Removal of Methyl Blue from Aqueous Solution Using Magnetic Loquat (*Eriobotrya japonica*) Seed

ABSTRACT

Aims: In this study, biochar and magnetic biochar were obtained from loquat seeds. The obtained biochars were used to remove methyl blue from the aqueous solution.
Study design: The effects of adsorbent substance dosage, pH, initial methyl blue concentration, time and temperature on the adsorption process were investigated.
Place and Duration of Study: Department of Chemistry, Graduate School of Applied and Natural Sciences, Süleyman Demirel University, between February 2022 and February 2023.
Methodology: In this study, batch adsorption method, which is an easily applicable and common method, was used to remove dye from aqueous media. Modified loquat seeds were characterized by FTIR, BET analysis. The adsorption process was investigated in terms of kinetics, equilibrium and thermodynamics.
Results: The maximum adsorption capacity was 31.746 mg/g for biochar and 67.568 mg/g for magnetic biochar. According to the kinetic data, the adsorption rate is pseudo-second-order. According to the thermodynamic data, negative ΔG values indicated that adsorption of methyl blue occurred spontaneously. According to negative ΔH values, the adsorption process was exothermic. When the adsorption isotherms were examined, it was seen that loquat biochar and modified loquat biochar were suitable for the Langmuir adsorption isotherm.
Conclusion: Modified loquat seeds can be used to remove methyl blue dye from aqueous solutions. The adsorbents used can be modified with different chemicals to increase the adsorption capacity and contribute to the literature.

Keywords: loquat seed, biochar, methyl blue, adsorption, langmuir, freundlich

1. INTRODUCTION

Water is an important resource for industrial, domestic and agricultural activities. The increasing population and the expansion of industrial activities cause water and environmental pollution. Dyes are used in many fields, especially in textile, cosmetics and paper. These substances, which dissolve well in water and have low biodegradability, are the main pollutants in wastewater [1]. In general, dyes are classified as anionic, cationic, and non-ionic according to their charge in aqueous solution. Methyl blue is an anionic dye used to dye leather, cotton and fiber [2]. Dyes in wastewater pose a danger to humans and the environment. For this reason, industrial wastewater must be treated before being discharged into the environment. Various techniques such as reverse osmosis, ion exchange, precipitation, photocatalysis are applied to remove dyes from the aqueous medium. Among them, adsorption is an effective method that is widely used [3]. Loquat (Eriobotrya japonica), with its common name, belongs to the Rosaceae family [4]. The homeland of loquat is China, Japan and North India. Loquat fruit is grown in limited areas in Turkey, where the climatic conditions are suitable, in the coastal regions of the Mediterranean and Aegean regions and partially on the coastline of the Black Sea [5]. Various adsorbents are used to remove dyes from the aqueous medium. Among the economical and environmentally friendly adsorbents, biochars are widely used [6]. Biochar is obtained as a result of the

thermochemical decomposition of biomass in a limited oxygen environment. Biochar is a stable material with a porous, highly aromatic carbon structure. Waste water is used to improve the soil structure as well as to purify the gases [7]. Biochars can be easily prepared from domestic and industrial wastes, especially agricultural wastes. The high carbon content, cation exchange capacity and porous structure have increased the interest in this material [8].

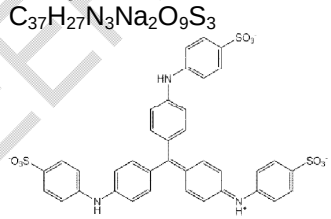
In this study, batch adsorption method, which is an easily applicable and common method, was used to remove dyes from aqueous media. Loquat (Eriobotrya japonica) seeds, which are discarded after the fruits are eaten, were turned into biochar and used as an adsorbent. This material was chosen because it is abundant and economical, and it was modified with iron compounds to increase its adsorption capacity and turned into nanomagnetic biochar. The prepared materials were characterized by FTIR, BET analysis. Since there are not many studies on the adsorption of methyl blue dye in the literature review, this dye was preferred. The adsorption process was investigated in terms of kinetics, equilibrium and thermodynamics using different parameters.

2. MATERIAL AND METHODS

2.1 Properties of dye

Methyl blue (MM) is from Isolab chemicals. Its properties are given in Table 1.

