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EGE UNIVERSITY
Graduate School of Applied and Natural Science



INVESTIGATING THE ADSORPTION PROPERTIES OF OLIVE STONE DERIVED ACTIVE CARBON

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Mert Can HENDEKÇİ

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Supervisor : Prof. Dr. Bıkem ÖVEZ

Chemical Engineering Department
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Mert Can HENDEKÇİ tarafından Yüksek Lisans tezi olarak sunulan “Zeytin çekirdeđi esaslı aktif karbonun adsorpsiyon özelliklerinin incelenmesi” başlıklı bu çalışma EÜ Lisansüstü Eğitim ve Öğretim Yönetmeliđi ile EÜ Fen Bilimleri Enstitüsü Eğitim ve Öğretim Yönergesi’nin ilgili hükümleri uyarınca tarafımızdan değerlendirilerek savunmaya değeri bulunmuş ve 15.09.2023 tarihinde yapılan tez savunma sınavında aday oybirliđi ile başarılı bulunmuştur.

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15/09/2023

Mert Can HENDEKÇİ

ÖZET**ZEYTİN ÇEKİRDEĞİ ESASLI AKTİF KARBONUN ADSORPSİYON
ÖZELLİKLERİNİN İNCELENMESİ**

HENDEKÇİ, Mert Can

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Temiz suya ulaşım, endüstriyel faaliyetlerle ortaya çıkan atıkların mevcut su kaynaklarımızı kirletmesiyle günden güne daha zor hale gelmektedir. Atık suların, su kaynaklarına kontrolsüz deşarjıyla birlikte karasal ve sucul yaşama büyük zarar verdiği görülmüş ve kontaminantların besin zincirine dâhil olarak canlı sağlığını tehdit ettiği yapılan çalışmalarla ortaya konmuştur. Tüm bu çevre ve sağlık problemlerinin önüne geçilebilmesi için atık suların arıtılması oldukça önem taşımaktadır. Adsorpsiyon, kolay uygulanabilirliği, uygun ekonomisi ve çevre dostu olmasıyla su arıtma yöntemleri arasında öne çıkmaktadır.

Bu çalışmada, düşük maliyetli, tarımsal bir biyoatık olan zeytin çekirdeği aktif karbon üretiminde hammadde olarak kullanılmıştır. $ZnCl_2$, KOH ve H_3PO_4 kimyasalları ile aktive edilerek kullanımı birçok alanda yaygın olan ve toksik etkiye sahip Rodamin B boyasının sulu çözeltiden adsorpsiyonu incelenmiştir. Zaman, konsantrasyon, pH, sıcaklık, adsorbent miktarı ve farklı iyonların varlığı gibi parametrelerin adsorpsiyon performansı üzerine etkileri araştırılmıştır.

Gerçekleştirilen kinetik çalışma sonucunda denge süresi 6 saat olarak belirlenirken, en yüksek adsorplama kapasitesine zeytin çekirdeklerinden hazırlanan $ZnCl_2$ ile aktive edilmiş aktif karbon (190,67 mg/g) ulaşmıştır. Sonrasında sırasıyla KOH ile aktive edilmiş (118,26 mg/g) ve H_3PO_4 ile aktive edilmiş (49,81 mg/g) aktif karbonlar takip etmektedir.

Farklı pH değerlerinde (2-10) pH'ın adsorplama kapasitesi üzerinde çok fazla bir etkisinin olmadığı gözlemlenmiştir. Rodamin B başlangıç konsantrasyonu 10-300 mg/L aralığında artarken adsorplama kapasitesi de artmış ve 200 mg/L'de dengeye ulaştığı görülmüştür. 0,01 gram $ZnCl_2$ ile aktive edilmiş aktif karbon %40 giderme performansına sahipken 0,05 gram adsorbent miktarının Rodamin B'yi %100 gidermek için yeterli olduğu saptanmıştır.

Farklı sıcaklıklarda (30, 40, 50 °C) gerçekleştirilen deneyler sonucunda sıcaklık artışının adsorpsiyon kapasitesi üzerinde arttırıcı bir etkisi olduğu saptanmıştır. Termodinamik sabitlerin hesaplanmasıyla birlikte adsorpsiyonun endotermik olduğu ($\Delta H^\circ=14.91$ kJ/mol) ve termodinamik olarak elverişli ($\Delta G^\circ<0$) olduğu ortaya konmuştur.

Kinetik çalışma sonuçlarına göre, yalancı ikinci dereceden modelin ($R^2=0.993$) deneysel verilere en uygun olduğu belirlenmiştir. Gerçekleştirilen denge çalışmasına göre iki ve üç parametrelili denge modellerinden sırasıyla Langmuir ($R^2=0.986$) ve Redlich-Peterson ($R^2=0.992$) modellerinin uygun olduğu görülmüştür.

$ZnCl_2$ ile aktive edilmiş zeytin çekirdeği aktif karbonunun yeniden kullanılabilirliği adsorpsiyon/desorpsiyon döngüsü ile araştırılmıştır. 5. döngünün sonunda adsorplama kapasitesinde ve giderim performansında ciddi bir azalma meydana gelmemiştir. $ZnCl_2$ ile aktive edilmiş zeytin çekirdeği aktif karbonunun, Rodamin B gideriminde etkili ve tekrar kullanılabilir olduğu görülmüştür.

Anahtar kelimeler: sürdürülebilir atık yönetimi, zeytin çekirdeği, yüzey modifikasyonu, Rodamin B, adsorpsiyon, optimizasyon

ABSTRACT**INVESTIGATING THE ADSORPTION PROPERTIES OF OLIVE
STONE DERIVED ACTIVATED CARBON**

HENDEKÇİ, Mert Can

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Access to clean water is getting more difficult day by day as the wastes generated by industrial activities pollute our existing water resources. It has been seen that waste waters cause great damage to terrestrial and aquatic life, and it has been revealed by studies that contaminants threaten the health of living beings by entering in the food chain. To prevent all these environmental and health problems, it is crucial to treat wastewater. Adsorption stands out among water treatment methods with its easy applicability, convenient economy, and environmental friendliness.

In this study, activated carbon derived from olive stones which is a low-cost, agricultural biowaste was the main precursor for the adsorption process. The olive stones were further impregnated with ZnCl_2 , KOH and H_3PO_4 and the performance of these different activated carbons in removal of Rhodamine B, which is commonly used dye in many areas and has toxic effects, was investigated. The effect of parameters time, initial Rhodamine B concentration, pH, temperature, adsorbent dosage, and presence of background ions on the adsorption performance of activated carbons were investigated.

In kinetic study, the equilibrium time was determined as 6 hours, and the highest adsorption capacity was achieved by ZnCl_2 impregnated olive stone activated carbon (190.67 mg/g). It was followed by activated carbons impregnated with KOH (118.26 mg/g) and H_3PO_4 (49.81 mg/g), respectively.

It was observed that at different pH values (2-10), pH did not have much effect on the adsorption capacity. While the initial Rhodamine B concentration increased between the range of 10-300 mg/L, its adsorption capacity also increased and it was observed that it reached equilibrium at 200 mg/L. 0.01 gram of ZnCl_2 impregnated activated carbon had 40% removal performance, while 0.05 gram of adsorbent amount was found to be sufficient to 100% remove Rhodamine B.

As a result of the experiments performed at different temperatures (30, 40, 50 °C), the temperature increase had an increasing effect on the adsorption capacity. According to calculated thermodynamic parameters, it was revealed that the adsorption is endothermic ($\Delta H^\circ = 14.91$ kJ/mol) and thermodynamically favorable ($\Delta G^\circ < 0$).

Pseudo-second order model ($R^2=0.993$) was most suitable for the experimental data among kinetic models. According to the equilibrium modelling, Langmuir ($R^2=0.986$) and Redlich-Peterson ($R^2=0.992$) models were found to be suitable, respectively, among the two- and three-parameter models.

The reusability of ZnCl_2 impregnated olive stone activated carbon was investigated by performing adsorption/desorption cycle. At the end of the 5th cycle, there was no significant decrease in adsorption capacity and removal performance. ZnCl_2 impregnated olive stone activated carbon was found to be effective and reusable in Rhodamine B removal.

Keywords: sustainable waste management, olive stone, surface modification, Rhodamine B, adsorption, optimization

PREFACE

Water crisis is one of the crucial problems that everyone should care about it and take some actions to leave a better world to future generations. I am happy and proud to contribute this topic.

It was a long and tough journey from the day started to my master's degree until now. I have gained lots of experience during this period. After many misfortunes like global pandemic, Prof. Dr. Bikem ÖVEZ brought us together with Dr. Duygu OVA ÖZCAN and then this study was proposed. I would like to express my gratitude once again for their valuable contributions to this study and my life.

I want to dedicate this thesis to memory of my supervisor Prof. Dr. Serap CESUR and my grandfather Ahmet AVLAR. I know and believe that they are watching me from somewhere and proud of me.

İZMİR

Mert Can HENDEKÇİ

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NOMENCLATURE

<u>Symbol</u>	<u>Definition</u>
q_{exp}	experimental adsorption capacity (mg/g)
C_i	initial concentration of solution (mg/L)
C_f	final concentration of solution (mg/L)
m	mass of adsorbent (g)
V	volume of the solution (L)
k_1	pseudo first order rate constant (min^{-1})
k_2	pseudo second order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$)
q_1	theoretical adsorption capacity (mg g^{-1})
q_2	theoretical adsorption capacity (mg g^{-1})
q_t	experimental adsorption capacity (mg g^{-1})
t	time (min^{-1})
a	Elovich's adsorption constant (g mg^{-1})
b	Elovich's first rate ($\text{mg g}^{-1} \text{min}^{-1}$)
K_F	Freundlich constant ($(\text{mg/g})(\text{L/mg})^{1/n}$)
K_a	Langmuir constant (L mg^{-1})
$1/n$	Heterogeneity factor (dimensionless)

q_e	equilibrium adsorption capacity (mg g ⁻¹)
q_m	maximum adsorption capacity (mg g ⁻¹)
C_f	equilibrium concentration (mg L ⁻¹)
K_{RP}	Redlich-Peterson constants (L mg ⁻¹)
a_{RP}	Redlich-Peterson constants (L ^β /mg ^β)
β	Redlich-Peterson exponent (dimensionless)
K_{eq}	Sips constant (L g ⁻¹)
n	heterogeneity factor (dimensionless)
q_T	Toth maximum adsorption capacity (mg g ⁻¹)
b_T	Toth constant (L mg ⁻¹)
n_T	Toth exponent (dimensionless)
K_0	adsorption equilibrium constant (dimensionless)
T	temperature (K)
R	universal gas coefficient (8.31 × 10 ⁻³ kJ mol ⁻¹ K ⁻¹).
ΔG°	Gibbs free energy (kJ mol ⁻¹)
ΔH°	standard change in enthalpy (kJ mol ⁻¹)
ΔS°	standard change in entropy (kJ mol ⁻¹ K ⁻¹)
R^2	correlation coefficient

<u>Abbreviations</u>	<u>Definition</u>
RB	Rhodamine B
AC	Activated carbon
PAC	Powdered activated carbon
OSAC	Olive stone activated carbon
KOSAC	KOH impregnated olive stone activated carbon
ZOSAC	ZnCl ₂ impregnated olive stone activated carbon
HOSAC	H ₃ PO ₄ impregnated olive stone activated carbon
UV/VIS	Ultraviolet visible spectroscopy
FT-IR	Fourier Transform Infrared
TDS	Total Dissolved Solids
COD	Chemical oxygen demand
BOD	Biological oxygen demand
HCl	Hydrogen chloride
NaOH	Sodium hydroxide
KOH	Potassium hydroxide
ZnCl ₂	Zinc chloride
H ₃ PO ₄	Phosphoric acid

Cu(II)	Copper
Cd(II)	Cadmium
Pb(II)	Lead
Cr(VI)	Chromium
ANOVA	Analysis of Variance
IOC	International Olive Council
UNESCO	United Nations Educational, Scientific and Cultural Organization
UNICEF	United Nations International Children's Emergency Found

1.0 INTRODUCTION

As a result of the climate crisis, rapidly increasing population and industrialization, the depletion of water resources poses a great threat to our future which is required for the continuity of life. Water resources are getting contaminated by human activities and this issue poses a threat to environment and all aquatic and terrestrial organisms.

One of the most important precautions that can be taken is to ensure that the wastewater produced by industrial facilities with high water consumption is cleaned and reused. Adsorption is a preferred method in water treatment owing to its advantages.

Rhodamine B has a reddish-violet color which is commonly used dye in many industries, and it causes serious environmental and health issues because of discharge of its effluents into water sources. To eliminate these effects, Rhodamine B must be effectively removed from the effluents.

There are several processes to treat contaminated water, and adsorption stands out among these methods with its easy applicability, economy, and environmental friendliness. The choice of adsorbent is important for a highly efficient adsorption. The development of low-cost and high-performance adsorbent from agricultural waste is one of the important research topics.

Türkiye, which ranks in first five countries in olive production in the world, has a high potential in terms of olive stone, which is an agricultural waste. Instead of using this biowaste as fuel, it could be passed through a series of processes to produce activated carbon and make it a value-added product which is planned to be used in adsorption of contaminants from water.

In this thesis, the adsorption performance of Rhodamine B from water was studied with olive stone activated carbons. The effect of time, initial concentration, pH, temperature, adsorbent dosage, and existing background ions was parametrically investigated in batch systems. The adsorption capacity of olive stone

activated carbon was compared with powdered activated carbon. The adsorption kinetic and equilibrium modeling were performed to figure out the adsorption mechanism. To see the nature and feasibility of the adsorption process, thermodynamic parameters were determined. Optimization study was done based on temperature and initial concentration parameters and optimum conditions were determined for maximum adsorption capacity. The reusability of olive stone activated carbon was researched by adsorption/desorption cycles.



2.0 LITERATURE SURVEY

2.1 Water Contamination

Without water, no sign of life can be expected to be observed on the earth. So, that makes water is a necessary and irreplaceable element for life. Water has a crucial role in preserving and sustaining the ecology. Although almost 70% of the earth is covered by water, 97.5% of water is not eligible for consumption due to its salinity. In the remaining part, only 0.4% of water is available and the rest of water is trapped under the earth's surface and in polar ice caps. Since the freshwater supply will be insufficient to meet the demands of the future generations, water scarcity is regarded as a serious concern in today's world (Boretti and Rosa, 2019; Singh et al., 2018; Sirajudheen et al., 2021).

Due to the increase in population and industrialization, freshwater resources are rapidly depleting day by day (Premkumar et al., 2018). Contaminants pollute the water bodies and adversely affect the quality of water. Any unwanted substances in water can be considered as contaminant (Bashir et al., 2023). Main examples of contaminants are given in Figure 2.1.

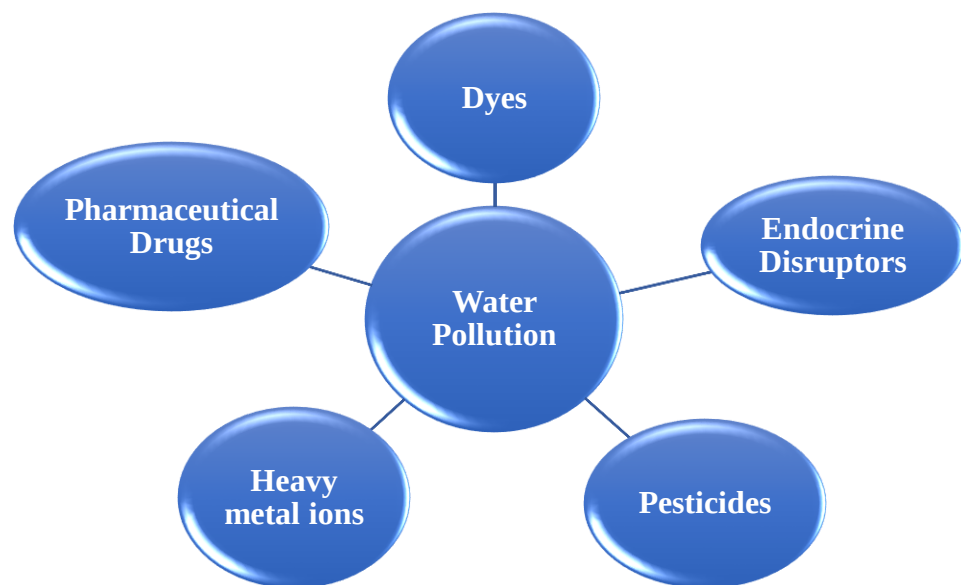


Figure 2.1 Main water contaminant groups

The primary contaminants that caused by industrial activities includes dyes, pesticides, heavy metal ions, pharmaceutical drugs and endocrine disruptors which are negatively affect the potable quality of water resources.

Dyes are one of the hazardous contaminants which affect environment and human health due to high resistance to degradation (Bashir et al., 2023). Heavy metals can pose a danger to human health when they are above their critical limits in water and soil (Anyanwu et al., 2022). Pesticides, extensively used in agricultural activities, are another type of contaminant commonly found in soil and surface waters in many countries of the world. (Rad et al., 2022) Similarly, pharmaceutical drugs have adverse effects on the aquatic life due to their persistence and accumulation in bodies (Gopal et al., 2021). Kasonga et al., (2021) reported that chronic exposure to endocrine disruptors can cause different diseases by altering to hormones.

From different locations in the world, mainly from rivers, samples were taken and analyzed the contamination level of different contaminants (Venault et al., 2018). Chiang et al., (2012) detected Rhodamine B dye in Taichung River, Taiwan with a concentration of 0.0048 $\mu\text{g/L}$. Roznere et al., (2023) showed that Atrazine, widely used herbicide, detected in Maumee River, US at concentration level of 0.7205 $\mu\text{g/L}$. Raj et al., (2023) reported that high level of Zn(II) and Al(III) heavy metal ions, 8520 and 14740 $\mu\text{g/L}$, respectively, found in Cooum River, India. Ibuprofen (1.834 $\mu\text{g/L}$) and diclofenac (1.130 $\mu\text{g/L}$) which are common pharmaceutical drugs, were detected in Arkavathi River, India by Gopal et al., (2021). Valbonesi et al., (2021) detected BPA in Forli-Cesena, Italy at concentration level of 0.00925 $\mu\text{g/L}$. All studies about determination of contamination in water sources are listed in Table 2.1.

The discharge of industrial activities is a crucial problem that can be harmful to the ecological, environmental, and human health (Kalaitzidou et al., 2020). In UNESCO report, it was stated that more than 80 percent of the wastewater is directly discharged into the environment (UNESCO, 2017). It was mentioned that the drinking of contaminated water is responsible for millions of people's death due to waterborne diseases (UNICEF, 2019).

Publics and governments are agreed that management of wastewater should be carried out in a sustainable manner. Numerous researchers have been working to develop a sustainable treatment method and find a solution for water treatment (Teo et al., 2022).



