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ARAŞTIRMA MAKALESİ / **RESEARCH ARTICLE**

Elaeagnus angustifolia STONE AS A LOW-COST BIOSORBENT PRECURSOR FOR REMOVAL OF METHYLENE BLUE FROM AQUEOUS SOLUTION

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ABSTRACT

In this study, the removal of methylene blue from aqueous solutions by biosorption onto *Elaeagnus angustifolia* stone has investigated. Optimum biosorption conditions have determined as a function of pH, biosorbent dosage, initial methylene blue concentration, contact time and temperature of the solution for the removal of methylene blue. Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm models have used to describe the biosorption isotherm model. The experimental data have fitted to pseudo-first order, pseudo-second order and intraparticle diffusion model to examine the sorption kinetics. The values of ΔG°, ΔH° and ΔS° have calculated by thermodynamic study to determine the nature of biosorption process. Experimental results have shown that *Elaeagnus angustifolia* stone can be used as an effective and low cost biosorbent precursor for the removal of methylene blue from aqueous solutions.

Keywords: Biosorption, Methylene blue, Biomass, *Elaeagnus angustifolia.*

SULU ÇÖZELTİDEN METİLEN MAVİSİ GİDERİMİNDE DÜŞÜK MALİYETLİ BİYOSORBENT KAYNAĞI OLARAK *Eleagnus angustifolia* ÇEKİRDEĞİNİN KULLANILMASI

ÖZ

Bu çalışmada, biyosorpsiyon ile sulu çözeltilerden metilen mavisinin *Elaeagnus angustifolia* çekirdeği ile giderimi araştırılmıştır. Optimum biyosorpisyon koşulları pH, biyosorban miktarı, başlangıç metilen mavisi derişimi, temas süresi ve sıcaklığın fonksiyonu olarak belirlenmiştir. Biyosorpsiyon izoterm modelinin belirlenmesi amacıyla Langmuir, Freundlich ve Dubinin-Radushkevich (D-R) izoterm modelleri kullanılmıştır. Deneysel veriler sözde-birinci dereceden, sözde-ikinci dereceden ve partikül içi difüzyon modellerine uygulanarak giderim işleminin kinetik ifadeleri belirlenmiştir. Biyosorpsiyon işleminin doğasını incelemek için ise ΔG°, ΔH° ve ΔS° değerleri hesaplanmıştır. Deneysel sonuçlar, sulu çözeltilerden biyosorpsiyon ile metilen mavisinin gideriminde *Elaeagnus angustifolia* çekirdeğinin etkili ve ucuz bir biyosorban kaynağı olarak kullanılabileceğini göstermiştir.

Anahtar Kelimeler: Biyosorpsiyon, Metilen mavisi, Biyokütle, *Elaeagnus angustifolia*.

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1. INTRODUCTION

Among the different pollutants of aquatic ecosystem, dyes are a large and important group of chemicals. They are widely used in industries such as textile, leather, printing, food, paper, rubber, plastics, cosmetics, etc., to color their products (Aksu et al., 2010; Vargas et al., 2011). These dyes are invariably left in the industrial wastes and consequently discharged mostly to surface water resources. With rapid industrialization, the discharge of industrial wastewater has increased. Their presence in water resources, even in low concentrations, consumes the dissolved oxygen and therefore affects the aquatic life and food web, causing thus environmental problems in eco system (El-Sharkawy et al., 2007).

Basic dyes are cationic due to the positive charge delocalized throughout the chromophoric system and have affinity towards materials with negatively charged functional groups, such as wool, silk, nylon and acrylics, where bright dyeing is the prime consideration. Among basic dyes, methylene blue (MB) is the most common water-soluble dye, widely used for dyeing leather, printing calico, cotton and tannin, and for medicinal purposes in its purified zinc-free form (Fernandez et al., 2010). It is stable to sunlight and natural oxidizing agents, and resists to biodegradation (Hajjaji and El Arfaoui, 2009). MB is not strongly hazardous to human being, it can cause some harmful effects. Acute exposure to MB can cause increased heart rare, vomiting, shock, Heinz body formation, cyanosis, jaundice, quadriplegia, and tissue necrosis in humans (Hameed et al., 2007). Therefore, it is important to remove such dye from waters and wastewaters before they are released to the environment.