Table 1. Structure and properties of methyl blue

Methyl Blue Properties	
Name	Methyl blue
Molecule Formula	$C_{37}H_{27}N_3Na_2O_9S_3$
Chemical Structure	
Molecular Weight	799.810 g/mol
Type	Anionic

Wavelength scanning was performed for methyl blue using a Peak Instruments C-7100 brand UV/VIS device. The maximum absorbance value was found at 600 nm.

2.2 Preparation of biochar

Loquat fruit was bought from the public market in May. The fruits are cut and the seeds are separated. The seeds were washed with distilled water and dried in a Nuve FN500 oven for 24 hours. The dried seed were converted into biochar by heating at 450 °C for 4 hours in a Carbolite ELF 11/6B brand muffle furnace [9]. The obtained biochar (b-ER) was ground into powder. The biochar was divided into two part, the second part was modified with iron compounds and a new magnetic biochar was obtained. The $FeSO_4.7H_2O$ and $FeCl_3.6H_2O$ compounds are from Isolab chemicals. 100 mL aqueous solution was prepared by using 8 g $FeSO_4.7H_2O$ and 12 g $FeCl_3.6H_2O$. The pH of the solution was adjusted to 10 using 0.1 M NaOH. 10 g of biochar was taken into a three-necked balloon and iron solution was added to it. It was stirred at 70 °C in the presence of nitrogen gas for 1 hour. The mixture was filtered and the solid remaining on the filter paper was washed several times with distilled water.

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Nanomagnetic biochar (mb-ER) was dried in an oven at 70 °C for 24 hours. It was stored in a closed container for use in experiments [10]

2.3 Characterization of biochar

The point of zero charge was found for the prepared b-ER and mb-ER. The surface area was measured by the Brunauer-Emmett-Teller (BET) method. Infrared spectrometry (FTIR) was used to determine the surface functional groups.

2.3.1 Point of zero charge

In order to find the pH values at which the surface charge of the adsorbents is zero, 0.1 M NaCl aqueous solutions with pH values between 2 and 12 were used. pH were adjusted using 0.1 M HCl and 0.1 M NaOH solutions. 40 mL of each solution was added onto 0.1 g adsorbent, and it was shaken at 150 rpm for 24 hours. The mixtures were filtered and pHs were measured using Hanna HI2020-02 edge brand pH meter. Point of zero charges were found by plotting the final pH versus ΔpH [11].

2.3.2 FTIR spectroscopy

FTIR Spectroscopy analyzes of biochar and loquat seeds that were made into nanomagnetic biochar were performed with JASCO FT/IR-4700 typeA brand device. Surface functional groups were determined before and after adsorption of adsorbents with methyl blue (MM) in the wave number range of 4000-400 cm^{-1}.

2.3.3 BET analysis

BET Analysis was performed at Anadolu University, Plant, Medicine and Scientific Research Application and Research Center. Micromeritics brand and TriStar II 3020 model device were used in the analysis. In order to remove and purify the water, the adsorbents were left in the degas unit at 300 °C for 24 hours. Then, surface areas were measured based on nitrogen gas adsorption-desorption isotherms at a temperature of 77.350 K.

2.4 Batch adsorption experiments

Experiments were carried out by changing the parameters such as pH, initial methyl blue concentration, temperature, dosage of adsorbent substance and contact time using the batch adsorption method. For the experiments of pH, it was studied in the range of 2-9. pH adjustments were made with 0.1 M HCl and 0.1 M NaOH. The pH meter was calibrated with Isolab brand pH buffer solutions. 25 °C-55 °C was chosen for the temperature. Using the stock methyl blue solution, solutions were prepared at concentrations ranging from 10 mg/L to 100 mg/L. The dosage of adsorbent was studied in the range of 0.05 g-0.25 g and for the effect of contact time between 15 min-240 min. The dosage of methyl blue adsorbed on b-ER and mb-ER during the equilibrium process was calculated using Equation1 [12].

$$q_e = \frac{(C_0 - C_e)V}{W} \qquad \text{Equation 1}$$

C_0 is the initial concentration of methyl blue (MM), Ce is the equilibrium concentration. W (g) is the dosage of b-ER and mb-ER used as adsorbent and V (mL) is the volume of solution.

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3. RESULTS AND DISCUSSION

Methyl blue was removed from the aqueous medium with biochar and magnetic biochar obtained from loquat seeds. The effects of parameters such as adsorbent dosage, temperature, methyl blue initial concentration, pH and contact time on the adsorption process were investigated. The obtained adsorption data were analyzed in terms of equilibrium isotherms, kinetics and thermodynamics.

