. 5.5b). In the first 2 minutes, it is seen that the removal of MB from the binary mixture very quickly and the percentages of removal of MB was found to be 96%. After 30 minutes, the percentages of removal of MO and MB from the binary dye mixture were found to be 13% and 98%, respectively. This is supported with the corresponding photograph (Fig. 5.6a) that the binary solution is almost yellow after adsorption.



a)

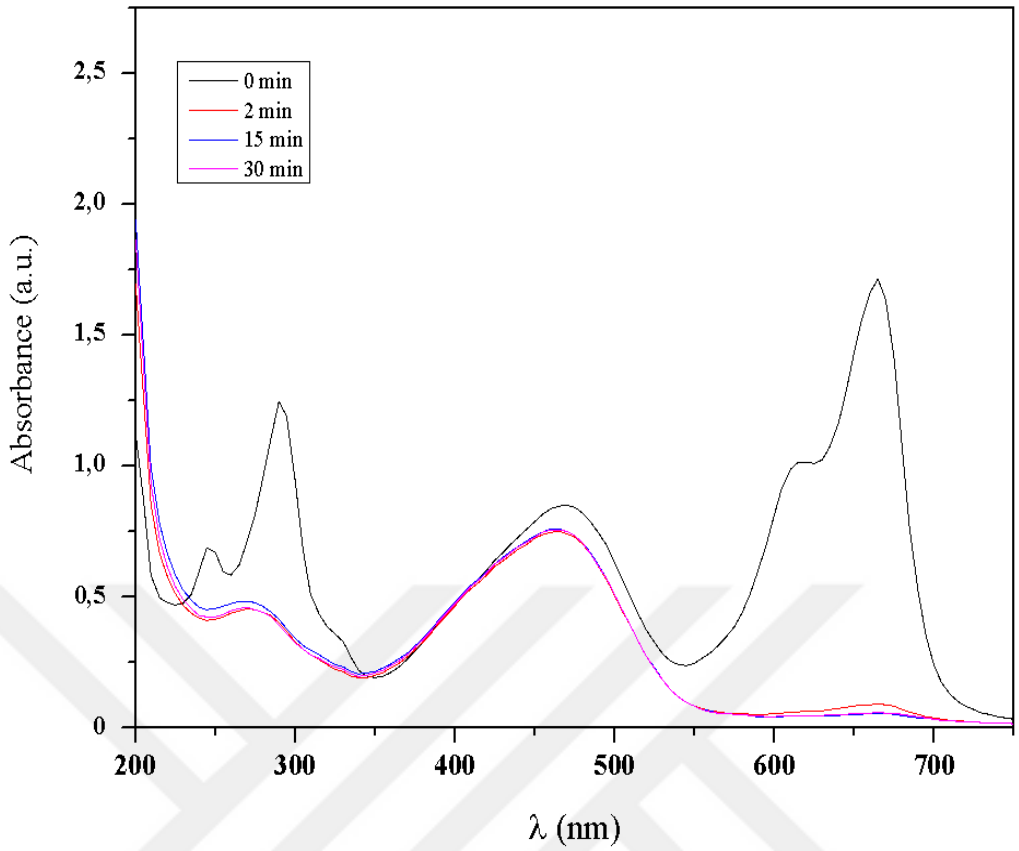


Figure 5.6 a) The color change of the MO and MB solutions and b) UV-Vis spectra of MO and MB binary solution with increasing time

According to the selective dye adsorption results, EA showed the best removal capacity in MB and CR dyes. Therefore, the individual dye adsorption analyses were carried out for these dyes.

5.3 Individual Dye Adsorption

The effect of various parameters on the individual MB and CR adsorption was investigated in this section.

5.3.1 Effect of Time

The graph of the influence of time on the individual adsorption of cationic MB and anionic CR from an aqueous solution by EA is shown in Figure 5.7. According to the graphs, it is seen that the capacity of EA to remove MB is more than CR. The increase in the amount adsorbed as a function of time as the remaining MB concentration decreased, signaled that the adsorption of the cationic dye approached to steady, and the adsorption equilibrium was reached. In comparison to the CR, which reached the equilibrium after 90 minutes, the MB showed a faster approach to the equilibrium after 15 minutes. In addition, the dye removal capacity reached 94% in the first 5 minutes of MB adsorption, which shows that MB adsorption by EA is very fast. The removal capacity of CR (83%) on the EA was clearly lower than that of MB (98%).

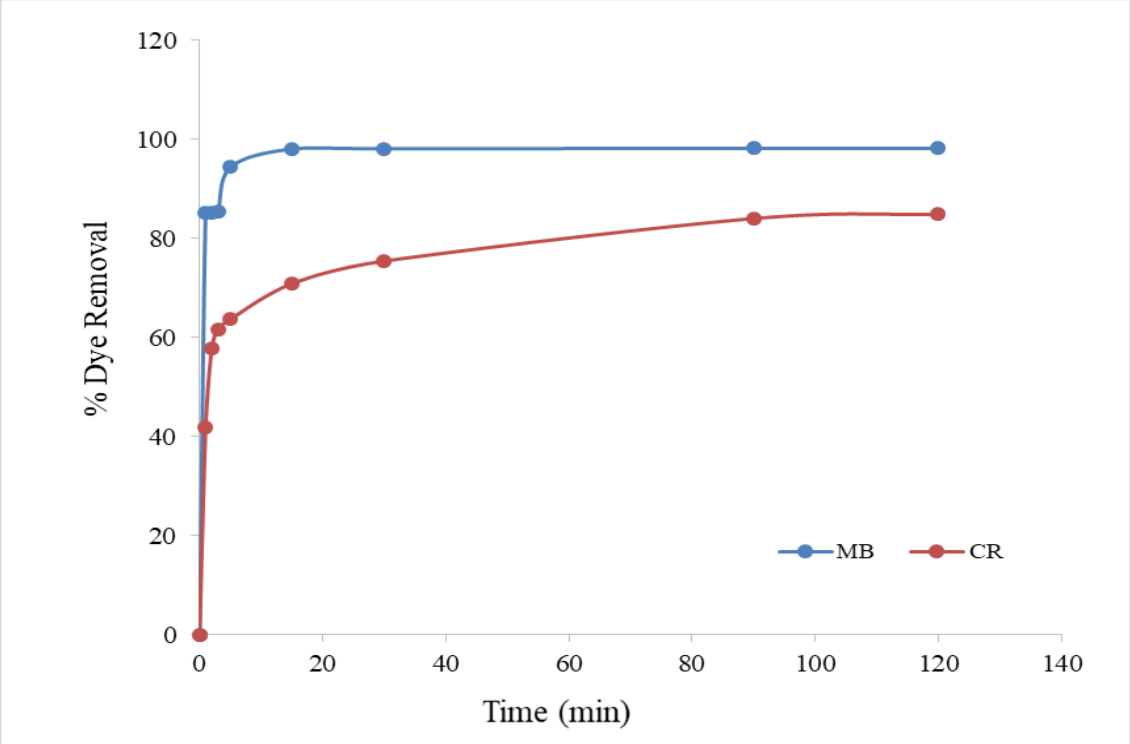


Figure 5.7 Plots of dye removal versus time onto the EA (Conditions: Amount of EA: 0.075gr, initial dye concentration: 20 ppm)

In addition, the removal capacity of CR onto the calcined eggshell was investigated in this thesis. The variation of CR removal capacity of eggshell over time is given in the Figure 5.8. The calcined eggshell was found to be able to adsorb 74% of dye from the aqueous solution of 20 mg/L at the 90th minute. Accordingly, it was observed that the CR removal capacity of EA was higher than that of the calcined eggshell.