Several methods have been developed to remove dyes from waters and wastewaters in order to decrease their impact on the environment. The processes developed consist in decolorizing by photo-catalytic oxidation, microbiological or enzymatic decomposition and adsorption on inorganic or organic matrices (Pavan *et al.*, 2008). Among them activated carbon is commonly used to remove dyes from industrial effluents because of its high removal efficiency. However, the cost associated with using activated carbon is relatively high and additionally not applicable to industrial effluents containing low concentrations of dyes (Tan *et al.*, 2010). In order to decrease the cost of treatment, some attempts have been made to find low-cost alternative adsorbents (Özer et al., 2007).

Biosorption, if compared with other available technologies above, gives comparable performance at a very low cost. It can be defined as sequestering of organic and inorganic species including metals, dyes and odor causing substances using live or dead biomass or their derivatives. Apart from cost effectiveness and competitive performance, the other advantages are possible regeneration at low cost, availability of known process equipment, sludge free operation and recovery of the sorbate (Doğan et al., 2009). Non-conventional adsorbents, including natural materials such as waste from agro-industrial activities, have been used successfully, as low-cost adsorbents for the removal of several dyes from aqueous solution and the evaluation of waste biomass is getting increased attention in all over the world (Pavan et al., 2008; Karagöz et al., 2008).

Agricultural by products and waste materials used for cheaper and effective adsorbents for removal of methylene blue from aqueous solution include hazelnut shell (Ferrero, 2007), garlic peel (Hameed and Ahmad, 2009), mango seed kernel powder (Kumar and Kumaran, 2005), Indian rosewood sawdust (Garg et al., 2004), peanut hull (Özer at al., 2007), yellow passion fruit waste (Pavan et al., 2008), rice husk (Chandrasekhar and Pramada, 2006).

In this study, methylene blue removal from aqueous solutions by biosorption onto *Elaeagnus angustifolia* stone was studied. Experimental parameters affecting the biosorption process such as pH, amount of biosorbent, initial dyestuff concentration, contact time and temperature of solution were optimized. Important parameters such as equilibrium isotherm, kinetics and thermodynamic studies were carried out to complement the usability of *Elaeagnus angustifolia* stone as an alternative and low-cost biosorbent.

EXPERIMENTAL PROCEDURE

Elaeagnus angustifolia, commonly known as Russian olive, is a member of *Elaeagnus*. Although having a dryish and mealy texture the fruits are edible and sweet. Production amount of Turkey is about 8000 tons/year and nearly 50 % of *Elaeagnus angustifolia* consist of shell, thus shells generated from industrial usage can be utilize as an alternative sorbent precursor for removal of basic dyes from aqueous solution.

Elaeagnus angustifolia was collected from Aegean region in August. Stones were washed, dried and ground in a high-speed rotary cutting mill. The resulting material was sieved and a particle size lower than 250 µm was used for biosorption experiments.

Methylene blue (C.I. 52015, $C_{16}H_{18}N_3SCl$, MW 319.87 g mol^{-1}) was obtained from Merck, Germany with analytical grade and used without further purification. Double deionized water (Milli-Q Millipore 18.2 MΩ cm^{-1} conductivity) was used for all solutions. The stock solution was prepared by dissolving accurately weighted dye in distilled water to the concentration of 1000 mg L^{-1} and the other concentrations for the experiments were obtained by diluting the dye stock solution to the required concentrations. Batch equilibrium biosorption experiments were performed using 200 mL of basic dye solution. The initial pH of each metal solution was adjusted to the required pH value by using 0.1 mol L^{-1} NaOH and 0.1 mol L^{-1} HCl solutions. Samples were collected at different contact time intervals and then they were centrifuged. The supernatant solution was analyzed using UV-VIS spectrophotometer at 664 nm. To investigate the effects of biosorption parameters such as, pH (3-12), biosorbent dosage (1-10 g L^{-1}), initial basic dye concentration (100-250 mg L^{-1}), contact time (10-240 min) and temperature (20-50°C) on removal of methylene blue by *Elaeagnus angustifolia* stone were studied in a batch mode of operation.

