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Effective and rapid removal of cationic and anionic dyes from aqueous solutions using *Elaeagnus angustifolia* L. fruits as a biosorbent

Tülay Oymak[a,*], Nuraniye Eruygur[b]

[a]*Department of Analytical Chemistry, Faculty of Pharmacy, Cumhuriyet University, 58140 Sivas, Turkey, Tel. +903462191260; Fax: 034621916634; email: tulayoymak@cumhuriyet.edu.tr*
[b]*Department of Pharmacognosy, Faculty of Pharmacy, Selcuk University, 42250, Konya, Turkey, Tel. +90 3322233919; Fax: +90322412499; email: nuraniye.eruygur@selcuk.edu.tr*

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ABSTRACT

This study focused on the removal of both cationic and anionic dye from an aqueous solution using a natural product. Evaluation was made of the biosorption of methylene blue (MB) and Indigo carmine (IC) as a basic dye and an acid dye, respectively, from an aqueous solution using the dried fruits of *Elaeagnus angustifolia*. The experimental parameters such as pH of the solution, initial dye concentration, and contact time, were optimized to achieve quantitative removal. The quantitative biosorption of dyes was achieved as 200 mg L^{-1} of MB within 10 min at pH 7, 25 mg L^{-1} of IC within 10 min at pH 2. The maximum biosorption capacity was 344.8 mg g^{-1} for MB and 9.7 mg g^{-1} for IC at room temperature. The pseudo-first-order model and pseudo-second-order models were used to explain the biosorption kinetics. The second order model best explained MB and IC biosorption onto *E. angustifolia*. The experimental results showed that the use of *E. angustifolia* as a biosorbent is fast and effective, thereby indicating that it could be an attractive alternative for the removal of anionic and cationic dyes from dye wastewater.

Keywords: E. angustifolia; Dye molecules; Biosorption

1. Introduction

The current increasing widespread use of synthetic dyes in light industries from food to textiles results in the discharge of water contaminated with dyes into the ecosystem, which then threatens aquatic life. The removal of synthetic dyes from water is very important in terms of environmental protection. The degradation products of some dyes are toxic and carcinogenic even in small amounts [1,2]. Most of the dyes are difficult to biodegrade due to the complex aromatic molecular structure [3]. In this context, in order to decrease their impact on the environment, various physical, chemical and biological methods such as adsorption, biosorption, coagulation/flocculation, oxidation, ozonation, membrane filtration and liquid–liquid extraction have been widely employed for the treatment of wastewater containing dyes with different degree of success [4]. Various conventional methods that have been used, such as ferric chloride and alum for removing dyes, are not economically viable, require a sludge-handling process and are not very effective [5,6]. Among the removal methods of dyestuff from water and wastewater, the biosorption technique has been accepted as one of the most effective wastewater treatment processes because of its superiority in terms of simplicity of implementation, lower cost and abundant availability. The use of inexpensive adsorbent materials that do not require pretreatment seems to be more promising [7,8]. Therefore, many researchers are researching low-cost and more efficient alternative adsorbent materials [9–11]. Different adsorbents have been investigated in respect of the removal of cationic and anionic dyes from aqueous media.

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* Corresponding author.

Some of these alternative adsorbents include hazelnut shells [12], tea [13], peanut shells [14], wheat bran [6], garlic peel [15], and tamarind fruit shells [16].

Methylene blue is a cationic dye, which is widely used in the coloring of textiles, paper, and hair (as temporary colorants). However, MB has numerous harmful effects on human health and the environment due to its structural stability and complexity [17]. Indigo carmine is a synthetic anionic dye, used as an antibacterial and dermatological agent, and as biological staining [18]. However, it is also toxic and carcinogenic to mammalian cells [19]. There have been many studies on different types of adsorbent for removing methylene blue dye [12,17] but there have been few reports on indigo carmine dye [20].

Elaeagnus, which is the genus of Elaeagnaceae family, is used widely in Anatolia and is easily available in large quantities [21]. Of these, *E. angustifolia* is well-known for its medicinal use around the world. It has been used as an analgesic, tonic, anti-diarrheal, antipyretic, diuretic, and in the treatment of gastric and kidney disorders in folk medicine [22,23]. Previous phytochemical studies on *Elaeagnus* sp. have revealed that they contain a variety of compounds such as flavonoids, polyphenolics, alkaloids, sugars, and complex sterols. Biological activity studies have demonstrated that *Elaeagnus* have antioxidant, antibacterial, antinociceptive, anti-inflammatory, and antiproliferative effects [24].