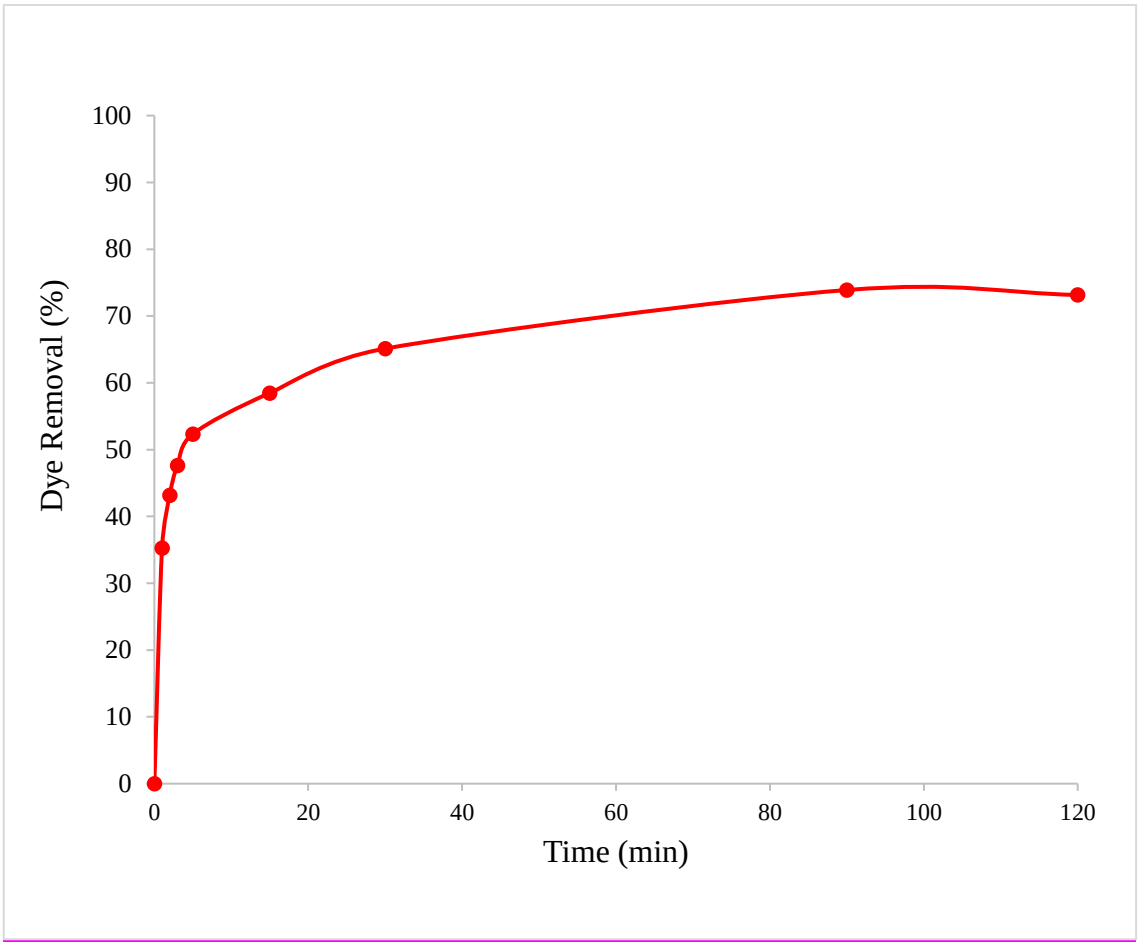


Figure 5.8 Plots of CR removal versus time onto the eggshell (Conditions: Amount of EA: 0.075gr, initial dye concentration: 20 ppm)

5.3.2 Effect of Initial Concentration

The graph of the influence of initial concentration on the individual adsorption of cationic MB and anionic CR from an aqueous solution by EA is shown in Figure 5.9. While similar adsorption trends were observed for both dyes at initial dye concentrations between 10 ppm and 50 ppm, when the initial concentration was 100 ppm, MB removal capacity decreased, and CR removal capacity remained constant. The result could be attributed to the amount of adsorption sites that have been determined by a given adsorbent dosage. This means that as the initial dye concentration rises, the adsorption rate rises as well, owing to the increased mass transfer from the concentration gradient, but the concentration effect has the opposite effect on the adsorption frequency, which indicates that the adsorption rate remains constant due to the limited adsorption sites available for adsorbate uptake.

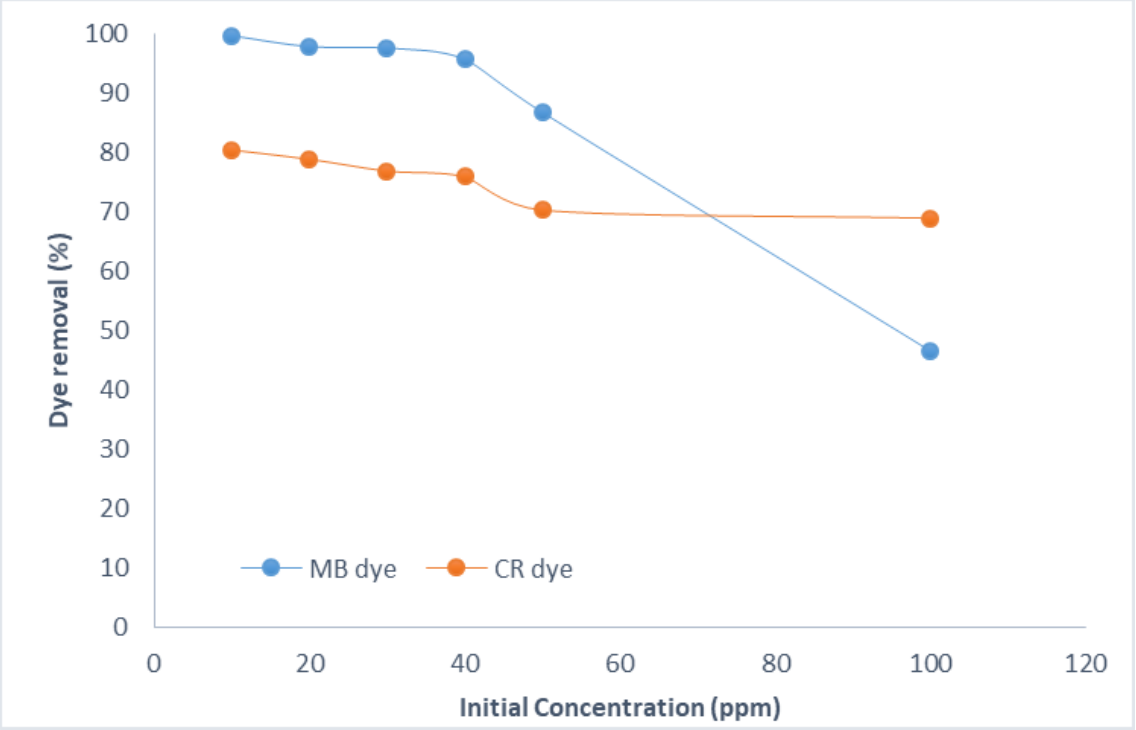


Figure 5.9 Effect of Initial Concentration on removal of MB and CR by EA (Conditions: Amount of EA: 0.075gr, Time: 30 min)

5.3.3 Effect of Adsorbent Dosage

The graph of the influence of adsorbent amount on the individual adsorption of cationic MB and anionic CR from an aqueous solution by EA is shown in Figure 5.10. When the amount of adsorbent increased from 0.05 to 0.075 gr, the adsorption efficiency increased for both dyes. However, as the adsorbent dose was further increased, the adsorbability reduced, meaning that the amount of dye adsorbed per unit mass of EA (i.e., adsorption capacity) dropped for both dyes.

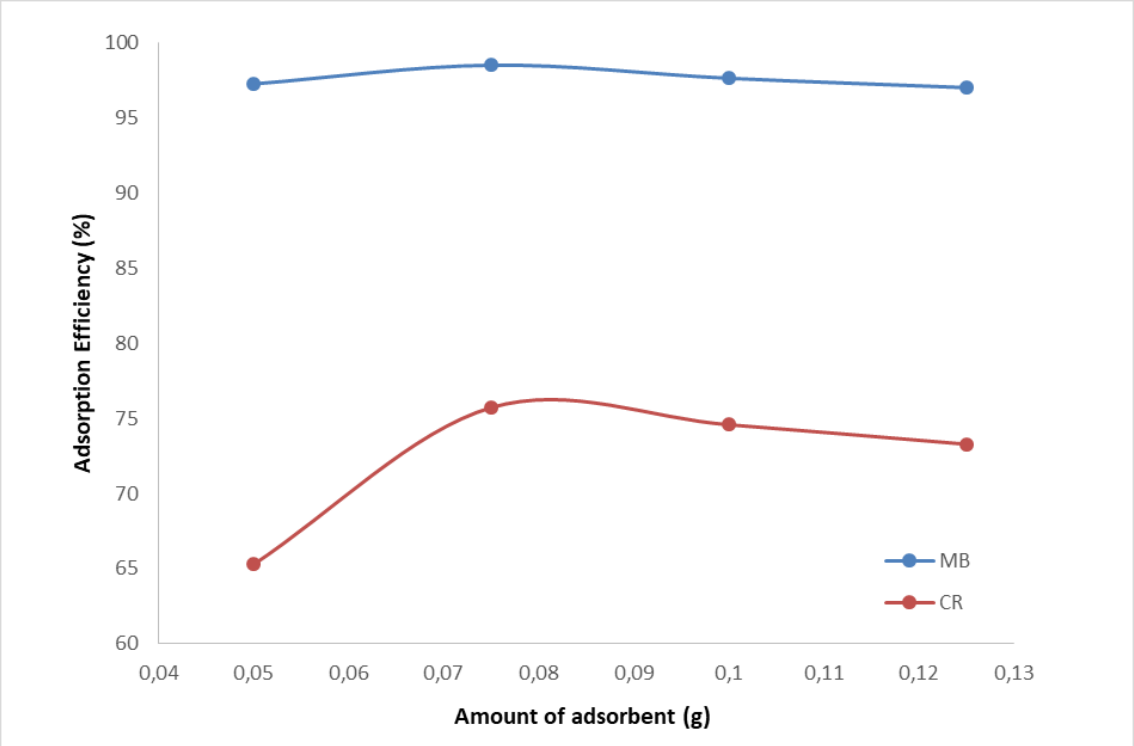


Figure 5.10 Effect of adsorbent quantity of EA on the removal of MB and CR (Conditions: Time:30 min, initial dye concentration: 20 ppm)

5.3.4 Effect of Pretreatment Process

When the effects of various parameters on dye adsorption were examined, it was observed that EA was more effective in MB removal than CR removal. For this reason, only the studies on MB are given in the continuation of the experimental studies.