Table 2.1 Different contaminations detected around world

Contaminant Class	Contaminant Name	Concentration [$\mu\text{g/L}$]	Location	Reference
Dyes	Rhodamine B	0.0048	Taichung River, Taiwan	(Chiang et al., 2012)
	Malachite green	0.62	Dong Lin River, China	(Zhang et al., 2012)
	Disperse Violet 93	2.81	Quilombo River, Brazil	(Vacchi et al., 2017)
Pesticides	Chlorpyrifos	0.183	Cachapoal River, Chile	(Climent et al., 2018)
	DET	21.89		
	Atrazine	0.7205	Maumee River, US	(Roznere et al., 2023)
Heavy Metal Ions	Cu(II)	210	Ikwu River, Nigeria	(Anyanwu et al., 2022)
	Pb(II)	40		
	Zn(II)	8520	Cooum River, India	(Raj et al., 2023)
	Al(III)	14740		
Pharmaceutical Drugs	Venlafaxine	0.1	Molonglo River, Australia	(Roberts et al., 2016)
	Ibuprofen	1.834	Arkavathi River, India	(Gopal et al., 2021)
	Diclofenac	1.13		
	Iopamidol	0.761	Maumee River, US	(Roznere et al., 2023)
Endocrine Disruptors	Propylparaben	0.089	Arkavathi River, India	(Gopal et al., 2021)
	BPA	0.00925	Forli-Cesena, Italy	(Valbonesi et al., 2021)
	PFOA	0.00479	Ravenna, Italy	

2.2 Dye Contamination

Dyes are one of the major contributor chemicals to water pollution. They are classified into two groups based on the origin as natural or synthesized. Synthetic dyes, almost 60% of total dyes, are generally obtained by chemically modification of the natural dyes. Azo dyes are the largest dye group used as colorant in paper, leathering and plastic coloring (Al-Gheethi et al., 2022). Acidic dyes, reactive dyes, disperse dyes, vat dyes, pigment dyes, and sulfur dyes are the members of the azo dyes group (Shabir et al., 2022).

Annually, more than 10,000 types of dyes are produced, and they are extensively used in textile, leather, plastic, paint, printing, and cosmetics. Approximately 7×10^5 tons of dye is discharged by these industries in every year (Daud et al., 2019).

Main industries are responsible for discharging dye-containing wastewater in nearby water bodies as shown in Figure 2.2. Among these industries, a significant portion of dye effluent, more than 50%, are discharged into environment by textile industry. In textile industry, over 10,000 tons of dyes is used annually and according to reports, incomplete washing and exhaustion processes result in the loss of 10–20% of dyes in residual liquors (Shabir et al., 2022; Uddin et al., 2021).

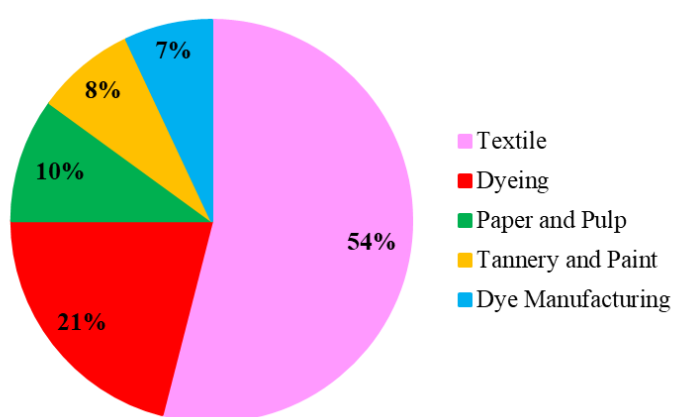


Figure 2.2 Responsible industry for dye effluents

Khan et al., (2014) and Khan et al., (2019) reported that methylene blue and malachite green dyes were detected in laundry, paper, printing, and textile effluents. Chiang et al., (2012) reported that Rhodamine 6G and Rhodamine B dyes in wastewater samples which were taken from two wastewater treatment plants. Lou et al., (2018) detected seven different dyes in textile effluent. In Table 2.2, other detected dyes in wastewater and effluents of different industries are listed.



Table 2.2 Detected dyes in wastewater

Type of wastewater	Dye Name	Concentration determined [$\mu\text{g/L}$]	Reference
Wastewater	Rhodamine 6G	0.0007-0.00014	(Chiang et al., 2012)
	Rhodamine B	0.037–0.081	
Wastewater	Methylene Blue	1530	(Razmara et al., 2011)
Laundry Effluent	Methylene Blue	360	(Khan et al., 2014)
Paper Effluent		540	
Printing Effluent		830	
Textile Effluent		1080	
Wastewater	Disperse Red 1	0.03–0.19	(Vacchi et al., 2017)
	Disperse Blue 373	0.08–0.35	
	Disperse Blue 291	0.05	
Textile Effluent	Disperse Red 1	12–34	(Lou et al., 2018)
	Disperse Orange 3	17	
	Disperse Yellow 49	23–428	
	Disperse Orange 37/76	53	
	Disperse Red 17	63	
	Disperse Yellow 1	90–306	
	Disperse Brown 1	109	
Laundry Effluent	Malachite Green	1320	(Khan et al., 2019)
Paper Effluent		620	
Printing Effluent		790	
Textile Wastewater		1680	
Textile Wastewater	Brilliant Green	3220	(Damirchi et al., 2019)

As well as in textile industry, dyes are also employed in food, cosmetic and pharmaceutical industry to make products more attractive. In pharmaceutical industry, dyes are commonly used in hard or soft capsules, lozenges, syrups and tablets owing to its convenient economy and high stability. Also, dyes are widely used in make-up products and skin care products formulations in cosmetic industry. Because of their long-lasting properties, synthetic dyes are more preferable rather than natural dyes (Šuleková et al., 2017; Tkaczyk et al., 2020). In Table 2.3, some examples of commonly used dyes in different industries are listed.

Table 2.3 Commonly used dyes in different industries

Industry	Common name	Class
Textile	Auramine O	Diphenylmethane
	Malachite Green	Triarylmethane
	Nile Blue	Oxazine
	Rhodamine B	Xanthene
Food & Pharmaceutical	Chocolate Brown HT	Azo
	Food Blue 2	Triphenylmethane
	Food Green S	Triphenylmethane
	Erythrosine B	Xanthene
Cosmetic	Acid Red 33	Azo
	Basic Brown 17	Azo
	Basic Red 76	Azo
	Disperse Red 17	Azo

Since their negative environmental and health effects, dyes are restricted or banned under some regulations according to usage area. In the European Union (EU), application of dyes is regulated by EU laws and in Table 2.4 these regulations are given.

Table 2.4 Dye regulations for industries

Industry	Regulation
Textile	EU- Ecolabel Textile Restricted Substances List Commission Decision: (EU) 2014/350;(EU) 2017/1392
Food	EU- European Food Safety Authority (EFSA) Regulation No: 1129/2011
Cosmetic	EU- European Parliament and of the Council (EC) Regulation (EC) No: 1223/2009
Pharmaceutical	EU- European Parliament and of the Council (EC) Directive 2009/35/EC

According to Ecolabel Textile Restricted Substances List, some examples of restricted dyes are given in Table 2.5 due to their carcinogenicity, mutagenicity, and toxicity.

Table 2.5 Examples of restricted dyes in textile

Dye Class	Dye Name
Acidic	Acid Red 24
	Acid Violet 12
	Acid Brown 415
	Acid Black 29
Basic	Basic Yellow 82
	Basic Red 42
	Basic Brown 4
	Basic Red 114
Direct	Direct Black 4
	Direct Blue 8
	Direct Brown 33
	Direct Red 28
Disperse	Disperse Blue 102
	Disperse Brown 1
	Disperse Orange 76
	Disperse Red 17

Although using of rhodamine B and malachite green in textile industry is permitted, using these dyes in food industry is banned. Similarly, they are banned to use by regulation (EC) No. 1223/2009 in cosmetics (Tkaczyk et al., 2020).

Consequently, drinking water sources is polluted by about 15% of these dyes which may cause harmful diseases (Daud et al., 2019). These dyes are considered as toxic and potentially carcinogenic and non-degradable because of its chemical stability (Hu et al., 2021).

2.2.1 Effect of dye contamination on environment

When dye effluents are directly discharged to the environment, huge amounts of dyes accumulate in water and soil near the dye processing plants and the quality of the ecosystem is adversely influenced. Synthetic dyes detected in rivers are listed in Table 2.6.

Table 2.6 Synthetic dyes detected in rivers

Dye Name	Concentration determined (µg/L)	Location	Reference
Disperse Violet 93	0.0118	Cristais River, Brazil	(Carneiro et al., 2010)
Disperse Orange 37	0.397		
Disperse Blue 373	0.0649		
Rhodamine B	0.0048	Taichung River, Taiwan	(Chiang et al., 2012)
Rhodamine 6G	0.0013		
Malachite Green	0.62	Dong Lin River, China	(Zhang et al., 2012)
Crystal Violet	0.87		
Disperse Blue 291	0.04	Piracicaba River, Brazil	(Vacchi et al., 2017)
Disperse Yellow 3	0.03		
Disperse Red 1	0.52		
Disperse Blue 373	3.13		
Disperse Violet 93	6.81		
Disperse Orange 30	0.14	Quilombo River, Brazil	
Disperse Red 1	0.15		
Disperse Yellow 3	0.41		
Disperse Blue 373	1.38		
Disperse Violet 93	2.81		

Contaminants are harmful to aquatic life when they enter the water sources. Aquatic ecosystem is sensitive to changes in their environment. The water parameters like pH, salinity, dissolved oxygen etc., are influenced by contamination. Therefore, it will be difficult to survive and reproduce for aquatic organisms. The toxic substances are accumulated in the organism bodies either absorbed through skin or ingestion. The toxic effect may continue until become deadly to the organism. Also, the toxins can pass through from lower organism to higher organism in the food chain and it is called biomagnification. From lowest to highest level of food chain, the toxic substances are increasingly accumulated in bodies (Varsha et al., 2022). Belpaire et al., (2015) reported that crystal violet, brilliant green and malachite green dyes were detected in European eel (*Anguilla Anguilla*) from 91 different locations in Belgian rivers.

Dye contamination decreases dissolved oxygen level in water which affects all aquatic ecosystem. Also, the penetration of light is inhibited by dyes into the water and the rate of photosynthesis is negatively affected in the water bodies (Rehman et al., 2018). Dyes can cause serious problems even death for different species like algae, crustaceans, and fishes. In Table 2.7, toxicity of dyes on aquatic species are listed in terms of effective and lethal concentration.

Dye effluents change the chemistry of soil and balance of microbial flora in soil and this change affects growing of plants (Zou et al., 2019). Dissolved oxygen level needed for seedlings and chlorophyll content of plants decreases by contamination which cause slow growth (Sharma et al., 2020).

Dye effluents inhibit plant growth by reducing photosynthesis rate, inability to metabolize nitrogen required for protein synthesis, lowering potential to metabolize carbon dioxide, and low aerobic microbial biodegradation (Chandanshive et al., 2018).

Jolly et al., (2012) performed research to observe the effect of dye contamination on wheat cultivation. The germination of wheat seeds was greatly reduced with the increasing dye concentration.

Zhou (2001) collected soil samples from five different locations in China and detected Reactive Red X-3B dye in varying concentrations between 20.5 to 38.3 mg per kg soil. In the same study, it was also demonstrated that eight different types of agricultural products were contaminated with Reactive Red X-3B dye with a range of 0.01-11.3 mg per kg dry weight of crop. This study proves that the crops cultivated in the contaminated soil, also contaminated from this pollution. Dyes can enter food chain by this way and may cause many health problems.

Table 2.7 Toxicity of different dyes on aquatic species

Taxon	Species	Dye Name	EC₅₀/LC₅₀ [mg/L]	References
Algae	<i>Chlorella sp.</i>	Basic Red 14	10.8	(Vinitnantharat et al., 2008)
		Reactive Red 141	95.5	
Algae	<i>P. subcapitata</i>	Reactive Black 5	29	(de Luna et al., 2014)
		Food Red 17	61	
		Food Yellow 3	72	
		Acid Orange 7	100	
		Acid Black 1	54.20	
Algae	<i>Selenastrum capricornutum</i>	Acid Orange 33	65.95	(Croce et al., 2017)
		Acid Green 111	71.82	
		Acid Blue 113	78.21	
		Acid Brown 354	92.25	
		Rhodamine B	14	
Algae	<i>R. subcapitata</i>	Rhodamine WT	91	(Skjolding et al., 2021)
		Reactive Red 141	95.5	
		Direct Blue 218	3.6	
Crustaceans	<i>D. magna</i>	Direct Blue 218	3.6	(Bae et al., 2006)
Crustaceans	<i>M. macropora</i>	Basic Red 14	4.9	(Vinitnantharat et al., 2008)
		Reactive Red 141	18.2	
Crustaceans	<i>D. similis</i>	Disperse Red 1	0.12	(Ferraz et al., 2011)
		Disperse Red 13	0.18	
Crustaceans	<i>D. similis</i>	Disperse Red 1	0.13	(Vacchi et al., 2013)
Fish	<i>Channa punctatus</i>	Vat Blue 4	148	(Olaganathan and Patterson, 2013)
	<i>Cyprinus carpio</i>	Vat Green 1	180	
Fish	<i>D. rerio</i>	Rhodamine B	18	(Skjolding et al., 2021)
		Rhodamine WT	200	
Fish	<i>D. rerio</i>	Maxilon blue 5G	166.04	(Köktürk et al., 2021)
		Reactive blue 203	278.32	

2.2.2 Effect of dye contamination on health

Dye effluents endanger human health due to their toxicity and carcinogenicity. Toxic substances can be entered human body by absorption through skin when the pores are open and direct ingestion of toxic substances by food chain. Dyes can cause skin problems such as dermatitis and allergic reactions. Inhalation or ingestion of dyes may cause skin and eyes irritation. They are also harmful to human reproductive systems by effecting ovulation and spermatogenesis. Azo dyes can be converted carcinogenic metabolites by enzymatic reactions and linked to bladder cancer in humans (Al-Tohamy et al., 2022). In Table 2.8, health effects of several dyes are listed.

Table 2.8 Health effects of dyes

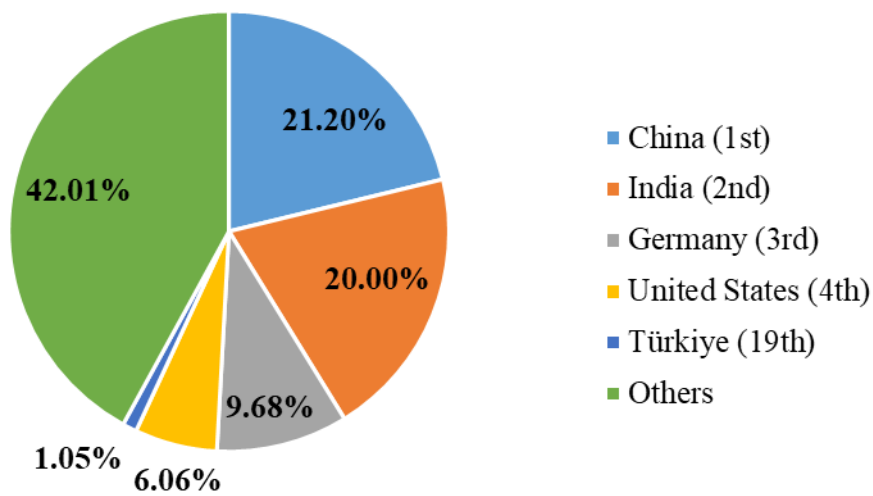
Dye	Health Effect	Reference
Malachite Green	Carcinogenic Mutagenic Teratogenic	(Srivastava et al., 2004)
Rhodamine-B	Eyes and skin infections Diseases of gastrointestinal	(Hamdaoui, 2011)
Brilliant Green	Shortness of breath Diseases of gastrointestinal Skin irritation	(Mane and Babu, 2011)
Crystal violet	Carcinogenic	(Belpaire et al., 2015)
Reactive Green 19	Genotoxic	(Leme et al., 2015)
Sunset Yellow	Allergies Kidney tumors Chromosomal damage	(Šuleková et al., 2017)
Methylene Blue	Cyanosis Tissue necrosis Enhanced heartbeat rate	(Oladoye et al., 2022)

Pharmacokinetic studies can help to understand the adsorption and biodistribution of toxic substances. Cheng and Tsai, (2016) carried out pharmacokinetic study of rhodamine B in animal. 1 mg/kg oral administration of rhodamine B did not cause pink urine in rats. In another study performed by Cheng and Tsai, (2017) 10 mg/kg oral administration of rhodamine B caused pink skin and urine and also red feces and it was observed that rhodamine B was mainly accumulated liver and kidney.

2.3 Dye Production and Economy

Synthetic dyes were the world's 262nd most traded product in 2021, with a total trade of \$15.5 billion (Figure 2.3). The export of these products was increased from \$12.5 billion to \$15.5 billion, with a grow rate of 24.2% between 2020 and 2021. China, India, Germany, United States were the top synthetic dye exporters. While Türkiye was the 19th biggest synthetic dye exporter, also was the 5th biggest synthetic dye importer (OEC, 2021).

a)



b)

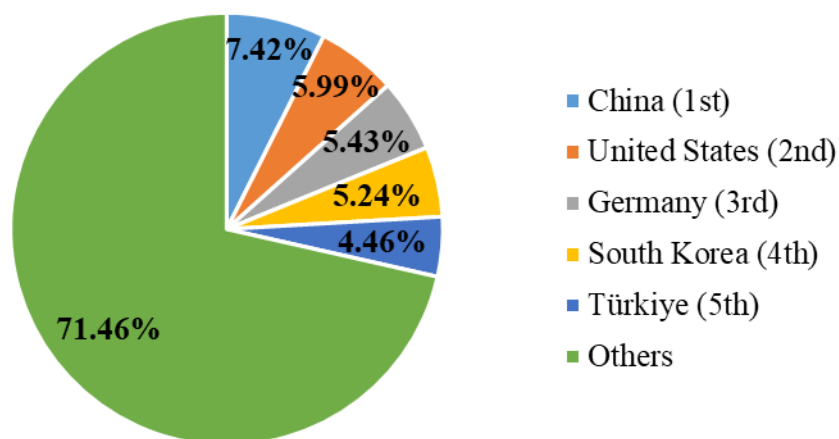


Figure 2.3 Global Synthetic Dye Trade a) Exporters b) Importers

Trade data of synthetic dyes focused on Turkish Market is given in Table 2.8. Türkiye exported synthetic dyes about \$163M in 2021 and Uzbekistan, Egypt, Pakistan, Iran, and Bangladesh were the top five target countries. On the other hand, Türkiye imported huge amount of synthetic dyes about a value of \$692M which was almost 4 times bigger than export value.