In the present study, the use is reported of *E. angustifolia* fruit which is unusable and readily available in Turkey, as a biosorbent for the removal of MB and IC dye from an aqueous solution. In this work, the efficiency of *E. angustifolia* fruits in biosorption of MB and IC dye were investigated in respect of the effects of contact time, pH, initial MB, and IC concentration and biosorbent dosage. The aim of this study was to investigate the removal of harmful substances from wastewater using more economical biomaterials of natural origin.

2. Materials and methods

2.1. Chemicals and instrumentation

All the chemicals used in this study were of analytical grade. MB and IC were obtained from Merck, Germany. A multirotator (Biosan R 24) was employed for effective mixing of sorbent and solution. MB and IC stock solution was prepared by dissolving the appropriate amount in extra pure water. Then the working solution of MB and IC was prepared by diluting the stock solution to the desired concentrations, determined at 612 and 664 nm by UV–1600 spectrophotometer (Shimadzu, Japan). The pH measurement of the solutions was carried out using a pH meter (Mettler Toledo, USA). All the solutions were prepared in ultra-pure water. The pH of the solutions was adjusted with Britton–Robinson Buffer (boric, acetic, and phosphoric acid, each of 0.04 M) and base (0.2 M of NaOH) solutions.

2.2. Preparing the biosorbent

Elaeagnus angustifolia fruits were collected from the yard of the Faculty of Science, Cumhuriyet University, and dried in the oven at 50°C for a day. After manually separation of the peel and stones, the fruits were washed several times with de-ionized water to remove primary impurities. The prepared samples were then dried in the oven and pulverized into particle size <50 μm through standard sieves to be used as biosorbent.

E. angustifolia fruits are of different sizes. The small fruits are not preferred for human consumption. In this study, investigation was made of the biosorbent use of the small fruits of *E. angustifolia* that are not consumed by the public.

2.3. Biosorption procedure

For the biosorption of dyes (50 mg L^{-1} MB and 25 mg L^{-1} IC) on *E. angustifolia* dried fruits (25 mL, the model dye solution was treated with 200 mg of *E. angustifolia* dried fruits, and each sample was then adjusted to pH 7 for MB and pH 2 for IC with BR buffer. After reaching equilibrium (10 min), the absorbance of the supernatant was monitored spectrophotometrically at 612 and 664 nm against reagent blank. The final concentration of dye was determined with the calibration plot method.

The percentage dye removal (%) was calculated using the following equation:

$$\text{Removal\%} = \frac{C_0 - C_f}{C_0} \times 100 \tag{1}$$

The effect of pH, adsorption time and initial dye concentration studies were conducted in the same way with changes made only to the related experimental parameter.

3. Results and discussion

3.1. Characterization of E. angustifolia dried fruits

Scanning electron microscopy (SEM) studies were performed on a Tescan Mira 3XMU with an Oxford EDS analysis system. As can be seen from Fig. 1, the surface morphology of *E. angustifolia* fruits changed after biosorption of the dyes. A significant difference was seen in the surface roughness on the SEM images of *E. angustifolia* fruits before and after biosorption of dyes. MB and IC were observed to be adsorbed through the pores of *E. angustifolia* fruit and between the layers.

3.2. Point of zero charge

The point of zero charge method was used for determination of the surface charge on *E. angustifolia* fruit. Briefly, 100 mg of biosorbent was introduced into 25 mL of solutions with varying pH from 2 to 12 and stirred for 24 h. (2–11, prepared from 0.1 M HCl and 0.1 M NaOH). The final pH values were then measured with a pH meter. The ΔpH value was calculated from the difference between the initial and final pH values. A plot of ΔpH vs. pH was used for determination of the point of zero charge. The value of pH corresponding to ΔpH = 0 was taken as the point of zero charge [7,9]. The experimental results determined point of zero charge to be at pH 6.7. At lower pH values (pH < 6.7) the surface of the biosorbent became positively charged and at these pH ranges, biosorption of anionic dyes, such as IC, seems possible. At higher pH ranges (pH > 6.7), the surface of the *E. angustifolia* fruits was negatively charged. Therefore, cationic species were more feasible for biosorption on to *E. angustifolia* fruits in this range. The point of zero charge of *E. angustifolia* fruit is shown in Fig. 2.