In order to find the pretreatment effect on dye adsorption, the time-dependent MB adsorption of EA, untreated U.Lactuca, and the calcined eggshell at 600 °C was carried out (Figure 5.11). As seen from the results, untreated U. Lactuca exhibited the lowest MB adsorption capacity of 67%, while the calcined eggshell and EA got a removal capacity of 83% and 98%, respectively. Within 5 minutes, the EA was able to remove 94% of the MB. It was found that when U. Lactuca was treated with eggshell, MB adsorption capacity of EA increased due to increased electronegativity of the adsorbent [93]. Consequently, calcined eggshells can be used as an alternative base material to $Ca(OH)_2$.

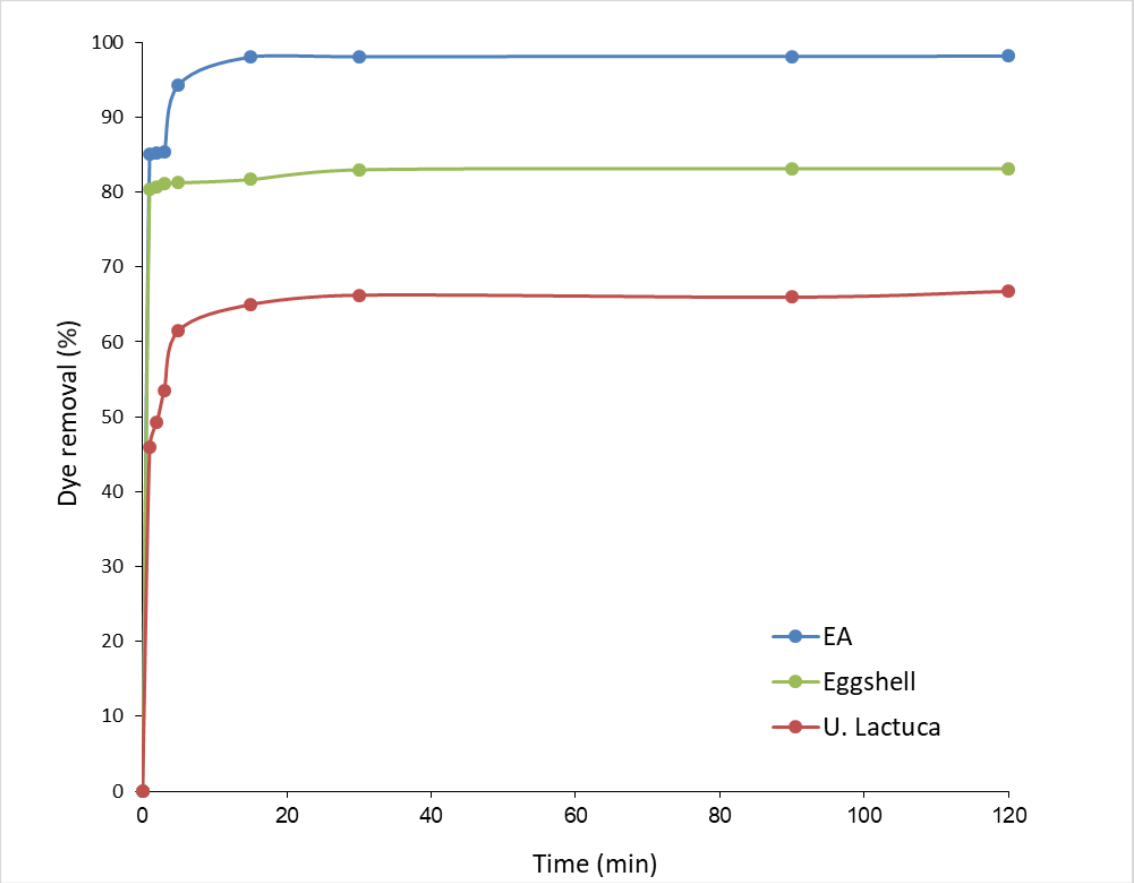


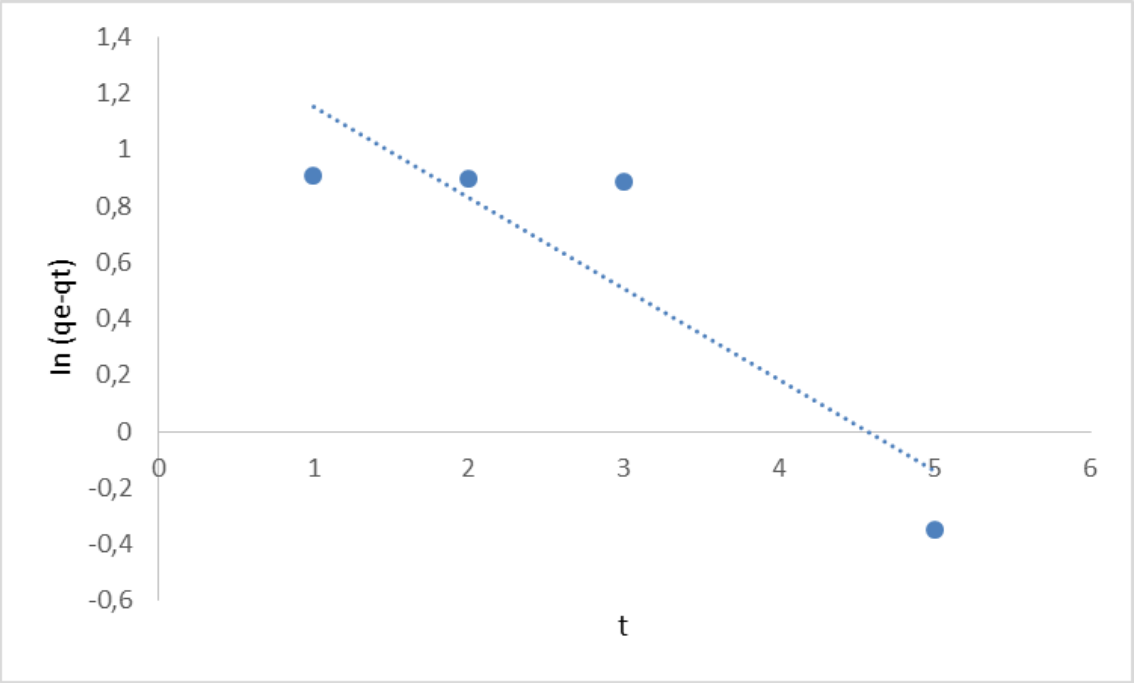
Figure 5.11 Effect of pretreatment process on the removal of MB

5.3.5 Adsorption Kinetics

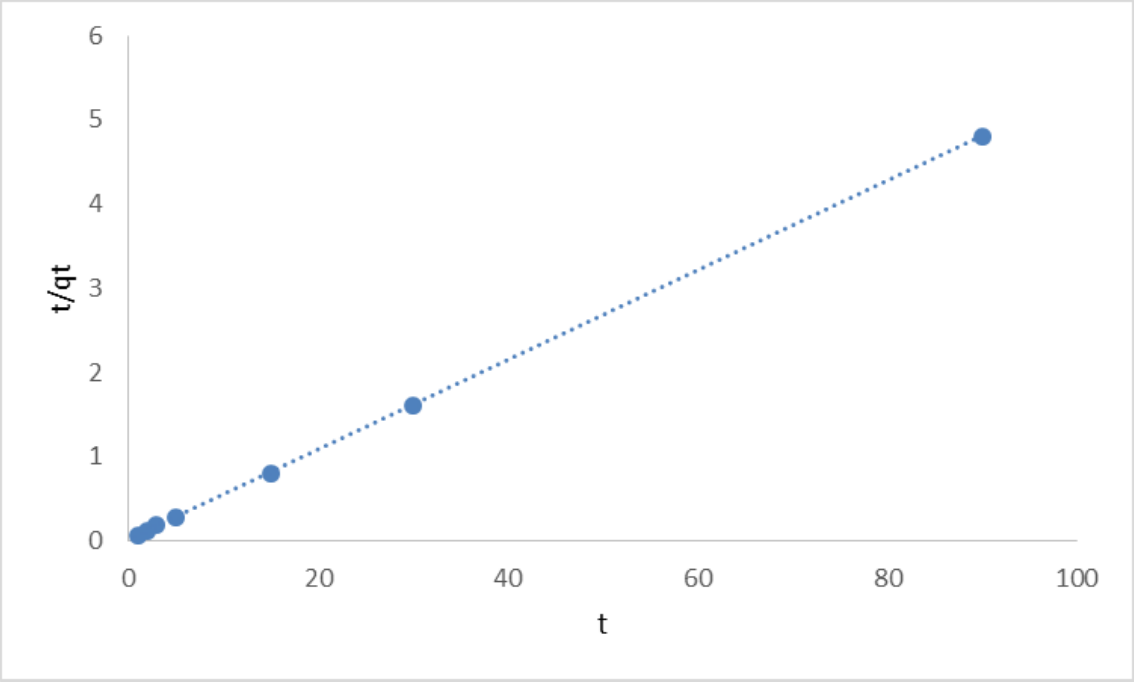
P1 and P2 kinetic models were used to investigate the adsorption mechanism of MB dye on EA. The order of the adsorption process was determined by fitting the experimental data into the P1 and P2 equations 3.12 and 3.13, respectively, in order to understand the adsorption kinetics. A UV-Vis spectroscopy was used to calculate the equilibrium adsorption capacity (q_t) towards MB dye at different time intervals (t) using a 20-ppm starting aqueous solution of MB dye with 75 mg EA. The experimental data were represented after linearization in Figure 5.12a and 5.12b, with K_1, K_2, and q_e calculated from the intercept and slope, respectively. The obtained values are displayed in Table 5.1. The equilibrium adsorption capacity q_e is reached in 15 min. and remains constant when the time interval is increased. The first-order correlation coefficient showed a lower value than the second-order which obtained a value of 1, as seen in Table 5.1. Moreover, the q_e value obtained from the experimental result and the q_e value from P2 were close to each other. As a result, the adsorption mechanism can be concluded to follow a P2 kinetic model, implying physiochemisorption [94].