Table 2.8 Synthetic Dye Trade in Turkish Market (2020-2021)

Export Destination				Import Origin			
Rank	Country	Trade Value (\$)	Percentage (%)	Rank	Country	Trade Value (\$)	Percentage (%)
1	Uzbekistan	24.3M	14.8	1	India	249M	35.9
2	Egypt	20.1M	12.3	2	China	195M	28.2
3	Pakistan	16.9M	10.3	3	Germany	53.2M	7.69
4	Iran	10.5M	6.44	4	Switzerland	28M	4.05
5	Bangladesh	10.1M	6.21	5	Spain	22.6M	3.27
Sub total		81.9M	50.05	Sub total		547.8M	79.11
Total		163M	100	Total		692M	100

According to Istanbul Chemicals and Chemical Products Exporters' Association (İKMİB), export data of different dye types in 2021 and 2022 was tabulated in Table 2.9. While the export value of basic and direct dyes increased, the export value of other type of dyes decreased from 2021 to 2022.

Table 2.9 Comparison of export values of different dyes in Türkiye

Type of Dye	2021 (\$)	2022 (\$)	Change (%)
Basic dyes and preparations based thereon	337K	598K	77.66
Acidic dyes and preparations based thereon	244K	224K	-8.00
Dispersive dyes and preparations based thereon	1.24M	514K	-58.61
Direct dyes and preparations based thereon	631K	1.03M	63.95
Reactive dyes and preparations based thereon	3.03M	2.32M	-23.22
Vat dyes and preparations based thereon	228K	6.4K	-97.18

2.4 Rhodamine B

Rhodamine B (RB) is a reddish violet colored powder and a member of xanthene dye class. RB is chemically stable and non-biodegradable dye (Hamdaoui, 2011; Imam and Babamale, 2020). Due to good water solubility, brightness and stability, RB has been widely preferred in many industries mainly textile, painting, etc. (Al-Gheethi et al., 2022; Imam and Babamale, 2020).

RB is a preferable dye owing to its desirable properties; however, it can be hazardous to environment and health. Its carcinogenic and toxic effects may cause respiratory, gastrointestinal, skin and eyes problems. Exposure to RB by inhalation or ingestion may cause liver and thyroid problems, skin and eye irritation. (Bhat et al., 2020; Hamdaoui, 2011).

Although rhodamine B is commonly used in textile industry, it is forbidden used in food additives and cosmetic products (Li et al., 2013).

The discharging of effluents containing even 1 mg/L of rhodamine B, gives a powerful color to water makes it unsuitable for aquatic life and human consumption (Adegoke et al., 2022).

2.5 Water Treatment Methods

Due to their toxic effects, dye effluents pose a danger to animals and humans. Majority of dyes are carcinogenic and toxic which makes them hazardous to aquatic life, microorganism, and human health (Gao et al., 2018). Therefore, wastewater treatment is a crucial issue for the treatment of dyes effluents before it is discharged into water streams. These methods have been categorized as physical, chemical, biological and hybrid (Figure 2.4). The comparison of water treatment methods given in Table 2.10.

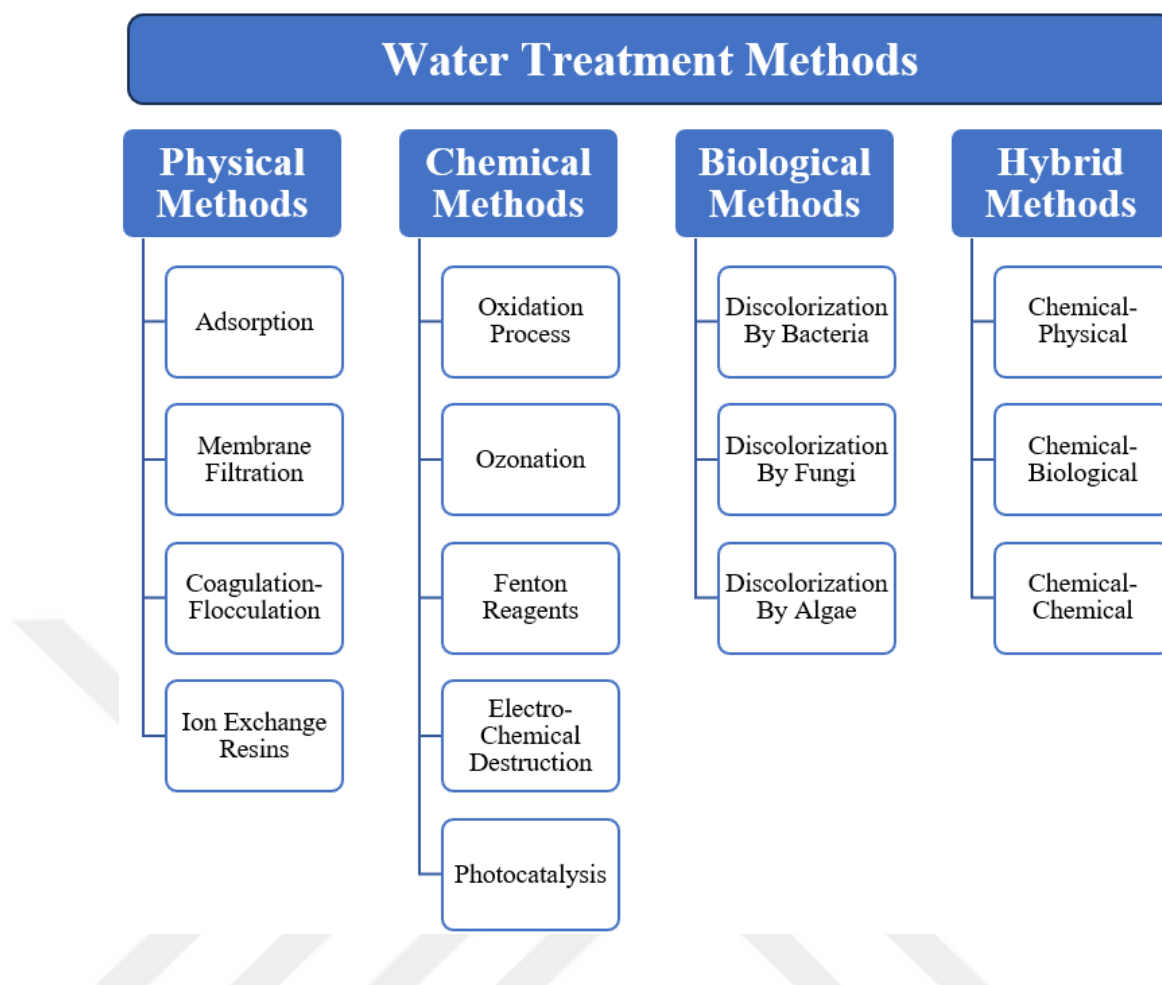


Figure 2.4 Methods for the treatment of dyes

Mass transfer process is the principle of physical treatment methods. Adsorption, membrane filtration and ion exchange are the common physical methods. In physical methods, less amount of chemicals is used rather than biological and chemical methods (Holkar et al., 2016).

Although the chemical techniques are more efficient than physical and biological techniques, these techniques require more capital and operating cost (Wang et al., 2017). After treatment process, hazardous by-products are formed (Katheresan et al., 2018). There are some constraints for biological techniques. Used biomass in these technique cannot be applicable for all types of dye removal (Noman et al., 2021).

Flocculation and coagulation, membrane filtration and ion exchange are also efficient physical methods in the dye removal. On the other hand, formation of toxic

secondary products, high energy demand, fouling, limited application are some disadvantages of these methods.

Among these techniques, owing to its high removal efficiency adsorption process is preferred in removal of dyes from wastewater and, also no hazardous by-products are formed at the end of process. One of the limitations of adsorption process is finding a suitable adsorbent. Developing a low-cost and efficient adsorbent makes the adsorption most applicable and best economical method in dye removal from the effluents (Kadirvelu et al., 2005; Naga Babu et al., 2019).



Table 2.10 Comparison of treatment methods

Treatment Method	Advantages	Disadvantages
Adsorption	• Convenient economy • High color removal	• Chemical derivation to boost their capacity • Regeneration issues
Membrane Filtration	• Removes all dye types • Small demand for space	• High maintenance and high energy demands • Fouling
Coagulation and Flocculation	• COD and BOD reduction • High applicability	• Includes the addition of non-reusable chemicals • High residual aluminum concentration
Ion Exchange	• Produce high quality of water • Low maintenance cost	• Applicable for limited number of dyes • Sensitive to pH
Incineration	• Highly effective • Degrade all types of dyes	• High operating cost • Formation of pollutants
Oxidation	• Fairly suitable dye removal method • Pollutant mineralization	• Takes long time • Technical limitations
Ozonation	• Effective and quick dye removal technique • Good decolorization and COD reduction	• High cost • Requires additional treatment for heavy metals
Electro-Chemical	• Space saving and high-performance processing • Direct or indirect oxidation flexibility	• High electricity demand • High price of electrical energy
Biological methods	• Convenient economy • Environmentally friendly	• Requires long time • Not applicable for all dyes

2.6 Adsorption

Adsorption is a physical technique which is widely used in water treatment. Adsorption can be described as the exchange of materials at the interface between two immiscible phases in contact with one another. Adsorbent is a porous material which has a high surface area and adsorbs substances by intermolecular forces onto its surface. The substance (e.g., dye molecules) adsorbed or attached is called the adsorbate. The detaching of substance from the adsorbent surface is called desorption (Premkumar et al., 2018).

Physical adsorption (Physisorption) can be described as the adsorption of molecules onto adsorbent by weak physical forces or van der Waal's forces. This type of adsorption called multi-layer adsorption and usually observed at low temperature. It has relatively low enthalpy of adsorption which is between 20–40 kJ/mol. Chemisorption (chemical adsorption) can be defined as the adsorption of molecules onto adsorbent by forming chemical bonds between adsorbent and adsorbate. In chemisorption, monolayer adsorption is observed and requires high temperatures and high value of enthalpy which is between 80-240 kJ/mol (Soliman and Moustafa, 2020).

External diffusion, internal diffusion, and adsorption on active sites are the three mass transfer steps of adsorption.

i) External diffusion, which is the transport of adsorbate from the bulk phase to the external surface of adsorbent.

ii) Internal diffusion, which is the transport of adsorbate from the external surface into the pores of adsorbent.

iii) Adsorption on active sites, which is the attachment of adsorbate to the active sites of adsorbent.

Adsorption capacity can be defined as the amount of adsorbate adsorbed by adsorbent per unit mass. Percent removal is an indicator that shows the performance

of adsorbent to remove adsorbate from the solution. The equations of adsorption capacity and percent removal are given below:

$$q_{exp} = \frac{C_i - C_f}{m} \times V \quad (\text{Eq. 1})$$

$$\text{Removal (\%)} = \frac{C_i - C_f}{C_i} \times 100 \quad (\text{Eq. 2})$$

where q_{exp} is the adsorption capacity (mg/g), C_i and C_f are the initial and final concentrations of solution (mg/L), m is the mass of adsorbent (g) and V is the volume of the solution (L).

2.7 Parameter Affecting Adsorption Capacity

Adsorption capacity depends on different factors. Optimization of these factors is important to achieve higher adsorption capacities. Contact time, initial concentration, pH, temperature, adsorbent dosage and background ions are the main parameters that have a great effect on adsorption capacity (Rápó and Tonk, 2021).

2.7.1 Contact time

Adsorbate removal rate increases generally with an increasing contact time. When all available sites on the adsorbent surface are deposited of adsorbate, the adsorption capacity will not be affected by time. At this point, the process reaches equilibrium and the time required to attain equilibrium called equilibrium time (Bharathi and Ramesh, 2013; Mohammad Razi et al., 2017; Salleh et al., 2011).

2.7.2 Initial concentration

Initial adsorbate concentration is strictly related to adsorption capacity and removal. With an increasing initial adsorbate concentration, the active sites on the adsorbent will be saturated and this led to a decrease in the percent removal. However, higher concentration difference will cause higher mass transfer driving

force which will increase the adsorption capacity (Dang Son et al., 2016; Soltani et al., 2021).

2.7.3 pH

pH of the solution, which has an important effect on the degree of ionization, surface charge density, and adsorption capacity of the adsorbent, is crucial for adsorption process. The adsorption capacity varies with the medium pH change, and it also depends on the characteristics of adsorbent and adsorbate (Salleh et al., 2011).

2.7.4 Temperature

Temperature is also an important factor for adsorption. It may have incremental or decremental effect on the adsorption capacity depending on the thermodynamic nature of the adsorption is exothermic or endothermic. For exothermic adsorptions, the increase of temperature will decrease the adsorption capacity because the forces between adsorbate and adsorbent will become weaker. On the contrary, for endothermic adsorptions, the active sites on the adsorbent and mobility of large adsorbate molecules will increase by temperature increasing which led to achieve higher adsorption capacities (Rápó and Tonk, 2021).

2.7.5 Adsorbent dosage

With an increasing adsorbent dosage, removal efficiency will also increase because of the increase in the active sites. Contrary, adsorption capacity will decrease because the amount of adsorbate per adsorbent will decrease. Adsorption efficiency should be optimized using minimum adsorbent dosage (Bushra et al., 2021).

2.7.6 Background ion

If electrostatic forces are attractive, the adsorption capacity reduces by increasing ionic strength. On the contrary, for repulsive forces, the adsorption capacity increases by increasing ionic strength (Bharathi and Ramesh, 2013).

2.8 Modeling

Models are critical to design adsorption processes. Interaction between adsorbate and adsorbent can be described and performance of adsorbent can be evaluated using modeling.

2.8.1 Kinetic modeling

The adsorption kinetic helps to understand the adsorption rate, performance of adsorbent and mass transfer mechanism. Adsorption kinetics can be described using the classical pseudo-first order (PFO), pseudo-second order (PSO) models, and Elovich model.

Pseudo first order (PFO) model

Pseudo first order model was firstly described by Lagergren (1898) to find out the adsorption mechanism.

$$q_t = q_l (1 - \exp(-k_l t)) \quad (\text{Eq. 3})$$

where k_l is the pseudo first order rate constant (min^{-1}), q_l is the theoretical adsorption capacity (mg g^{-1}), q_t experimental adsorption capacity (mg g^{-1}), and t is the time (min^{-1}).

Pseudo second order (PSO) model

Pseudo second order model is widely used to describe the adsorption mechanism, was firstly applied by Ho et al. (1996).

$$q_t = \frac{t}{\left(\frac{1}{k_2 q_2^2}\right) + \left(\frac{t}{q_2}\right)} \quad (\text{Eq. 4})$$

where k_2 is the pseudo second order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$), q_2 is the theoretical adsorption capacity (mg g^{-1}), q_t experimental adsorption capacity (mg g^{-1}), and t is the time (min^{-1}).

Elovich model

The Elovich model is an empirical model without physical meanings and described by Elovich and Larinov (1962).

$$q_t = \frac{1}{a} \ln(1+abt) \quad (\text{Eq. 5})$$

where a is Elovich's adsorption constant (g mg^{-1}), b is Elovich's first rate ($\text{mg g}^{-1} \text{min}^{-1}$), q_t experimental adsorption capacity (mg g^{-1}), and t is the time (min^{-1}).

2.8.2 Isotherm modeling

Adsorption isotherms are significant designing, optimizing, and troubleshooting. They describe the equilibrium performances of adsorbents. Freundlich, Langmuir, Redlich-Peterson, Toth and, Sips models are generally used to investigate the equilibrium of adsorption.

Freundlich model

The Freundlich model is an empirical equation without physical meaning and one of the most widely used isotherm in adsorption (Freundlich, 1906).

$$q_e = K_F C_f^{1/n} \quad (\text{Eq. 6})$$

where K_F is Freundlich constant $((\text{mg/g})(\text{L/mg})^{1/n})$, $1/n$ heterogeneity factor (dimensionless), q_e is the equilibrium adsorption capacity (mg g^{-1}) and C_f is the equilibrium concentration (mg L^{-1}).

Langmuir model

Langmuir isotherm was firstly used to describe the gas-solid adsorption (Langmuir, 1916). Langmuir model assumes equilibrium condition as monolayer homogeneous adsorption.

$$q_e = \frac{q_m K_a C_f}{1 + K_a C_f} \quad (\text{Eq. 7})$$

where q_m is the maximum adsorption capacity (mg g^{-1}), K_a is Langmuir constant (L mg^{-1}), q_e is the equilibrium adsorption capacity (mg g^{-1}) and C_f is the equilibrium concentration (mg L^{-1}).

Redlich-Peterson model

Redlich-Peterson model is a hybrid model that combines Langmuir and Freundlich models and empirical model. (Redlich and Peterson, 1959):

$$q_e = \frac{K_{RP} C_f}{1 + a_{RP} C_f^\beta} \quad (\text{Eq. 8})$$

where K_{RP} and a_{RP} are Redlich-Peterson constants (L mg^{-1} , $\text{L}^\beta/\text{mg}^\beta$), β is Redlich-Peterson exponent (between 0-1), q_e is the equilibrium adsorption capacity (mg g^{-1}) and C_f is the equilibrium concentration (mg L^{-1}).

Sips model

Another hybrid model that combines Langmuir and Freundlich models is Sips model and it can be used to describe both homogeneous and heterogeneous adsorption (Sips, 1948).

$$q_e = \frac{q_m K_{eq} C_f^n}{1 + K_{eq} C_f^n} \quad (\text{Eq. 9})$$

where q_m is the maximum adsorption capacity (mg g^{-1}), K_{eq} is Sips constant (L g^{-1}), n is the heterogeneity factor (dimensionless), q_e is the equilibrium adsorption capacity (mg g^{-1}) and C_f is the equilibrium concentration (mg L^{-1}).

Toth model

Toth model was proposed to widen the application of the Langmuir model (Toth, 1971).

$$q_e = \frac{q_T b_T C_f}{[1 + (b_T C_f)^{1/n_T}]^{n_T}} \quad (\text{Eq. 10})$$

where q_T is Toth maximum adsorption capacity (mg g^{-1}), b_T is Toth constant (L mg^{-1}), n_T is Toth exponent (dimensionless), q_e is the equilibrium adsorption capacity (mg g^{-1}) and C_f is the equilibrium concentration (mg L^{-1}).