3.1 Point of Zero Charge

The pH at the point of zero charge (pHpzc) was determined 8.5 for b-ER and the pH at the point of zero charge (pHpzc) was determined 8.9 for mb-ER.

3.2 Batch adsorption experiments

The surface functional groups after the adsorption of biochar obtained from loquat seeds, nanomagnetic biochar and biochars with methyl blue were determined by FTIR spectrometry. The results are given in Figure 1.

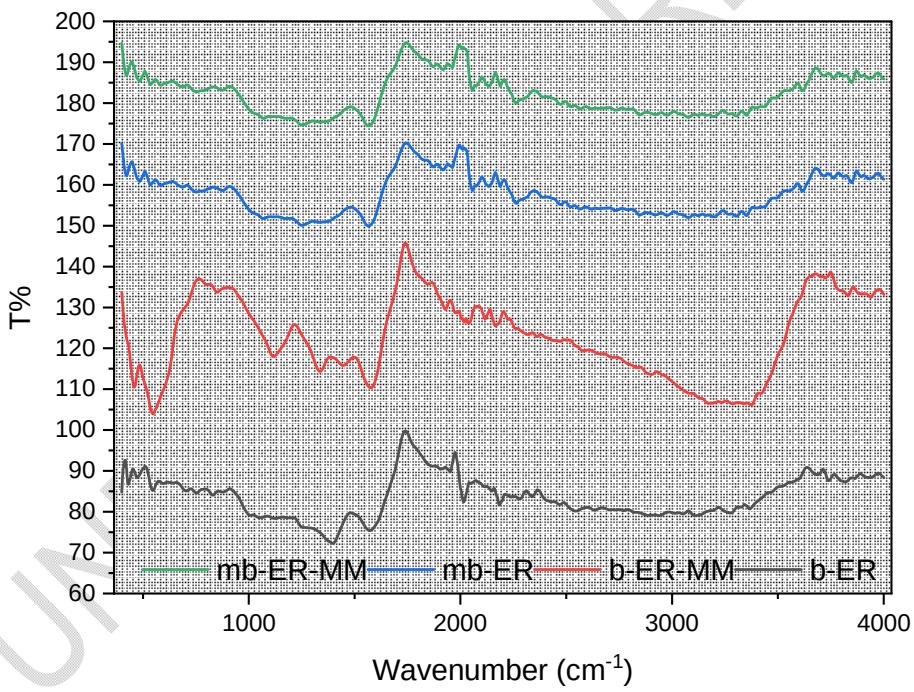

Fig. 1. FTIR images (Biochar b-ER, methyl blue and biochar b-ER-MM**, nanomagnetic biochar mb-ER, methyl blue and nanomagnetic biochar mb-ER-**MM**)**

Biochar has both aliphatic and aromatic groups on its surface [13]. The band at 3366 cm^{-1} in the b-ER FTIR spectrum might be assigned to the –OH stretching vibration and the band at 1569 cm-1 might be assigned to the C-H stretch in the aromatic ring [14]. When the b-ER and b-ER MM spectra are compared, the peaks observed sharply at 830 $cm^{-1,}$ 1569 cm^{-1}, 2015 cm^{-1} and 3272 cm^{-1} are shifted to 752 cm^{-1}, 1564 cm^{-1} ve 2057 cm^{-1} ve 3110 cm^{-1} after the contact of the adsorbent with methyl blue and lost their intensity. The peak seen at

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3375cm-^{1} in the mb-ER FTIR spectrum belongs to the –OH stretching vibration. When the mb-ER and mb-ER MM spectra are compared, the sharply observed bands at 1336 cm^{-1},1574 cm^{-1} and 3375 cm^{-1} shifted to 1349 cm^{-1}, 1560 cm^{-1}, and 3272 cm^{-1} bands, respectively, after the contact of the adsorbent with methyl blue. The sharp peak seen 1117 cm^{-1} in the mb-ER spectrum disappeared after adsorption and a new intense peak was formed at 2417 cm^{-1}. The bands observed at 543 cm^{-1} and 547cm^{-1} correspond to the Fe–O vibrational band [15]. The shift of some peaks and the formation of some new peaks after adsorption also suggest that methyl blue functional groups are involved during adsorption.