Table 5.1 P1 and P2 kinetics parameters for MB adsorption over EA biosorbent

$q_{e,\,exp}$	Pseudo First Order			Pseudo Second Order		
	$q_{e,\,cal}$	k_1	R^2	$q_{e,\,cal}$	k_2	R^2
18.69	4.3671	0.323	0.7831	18.7617	0.23097	1



a)



b)

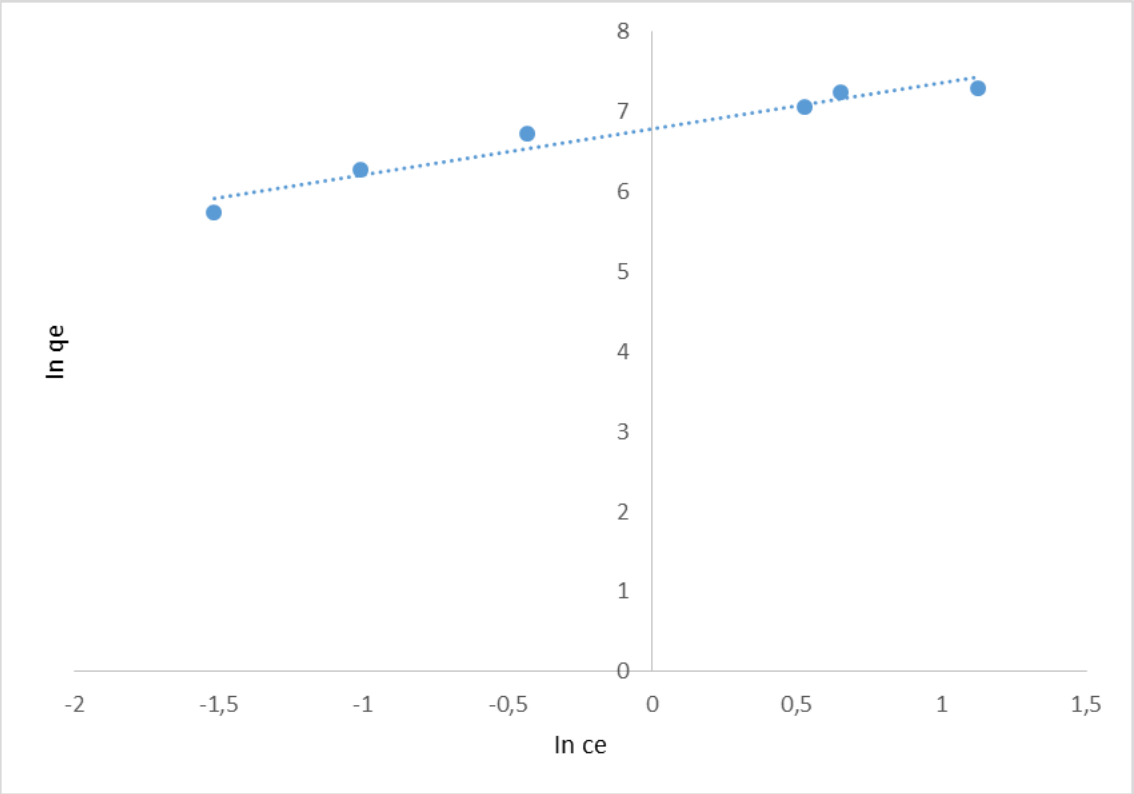
Figure 5.12 a) P1 and b) P2 plots

5.3.6 Adsorption Isotherms

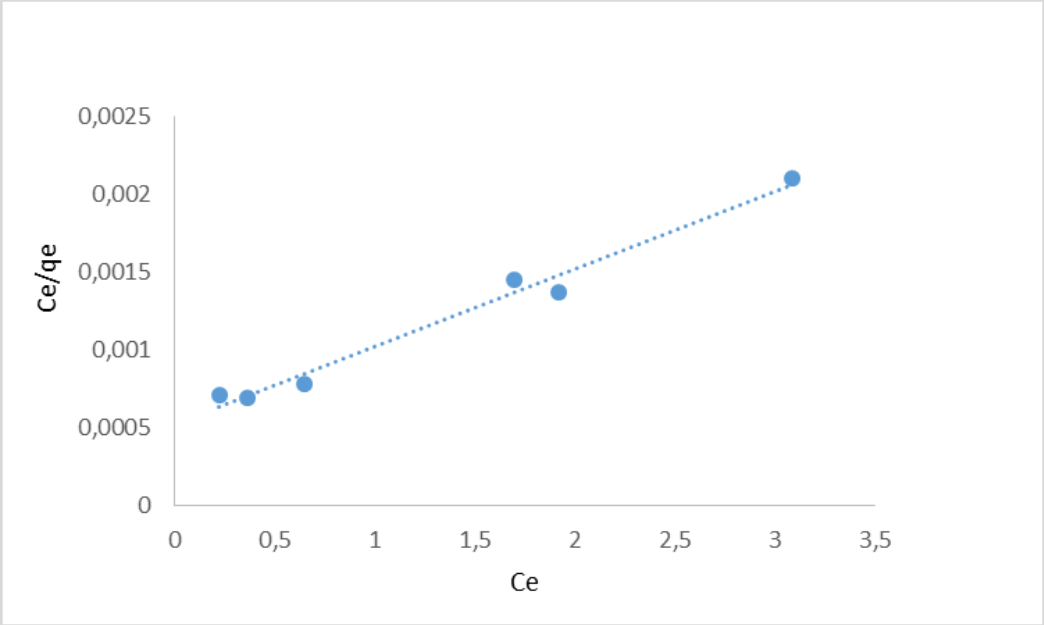
Two typical isotherm models were used to investigate the behavior of MB adsorption on the EA surface (Langmuir and Freundlich isotherm models). Figure 5.13 shows the results of the Langmuir and Freundlich isotherms fitted using the adsorption capacity data from the regression of Eq. (3.13). The Langmuir model was shown to have a somewhat better match than the Freundlich model, as evidenced by correlation coefficients (R_L^2) of 0.980 versus 0.947. The Langmuir isotherm model assumed that adsorption took place on a homogeneous surface in the form of a monomolecular layer, whereas the Freundlich isotherm model assumes that adsorption takes place on heterogeneous adsorption surfaces with multilayer adsorption. The experimental constants of the isotherm models are K_L, K_F, and n. The linear plots can be used to calculate these constants, as demonstrated in (Figure 5.13) and the findings are summarized in Table 5.2. The adsorption intensity or surface heterogeneity is measured by the slope 1/n, which ranges from 0 to 1. The adsorption is advantageous when 0>n>1. Adsorption is unfavorable when 1/n > 1. The fact that n=1 indicates that the adsorption is irreversible. In this experiment, the 1/n ratio is less than 1, indicating that MB adsorption on EA biosorbent is favorable. In addition, R_L was calculated as 0.038 demonstrates the desirable adsorption [95,96].

Table 5.2 Langmuir and Freundlich isotherms parameters for MB adsorption over EA biosorbent

Freundlich model			Langmuir model		
1/n	K_F	R^2	q_m	K_L	R^2
0.577	882.62	0.947	2000	1.00	0.980



a)



b)

Figure 5.13 a) Freundlich and b) Langmuir adsorption isotherms of MB from aqueous solutions onto EA

The maximum adsorption capacity (q_m) of MB was calculated 2000 $mg.g^{-1}$ by Langmuir Model. In comparison to the other q_m values for algae-based materials presented in the literature are examined, it is seen that this value is very high (Table 5.3). These findings suggest that the EA is a promising adsorbent for the adsorption of MB.

Table 5.3 Comparison of the maximum adsorption capacities of algae-based materials for various dyes

Dye	Sorbent	q_m (mg/g)	Reference
MB	Brown macroalga	729.93	[97]
MB	Biochar derived from seaweed	199.15	[98]
Reactive Red 120	Eucheuma spinosum biochar	331.97	[99]
MB	Chemical and pyrolysis activated U. Lactuca	625	[100]
Safranine O	U. Lactuca–based active carbon	526	[101]
Crystal Violet	Citric acid-functionalized brown algae	279.14	[102]
CR	Polypyrrole-microalgae composite	772.70	[103]
MB	Cu-BTC@Algal	162	[104]

5.4 Desorption Process

A green chemistry-compliant regenerable adsorbent can be both cost-effective and environmentally friendly. It is of great practical importance that active sites can be reconstituted using a simple desorption method for the removal of organic dyes. To achieve this, various eluents were used for the desorption of MB from the biosorbent within the scope of the thesis. This procedure was repeated several times to determine the regenerative capacity of the adsorbent based on the findings.