2.9 Adsorption Thermodynamics

The standard change in Gibbs free energy (ΔG° , kJ mol^{-1}) can be calculated from Equation 11. The relationship between Gibbs free energy and the standard change in enthalpy (ΔH° , kJ mol^{-1}) and the standard change in entropy (ΔS° , $\text{kJ mol}^{-1} \text{ K}^{-1}$) is given in Equation 12. The combination of Equation 11 and 12, a linear expression is formed (Equation 13). From this linear form, ΔH° and ΔS° can be obtained from slope and intercept by plotting ΔG° vs $1/T$ graph.

$$\Delta G^\circ = -RT \ln(K_0) \quad (\text{Eq. 11})$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (\text{Eq. 12})$$

$$\ln(K_0) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (\text{Eq. 13})$$

where K_0 is the adsorption equilibrium constant (dimensionless), T is the temperature (K), and R is the universal gas coefficient ($8.31 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$).

The feasibility of adsorption can be predicted from ΔG° , if $\Delta G^\circ < 0$ adsorption can be considered as feasible and spontaneous, if $\Delta G^\circ > 0$ adsorption can be considered as non-feasible and non-spontaneous. ΔH° indicates the nature of process. If $\Delta H^\circ < 0$ adsorption can be considered as exothermic behavior, if $\Delta H^\circ > 0$ adsorption can be considered as endothermic behavior (Doke and Khan, 2013).

The positive values of ΔS° shows the increased randomness at the solid/solution interface with some structural changes in the adsorbate and the adsorbent. The negative values of ΔS° indicates a decreased disorder at the solid/liquid interface during the adsorption process causing the adsorbate ions/molecules to escape from the solid phase to the liquid phase (Saha and Chowdhury, 2011).

2.10 Activated Carbon

The most important factor is selection of adsorbent for successful and effective adsorption process. Activated carbon is a proficient adsorbent for wastewater treatment and it has proven adsorption performance owing to its large surface area and porous structure. To remove synthetic and naturally occurring pollutants, activated carbons have been employed in many studies as adsorbent (Ifelebuegu et al., 2015; Isoda et al., 2014).

It has been discussed that developing low-cost adsorbent with high removal capacity as activated carbon for water treatment in scientific community. The researchers are searching for inexpensive and effective adsorbents from waste materials. Agricultural wastes can be used to produce adsorbents since these wastes are generated in large quantities around the world (Al-Gheethi et al., 2022; Nascimento et al., 2021).

High carbon content makes agriculture wastes are commonly preferable to prepare activated carbon and biochar. Even though agricultural wastes have no

economic value, turning them into activated carbon helps to provide new, inexpensive adsorbent which is efficient in removal of dyes from contaminated waters (Okieimen et al., 2007). Its porous structure and functional groups makes agricultural wastes a good candidate in adsorption of dyes (Dai et al., 2018).

As shells, stones and also parts of plants can be used to produce activated carbon. Aquatic biomass also can be a precursor in adsorbent development. Prior to activating a chosen precursor material, carbonization, a thermal process also known as pyrolysis, is used to enhance the carbon content under inert atmosphere. Activation of the biowaste, increasing porosity and the number of functional groups of the activated carbon requires additional physical, chemical, or physico-chemical treatments (Mariana et al., 2021; Mistar et al., 2020).

Activated carbon can be produced in two ways, the first is carbonization and the second is chemical impregnation followed by carbonization. Generally, carbonization takes place under 800 °C and in inert atmosphere. To obtain activated carbon has higher surface area, chemical activation is necessary. In Figure 2.5, a summary of biomass conversion to activated carbon is shown.

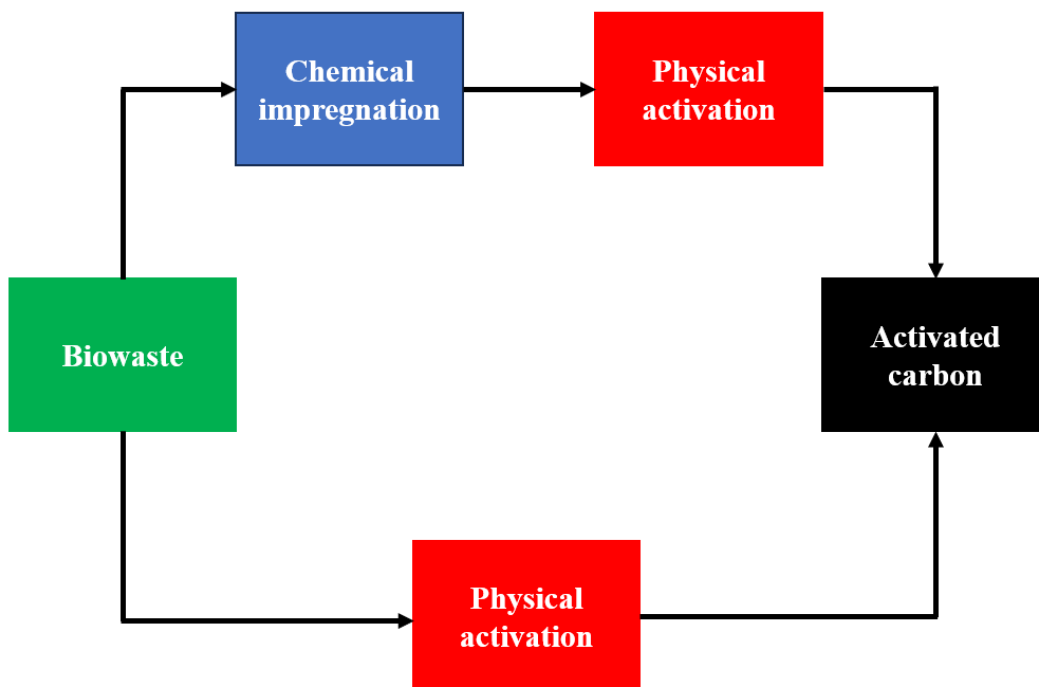


Figure 2.5 Schematic illustration of activated carbon production

Activated carbon can be obtained from different precursors. Cassava slug, banana peel, walnut shell, and pumpkin peel were utilized in dye removal studies. For the removal of pharmaceutical preparations, adsorbent was developed from shiitake mushroom, kola nut husks, orchard pruning residues, peanut shell. Apple shell, sesame stalk, orange peel, and sugar cane bagasse were used in pesticide removal studies. In heavy metal ion adsorption studies, plum stone, tea waste, cauliflower leaves, and date bead were the precursors of adsorbent development. In Table 2.11, the studies about developing activated carbon from different the agriculture waste sources to remove different pollutant types are listed.



Table 2.11 Biobased adsorbent studies for removal different types of pollutants

Pollutant type	Precursor	Activator	Adsorbate	q_{max} (mg/g)	References
Dyes	Walnut shell	-	Malachite Green	90.80	(Dahri et al., 2014)
	Banana peel powder	-	Reactive Black 5	49.20	(Munagapati et al., 2018)
	Pumpkin peel	HNO ₃	Methylene blue	198.15	(Rashid et al., 2019)
	Cassava slug	-	Rhodamine B	105.30	(Wu et al., 2020)
Pharmaceutical preparations	Orchard pruning residues	-	Diclofenac	7.25	(Y. Li et al., 2019)
	Shiitake mushroom	-	Paracetamol	34.20	(Menk et al., 2019)
	Peanut shells	-	Naproxen	324.00	(Tomul et al., 2020)
	Kola nut husks	H ₃ PO ₄	Ibuprofen	39.68	(Bello et al., 2021)
Pesticides	Apple shell	-	2,4-DP	40.08	(Okumuş et al., 2015)
	Sesame stalk	ZnCl ₂	2,4-D	36.16	(Kırbıyık et al., 2017)
	Orange peel	KOH	2,4,5-T	414.93	(Pandiarajan et al., 2018)
	Sugar cane bagasse	Acetone	Chlorpyrifos	3.20	(Jacob et al., 2020)
Heavy metal ions	Date bead	ZnCl ₂	Pb(II)	76.92	(Danish et al., 2011)
	Plum stone	H ₃ PO ₄	Cu(II)	48.31	(Parlayıcı and Pehlivan, 2017)
	Cauliflower leaves	-	Cd(II)	73.80	(Ahmad et al., 2018)
	Tea waste	NaOH	Cr(VI)	139.50	(Kabir et al., 2021)

2.11 Olive Stone

Olive tree (*Olea europaea* L.) is cultivated around the world. Almost 98% of the world's production settled in Mediterranean Region that makes olive is an important agricultural product of the Mediterranean countries (Calvano and Tamborrino, 2022).

Olive oil production in 2020/2021 crop year is given in Table 2.12 (IOC, 2021). Spain is the leader olive producer country in the world and meets approximately 50% of global olive oil production. Türkiye is the fourth biggest olive oil producer globally as it can be seen from the table. Türkiye is one of the world's leading olive and olive oil producers, along with other Mediterranean countries due to their geographical locations and Mediterranean climate characteristics.

Table 2.12 2020/2021 crop year olive oil production

Country	Production (tons, thousands)	Percentage of total (%)
Spain	1,300	46.83
Italy	315	11.35
Tunisia	240	8.65
Türkiye	228	8.21
Greece	225	8.11
Morocco	200	7.20
Portugal	120	4.32
Algeria	98	3.53
Argentina	30	1.08
Egypt	20	0.72

Besides the olive oil, different types of by-products can be obtained during pruning and harvesting of olive trees. From 1 hectares of olive trees, approximately 2500 kg of olives can be harvested which yields 500 kg of olive oil and 2000 kg of pomace. This pomace includes 400 kg olive stones, 40 kg pomace oil, 260 kg

pomace dry residues and 1300 kg wastewater. These agricultural wastes can be utilized in many applications (Espeso et al., 2021).

Since Türkiye is one of the biggest olive producers, huge amount olive by-products are available. It was aimed to use olive stone, one of the by-products in olive oil production, as an adsorbent by activating chemical and physical methods in this study.

2.12 Production of Olive Stone Activated Carbons

Olive stone based activated carbons used in this study were develop by Dr. Duygu OVA ÖZCAN in a previous study. The procedure for olive stone based activated carbon is given in Figure 2.6.

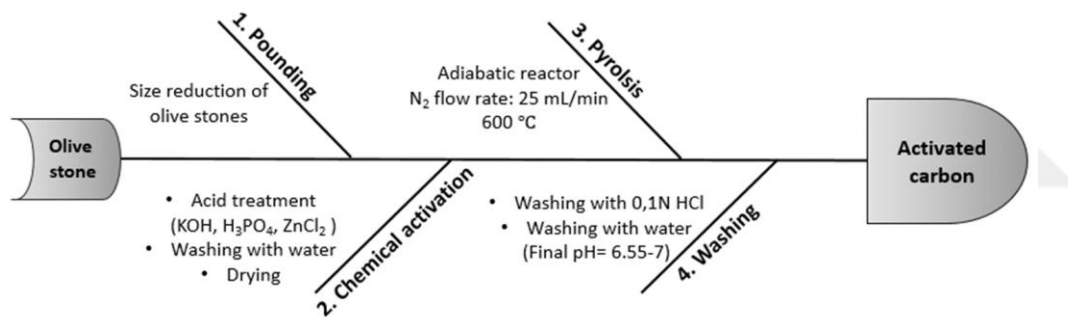


Figure 2.6 Olive stone activated carbon process

Firstly, olive stones, obtained from Tariş Olive Oil Factory (Aydın, Türkiye), were grinded and their particle size was reduced. Next, olive stones were impregnated with different acids such as ZnCl_2 , KOH , H_3PO_4 with 1:1.5 solid-liquid ratio then, washed with deionized water and impregnated olive stones were dried at 300°C . As a third step, pyrolysis process was carried out at 600°C temperature and 25 mL/min N_2 flow rate 7°C/min for 2 hours in an adiabatic reactor. At the end of pyrolysis, 0.1 N HCl solution and then, water was used to wash olive stones until neutral pH reached. After complete drying of olive stone activated carbons were ready to use in adsorption studies.

2.13 Olive Stone Activated Carbon and Rhodamine B Adsorption Studies

In Table 2.13 and Table 2.14, the adsorption studies about developing olive by-products based activated carbon and Rhodamine B removal are listed. Albanio et al., (2021) used olive stone impregnated with ZnCl_2 to remove Rhodamine B and the maximum adsorption capacity was 263.71 mg/g. Boukerzaza et al., (2021) carried out a study using olive stone without any thermal or chemical activation to remove Rhodamine B and achieved maximum adsorption capacities was 86.20 mg/g. When these two studies were compared, it can be said that activation has a crucial role to achieve higher adsorption capacity.

Walnut shell, paper waste, coconut coir, pomegranate peel, tapioca peel, sugarcane bagasse, olive pomace, waste tire scraps, bamboo shell, cassava slag, rosemary waste, and olive tree waste were used as precursor in Rhodamine B removal studies. Different types of chemical activators such as H_2SO_4 , CH_2O_2 , HCl , NaOH , H_3PO_4 , and ZnCl_2 were used to impregnate the biowaste. The achieved maximum adsorption capacities were between 2.29 and 263.71 mg/g.

Table 2.13 Adsorption studies with olive by-products activated carbon

Precursor	Thermal activation	Chemical activation	Adsorbate	t (min)	c_0 (mg/L)	pH	T (°C)	q_{max} (mg/g)	Reference
Olive stone	Yes	H ₃ PO ₄	Cu(II) Cd(II) Pb(II)	0-600	0.5-5 mmol/L	2-6	30	17.66 57.10 147.52	(Bohli et al., 2015)
Olive stone	-	-	Cu(II) Cd(II) Pb(II) Cr(VI)	0-120	1-10	6	20	0.56 0.30 0.58 2.34	(Amar et al., 2020)
Olive stone	Yes	-	Methylene blue	0-1440	50-1000	2-10	25	714.00	(Al-Ghouti and Sweleh, 2019)
Olive stone	Yes	ZnCl ₂	Methylene blue Methyl orange	0-1440	30-1000	2-12	25	303.00 277.80	(Mahmoudi et al., 2020)
Olive tree waste	Yes	ZnCl ₂	Rhodamine B	0-240	50-250	4.3	25, 35, 45	263.71	(Albanio et al., 2021)
Olive pomace	-	-	Rhodamine B	0-180	300-700	2-10	5, 22, 40	86.20	(Boukerzaza et al., 2021)

Table 2.14 Rhodamine B adsorption studies

Precursor	Thermal activation	Chemical activation	t (min)	c_0 (mg/L)	pH	T (°C)	q_{max} (mg/g)	Reference
Walnut shell	Yes	H ₂ SO ₄	0-120	10-60	2-8	40, 50, 60, 70, 80	2.29	(Shah et al., 2013)
Paper waste	No	H ₂ SO ₄	0-120	50	4.4	35, 40, 45	6.71	(Thakur and Kaur, 2017)
Coconut coir	Yes	CH ₂ O ₂ , HCl	0-60	50-100	7	25, 35, 45	22.00	(Nascimento et al., 2021)
Pomegranate peel	-	-	0-300	100	-	25, 35, 45	30.47	(Ghibate et al., 2021a)
Tapioca peel	Yes	-	0-150	25-150	2-10	25	33.10	(Vigneshwaran et al., 2021)
Sugarcane bagasse	-	-	0-1440	100-500	4-10	30, 40, 50	65.50	(Zhang et al., 2013)
Olive pomace	No	-	0-180	100-700	2-10	20	79.80	(Boukerzaza et al., 2021)
Waste tire scraps	Yes	-	0-210	2.5-15	3-10	20, 30, 40	85.26	(Özüdoğru, 2021)
Bamboo shell	Yes	HCl	0-180	2-300	-	0, 25, 40	85.50	(Hou et al., 2019)
Cassava slag	Yes	NaOH, H ₂ O ₂	0-720	25-500	2-12	35, 45, 55	105.30	(Wu et al., 2020)
Rosemary waste	Yes	H ₃ PO ₄	0-60	10-40	2-10	25, 35, 45, 55	125.00	(Naboulsi et al., 2023)
Olive tree waste	Yes	ZnCl ₂	0-240	50-250	4.3	25, 35, 45	263.71	(Albanio et al., 2021)

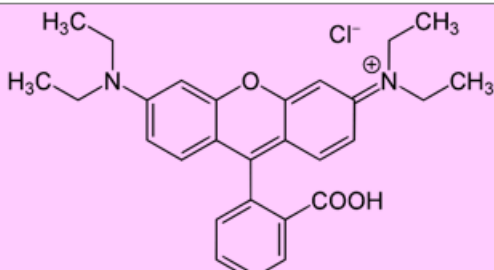
3.0 MATERIAL AND METHODS

3.1 Materials

3.1.1 Reagents

Rhodamine B dye ($C_{28}H_{31}N_2O_3Cl$, RB, Merck) was used as contaminant and in Table 3.1 its properties are given.

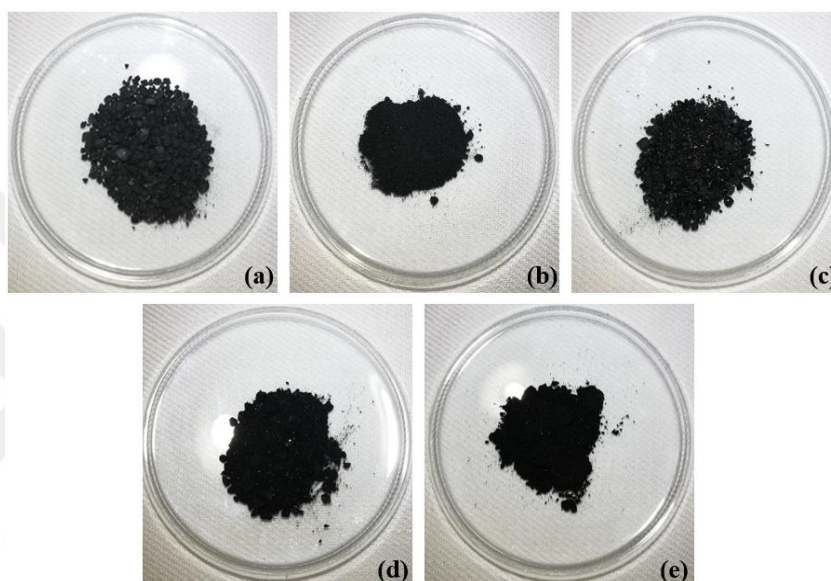
Table 3.1 Properties of Rhodamine B

IUPAC Name	[9-(2-carboxyphenyl)-6-diethylamino-3-xanthenyldenediethylammonium chloride]
Common Name	Rhodamine B
Molecular formula	$C_{28}H_{31}ClN_2O_3$
Molecular weight	479.02 g/mol
Solubility in water	5 g/ 100 mL
CAS number	81-88-9
Molecular structure	

The olive stone based activated carbons (OSACs) used in this study were produced in a previous study performed by Dr. Duygu Ova Özcan. Powdered activated carbon (PAC, Sigma-Aldrich) was used to compare the removal performances of OSACs. In Table 3.2, the activation methods of produced OSACs and PAC are listed and in Figure 3.1, their pictures are given.