3.3 BET analysis results

The BET surface area of b-ER was measured as 3,559 m^{2}/g total pore volume 0.011 cm^{3}/g, while the surface area of mb-ER was 17,320 m^{2}/g and the total pore volume was 0.102 cm3/g. The purpose of nanomagnetic biochar is to expand their surface area and increase capacity. When the BET analysis results are compared, the pore volume and surface area of nanomagnetic biochar have increased, thus the adsorption capacity has also increased.

3.4 Effect of adsorbent dosage

The effect of the adsorbent dosage on the sorption of methyl blue was investigated. 0.05 g, 0.10 g, 0.15 g, 0.20 g and 0.25 g b-ER and mb-ER were put into each beaker. 30 mL of 50 mg/L prepared methyl blue solution was added to each vessel. It was mixed with a shaker at 25 °C at 300 rpm for 60 minutes. The mixture was filtered with blue band filter paper and the remaining solution was made up to 50 ml. In order to calculate the dosage of methyl blue not adsorbed by b-ER and mb-ER, absorbances were measured in the UV device and calculations were made. The sorption change with the dosage of adsorbent is given in Figure 2.

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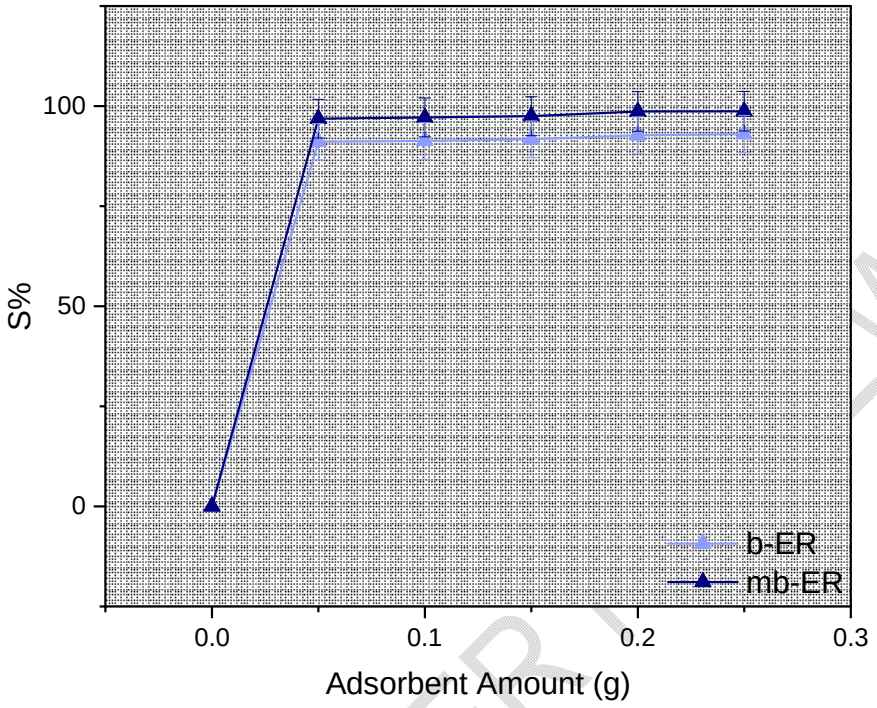

Fig. 2. Variation of sorption with the dosage of adsorbent

As the dosage of adsorbent increased, the number of active sites on the b-ER and mb-ER surface increased, and as a result, the sorption percentages increased. After the surface saturation, the increase in the sorption percentage decreased. The surface area of mb-ER is larger than that of b-ER. The total pore volume is greater. Therefore, the sorption percentage of methyl blue adsorbed on the mb-ER surface increased.

3.5 Concentration effect and adsorption isotherm

The effect of the initial dye concentration on the sorption of methyl blue was investigated. Methyl blue concentrations were determined as 10 mg/L-25 mg/L-50 mg/L- 75 mg/L-100 mg/L. Other parameters were kept constant. 30 ml was added to each beaker. It was mixed with a shaker at 25 °C at 300 rpm for 60 minutes. The mixture was filtered with blue band filter paper and the remaining solution was made up to 50 ml. In order to calculate the dosage of methyl blue remaining in the solution, absorbance measurement was made in the UV device. The effect of concentration change on adsorption is shown in Figure 3.