The amount of the dye biosorbed per unit mass of the biosorbent at equilibrium (q_e) was calculated by using the following mass balance equation,

$$q_e = \frac{(C_i - C_e)V}{W} \quad (1)$$

and the percent biosorption of the dye was calculated as follows:

$$\text{Biosorption (\%)} = \frac{(C_i - C_e)}{C_i} \times 100 \quad (2)$$

where C_i is the initial dye concentration (mg L^{-1}), C_e is the equilibrium concentration of the dye (mg L^{-1}), V is the volume of solution (L), and W is the mass of biosorbent (g).

The procedures of kinetic experiments were basically identical to those of equilibrium tests, but the aqueous samples were taken at different time intervals and the concentrations of dye were similarly measured. The amount of the dye biosorbed at time t (q_t) was calculated as follows:

$$q_t = \frac{(C_i - C_t)V}{W} \quad (3)$$

where C_i is the initial dye concentration (mg L^{-1}), C_t is the concentration of the dye at any time t (mg L^{-1}), V is the volume of solution (L), and W is the mass of biosorbent (g).

RESULTS AND DISCUSSION

Effect of pH

The pH is one of the most important factor controlling the biosorption of dye onto suspended particles. The pH of the solution affects the surface charge of the biosorbents as well as the degree of ionization of different pollutants. The hydrogen ion and hydroxyl ions are biosorbed quite strongly and therefore the biosorption of other ions is affected by the pH of the solution. Change of pH affects the biosorptive process through dissociation of functional groups on the biosorbent surface active sites. This subsequently leads to a shift in reaction kinetics and equilibrium characteristics of biosorption process (Doğan et al,. 2009). The effect of pH on biosorption of MB onto *Elaeagnus angustifolia* stone was investigated by varying pH from 2 to 12 and the results were given in Fig. 1. At lower pH**,** the surface charge may get positively charged, thus making (H^+) ions compete effectively with dye cations causing a decrease in the amount of dye biosorbed. When the pH increased, biosorbed MB also increases. This can be explained with the electrostatic interaction of MB with negatively charged surface. When the pH value increased, the surface of the biosorbent was negatively charged more. Thus, the maximum amount of biosorption of MB was observed at pH 7. Therefore, the remaining biosorption experiments were carried out at pH 7 (Hameed and El-Khaiary, 2008).

Effect of biosorbent dosage

The effects of biosorbent dosage on the removal ratios of dyes were shown in Fig.2. It is found that by increasing the biosorbent concentrations over the range of 1-10 g L^{-1} the removal efficiency increased but adsorption capacity (i.e. adsorption amount per unit mass) decreased. This can be attributed the fact that the number of available adsorption sites increased by an increase in adsorbent and this therefore resulted in an increase in removal efficiency. The decrease in adsorption capacity with an increase in the adsorbent concentration could be ascribed to the fact that some of the adsorption sites remained unsaturated during the adsorption process.