5.4.1 Eluents Choice

In order to avoid the accumulation of extra pollutant-loaded materials in the environment after the treatment process, the material used for pollution removal must also have good regeneration and reusability. As a result, as shown in Figure 5.14, the regeneration and reuse of EA for MB adsorption were assessed using four different desorption eluents of acidic and basic nature (NaOH, HNO_3, NH_4OH, and HCl). The highest MB desorption from dye-loaded EA was achieved using HCl solution, indicating the best desorbing agent, followed by HNO_3, NaOH, and NH_4OH. Accordingly, the fact that acidic eluents are more successful in MB desorption than basic eluents. The reason for this is that the biosorbent receives more H^+ ions from the acidic solution, resulting in more spontaneous cationic exchange and thus the cationic dye molecules pass from the adsorbent surface to the solution.

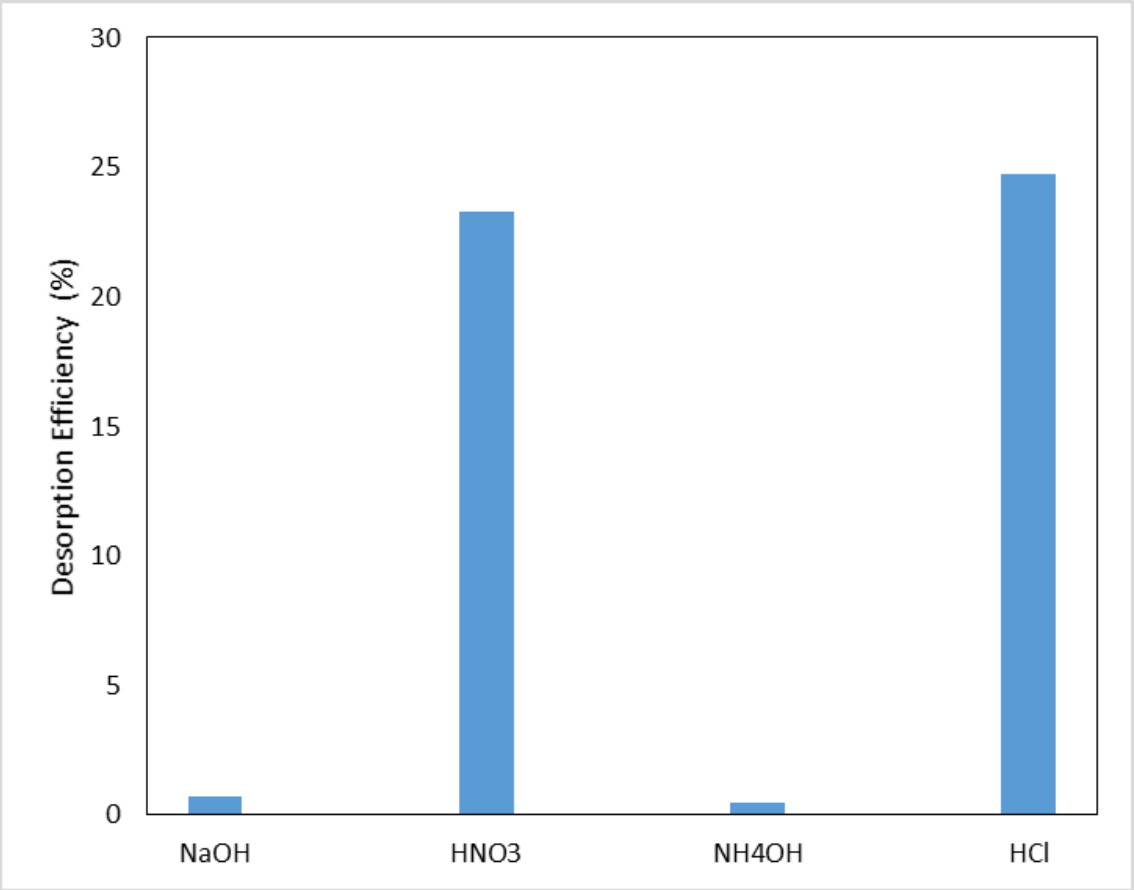


Figure 5.14 Desorption efficiencies for different eluents

5.4.2 Regeneration Capacity of Biosorbent

The regeneration studies employing HCl as desorbing eluent were done for five adsorption/desorption cycles. After each cycle, the concentration of the filtrate was measured by the UV-Vis spectrometer. Figure 5.15 depicts the adsorption and desorption efficiencies as a bar diagram for each cycle. Within the first four cycles, dye adsorption efficiency decreased from 97% in the first cycle to 86% in the fourth cycle, while dye desorption efficiency decreased from 60% to 50%. After the fourth cycle, a noticeable decrease in the adsorption and desorption efficiency was observed. The saturation of active sites on the surface of the biosorbent could cause a decrease in the adsorption/desorption efficiency.

The adsorption efficiency of various dyes by utilizing adsorbents has also been investigated in previous studies [97,98]. It is seen that the adsorption efficiency of many adsorbents dropped below 60% during the third cycle. By comparison our biosorbent demonstrates an adsorption efficiency of 86% after four cycles.

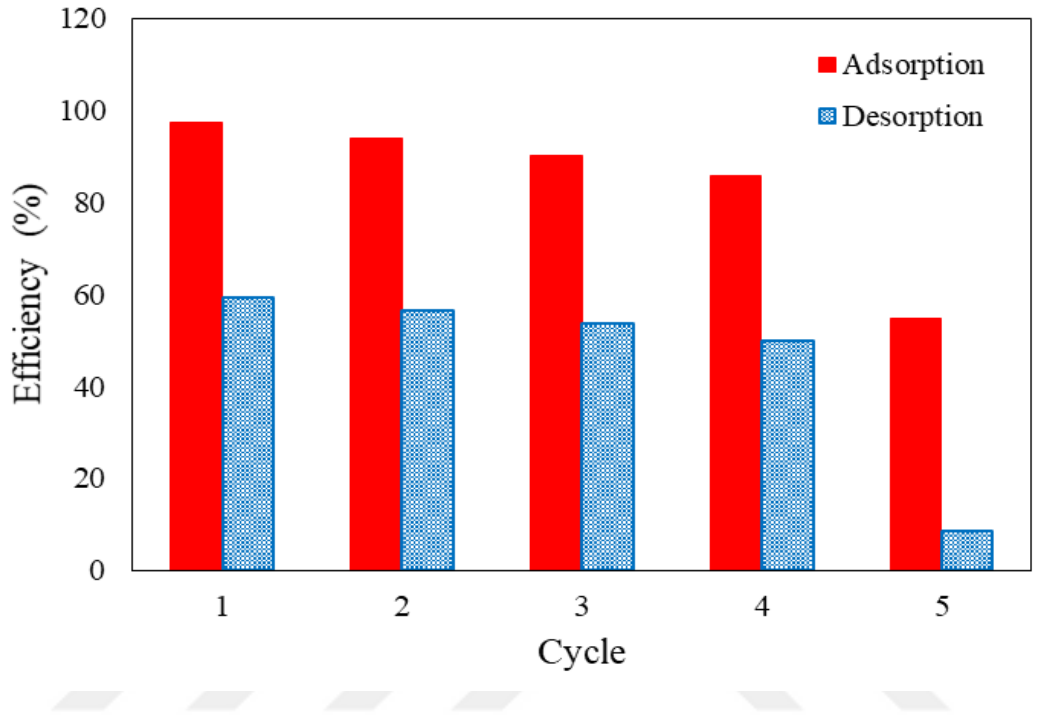


Figure 5.15 Reusability of EA for subsequent adsorption/desorption cycles of MB (Initial concentration: 20 ppm, adsorbent dosage=0.75 g, volume=25mL, contact time= 30 min.)

5.5 Adsorption Mechanism

To examine the MB and CR adsorption mechanisms, FTIR, TG, SEM, and XPS analyses were carried out, with the produced biosorbent showing the best adsorption capability.

5.5.1 FTIR Spectrum

Figure 5.16 shows the FTIR spectrum of EA following MB and CR adsorption. The peak of the -OH band still remained in the same wavelength after CR adsorption, while it shifted to 3432 cm^{-1} after MB adsorption, indicating the presence of H^- bonding interactions [99]. The peaks at 2515 cm^{-1} and 1799 cm^{-1} related to carbonate ion decreased after CR adsorption while they vanished after MB

adsorption. Additionally, the intensity of the carbonate ion peak at 1436 cm^{-1} reduced after CR adsorption, while it reduced sharply after MB adsorption. The same trend was observed at peaks at 876 cm^{-1} and 713 cm^{-1} which was ascribed to the C–O modes of the $CaCO_3$ and Ca-O, respectively. Also, new peaks were seen in the spectrums of EA after CR and MB adsorption. The new peaks at 1542 cm^{-1}, 1376 cm^{-1}, and 1261 cm^{-1} attributed to the stretching vibration of N-H bending, CH_2 group, and the aromatic and C-N amine group, respectively, in the spectrum of EA-MB, which confirmed the existence of MB in EA [100]. The new peaks at 1638 cm^{-1} and 1229 cm^{-1} are due to –N=N– stretching vibration near to aromatic ring and =C–N= stretching vibration adjacent to aromatic ring, respectively, in the spectrum of EA-CR, which confirmed the existence of CR in EA [101].