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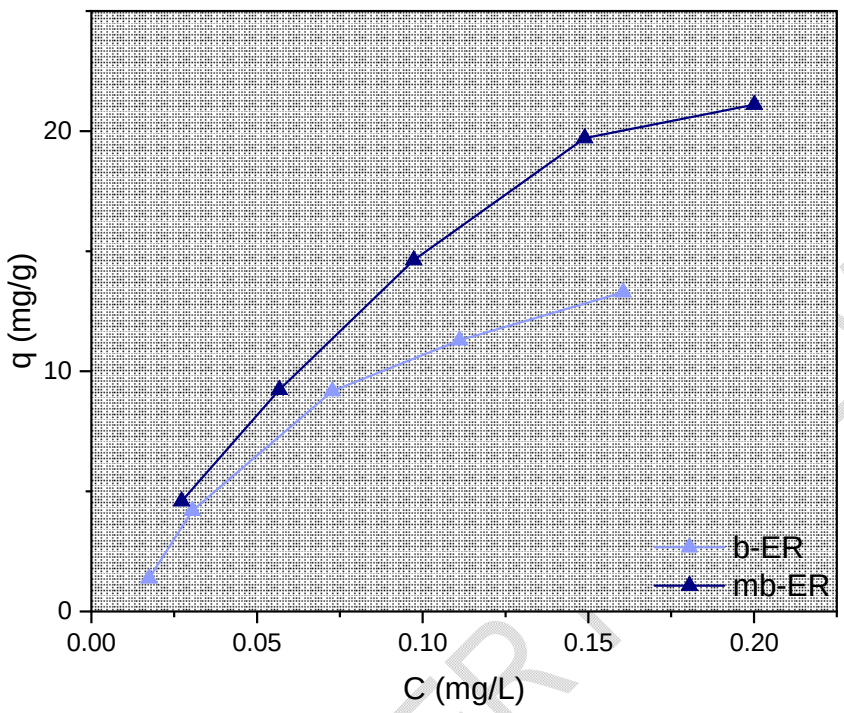

Fig. 3. Variation of adsorption capacity with equilibrium concentration

As the initial concentration increased, the equilibrium concentration increased, however, the adsorption capacity of b-ER and mb-ER increased. Adsorption isotherm models are important tools for studying adsorption behaviors and mechanisms. It reflects the interaction between adsorbent and adsorbate. Langmuir [16], Freundlich [17], Temkin-Phyzev [18] and Scatchard [19] isotherm models, which are widely used, were used to determine the sorption capacity of adsorbents. Equilibrium isotherm results are given in Table 2.

Table 2. Equilibrium isotherm results

Isotherm	Equations	Eq. No	Adsorbent	Isotherm parameters			
Langmuir	$\frac{1}{q_e} = \frac{1}{K_{L_{qmax}}} x \frac{1}{C_e} + \frac{1}{q_{max}}$	(2)		q_{max}	K_L	R^2	R_L
			b-ER	31.746	5.080	0.994	0.004
			mb-ER	67.568	2.690	0.998	0.007
Freundlich	$Logq_e = LogK_f + \frac{1}{n} LogC_e$	(3)		K_f	1/n	R^2	
			b-ER	51.927	0.704	0.972	
			mb-ER	84.101	0.788	0.980	
Scatchard	$\frac{q_e}{C_e} = Q_s K_s - q_e K_s$	(4)		Q_s	K_s	R^2	
			b-ER	28.470	5.904	0.877	
			mb-ER	56.558	3.368	0.846	
Temkin and Pyzhev	$q_e = B \ln K_T + B \ln C_e$	(5)		BT	K_t	R^2	
			b-ER	6.085	58.008	0.985	
			mb-ER	8.718	57.496	0.986	

*Biochar b-ER, nanomagnetic biochar mb-ER

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The Langmuir isotherm presupposes that each adsorption site has the same energy for adsorption and that the amount of active adsorption sites on the surface is what limits the adsorption process. Freundlich isotherm, the adsorption process is heterogeneous, indicating that various sites have various adsorption energies. Temkin isotherm assumes that the presence of an adsorption heat influences the adsorption process and that adsorption reduces the system's entropy. Adsorption isotherms were investigated and R^2 values were compared. According to these values, the sorption of both adsorbents was found to be in accordance with the Langmuir model (R^2= 0.994, q_{max}=31.746 mg/g for b-ER and R^2= 0.998, q_{max}=67.568 mg/g for mb-ER). The Langmuir isotherm is a single-layer adsorption model. In this model, it is assumed that the molecules adsorbed on the adsorbent surface can form a monolayer and that each molecule adsorbed on the surface has the same adsorption activation energy [20]. It can be thought that methyl blue is adsorbed in a monolayer on the b-ER and mb-ER surfaces. R_L is the separation factor. Equilibrium is a dimensionless constant used in concentration studies. If the R_L value is between $0<R_L<1$, it indicates that the adsorption process is suitable for removing the dye from the aqueous medium, while $R_L>1$ indicates that it is not suitable) [21]. It can be concluded that the sorption of methyl blue dye by b-ER and mb-ER is favorable (R_L=0.004 for b-ER and R_L=0.008 for mb-ER).