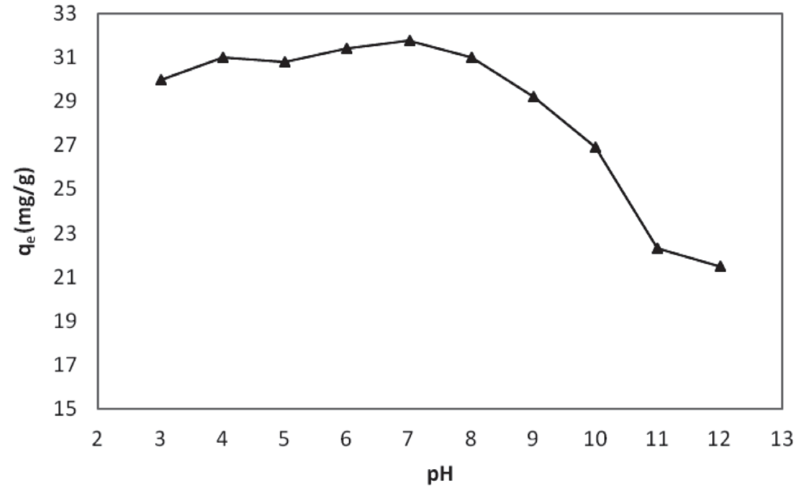

Figure 1. Effect of pH on MB sorption capacity

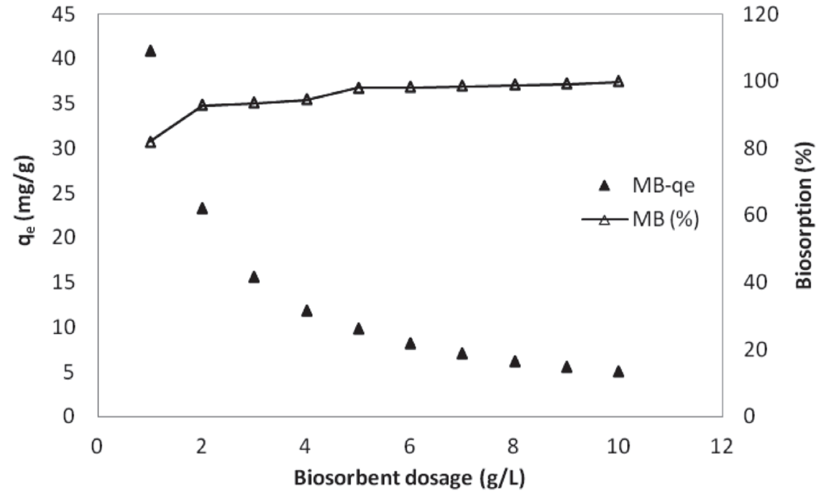

Figure 2. Effect of biosorbent dosage on MB sorption capacity

Another reason could likely be due to the interparticle interaction, such as aggregation, resulting from high adsorbent concentration. Such aggregation would lead to a decrease in the total surface area of the adsorbent and an increase in the diffusion path length (Wang et al., 2008). The biosorbent dosage was fixed at 2 g L^{-1} for further experiments.

Effect of initial MB concentration and contact time on temperature-dependent biosorption

The biosorption of MB was investigated at four different temperatures with changing biosorption times and initial concentrations and the results are shown in Fig. 3. As seen from Fig. 3, the amount of dye biosorbed (mg g^{-1}) increased with increase in time and then, reached equilibrium. The amount of dye removed at equilibrium increased with the increase in dye concentration. The initial dye concentration provides the necessary driving force to overcome the resistances to the mass transfer of MB between the aqueous and solid phases (Hameed and Ahmad, 2009). The biosorbed quantity of MB onto per unit mass of biosorbent (q_e) increased quickly with the beginning of biosorption, then after 120 min, the change became slow. Therefore, the biosorption of MB was speedy, and the reaction of sorption nearly reached equilibrium within 120 min. After this equilibrium period, the amount of biosorbed MB did not significantly change with time (Han et al., 2006). The biosorptive capacity of MB was also increased with temperature. This was due to the increasing tendency of biosorbate ions to biosorb from the solution to the interface with increasing temperature. The increase of the equilibrium biosorption with increased temperature indicated that the biosorption of MB ions is endothermic in nature (Han et al., 2007).