Table 3.2 Activated carbons used in this study

Activated carbon	Activation method
OSAC	Carbonization
KOSAC	Chemical (KOH) + Carbonization
ZOSAC	Chemical (ZnCl ₂) + Carbonization
HOSAC	Chemical (H ₃ PO ₄) + Carbonization
PAC	Analytical

**Figure 3.1** Activated carbons **a)**OSAC **b)**KOSAC **c)**ZOSAC **d)**HOSAC **e)**PAC

Deionized water, obtained from Ege University Chemical Engineering Department Laboratory, was used to prepare RB solution and in Table 3.3 the properties of deionized water are given.

Table 3.3 Characteristics of deionized water

Property	Value
pH	7.5
Conductivity	2.5 μ S/cm
Salinity	0%
Total Dissolved Solids (TDS)	1.1 mg/L

pH of solutions was modified by NaOH and HCl (Merck). KCl, NaCl, CaCl₂, MgCl₂, KNO₃, K₂SO₄ and KCH₃COO were used as background ions. All chemicals were analytical purity.

3.1.2 Instruments

The equipment used in the experiments were scale (AND HM-200, 0.0001 sensitivity) and water bath shakers (Memmert WNB 7-45, P Selecta Unitronic OR). pH of solutions was measured by pH meter (WTW pH 330). The concentration of RB was determined using UV spectroscopy where the maximum absorbance peak observed at 556 nm (PG Instruments T80).

3.2 Methods

3.2.1 Characterization of activated carbons

A set of 8 sieves with different mesh sizes (2000, 1000, 500, 250, 150, 106, 75 and 45 μm) was used to determine the particle size of ACs. 1 g of AC sample was poured onto the top sieve and shook for 10 minutes. At the end of the shaking period, each sieve was weighed individually, and the weight of the AC remaining in each sieve was calculated. Fourier Transform Infrared (FT-IR) spectroscopy was used to identify the functional groups of ACs before and after adsorption with a wavelength range of 600-4000 cm^{-1} (Perkin Elmer A100).

3.2.2 Preparation of stock solutions

RB stock solution with a concentration of 1000 mg/L was prepared by dissolving RB in deionized water. To determine the concentration of RB, UV spectroscopy was used, and maximum characteristic peak was found as 556 nm (see Figure 3.2). The solution was diluted into standard solutions (1-5 mg/L) and the calibration curve was prepared (see Figure 3.3 and Figure 3.4).

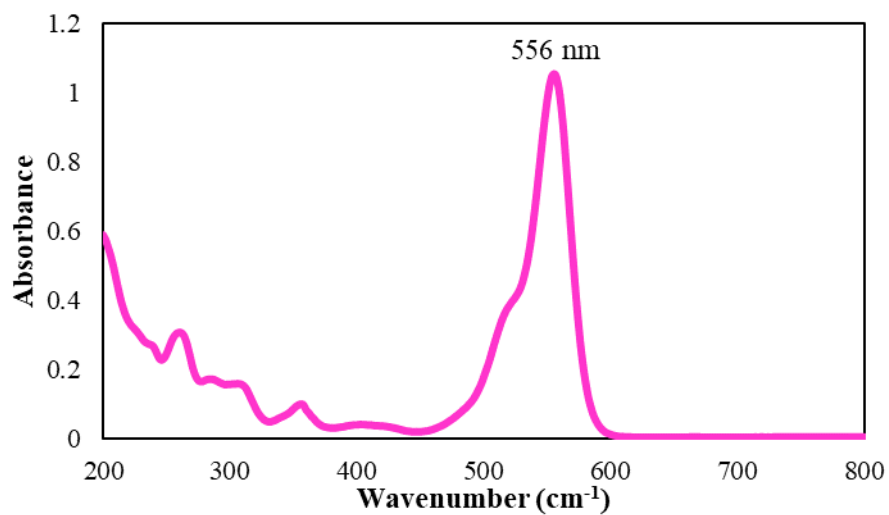


Figure 3.2 RB UV spectrum



Figure 3.3 RB stock solution and standard solutions

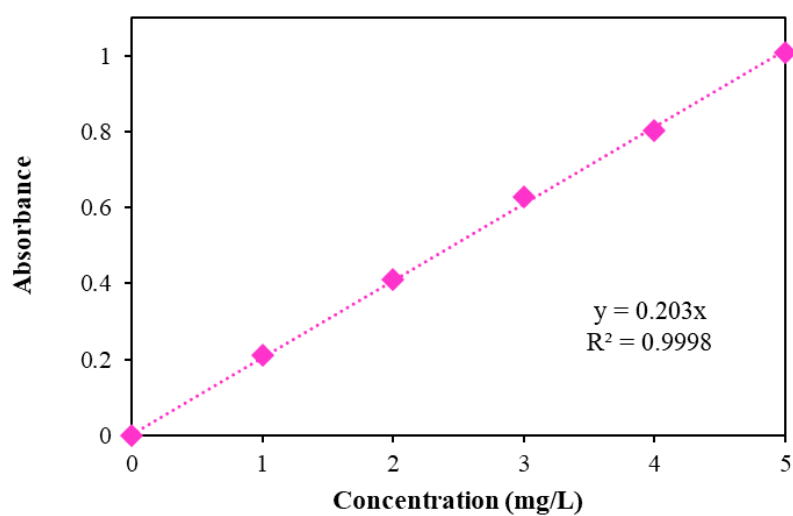


Figure 3.4 Calibration curve of RB

3.2.3 Adsorption experiments

The adsorption experiments were performed using the batch method. The effects of time, initial contaminant concentration, pH, temperature and adsorbent dosage on adsorption capacity of ACs were investigated. A certain amount of ACs was weighed into Erlenmeyer flasks then, 50 mL of solution was added. The Erlenmeyer flasks were placed into water bath shaker and agitated at 90 rpm for different time ranges (1, 2, 3, 4, 5, 6, 18 hours), different concentrations (10, 50, 100, 150, 200, 300 mg/L), different pH (2, 4, 6, 8, 10), different temperatures (30, 40, 50 °C) and different adsorbent dosage levels (0.01, 0.02, 0.05, 0.1 g). 100 ppm of KCl, NaCl, CaCl₂, MgCl₂, KNO₃, K₂SO₄ and KCH₃COO solutions were used to investigate the background electrolytes on RB adsorption. After shaking, the AC was separated from the solution using filter paper and then the filtered solution was taken to find the concentration of contaminant using UV spectroscopy. Experiment steps were shown in Figure 3.5.

The adsorption capacity (amount of contaminant adsorbed) and removal efficiency were calculated using equations below:

$$q_{exp} = \frac{C_i - C_f}{m} \times V \quad (\text{Eq. 1})$$

$$\text{Removal (\%)} = \frac{C_i - C_f}{C_i} \times 100 \quad (\text{Eq. 2})$$

where q_{exp} is the adsorption capacity (mg/g), C_i and C_f are the initial and final concentrations of solution (mg/L), m is the mass of adsorbent (g) and V is the volume of the solution (L).

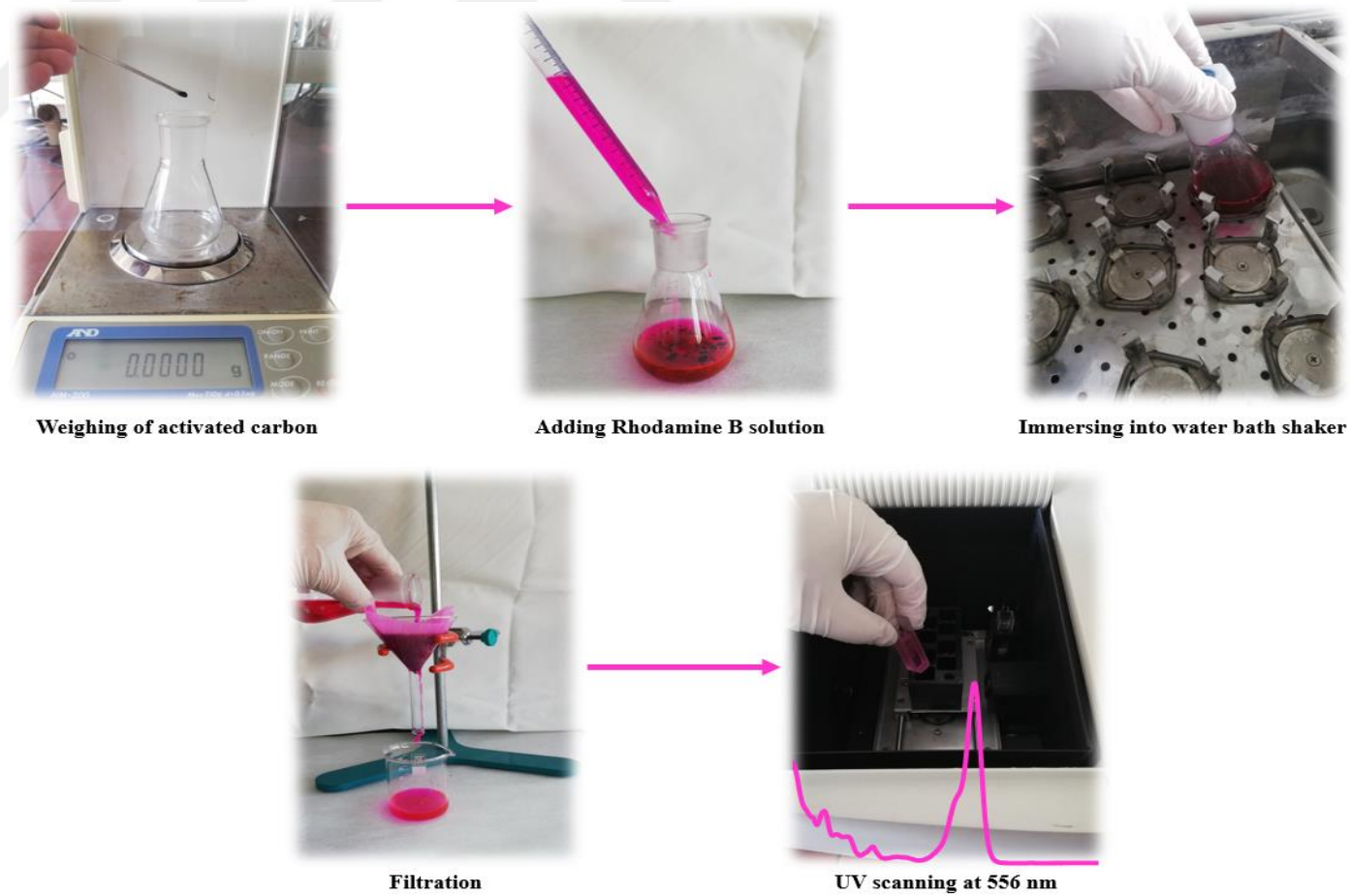


Figure 3.5 Adsorption experiment steps

3.2.4 Modeling

The kinetic and isotherm equations were modeled using *Curve Fitting Tool* in *MATLAB*.

3.2.4.1 Kinetic modeling

Elovich, pseudo first order (PFO) and pseudo second order (PSO) models were used for kinetic modeling.

3.2.4.2 Isotherm modeling

Langmuir, Freundlich, Redlich-Peterson, Toth and Sips models were used for isotherm modeling.

3.2.5 Thermodynamic calculations

ΔH° and ΔS° can be obtained from slope and intercept by plotting ΔG° vs $1/T$ graph.

3.2.6 Optimization study

To investigate the effects of temperature and concentration on adsorption capacity, *Design Expert* software was used. Analysis of Variance (ANOVA) was performed by developing a quadratic mathematical model. The significance of model terms and goodness of fit were determined by correlation coefficient (R^2), F-values and P-values. Optimum conditions were determined for maximum adsorption capacity.

3.2.7 Regeneration (desorption) study

To investigate the reusability, RB loaded activated carbons were regenerated by using 0.1 M NaOH solution as eluant. After each cycle of adsorption and desorption, % removal of RB was calculated. The cycles were repeated 5 times.

4.0 RESULTS AND DISCUSSION

4.1 Characterization of activated carbons

By performing sieve analysis, average particle size of activated carbons was determined. After calculating weights of activated carbons in each sieve, average particle size was found plotting histogram of data. In Table 4.1, the average particle sizes are listed.

Table 4.1 Average particle size of activated carbons

Activated carbon	Average particle size, D (μm)
OSAC	568.80±388.10
KOSAC	218.90±171.50
ZOSAC	422.30±391.60
HOSAC	663.30±375.00
PAC	135.10±38.93

Average particle size of activated carbons can be ordered from largest to smallest as follows:

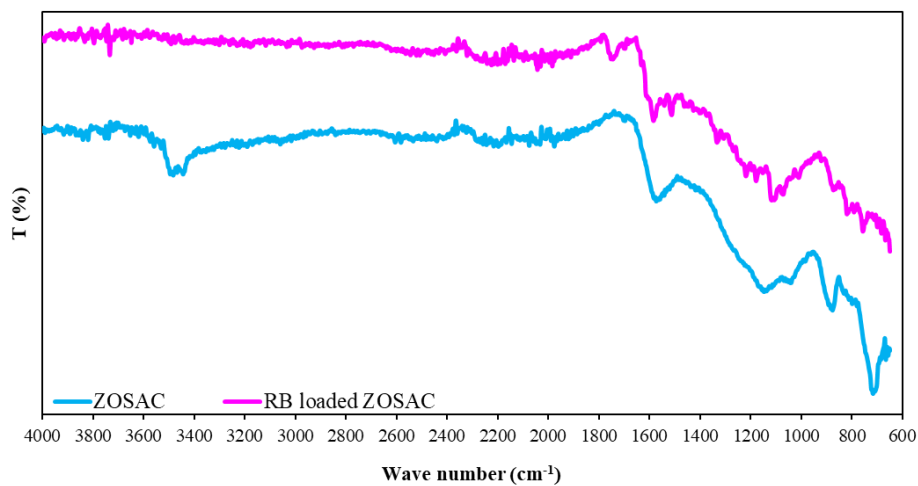
$$D_{\text{HOSAC}} > D_{\text{OSAC}} > D_{\text{ZOSAC}} > D_{\text{KOSAC}} > D_{\text{PAC}}$$

It can be said that HOSAC, OSAC and ZOSAC are more like granular form, while KOSAC and PAC are more like powdered form.

FT-IR analysis was used to identify the activated carbons and determine the functional groups. FT-IR spectra of OSACs and PAC are given in Figure 4.1 and their functional groups are tabulated in Table 4.2.

Table 4.2 Characteristic FT-IR peaks for OSAC and PAC

Adsorbent	Functional group	Wave number (cm ⁻¹)	Reference
OSAC	C-O stretching C-N bending	1170	(Al-Ghouti and Sweleh, 2019)
	N-H stretching	1560, 1590	(Al-Ghouti and Sweleh, 2019)
	C=O stretching	1650	(Mahmoudi et al., 2020)
	C=C stretching	2160	(Al-Ghouti and Sweleh, 2019)
	O-H stretching	3450	(Mahmoudi et al., 2020)
PAC	N-H bending	825	(Gondek et al., 2021)
	C-H bending	880	(Gondek et al., 2021)
	C-N stretching	1060, 1090, 1235	(Shang et al., 2015)
	CH ₃ symmetric bending	1460-1415	(Rajak et al., 2018)
	C=C stretching C-C stretching	1590	(Mehrasbi et al., 2009)
	CO ₂ asymmetric stretching	2380	(Gondek et al., 2021)
	O-H stretching	3450	(Gondek et al., 2021)

a)

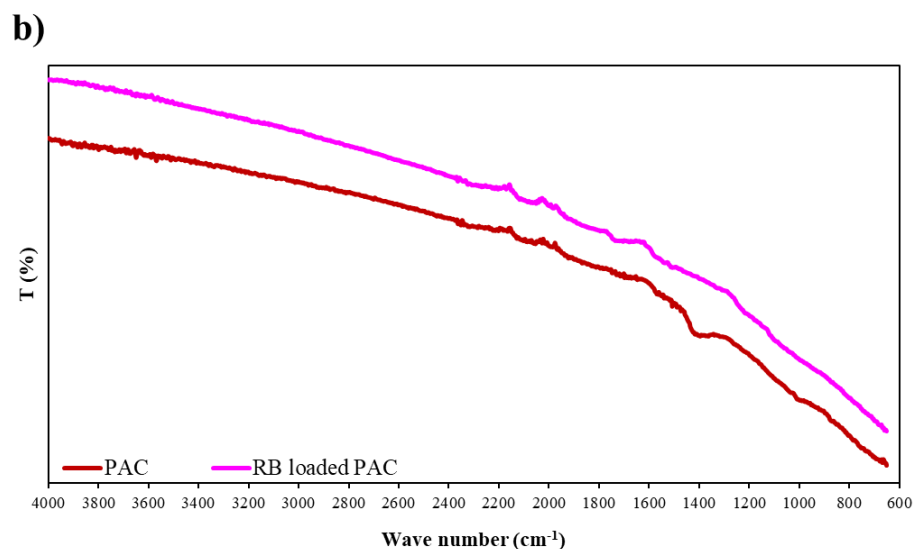


Figure 4.1 FT-IR spectra of a) ZOSAC b) PAC before and after RB adsorption

The presence of the band at 3450 cm^{-1} is related to O-H stretching comes from absorbed water onto the material. This band is only seen in the structure of ZOSAC. The peak at 2160 cm^{-1} confirms the presence of C=C stretching. The peak around 1650 cm^{-1} can be related to C=O stretching. Two peaks at 1560 and 1590 cm^{-1} are N-H stretching belongs to amine group in the structure. The peak at 1170 cm^{-1} is related to C-O stretching and C-N bending.

For PAC, the weak peak at 2935 cm^{-1} is the asymmetric C-H stretching vibration of CH_2 . Absorption at a wave number of 2380 cm^{-1} can be related to CO_2 asymmetric stretching vibration. The peak observed at 1590 cm^{-1} is to the effect of C=C stretching at the aromatic C-C bond. The peaks at 1460 and 1415 cm^{-1} are due to the symmetric bending of CH_3 . The peaks around 1235 , 1090 , and 1060 cm^{-1} can be ascribed to C-N stretching in aromatic tertiary amines. The peak 880 cm^{-1} indicates C-H out-of-plane bending in an aromatic ring. The band at 825 cm^{-1} is a result of N-H out of plane bending vibration.