3.6 Effect of pH

pH is an important factor in the adsorption process. The effect of pH change on sorption in the removal of methyl blue with b-ER and mb-ER is given in Figure 4.

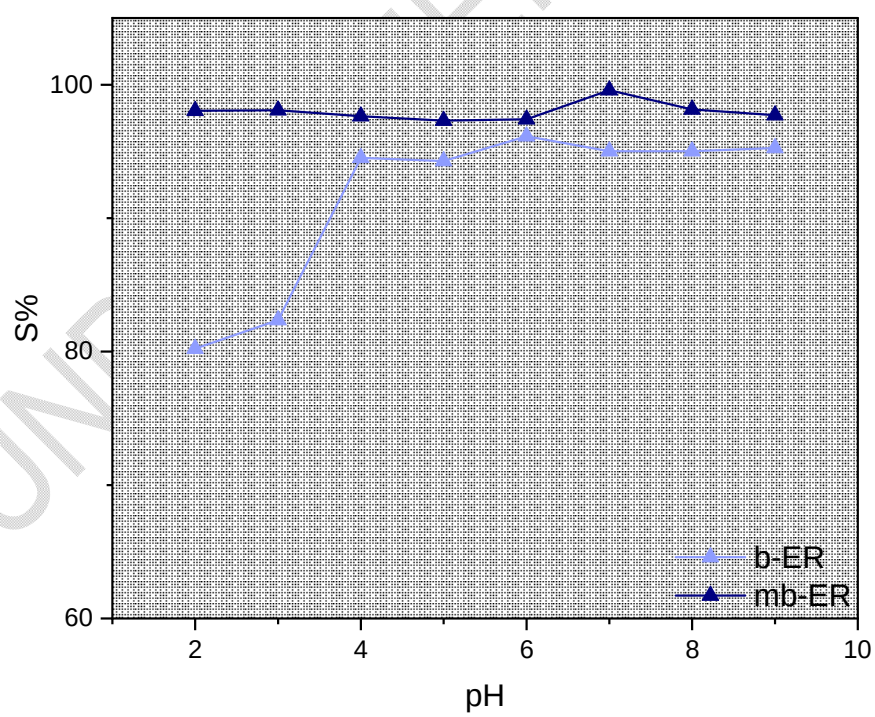

Fig. 4. Variation of sorption with pH

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Methyl blue is an anionic dye. Maximum dye adsorption for b-ER was observed at pH 6. Maximum adsorption for mb-ER was observed at pH 7. At low pH, the electrostatic attraction force between the negatively charged anionic methyl blue and the adsorbent surfaces increases. After pH 7, OH^- ions increase in the basic region, and it is thought that the sorption percentage decreases as they compete with the anions in the dye structure. While the point of zero charge pH for b-ER was 8.5, it was 8.9 for mb-EA. In the case of $pH \leq pH_{pzc}$, that is, at values lower than pH values where the total surface charge is zero, the adsorbent surface is positively charged [22]. b-ER and mb-ER showed maximum adsorption at pH values below point of zero charges.

3.7 Temperature effect and adsorption thermodynamics

Adsorption is a temperature dependent process. While researching the temperature effect, 25 °C, 35 °C, 45 °C, 55 °C values were selected and other parameters were fixed. The effect of pH change on sorption in the removal of methyl blue with b-ER and mb-ER is given in Figure 5.