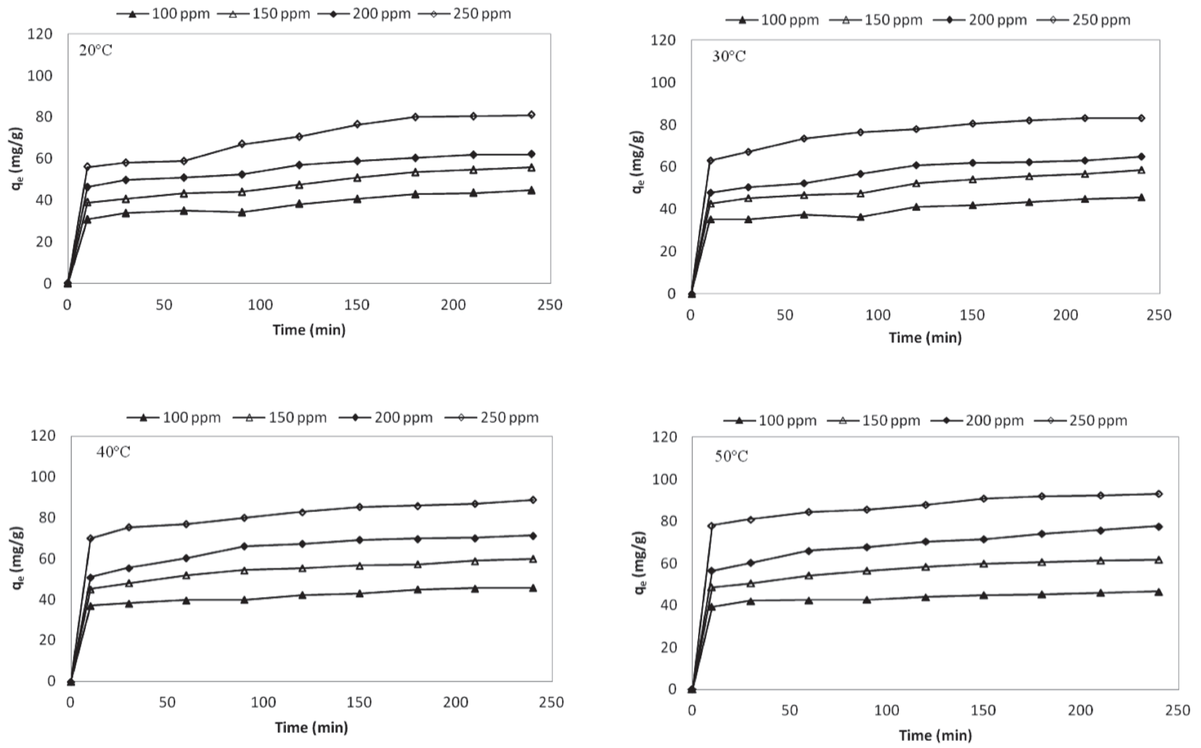

Figure 3. Effect of initial MB concentration and time at 20-30-40-50 °C

Biosorption isotherm models

The isotherm models are widely used parameters to describe the equilibrium between biosorption capacity (q_e) and sorbate concentration (C_e) at a constant temperature (Akar et al., 2009). In this study, the equilibrium data were experimentally determined and three different models, the Langmuir (Langmuir, 1916; Langmuir, 1918; Sawalha et al., 2006), Freundlich (Freundlich, 1906) and Dubinin-Radushkevich (D-R) (Dubinin and Radushkevich, 1947; Lodeiro et al., 2006; Fan et al., 2008) were fitted to experimental data which are given in Table 1.

Table 2 shows the experimental results for the Langmuir, Freundlich, and D-R isotherm models. According to experimental data the Freundlich isotherm fitted quite well with the high R^2 value indicating that the surface of the sorbent has some heterogeneity, and sorption is local. This situation is attributed to the fact that various active sites on sorbents have different affinities to MB molecules (Ertaş et al., 2010).