4.2 Adsorption experiments

4.2.1 Effect of contact time

Contact time was studied with a time range of 1 to 18 hours. It can be said that the adsorption capacities of ACs were increased gradually between 1 and 6

hours, however, after 6 hours there was no significant increment in adsorption capacity (Figure 4.2). It can be explained that available active sites on the activated carbon's surfaces and higher mass gradients at the initial stages of adsorption (Georgin et al., 2021; Kabir et al., 2021)

When the adsorption capacities of adsorbents are compared, the order of adsorption capacity (mg/g) from the highest and lowest is:

$$q_{PAC} (254.30) > q_{ZOSAC} (190.67) > q_{KOSAC} (118.26) > q_{HOSAC} (49.81) > q_{OSAC} (21.57)$$

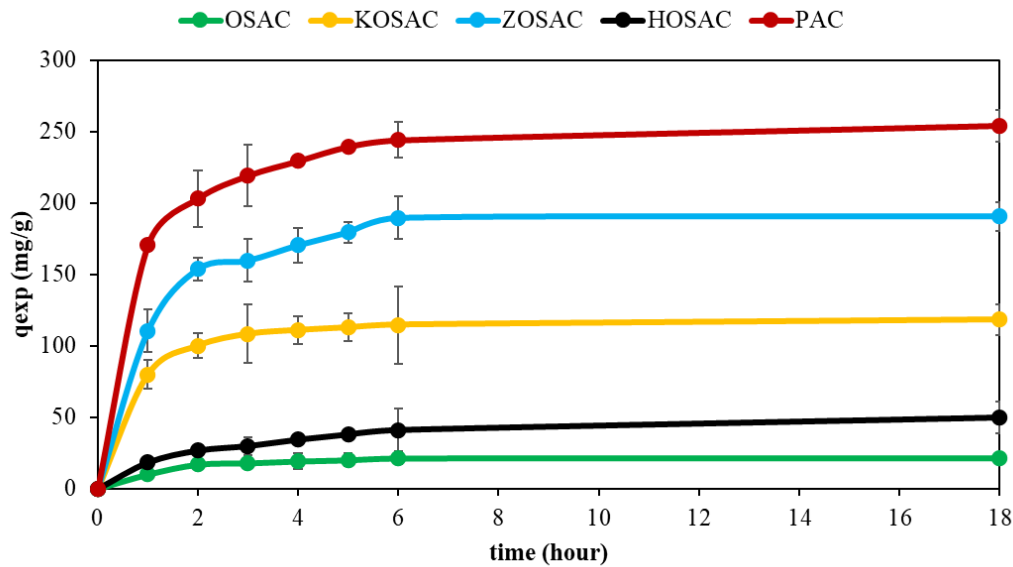


Figure 4.2 Effect of contact time on adsorption

Different levels of adsorption capacity can be associated with the steric hindrance effect of adsorbate and pore sizes of activated carbons (Wu et al., 2020). Larger molecules like RB could block attaching of other RB molecules to the active sites and this led to lower adsorption capacity. On the other hand, activated carbon with larger pore size will allow RB to reach active sites on the adsorbent, higher adsorption capacity could be achieved.

For further adsorption studies, ZOSAC and PAC were selected as adsorbents due to their high adsorption capacities and the equilibrium time was determined as 6 hours for next studies.

4.2.2 Effect of initial concentration

Initial contaminant concentration is another factor and plays an important role in adsorption. Figure 4.3 shows the isotherm study results with a concentration range of 10-300 mg/L. It can be said that the adsorption capacity was increased proportionally with initial concentration. The increment in concentration led to achieving higher adsorption capacities for both adsorbent. The higher pollutant concentration causes a higher driving force which accelerates the mass transfer from solution to adsorbate (Batoool and Valiyaveetil, 2021; Hou et al., 2019; Tang et al., 2021).

At $c_i=200$ mg/L, maximum values of the adsorption capacities were achieved which were 279.90 mg/g and 229.20 mg/g for PAC and ZOSAC, respectively. Higher than 200 mg/L initial concentration, adsorption capacity remained the same.

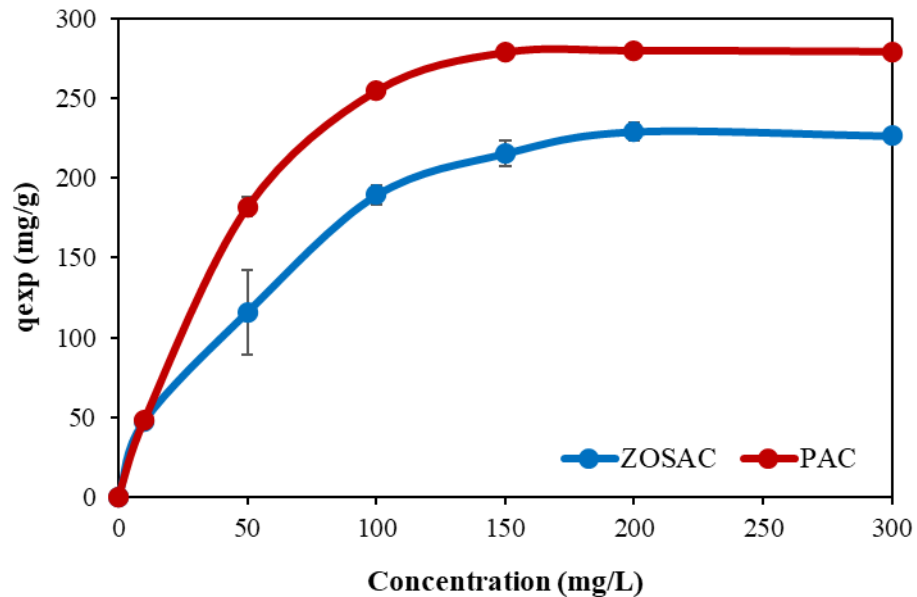


Figure 4.3 Effect of initial concentration on adsorption

4.2.3 Effect of pH

As another important parameter, pH was studied between 2-10, and the experimental results were given in Figure 4.4. It can be said that pH is not effective on adsorption capacity. The highest adsorption capacity for both ZOSAC and PAC was achieved at pH 4 which were 190 and 255 mg/g, respectively. Zhang et al., 2013 and Shah et al., 2013 also achieved the maximum RB adsorption capacity at pH 4. Since RB is in cationic and monomeric molecular structure, RB can enter easily into the activated carbon's pores at acidic medium rather than alkaline medium (Bello et al., 2019).

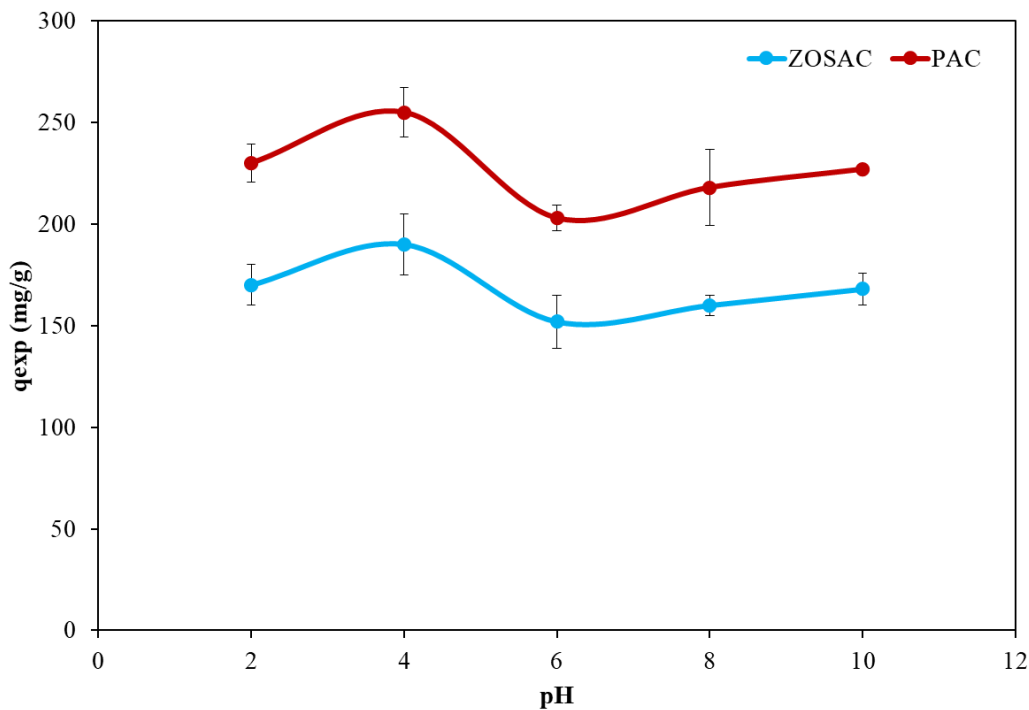


Figure 4.4 Effect of pH on RB adsorption

4.2.4 Effect of temperature

The effect of temperature on adsorption capacity by ZOSAC and PAC was studied at three different temperature levels (30, 40, 50 °C). According to Figure 4.5 and Figure 4.6, the adsorption capacities of ZOSAC and PAC were increased with temperature, so, the nature of the adsorption is determined as endothermic.

The adsorption capacities increased from 227 mg/g to 254.9 mg/g for ZOSAC and from 234 mg/g to 263.4 mg/g for PAC. The reason for this increment could be that the increment in the temperature increases the mobility of RB molecules and promotes the diffusion rate of RB molecules onto activated carbon's surface (Gören et al., 2021; He et al., 2022).

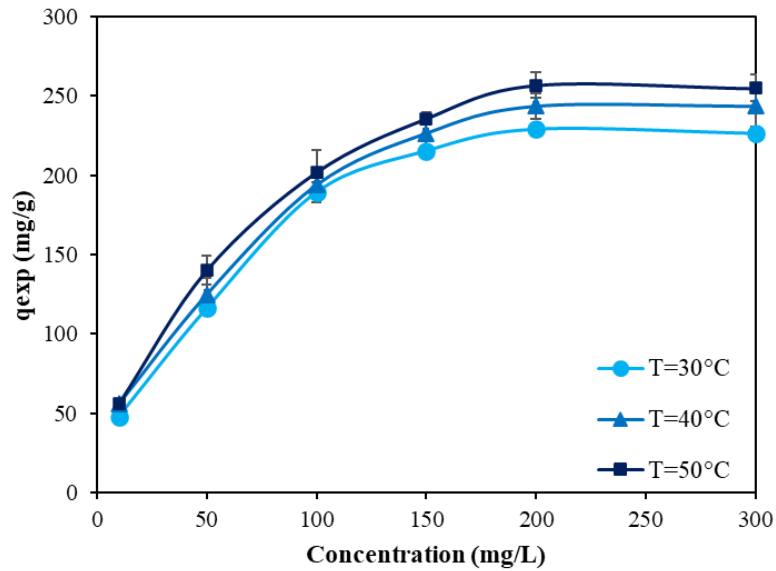


Figure 4.5 Effect of temperature on adsorption by ZOSAC

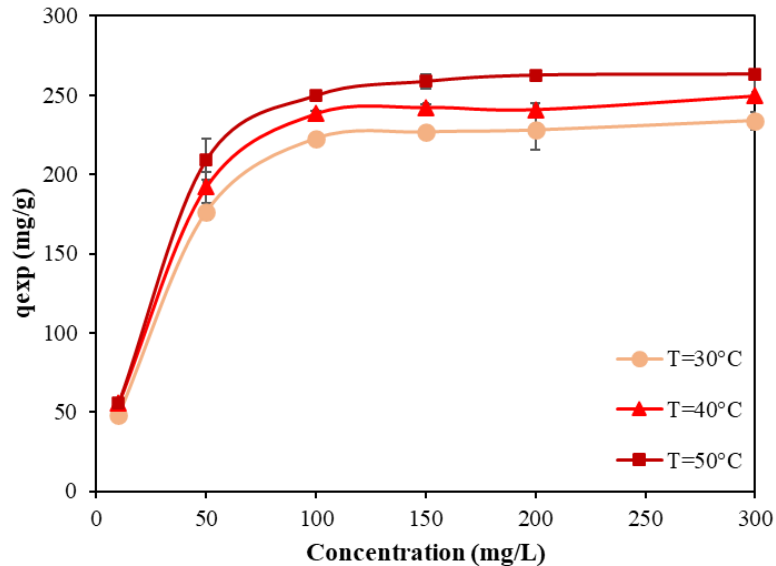


Figure 4.6 Effect of temperature on adsorption by PAC

4.2.5 Effect of adsorbent dosage

The effect of activated carbon dosage on adsorption was studied by different amounts of adsorbents (0.01-0.1 g). In Figure 4.7 and Figure 4.8, the obtained adsorption data for ZOSAC and PAC are given.

The removal increased from 39% to 100% for ZOSAC, and 52% to 100% for PAC. On the other hand, adsorption capacity is inversely proportional to the mass of adsorbent, hence, the adsorption capacity decreased by increasing adsorbent dosage. The adsorption capacity decreased from 190 to 49 mg/g for ZOSAC and from 255 to 49 mg/g for PAC. The increase in the removal efficiencies is due to the increase in the number of active sites and overall surface areas (Ni et al., 2022).

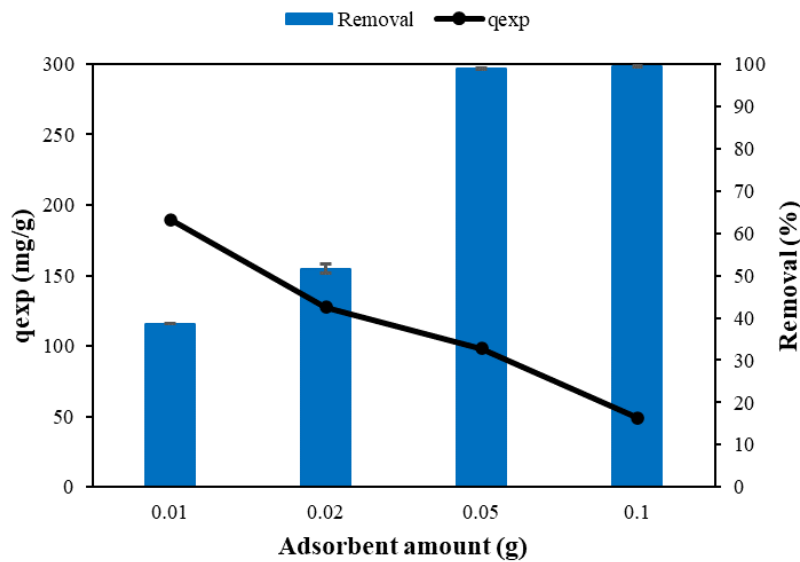


Figure 4.7 Effect of adsorbent dosage on adsorption for ZOSAC

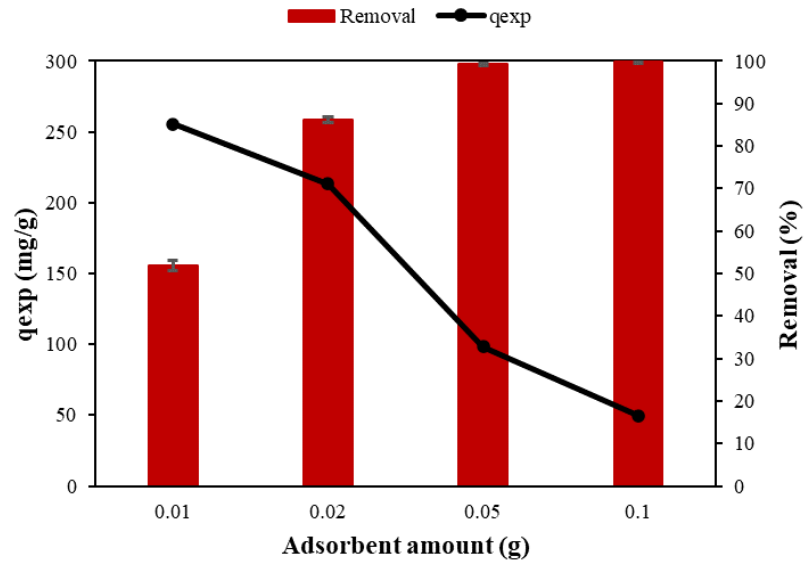


Figure 4.8 Effect of adsorbent dosage on adsorption for PAC

4.2.6 Effect of background ion

Wastewater does not contain a single contaminant in real cases. Especially, dye effluents also contain heavy metal ions and other substances. To simulate this, different types of ions were added to solution and effect on adsorption capacity was investigated (Figure 4.9). Addition of ions increased the adsorption capacity by decreasing the thickness of the electric layer between adsorbent and adsorbate (Kooh et al., 2016).

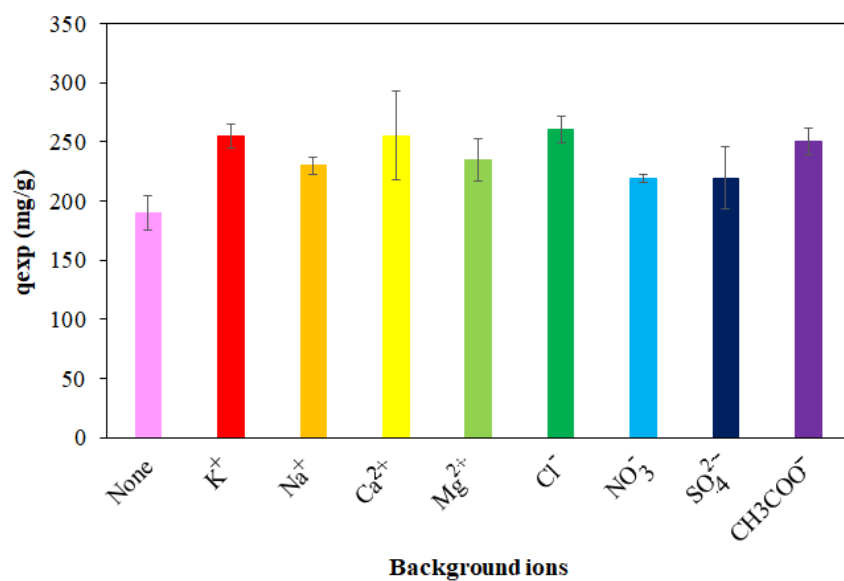


Figure 4.9 Effect of background ions

4.3 Modeling

4.3.1 Kinetic modeling

Elovich, pseudo-first order and pseudo-second order models were used to fit the experimental data and obtain the kinetic parameters. The parameters and correlation coefficients of three different models are listed in Table 4.3. The fitted curves and experimental data are shown in Figure 4.10 and Figure 4.11.

Table 4.3 Kinetic modeling results for RB adsorption

Model Name	Model equation	Model Parameters	Adsorbent	
			ZOSAC	PAC
Elovich	$q_t = \frac{1}{a} \ln \ln (1 + abt)$	a (mg g ⁻¹ min ⁻¹)	47.02	235.58
		b (g mg ⁻¹)	0.036	0.033
		R²	0.969	0.988
PFO	$q_t = q_1(1 - \exp(-k_1t))$	q₁ (mg g ⁻¹)	184.05	240.01
		k₁ (min ⁻¹)	0.0142	0.0181
		R²	0.989	0.986
PSO	$q_t = \frac{t}{\left(\frac{1}{k_2q_2^2}\right) + \left(\frac{t}{q_2}\right)}$	q₂ (mg g ⁻¹)	205.49	263.60
		k₂ (g mg ⁻¹ min ⁻¹)	1.03E-04	1.12E-04
		R²	0.993	0.999

Among these three kinetic models, it can be said that PSO model could describe the adsorption kinetics with highest coefficient of correlation (R²) values which were 0.993 and 0.999 for ZOSAC and PAC, respectively.