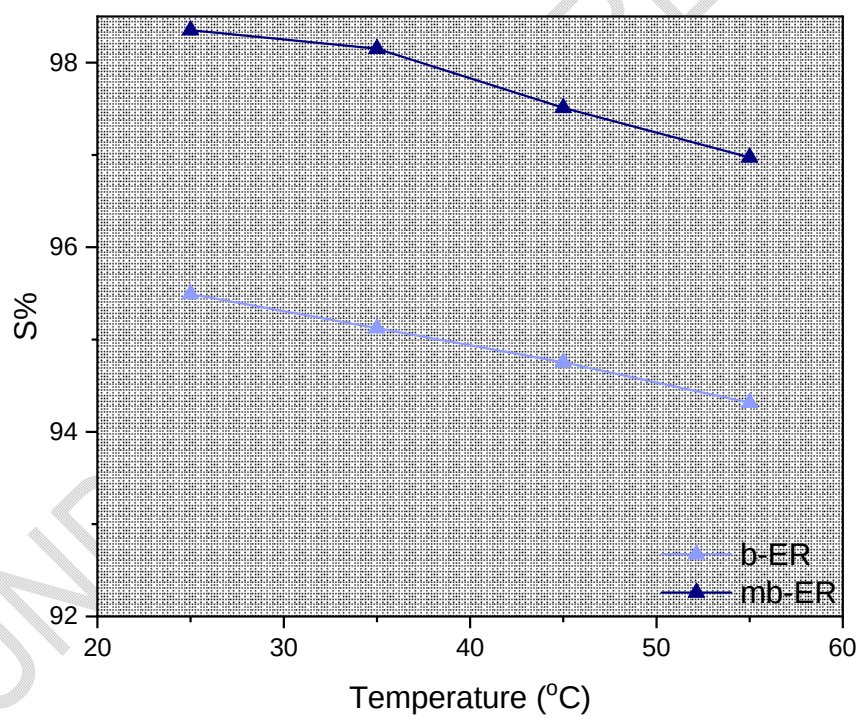

Fig. 5. Variation of sorption with temperature

A decrease in adsorption capacity was observed with the increase in temperature. Thermodynamic studies were carried out to examine the effect of temperature on the adsorption capacity. The results are given in Table 3.

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Table 3. Termodynamic parameters

Adsorbent	T(K)	ΔG° (kJmol^{-1})	ΔS° (jK^{-1} mol^{-1})	ΔH° (kJmol^{-1})
b-ER	298.150	-7.569	3.311	-6.587
	308.150	-7.611		
	318.150	-7.654		
	328.150	-7.663		
mb-ER	298.150	-1.135	24.668	-17.592
	308.150	-1.174		
	318.150	-9.702		
	328.150	-9.458		

*Biochar b-ER, nanomagnetic biochar mb-ER

It is seen that methyl blue sorption on b-ER and mb-ER decreases as the temperature increases. This shows that adsorption is an exothermic process. Negative enthalpy values confirm this situation. ΔH= -6.587 for b-ER and ΔH= -17.592 kJ/mol for mb-EA. Negative ΔG values indicate methyl blue adsorption spontaneous with b-ER and mb-ER. Positive ΔS values mean that the irregularity and randomness of the adsorbent-adsorbate interface increases during the adsorption of the dye [23].

3.8 Contact time effect and adsorption kinetics

While examining the effect of contact time, other parameters were kept constant. Experiments were carried out by changing the contact time to 15 minutes, 30 minutes, 60 minutes, 120 minutes, 180 minutes and 240 minutes. The effect of the contact time change on the sorption of methyl blue with b-ER and mb-ER is given in Figure 6.

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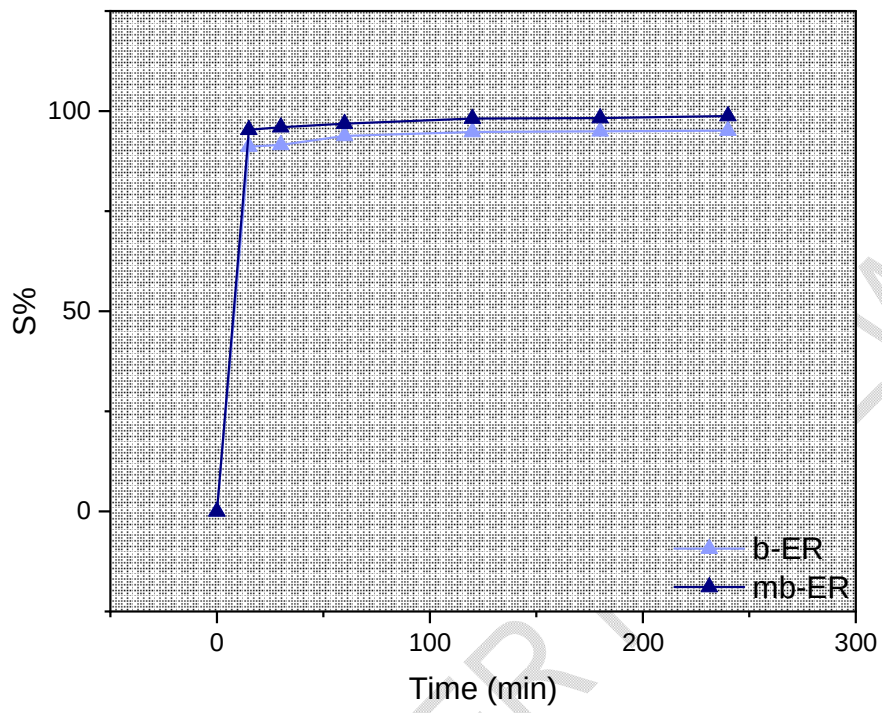