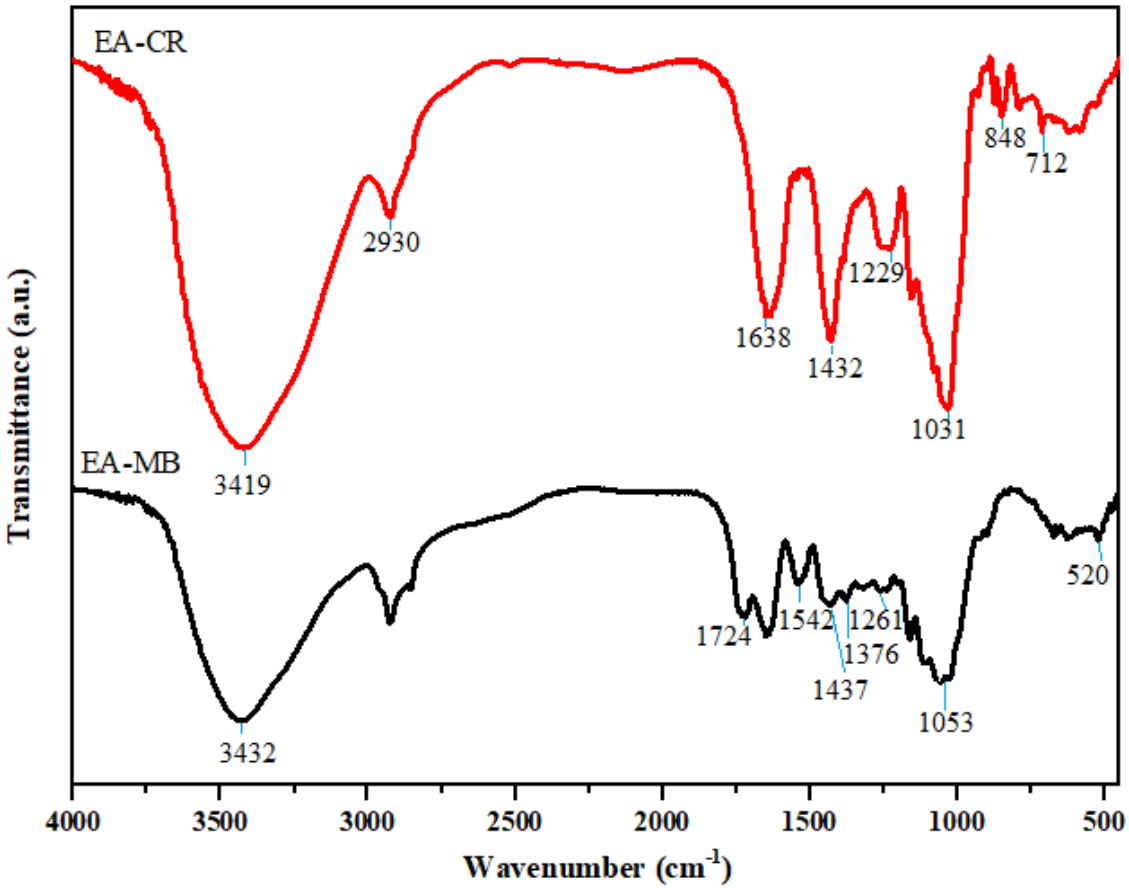


Figure 5.16 FTIR spectra of EA after MB and CR adsorption

5.5.2 XPS Analysis

XPS survey scan binding energy spectra of EA before and after CR and MB adsorption is demonstrated in Fig. 5.17a. The O 1s, Ca 2s, N 1s, Ca 2p, C 1s, and S 2p peaks detected in the survey spectra of EA. The intensities of the Ca 2p (347 eV) and Ca 2s (438 eV) peaks in the XPS survey spectrum of EA decreased after CR adsorption, while these peaks disappeared after MB adsorption. This finding was in line with the results of FTIR analysis. Accordingly, it can be concluded that unconverted $CaCO_3$ in EA were implicated in MB and CR adsorption. It has been observed that mineral phases such as CaO and $CaCO_3$ in the structure of the adsorbent are effective in removing dyes [102,103]. Electrostatic attraction may cause dye molecules to adsorb in the mineral phase [104,105,106]. Moreover, the new peak of element Cl in the XPS spectra of the EA-MB proves the presence of MB in the biosorbent.

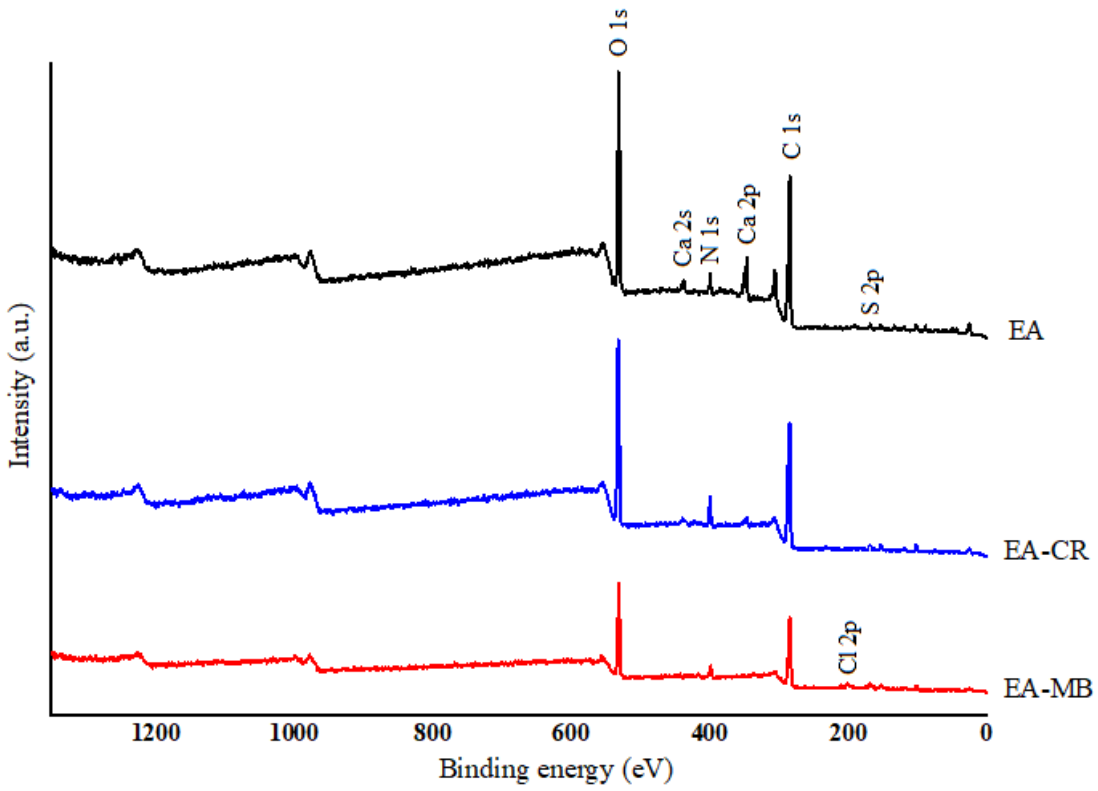


Fig.5.17a XPS survey spectra of EA before and after CR and MB adsorption

High-resolution XPS spectra of O 1s, C 1s, and N 1s are given in Figure 5.17b to show detailed bond changes of EA before and after dye adsorption. For O 1s, the peak located at 531 eV can be attributed to the O in the forms of carbonate [107]. This peak shifted to 531.4 eV after CR adsorption, while it vanished after MB adsorption. The other peak at 532 eV related to C-O/C=O bonds in the XPS spectra of the EA shifted to 532.5 eV for EA-CR and 532.2 eV for EA-MB, indicating the adsorption of CR and MB onto biosorbent [108]. For N1s, XPS spectra of the EA was fitted to two peaks located at 399.8 eV and 401.8 eV can be assigned as deprotonated amine and protonated amine groups respectively [109,110]. These peaks shifted to higher binding energies after CR adsorption while they shifted to lower binding energies after MB adsorption. Moreover, the new peak at 399.2 eV corresponding to the -NH [111] was detected after CR adsorption, implying that CR adsorbed onto EA. For C 1s, XPS spectra of the EA was fitted to four peaks at 284.7 eV, 286.2 eV, 287.8 eV, and 289.6 eV corresponding to C-C/C-H, C-O/C-N, C=O bonds, and carbonate, respectively [112,113]. After adsorption of MB and CR, the first three peaks slightly shifted to the lower binding energies, indicating interactions between dye and the biosorbent. Also, the third spectra (287.8 eV) can be divided into two peaks (287.54 eV and 287.47 eV) after MB adsorption. As expected, the intensity of the carbonate peak (289.6 eV) declined after CR adsorption while the peak vanished after MB adsorption.