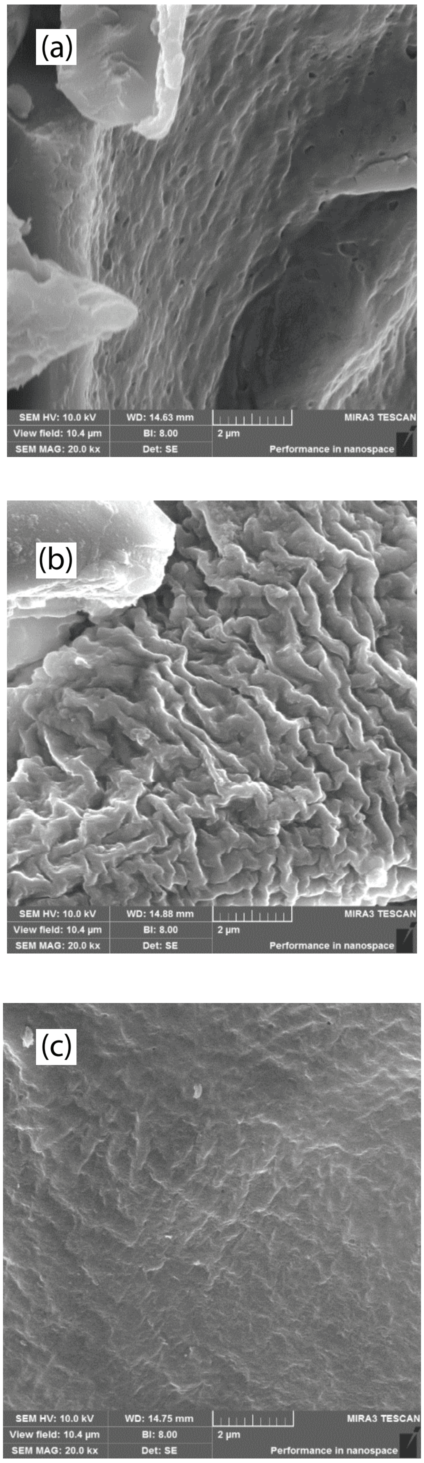

Fig. 1. SEM images of *E. angustifolia* fruits: (a) before biosorption; (b) after biosorption of MB; and (c) after biosorption of IC.

3.3. Surface area (BET)

The process of biosorption is a multistep, complex phenomenon affected by many factors. In the biosorption process, the pore size and total pore volume has a significant influence among these factors. The pore structure of the biosorbent and its surface chemistry significantly affect the biosorption of large molecules such as MB into its structure. MB has a molecular cross-sectional diameter of about 0.8 nm and therefore cannot easily enter into pores <1.3 nm. *E. angustifolia* has a significant surface area and wide pore size distribution [25,26]. The BET surface area of *E. angustifolia* is 10.12 $m^2 g^{-1}$, whereas the BJH biosorption/desorption surface area of the pores of *E. angustifolia* is 19.51/25.29 $m^2 g^{-1}$. The cumulative biosorption/desorption pore volume of the pores (17 Å < d < 3,000 Å) of *E. angustifolia* is 0.019823/0.019556 $cm^3 g^{-1}$ (Table 1). Thus, the *E. angustifolia* is found to consist of mesopores predominantly. This is exactly what is desirable for the adsorptive removal of metal ions and dyes from liquids.

3.4. X-ray diffraction

As an analytical technique, the X-ray diffraction (XRD) is employed to investigate crystal or polycrystalline structures, quantitative resolution of chemical compounds, qualitative identification of various chemical species and to measure the degree of crystallinity. The XRD, Rigaku SmartLab X-ray diffractometer, uses non-monochromatographic Cu Kα1-radiation (40 kV, 30 mA, λ = 1.5). Scanning in the range 5°–65° of 2θ patterns were recorded. The XRD pattern of *E. angustifolia* showed peaks at 2θ = 21.3° corresponding to cristobalite suggesting that the crystalline phase predominates in *E. angustifolia* (Fig. 3).