PSO model is related to chemisorption, which shows the adsorption process is a combination of simultaneous interactions of different mechanisms and

electrostatic attraction between activated carbons and RB molecules (Vigneshwaran et al., 2021).

Other researchers also reported that PSO model describes more adequately the adsorption kinetics (Ghibate et al., 2021b; Gören et al., 2021; Hou et al., 2019; Vigneshwaran et al., 2021).

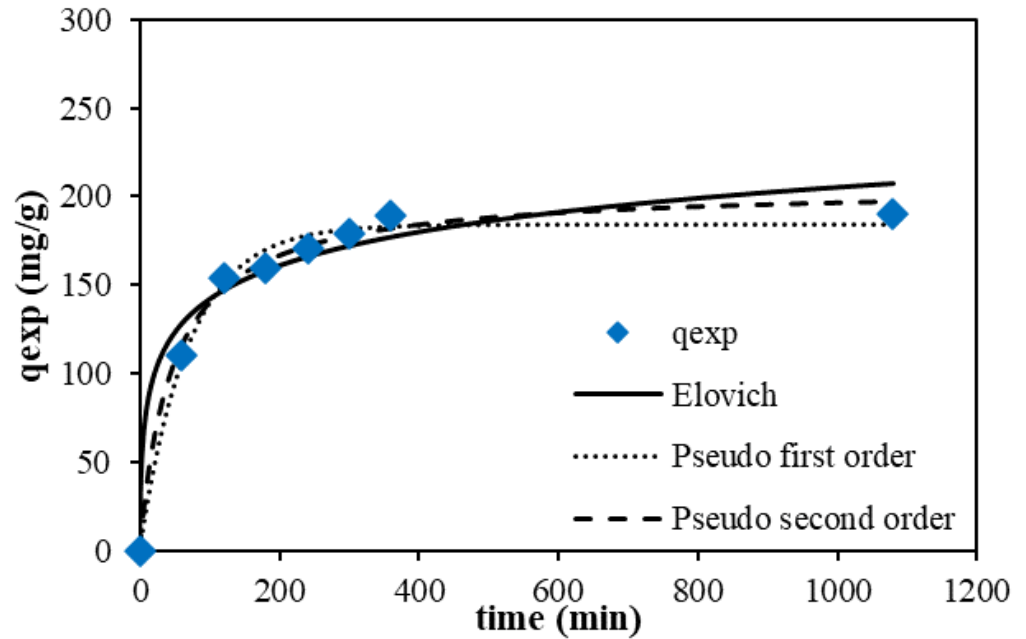


Figure 4.10 Kinetic models for ZOSAC-RB experimental data

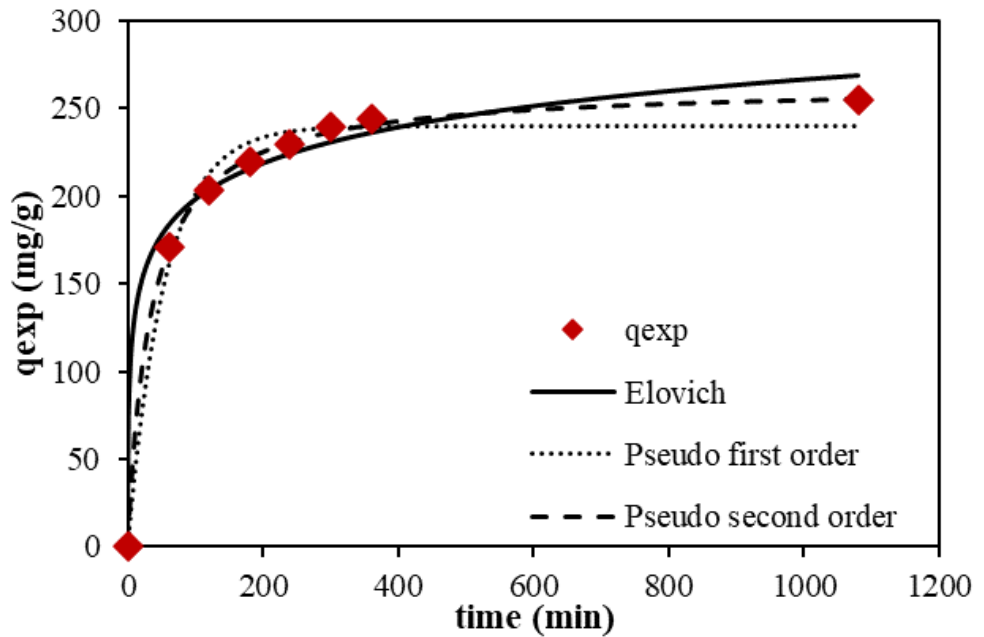


Figure 4.11 Kinetic models for PAC-RB experimental data

4.3.2 Isotherm modeling

Equilibrium study was carried out using Langmuir, Freundlich, Redlich-Peterson, Sips and Toth isotherm models to research the mechanism of adsorption. The model parameters are tabulated in Table 4.4. In Figure 4.12 and Figure 4.13, the fitted models for ZOSAC and PAC are given.

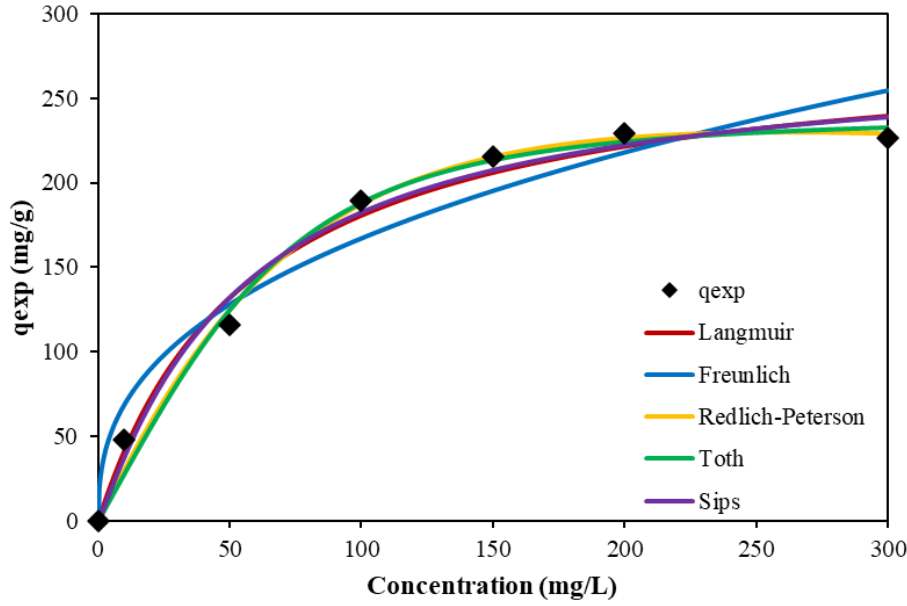


Figure 4.12 Isotherm models for ZOSAC-RB experimental data

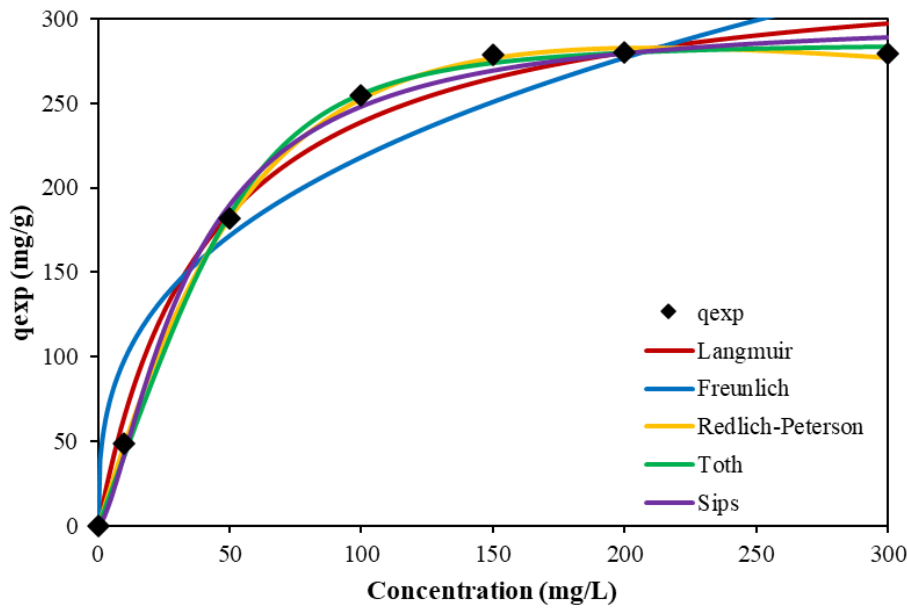


Figure 4.13 Isotherm models for PAC-RB experimental data

Table 4.4 Isotherm model parameters for ZOSAC and PAC

Isotherm model	Model equation	Parameter	Adsorbent	
			ZOSAC	PAC
Langmuir	$q_e = \frac{q_m K_a C_f}{1 + K_a C_f}$	q_m mg g ⁻¹	286.286	338.751
		K_a L mg ⁻¹	0.017	0.024
		R^2	0.986	0.987
Freundlich	$q_e = K_F C_f^{1/n}$	K_F (mg/g)(L/mg) ^{1/n}	28.660	44.687
		N	2.61	2.90
		R^2	0.953	0.925
Redlich-Peterson	$q_e = \frac{K_{RP} C_f}{1 + a_{RP} C_f^\beta}$	K_{RP} L mg ⁻¹	3.151	5.079
		a_{RP} L ^β /mg ^β	0.001	0.002
		B	1.386	1.361
		R^2	0.992	0.999
Toth	$q_e = \frac{q_m b_T C_f}{[1 + (b_T C_f)^{1/n_T}]^{n_T}}$	q_T mg g ⁻¹	238.860	285.052
		b_T L g ⁻¹	0.011	0.014
		n_T	0.456	0.373
		R^2	0.989	0.998
Sips	$q_e = \frac{q_m K_{eq} C_f^n}{1 + K_{eq} C_f^n}$	q_m mg g ⁻¹	275.695	301.4
		K_{eq} L g ⁻¹	0.013	0.006
		N	1.083	1.444
		R^2	0.987	0.996

The isotherm study can be divided into two groups as two-parameter models (Langmuir and Freundlich) and three-parameter models (Redlich-Peterson, Toth and Sips). It is assumed that adsorbent surface has uniform binding sites and equal adsorption energies in Langmuir model. Freundlich model is an empirical model

that explains the adsorption as multilayered on heterogeneous adsorbent surface (Zhao et al., 2020).

The goodness of fitting can be understood from correlation coefficient (R^2). It could be said that R^2 values of Langmuir isotherm were 0.986 and 0.987, they were closer to 1 than R^2 values of Freundlich isotherm were 0.953 and 0.925 for ZOSAC and PAC, respectively. This means that the adsorption can be characterized as monolayer adsorption. K_a values of 0.017 and 0.024 ($0 < K_a < 1$) also confirm that the adsorptions were favorable (Bedin et al., 2016). According to Langmuir model, the maximum adsorption capacities are 286.286 mg/g and 338.751 mg/g for ZOSAC and PAC, respectively.

The suitability of three-parameters models can be ordered by their correlation coefficients (R^2) as follows:

Sips ($R_{ZOSAC}^2=0.987$, $R_{PAC}^2=0.996$) < Toth ($R_{ZOSAC}^2=0.989$, $R_{PAC}^2=0.998$) < Redlich-Peterson ($R_{ZOSAC}^2=0.992$, $R_{PAC}^2=0.999$)

According to the modeling results, considering the highest R^2 value, Redlich-Peterson model is better fitting to the experimental data. Redlich-Peterson model is a combination of Langmuir and Freundlich models which makes this model more comprehensive and accurate. Redlich-Peterson model has a good adaptability in both low concentration and high concentration of adsorbate conditions (dos Reis et al., 2017).

4.4 Thermodynamic Calculations

To investigate the thermodynamic behavior of adsorption, Gibbs free energy change (ΔG°) was calculated using experimental data. The standard change in enthalpy (ΔH°) and the standard change in entropy (ΔS°) constants were found from slope and intercept of ΔG° versus $1/T$ plot. In Table 4.5 and Table 4.6, the calculated values for ZOSAC and PAC are tabulated.

Table 4.5 Thermodynamic parameters of ZOSAC-RB adsorption

Adsorbent	Temperature (°C)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol K)	R ²
ZOSAC	30	-4.67	14.911	0.0651	0.899
	40	-5.70			
	50	-5.97			

The negative values of ΔG° demonstrates the feasibility and spontaneity of the adsorption on ZOSAC and PAC. The absolute value of ΔG° was increased with temperature, hence, it can be said that temperature increasing is favorable to RB adsorption (Franco et al., 2021; Georgin et al., 2021).

The positive values of ΔH° shows the nature of the adsorption is endothermic and the positive values of ΔS° is related to the increase in randomness at the activated carbon-solution interface during RB adsorption (Ata et al., 2012).

According to previous researches, if ΔH° is less than 20 kJ/mol, adsorption can be considered as physisorption, if ΔH° is between 80 and 200 kJ/mol, adsorption can be considered as chemisorption (Ding et al., 2014). Since ΔH° values of ZOSAC-RB and PAC-RB adsorption were less than 20 kJ/mol, the adsorption can be described as physisorption in this study.

Table 4.6 Thermodynamic parameters of PAC-RB adsorption

Adsorbent	Temperature (°C)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol K)	R ²
PAC	30	-5.93	1.3789	0.0242	0.977
	40	-6.23			
	50	-6.41			

4.5 Optimization Study

To understand the relationship between parameters and adsorption capacity optimization study performed using Design Expert software. Temperature and

initial concentration were selected as parameter with the range of 30-50 °C and 10-300 mg/L, respectively.

Using Response Surface Methodology and Central Composite Design, experimental data was inserted into design and Analysis of Variance (ANOVA) performed and a quadratic model was suggested by software which achieved the highest coefficient of correlation (R^2).

In Table 4.7, ANOVA results and fit statistics are tabulated. The model F-values of 275.55 and 14.25 for ZOSAC and PAC, respectively, implies the significance of the design model.

The quadratic coded equations that express the relationship between parameters and adsorption capacity, q (mg/g), are given in Equation 14 and 15 for ZOSAC and PAC, respectively.

$$q_Z = 251.92 + 11.98 * A + 26.48 * B + 2.97 * AB - 0.6112 * A^2 - 39.44 * B^2 \quad (\text{Eq. 14})$$

$$q_P = 271.90 + 15.43 * A + 10.82 * B + 2.66 * AB - 0.2484 * A^2 - 45.60 * B^2 \quad (\text{Eq. 15})$$

where A is temperature (°C) and B is concentration (mg/L).

The model terms which have P-values less than 0.0500, are significant for the model. For ZOSAC model, A , B and B^2 are significant terms, while for PAC, only B^2 is a significant term for the model. Other terms except these terms are not significant.

Higher values of the correlation coefficients (R^2) confirm the goodness of fitting. ZOSAC model has a R^2 of 99.14% and PAC model has a R^2 of 85.58%. It can be said that ZOSAC model is well-fitted with experimental data rather than PAC model.

Table 4.7 Analysis of Variance (ANOVA) results for ZOSAC and PAC

ZOSAC				PAC			
Source	Degree of freedom	F-value	P-value	Source	Degree of freedom	F-value	P-value
Model	5	275.55	<0.0001	Model	5	14.25	0.0001
A	1	18.58	0.0010	A	1	1.82	0.2017
B	1	91.09	<0.0001	B	1	0.9002	0.3614
AB	1	1.54	0.2377	AB	1	0.0733	0.7912
A ²	1	0.0234	0.8809	A ²	1	0.0002	0.9882
B ²	1	333.25	<0.0001	B ²	1	26.37	0.0002
Residual	12			Residual	12		
Cor Total	17			Cor Total	17		
Fit Statistics				Fit Statistics			
Std. Dev.	7.99			Std. Dev.	32.82		
Mean	180.99			Mean	203.06		
C.V. %	4.41			C.V. %	16.16		
R ²	0.9914			R ²	0.8558		
Adjusted R ²	0.9878			Adjusted R ²	0.7958		
Predicted R ²	0.9810			Predicted R ²	0.6529		
Adequate Precision	45.7750			Adequate Precision	11.1363		

2D contour and 3D surface graphs help to understand the relationship between independent variables and response variable. The 2D contour and 3D surface plots are given in Figure 4.14 and Figure 4.15 for ZOSAC and PAC, respectively.