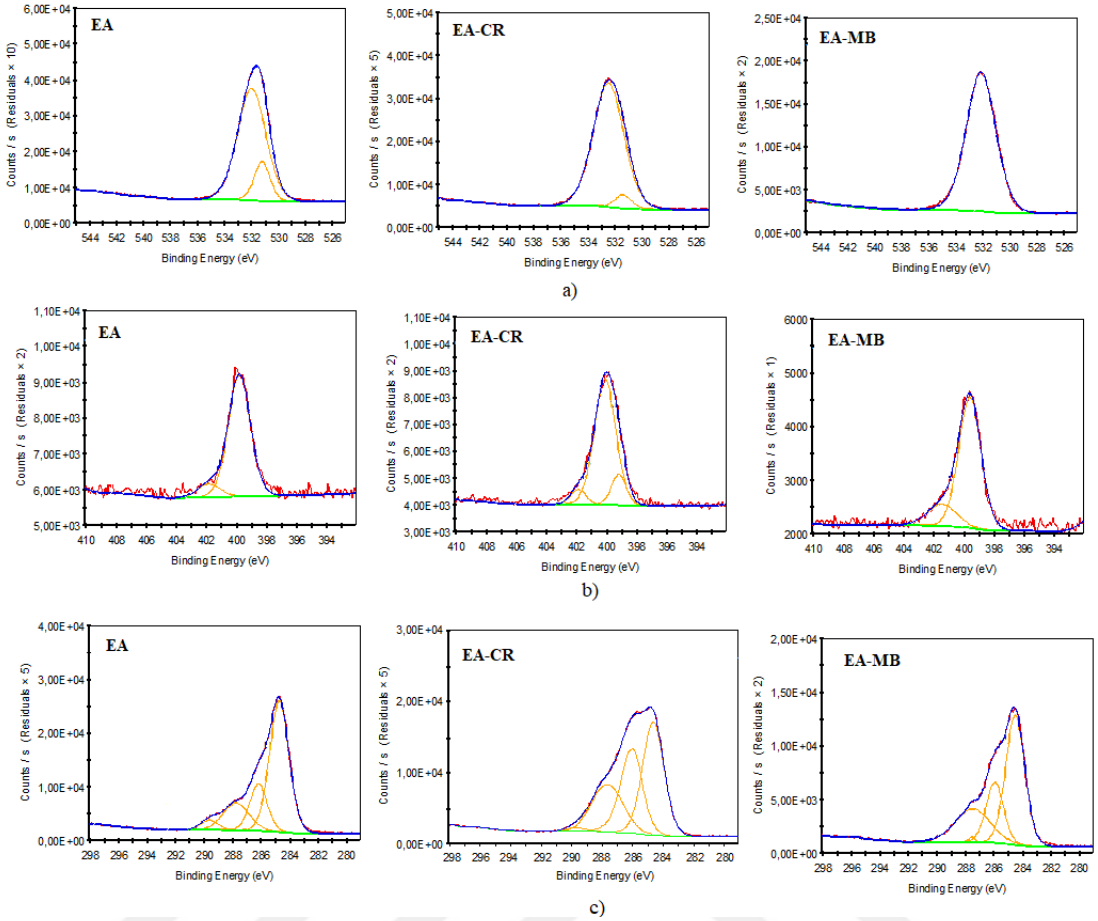


Fig.5.17b The high-resolution XPS spectra a) O 1s, b) N 1s, and c) C 1s

5.5.3 TG Analysis

Thermogravimetric (TG) analysis of EA was done before and after CR and MB adsorption to study the adsorbent's thermal characteristics. Three-step degradation was found in all three samples as shown in Figure 5.18. The weight loss in the first stage, which was induced by the evaporation of water and some volatile compounds adhering to the macroalgae surface, lasted up to 190°C in EA and EA-CR, and up to 145°C in EA-MB [114]. The decomposition of organic molecules such as carbohydrates, proteins, and lipids cause weight loss in the second stage, which can last up to 570°C in EA [115].

In EA-CR, the second breakdown stage can go up to 570°C, while in EA-MB, it can go up to 320°C. The adsorbed dye molecules begin to disintegrate in this second stage, which can last up to 900°C. The last stage of EA results in weight loss due to the burning of carbonaceous materials [116]. Furthermore, EA has a total weight loss of 59.85%, with total weight losses of 73.92 percent and 74.47 percent after CR and MB adsorption, respectively. The degradation of the dyes put on the structure accounts for the differential in weight losses. This demonstrates that MB and CR adsorption on the macroalgae surface is possible. Furthermore, the macroalgae structure's varied thermal behavior, particularly after MB adsorption, could be attributable to the creation of an EA-MB complex from MB and EA with varying thermal stability [117].

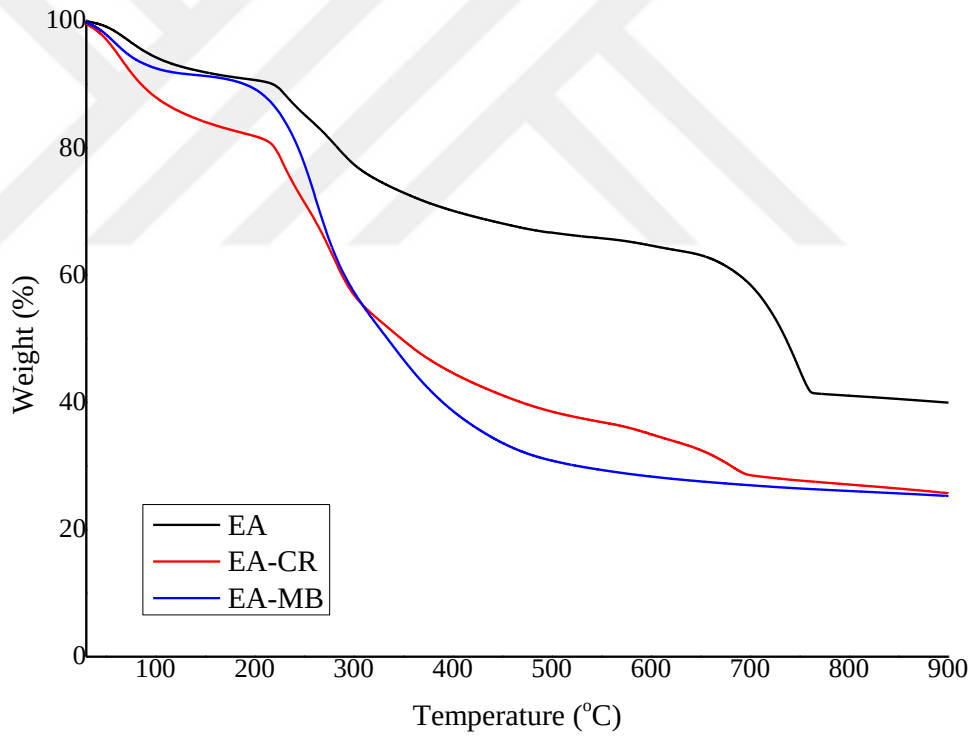
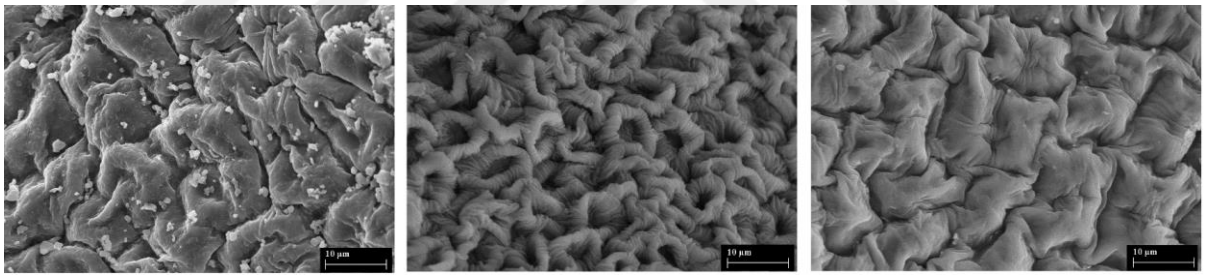


Figure 5.18 TG curves of EA, EA-CR and EA-MB

5.5.4 SEM Characterization

SEM examination was used to evaluate the morphological qualities and changes in surface characteristics of EA before and after adsorption. SEM images of EA before and after adsorption of MB and CR are shown in Figure 5.19. On the EA's surface, there are cell structures with fissures and many fine particles. These distributed tiny particles should be unconverted $CaCO_3$ in the calcined eggshell at 600C used in the treatment of U.Lactuca [118]. Dye application on the EA surface following adsorption reduced the size of these particles. In addition, after MB adsorption, there were considerable alterations on the EA surface. Due to the precipitation of MB ions surrounding the cell surface, the cells on the surface have become folded, and the fractures on the surface have vanished. Furthermore, the darkening of the MB-loaded adsorbent's surface confirmed MB's binding to the EA surface. With the introduction of CR into cells, the surface of EA seems to enlarge after CR adsorption [119].



a) b) c)

Figure 5.19 SEM image of EA a) before adsorption, after adsorption of b) MB and c) CR

Figure 5.20 shows surface pictures of EA before and after MB and CR adsorption, as well as corresponding EDS maps. In all three macroalgae structures, C, N, O, Na, Mg, S, P, K, and Ca components were found. The presence of Cl in EA only after MB adsorption indicates that macroalgae have successfully absorbed MB. After CR adsorption, the rise in S element in the macroalgae structure suggests that CR is adsorbed on the EA surface.