Biosorption kinetics

Kinetic models are used to determine the rate of the biosorption process (Hameed and Daud, 2008). Three kinetic models: pseudo-first-order (Lagergren, 1898; Febrainto et al., 2009), pseudo-second-order (Ho and McKay, 1999; Ho et al., 2000), and intraparticle diffusion (Weber and Morriss, 1963) models were used to investigate the biosorption process of MB (Table 3).

The rate constants of chemical sorption and intraparticle diffusion for the MB adsorption were determined and given in Table 4. The trend of the correlation coefficients values (R^2) were pseudo-second order > intraparticle diffusion ≥ pseudo-first order for all conditions. The correlation coefficients for pseudo-second order were higher for all initial concentrations and temperatures, strongly suggesting a second order chemical reaction process. A pseudo-second order fit indicates that the overall process is both dependent on the amount of dye and on the available sites in the sorbent. The process was also slightly influenced by temperature (Fernandes et al., 2007).

Table 2. shows the experimental results for the Langmuir, Freundlich, and D-R isotherm models. According to experimental data the Freundlich isotherm fitted quite well with the high R^2 value indicating that the surface of the sorbent has some heterogeneity, and sorption is local. This situation is attributed to the fact that various active sites on sorbents have different affinities to MB molecules (Ertaş et al., 2010).

Table 1. Biosorption isotherm models

Isotherm	Linearized Form	Parameters
Langmuir	$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$	q_e (mg g^{-1}): the amount of metal ion biosorbed at equilibrium
		q_m (mg g^{-1}): complete monolayer biosorption capacity
		C_e (mg L^{-1}): the equilibrium concentration
		K_L (L mg^{-1}): the Langmuir biosorption constant
Freundlich	$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	n: the empirical parameter relating the biosorption intensity, which varies with the heterogeneity of the material (dimensionless)
		K_F ((mg g^{-1})(L mg^{-1})$^{1/n}$): the Freundlich biosorption constant
D-R	$\ln q_e = \ln q_m - \beta\varepsilon^2$	β (mol^2 (kJ^2)$^{-1}$): the biosorption energy constant ε : the Polanyi potential R (8.314 J (mol K)$^{-1}$): the gas constant T (K): the absolute temperature E (kJ mol^{-1}): the mean free energy
	$\varepsilon = RT \ln\left[1 + \frac{1}{C_e}\right]$	
	$E = \frac{1}{\sqrt{2\beta}}$	

Table 2. Isotherm constants for the biosorption of MB

	Langmuir			Freundlich			D-R			
T (°C)	q_m	K_L	R^2	K_F	n	R^2	q_m	β	E	R^2
20	90.09	0.025	0.925	11.292	2.671	0.936	61.17	$5*10^{-5}$	$1.00*10^{2}$	0.735
30	101.01	0.029	0.910	13.520	2.679	0.927	72.17	$4*10^{-5}$	$1.12*10^{2}$	0.742
40	107.53	0.033	0.918	14.182	2.585	0.944	67.82	$3*10^{-5}$	$1.29*10^{2}$	0.711
50	105.26	0.046	0.941	17.807	2.846	0.954	74.39	$1*10^{-5}$	$2.24*10^{2}$	0.763

Table 3. Biosorption kinetic models

Isotherm	Linearized Form	Parameters
Pseudo-first order	$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$	q_e (mg g^{-1}): the biosorption capacity at equilibrium
		q_t (mg g^{-1}): the biosorption capacity at time t
		t (min): contact time
		k_1 (1 min^{-1}): the rate constant of pseudo-first order biosorption
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	q_t (mg g^{-1}): the biosorption capacity at time t
		k_2 (g (mg min)$^{-1}$): the rate constant of pseudo-second order biosorption
Intraparticle Diffusion	$q_t = k_p t^{1/2} + C$	q_t (mg g^{-1}): the biosorption capacity at time *t* k_p (mg (g min)$^{-1}$)$^{1/2}$)): the intraparticle diffusion rate constant C : the intercept