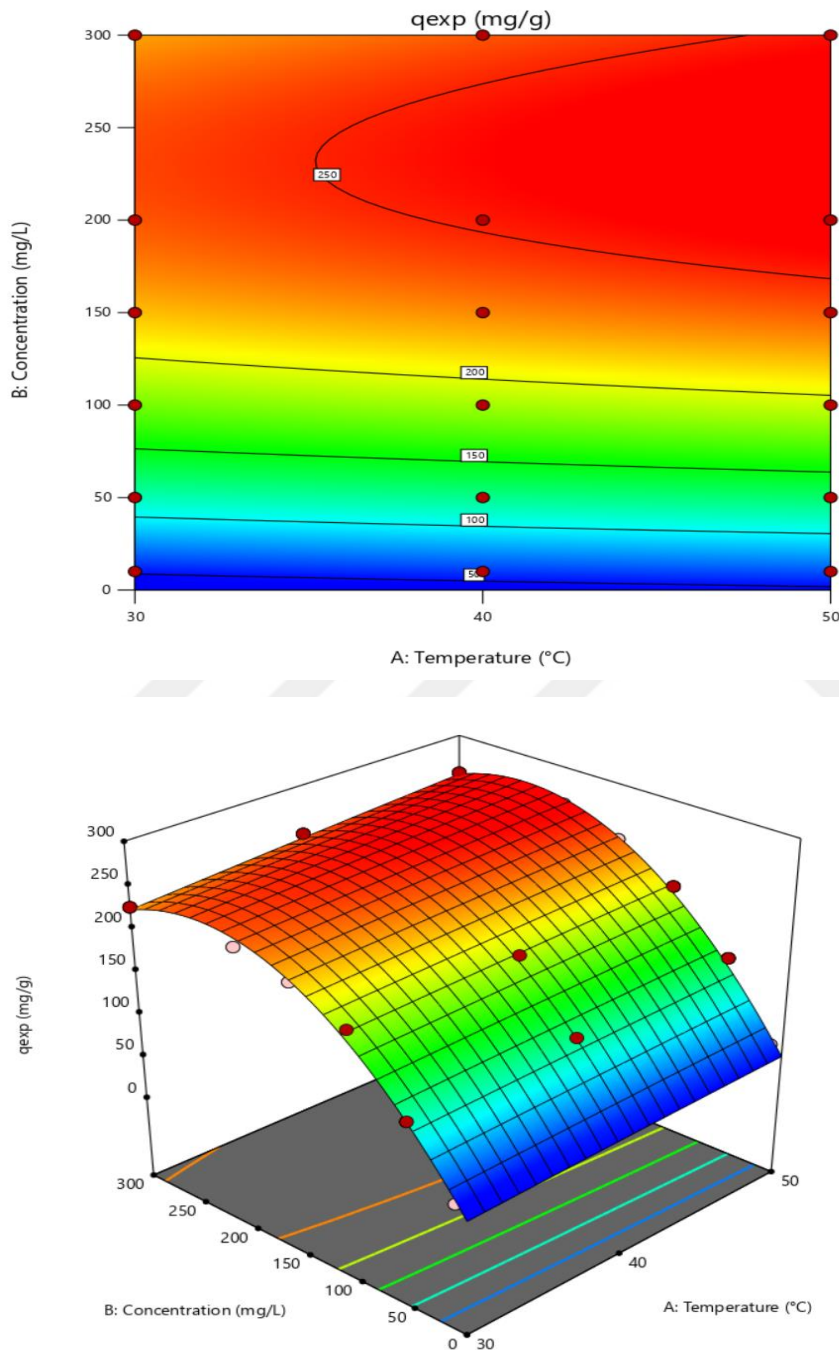


Figure 4.14 2D contour and 3D surface graphs for ZOSAC

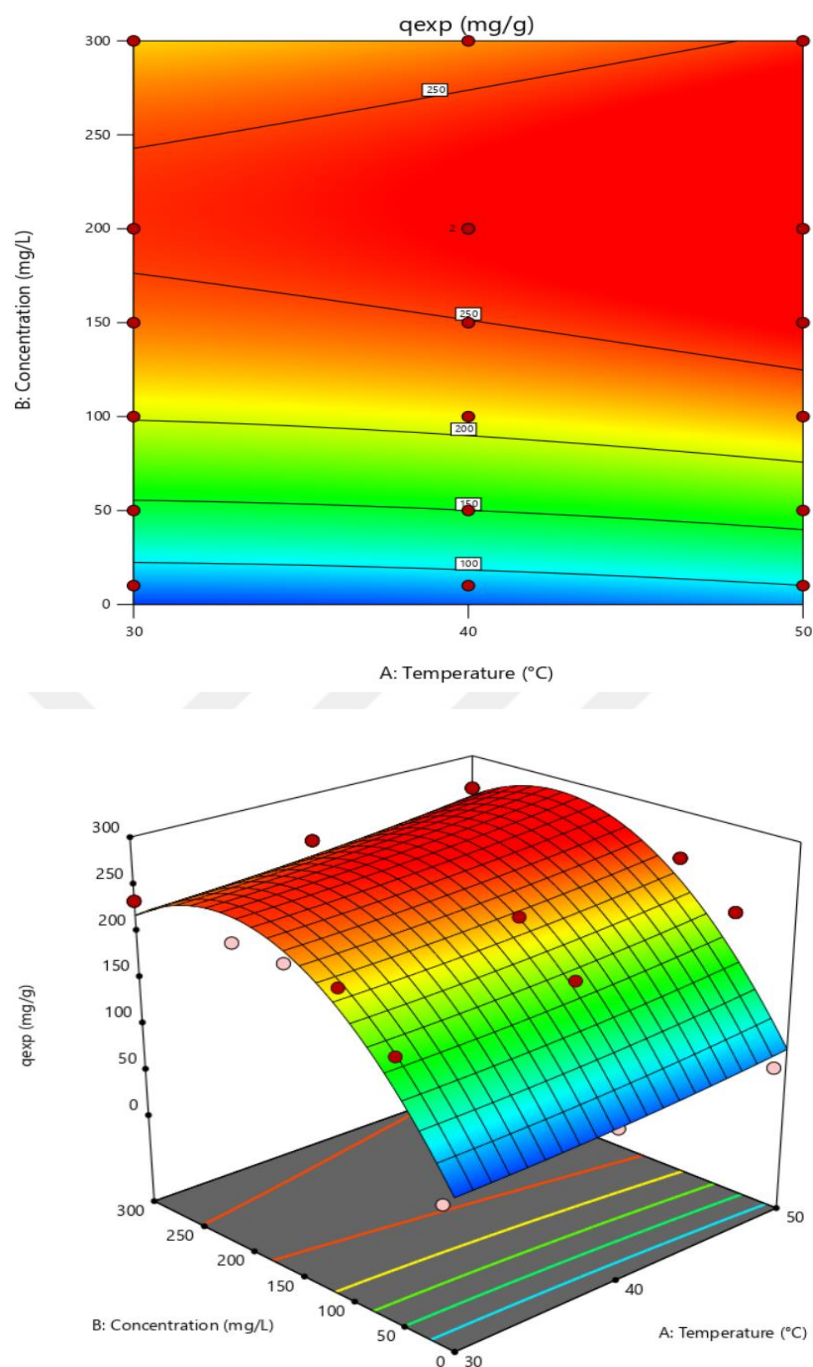


Figure 4.15 2D contour and 3D surface graphs for PAC

Simultaneous effects of temperature and initial contaminant concentration on adsorption capacity can be observed from graphs. With increasing temperature, the adsorption capacity was slightly increased. The diffusion of RB molecules onto the adsorbent surface was promoted by increasing temperature. In addition, the

relationship between temperature and adsorption capacity proves that the nature of the adsorption is endothermic.

Initial concentration also enhanced the adsorption capacity. The increment in concentration up to 200 mg/L, increased the adsorption capacity almost 5 times higher than at initial concentration 10 mg/L. The higher initial concentration values led to higher driving force which accelerates RB diffusion onto the activated carbons.

When the simultaneous effect of temperature and concentration is compared, the effect of initial concentration is greater than temperature on adsorption capacity.

To see the goodness of model, experimental data vs. theoretical value graph are plotted (Figure 4.16 And Figure 4.17). According to R^2 the model developed for ZOSAC-RB adsorption ($R^2=0.9989$) is better fitted compared to PAC-RB adsorption ($R^2=0.9845$).

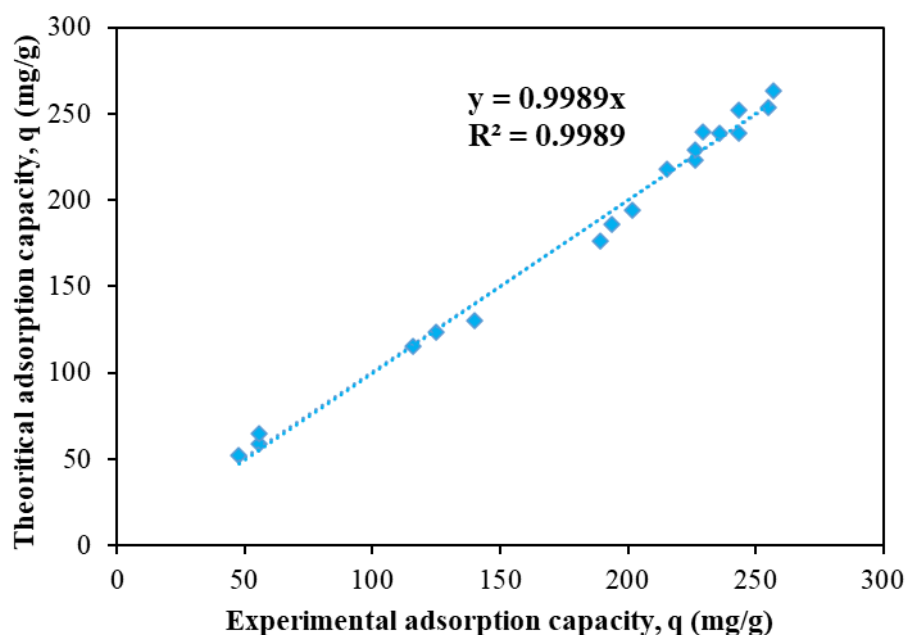


Figure 4.16 Goodness of model plot between experimental data and predicted values for ZOSAC

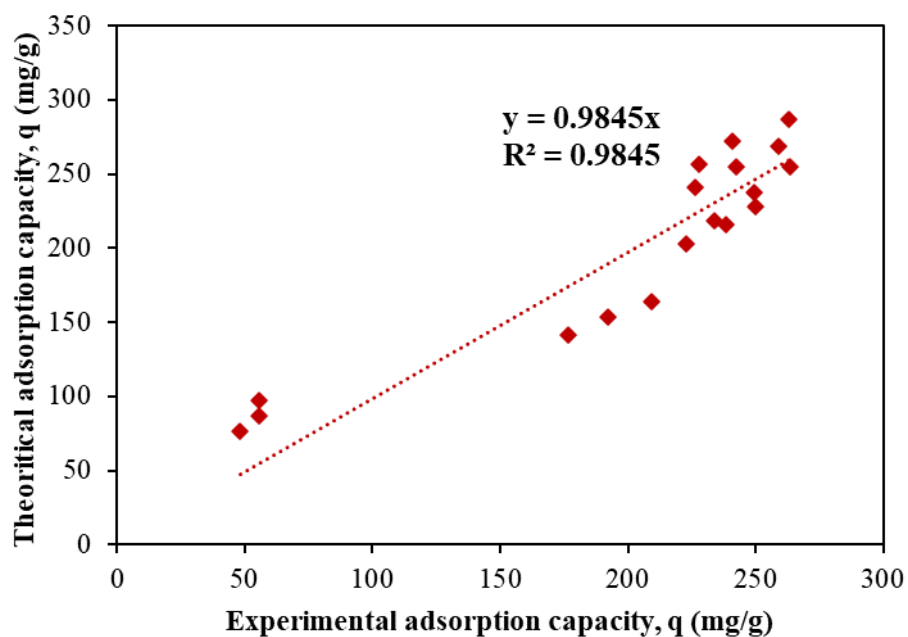


Figure 4.17 Goodness of model plot between experimental data and predicted values for ZOSAC

4.6 Regeneration (Desorption) Study

The reusability of ZOSAC was studied with adsorption-desorption cycles repeated for 5 times and removal efficiencies of each cycle are given in Figure 4.18. The adsorption capacity of ZOSAC decreased 100% to 94% at the end of reusability studies. It can be said that ZOSAC showed an excellent removal performance over 90% after the fifth adsorption stage.

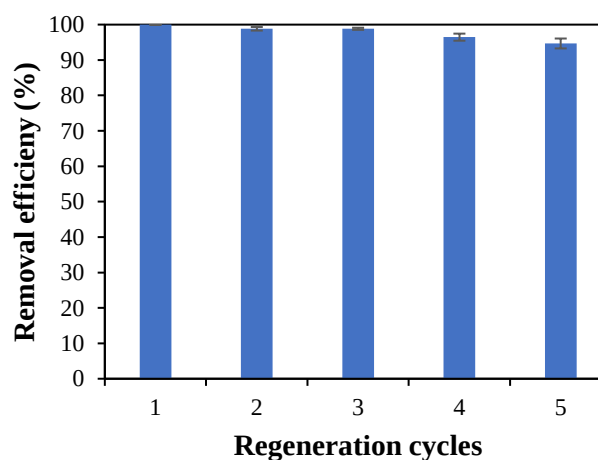


Figure 4.18 Reusability study of ZOSAC

In Table 4.8, the reusability of ZOSAC was compared with other RB removal studies with different precursors. This high removal performance makes ZOSAC a noticeable alternative adsorbent.

Table 4.8 Reusability of different biobased adsorbents

Precursor	Number of cycles	Removal efficiency (%)	Reference
Coal fly ash	5	66	(Ni et al., 2022)
Cassava slag	5	93	(Wu et al., 2020)
White sugar	7	98	(Xiao et al., 2020)
Olive stone	5	94	This study

4.7 Comparison of Study

Developing low-cost activated carbons became popular due to high demand for water treatment. To meet this demand, many bio-based activated carbons were produced, and their adsorption properties were investigated for different pollutants.

In Table 4.9, RB adsorption capacities of adsorbents studied in other research works and in this study were listed. Olive stone based activated carbons were compared with other bio-based adsorbents in terms of their maximum adsorption capacities.

Olive stone based activated carbons, especially ZOSAC, has a higher adsorption capacity than other biobased adsorbents. Recyclability study also showed that ZOSAC can be used in RB removal for many times due to its high removal efficiency in every cycle of adsorption and desorption. These adsorption features make ZOSAC a good alternative for RB removal.

Table 4.9 Comparison of RB adsorption onto different biobased adsorbents

Precursor	Activator	c_0 (mg/L)	T (°C)	pH	m_{ads} (g)	q_{max} (mg/g)	Reference
Walnut shell	H ₂ SO ₄	60	25	3	0.05	2.29	(J. Shah et al., 2013)
Coconut coir	CH ₂ O ₂ , HCl	100	45	7	0.1	22.00	(Nascimento et al., 2021)
Pomegranate peel	-	100	25	N/A	0.1	30.47	(Ghibate et al., 2021)
Tapioca peel	CH ₄ N ₂ S	150	N/A	8	0.1	33.10	(Vigneshwaran et al., 2021)
Rhamnus stone	-	20	30	8	0.1	39.00	(Al-Rudaini, 2017)
Sugarcane bagasse	-	250	30	4	0.05	65.50	(Zhang et al., 2013)
Bamboo shoot shell	HCl	300	25	N/A	0.04	85.80	(Hou et al., 2019)
Olive pomace	-	300	40	4	0.15	86.20	(Boukerzaza et al., 2021)
Elaeagnus stone	ZnCl ₂	200	25	7	0.05	281.69	(Geçgel et al., 2016)
Olive stone	-	100	30	4	0.01	21.57	This study
	H ₃ PO ₄	100	30	4	0.01	49.81	
	KOH	100	30	4	0.01	118.26	
	ZnCl ₂	200	50	4	0.01	256.80	

5.0 CONCLUSION

Water resources are getting polluted by industrial waste discharges. Developing an efficient, low-cost, sustainable and biowaste based adsorbent can be a good alternative to solve this water issue. In this study, Rhodamine B adsorption characteristics of olive stone based activated carbons were investigated in aqueous solution with the parametric study.

ZOSAC, KOSAC, HOSAC were prepared by impregnation with ZnCl_2 , KOH, H_3PO_4 , respectively, and then carbonization. To compare the performances of activated carbons, only physically activated olive stone (OSAC) and powdered activated carbon (PAC) were used. Deionized water was used to prepare the solution and its properties were pH 7.7, conductivity $2.5 \mu\text{S/cm}$, salinity 0‰ and 1.1 mg/L TDS.

The order of the maximum adsorption capacity (mg/g) is:

$\text{PAC (254.30)} > \text{ZOSAC (190.67)} > \text{KOSAC (118.26)} > \text{HOSAC (49.81)} > \text{OSAC (21.57)}$

According to isotherm study, it can be said that the initial RB concentration was proportional to adsorption capacity until at $c_0 = 200 \text{ mg/L}$ that the adsorption reached the equilibrium. The higher initial concentrations led to a driving force that accelerates the mass transfer from solution onto adsorbate. The maximum adsorption capacity achieved was 229.20 mg/g for ZOSAC which means the change of the initial concentration from 100 mg/L to 200 mg/L caused a 20% increment in terms of adsorption capacity at pH 4.

Adsorption capacity was calculated between 152 mg/g and 190.67 mg/g in the pH range of 2-10. At pH=4 environment, the maximum adsorption capacity was achieved. Due to its structure, acidic medium is more favorable for adsorption rather than alkaline medium.

Temperature has also an enhancing effect on adsorption capacity. Adsorption capacity increased 229.20 mg/g to 256.80 mg/g for temperature change 30 °C to 50 °C. As a result of thermodynamic study performed at three different temperature level, negative value of ΔG° shows the feasibility and spontaneity of adsorption on ZOSAC. The positiveness of ΔH° and ΔS° indicates the adsorption has endothermic behavior and increased randomness between adsorbent and solution interface.

For the adsorbent dosage change from 0.01 g to 0.05 g, removal percentage increased from 39% to 100%. This increase in the percent removal is associated with a great increase in the number of active sites on the adsorbent surface. In addition, another point to be considered is adsorption capacity is inversely proportional to percent removal. Adsorption capacity decreased from 190 mg/g to 98 mg/g for the same adsorbent dosage change.

Pseudo second order model ($R^2=0.993$) was selected best to describe the adsorption among the kinetic models. Langmuir ($R^2=0.986$) and Redlich-Peterson ($R^2=0.992$) models were the best models to represent the adsorption. The fitness of equilibrium data to Langmuir model indicates that adsorption can be considered as monolayer adsorption.

Experimentally, maximum adsorption capacity of ZOSAC (256.80 mg/g) was achieved at 50 °C and 200 mg/L initial concentration. Using Design Expert, it was found that at optimum conditions of 45 °C and 252 mg/L initial concentration, adsorption capacity reached a maximum value of 261.86 mg/g. ANOVA result also implies the significance of the quadratic design model based on temperature and initial concentration parameters.

The reusability of ZOSAC was investigated by performing adsorption and desorption cycles. At the end of 5 cycles, ZOSAC showed a retention of 94% removal efficiency which means it is possible to reuse ZOSAC for several cycles without a notable decrease in removal efficiency.

Finally, the study can be concluded that ZnCl_2 -impregnated olive stone activated carbon is a promising adsorbent candidate for employment in Rhodamine B adsorption due to its high removal efficiency and recyclability.



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Mert Can HENDEKÇİ

PERSONAL INFORMATION

WORKING EXPERIENCE

10.2022 – ... R&D Engineer, Vestel Dishwasher Plant, Manisa
06.2017 – 07.2017 Intern, Gema Elektro Plastik, İzmir
07.2016 – 08.2016 Intern, Amcor Tobacco Packaging, İzmir

EDUCATION

09.2020 – 09.2023 Chemical engineering, Ege University, Master's Degree
09.2018 – 09.2019 Kumamoto University, Exchange Student
09.2012 – 07.2017 Chemical engineering, Ege University, Bachelor's Degree

PROJECTS

08.2022 – 08.2023

Investigating The Adsorption Properties of Olive Stone Derived Activated Carbon,
Master's Thesis

09.2016 – 09.2017

Interface Development and Biodegradable Packaging Applications in Cellulosic Added Polymeric Composites, Diploma Project supported by TÜBİTAK 2209/A Project

LANGUAGES

Turkish	Native
English	Working proficiency
German	Elementary
Japanese	Elementary (JLPT N5 Certificate)

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