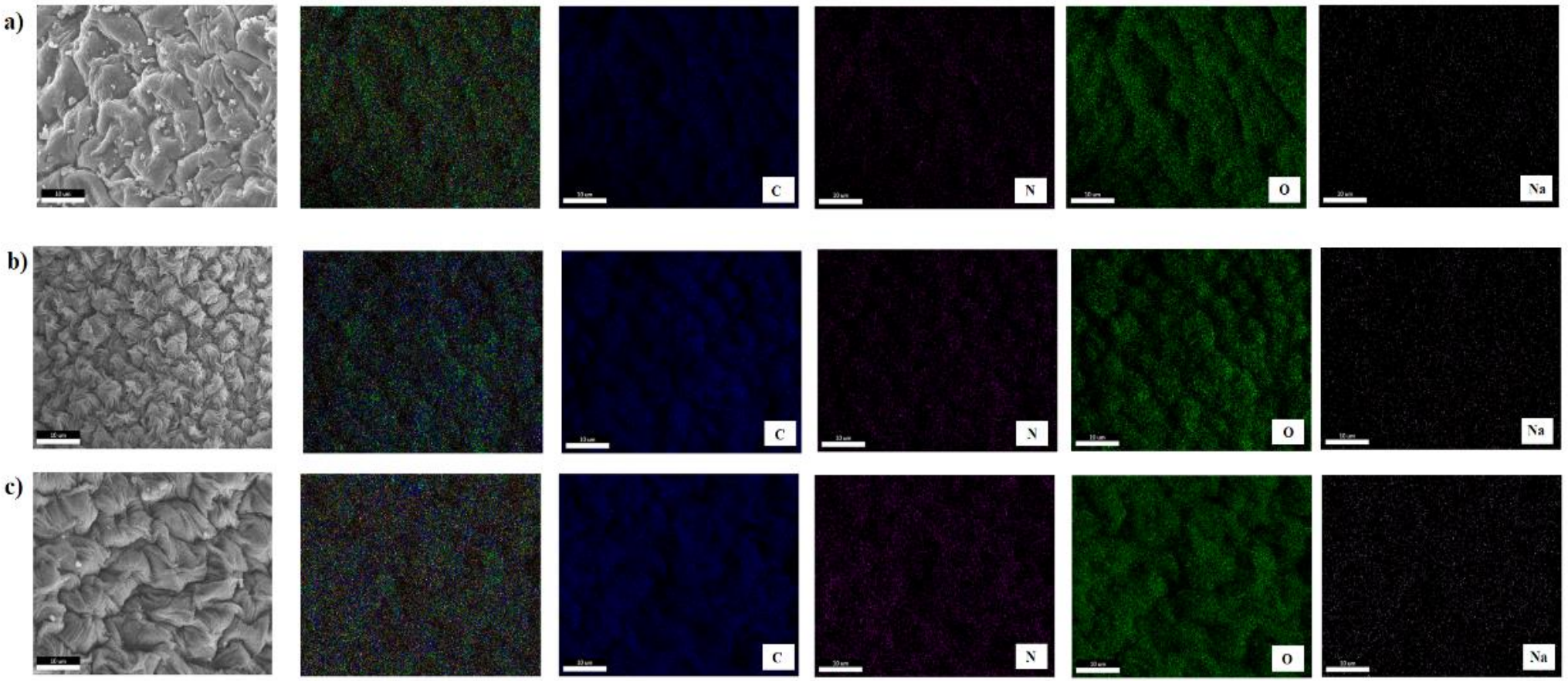


Figure 5.20a SEM images and EDS mapping of a) EA, b) EA-MB, and c) EA-CR

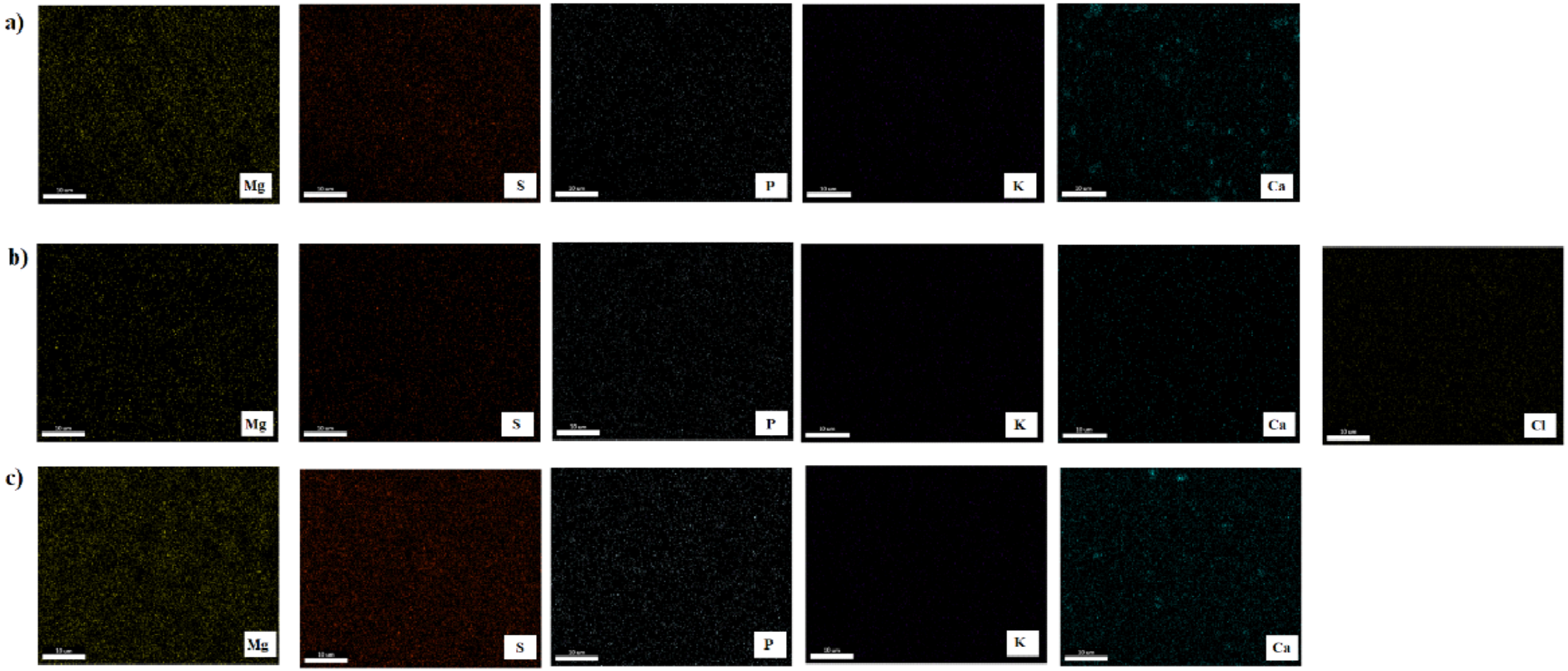


Figure 5.20b SEM images and EDS mapping of a) EA, b) EA-MB, and c) EA-CR

6
CONCLUSION AND RECOMMENDATIONS

The goal of this study was to create a new biobased adsorbent made from calcined eggshell and macroalgae U. Lactuca for selective dye adsorption and the removal of MB and CR dyes from industrial wastewater, thereby helping to protect the environment and natural water resources while using a simple, cheap, easy-to-apply, and time-saving process. For this reason, calcined eggshell with a high CaO content was employed as a low-cost activation substitute for macroalgae alkali treatment. Firstly, the selective adsorption of the treated U. Lactuca (EA) to MB/CR, MB/R-B, and MB/MO were investigated. EA had the best removal capacity in MB and CR dyes, according to the selective dye adsorption results. Thus, the individual dye adsorption was carried out for these dyes. Accordingly, the removal percentage of CR and MB was found as 83% and 98%, respectively. That is, EA exhibited a superior adsorption capacity for MB than the CR dye. Therefore, the adsorption kinetics and isotherms were determined for the removal of MB. To find the pretreatment effect on the MB adsorption, the adsorption performances of untreated macroalgae, calcined eggshell, and EA were examined. The order of the MB removal capacity was untreated macroalgae < calcined eggshell < EA. In addition, EA removed 94% of MB in just 5 minutes, which shows that the adsorption of MB was very fast. According to these results, it was seen that treating EA with calcined eggshells had enhanced the adsorption of MB due to the increasing electronegativity of the biosorbent. As a result, the calcined eggshells can be utilized instead of commercial $Ca(OH)_2$.

The Langmuir isotherm and P2 models fitted well to the MB dye adsorption data onto EA, implying a monolayer adsorption and physiochemisorption, respectively. The maximum adsorption capacity of EA was calculated 2000 $mg.g^{-1}$, which is significantly greater than most previously reported algae-based adsorbents.

The regeneration and reuse of EA for MB adsorption were carried out utilizing HCl, HNO_3, NH_4OH, and NaOH as desorption eluents, with HCl showing the best

results. Also, the regenerated adsorbent still had 86% of its original adsorption ability after four adsorption-desorption cycles.

The possible adsorption mechanism of MB and CR onto EA was investigated by FT-IR, XPS, TG, and SEM analysis. According to analysis results, $CaCO_3$, which is not transformed as a result of calcination in the eggshells used in the treatment of U.Lactuca, has been found to be effective in the adsorption of dyes. Electrostatic attraction may cause dye molecules to adsorb in the $CaCO_3$ mineral phase. Especially, XPS, SEM and FTIR analysis indicating that the possible synergistic effect of MB and $CaCO_3$ was higher than of CR and $CaCO_3$. In addition, hydrogen bonding and electrostatic interaction are also suggested to have an effect on the adsorption of MB on EA.

The novel low-cost biosorbent EA can be proposed as a promising adsorbent for the removal of MB and CR dyes based on the findings of this thesis and the developed treatment method of U.Lactuca paves the way for practical effluent treatment.

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PUBLICATIONS FROM THE THESIS

Conference

1. The 12th International Scientific Research Congress, 17 - 18 December 2021 (Poster presentation)

Projects

1. Preparation of novel bio-based adsorbent for fast and selective adsorption of various dyes, YTU-BAPK, FYL-2021-4618., 2021-2022, Researcher.