Table 4. Kinetic parameters for the biosorption of MB

			pseudo-first order			pseudo-second order			intraparticle		
T (°C)	Co	$q_{e,t}$	k_1	q_e	R^2	k_2	q_e	R^2	k_p	C	R^2
20	100	38.20	0.007	6.34	0.531	0.034	34.84	0.999	0.875	36.14	0.981
	150	47.55	0.012	9.67	0.980	0.009	45.25	0.999	0.554	29.92	0.681
	200	57.00	0.009	10.72	0.930	0.010	53.19	0.999	0.895	44.06	0.936
	250	70.50	0.017	20.25	0.781	0.003	68.03	0.989	1.547	49.99	0.775
30	100	41.15	0.004	6.19	0.441	0.045	36.76	0.999	0.277	34.14	0.553
	150	52.20	0.008	9.79	0.950	0.012	48.31	0.999	0.776	40.47	0.964
	200	60.90	0.014	16.17	0.909	0.005	57.80	0.996	1.343	43.11	0.931
	250	78.00	0.029	23.17	0.987	0.003	79.37	0.998	2.216	55.66	0.989
40	100	42.30	0.010	5.63	0.927	0.019	40.32	0.999	0.486	35.51	0.959
	150	55.35	0.030	16.48	0.959	0.004	56.18	0.998	1.505	40.12	0.997
	200	67.35	0.032	28.71	0.900	0.002	68.97	0.995	2.364	43.01	0.986
	250	83.00	0.017	14.49	0.958	0.005	81.30	0.999	1.486	66.01	0.951
50	100	43.95	0.013	3.76	0.688	0.031	42.92	1.000	0.474	38.58	0.744
	150	58.35	0.021	13.01	0.983	0.005	57.80	0.999	1.258	44.36	0.978
	200	70.45	0.021	17.70	0.985	0.004	69.93	0.999	1.874	50.44	0.979
	250	88.00	0.018	11.64	0.981	0.007	86.96	0.999	1.235	74.26	0.979

Thermodynamic parameters

Thermodynamic parameters (energy and entropy) are used to determine whether a biosorption process will spontaneously occur. For such equilibrium reactions, K_D, the distribution constant, can be used to calculate the Gibbs free energy:

$$K_D = \frac{q_e}{C_e} \tag{4}$$

$$\Delta G° = -RT ln K_D \tag{5}$$

$$\ln K_D = -\frac{\Delta G°}{RT} = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R} \tag{6}$$

where R is the universal gas constant, 8.314 J $mol^{-1}K^{-1}$, and T is the absolute temperature in K. The ΔS° and ΔH° values were calculated from the slope and intercept of a Van't Hoff plot of lnK_D versus 1/T, respectively (Akar *et al.*, 2009). The calculated values of Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) changes are given in Table 5. The negative value of ΔG° indicates the spontaneous nature of biosorption. The value of ΔH° is positive, indicating that the biosorption reaction is endothermic. The positive values of ΔS° show the increasing randomness at the solid/liquid interface during the biosorption.

CONCLUSIONS

Batch biosorption studies for the removal of MB from aqueous solutions have been carried out by using *Elaeagnus angustifolia* stone. The biosorption capacity changed with the parameters such as pH, biosorption dosage, initial dye concentration, contact time and temperature. Freundlich isotherm fitted well with the obtained data indicating the heterogeneity of sorbent surface. Pseudo-second order model was used to describe the sorption kinetic and thermodynamic study showed that the biosorption process is spontaneous and endothermic. Due to its high biosorption capacity, low cost and availability, *Elaeagnus angustifolia* stone seems an effective and alternative biosorbent precursor for the removal of basic dyes from aqueous solutions.

Table 5. Thermodynamic parameters for the biosorption of MB

T (°C)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})	R^2
20	-11.73	20.42	73.93	0.985
30	-21.25			
40	-26.29			
50	-34.64			

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