Fig. 6. Variation of sorption with contact time

The percentage of removal of methyl blue dye increased with increasing contact time. Since there was space on the surface at the beginning, the adsorption process was fast, and both adsorbent surfaces reached saturation within 60 minutes. There was no significant change in the percentage of adsorption after 60 minutes. Pseudo-first-order and pseudo-second-order kinetic models were used to examine the adsorption process from a kinetic isotherm. The results are given in Table 4.

Table 4. Kinetic parameters

Adsorbent	Order	q_c (mg/g)	k_1(1/min)	k_2(g/mg.min)	q_e (mg/g)	R^2
b-ER	First	0.238	$-2.58x10^{-05}$	-	14.400	0.272
b-ER	Second	14.300	-	0.549	14.400	0.999
mb-ER	First	0.392	$-1.04x10^{-05}$	-	14.750	0.323
mb-ER	Second	14.720	-	1.480	14.500	0.999

*Biochar b-ER, nanomagnetic biochar mb-ER

$q_{calculated}$ and $q_{experimental}$ adsorption capacity values for both adsorbents were compared for first-order and second-order kinetic models. While these values (14.300 and 14.400) were very close in the second-order kinetic model for b-ER, very close values (14.720 and 14.500) were found for mb-ER in the second-order kinetic model. The R^2 values of both adsorbents

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were checked (b-ER R^2 = 0.999 and mb-ER R^2 = 0.999). As a result, the adsorption process was found to fit the so-called second-order kinetic model. The maximum adsorption capacities obtained in some studies on methyl blue adsorption are given in Table 5.

Table 5. Some studies on methyl blue

Adsorbent	Adsorption capacity (mg/g)	Referencees
Nitrogen-enriched carbon	228.950	[24]
Bacillus amyloliquefaciens DT biofilm	847.000	[25]
Magnetic Mn-Fe_2O_4	32.210	[26]
Loquat biochar	31.746	Present work
Magnetic loquat biochar	67.568	Present work

In the literature search, not many studies were found on the adsorption of methyl blue dye. Adsorption capacities were found to be high in the removal of methyl blue with b-ER and mb-ER.

4. CONCLUSION

Biochar is an efficient adsorbent in removing dyes from aqueous media with its low cost, environmentally friendly, porous and large surface area. Loquat seeds are made into a stable structure with abundant porosity and specific surface area by turning into biochar. By modifying it with iron compounds, the total pore volume and surface area were expanded. BET analysis results confirm this situation. Methyl blue, an anionic dyes showed maximum adsorption at pH 6 and 7. The adsorption capacity of b-ER and mb-ER increased with increasing initial dye concentration. The maximum adsorption capacity was 31.746 mg/g for biochar (b-ER) and 67.568 mg/g for nanomagnetic biochar (mb-ER). While the adsorption isotherm data were explained by the Langmuir model (R^2=0.994 for b-ER, R^2=0.998 for mb-ER), the adsorption was consistent with the pseudo-second order kinetic model. When thermodynamic data is evaluated, the adsorption process is spontaneous (ΔG= -7.569 $kJmol^{-1}$ for b-ER and ΔG=-1.135 $kJmol^{-1}$ for mb-ER) and exothermic (ΔH= -6.587 kJ/mol for b-ER and mb-ER). ΔH=-17.592 kJ/mol). As a result, low cost, easily available loquat seeds can be used to remove methyl blue dye from aqueous solutions by modifying them. There are not many studies on methyl blue. The adsorbents used can be modified with different chemicals to increase the adsorption capacity and contribute to the literature.

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