3.4.1. Effect of initial pH on the biosorption

The initial pH of the solution is one of the significant parameters influencing the biosorption of dyes on the

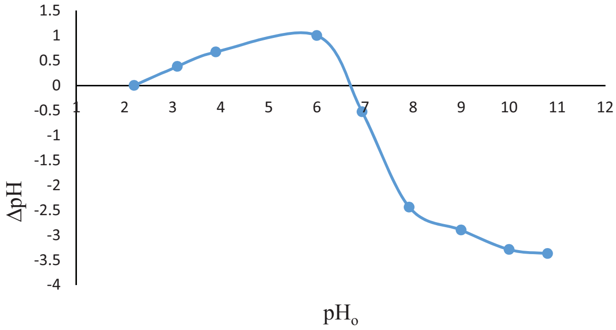

Fig. 2. Point of zero charge of *E. angustifolia* fruits.

Table 1
Surface properties of *E. angustifolia*

Surface properties	Value
BET surface area	10.12 m^2g^{-1}
Average pores volume	0.033 $cm^3 \cdot g^{-1}$
Average pore diameter	65.71 Å

biosorbent. Therefore, the biosorption of dyes on 200 mg dried fruit of *E. angustifolia* were studied by varying the pH 4–9 for MB and pH 2–6 for IC. The pH of the 25 mL dye solutions was adjusted using the relevant buffer solutions. The effect of pH on the removal of IC and MB is shown in Fig. 4. The maximum biosorption (≥95%) for the dyes studied was obtained at pH 6–8 for 50 mg L^{-1} MB and at pH 1–2 for 25 mg L^{-1} IC. Therefore, pH 7 for MB and pH 2 for IC were selected as optimum pH for subsequent experiments. Fig. 5 shows the UV–Vis spectrum of MB and IC before and after biosorption and is a photograph image of 50 mg L^{-1} MB and IC before and after biosorption.

3.5. Effect of the initial dye concentration

In the present study, the effect of the initial dye concentration was studied by changing MB and IC concentration from 50 to 200 mg L^{-1} and from 25 to 200 mg L^{-1}, respectively (25 mL, 0.2 g of biosorbent). Fig. 6 shows the effect of initial dye concentration on biosorption. As seen in

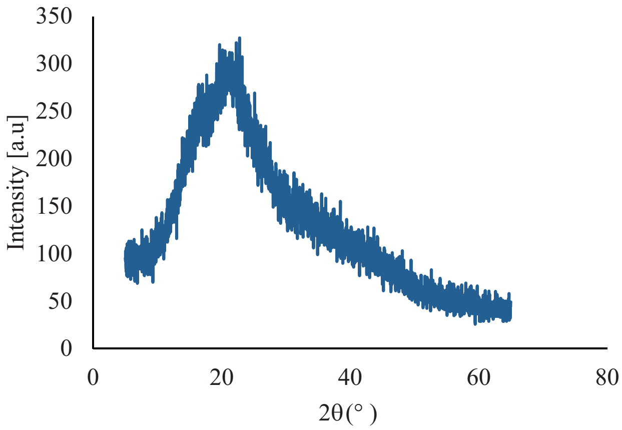

Fig. 3. XRD analyses of *E. angustifolia*.

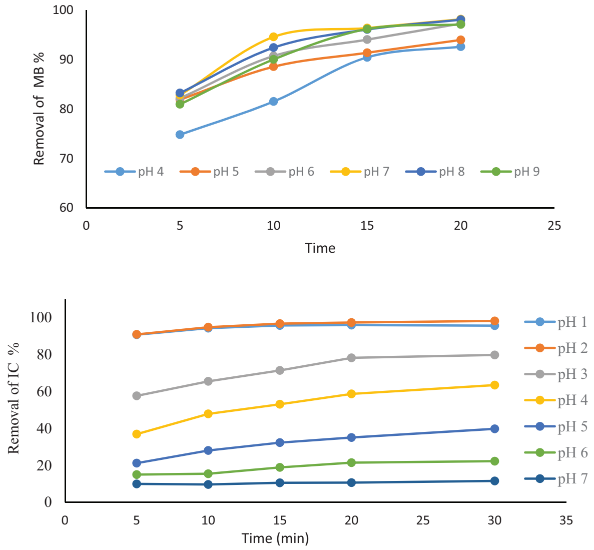

Fig. 4. Effect of pH on the removal of IC and MB solution at different time intervals.

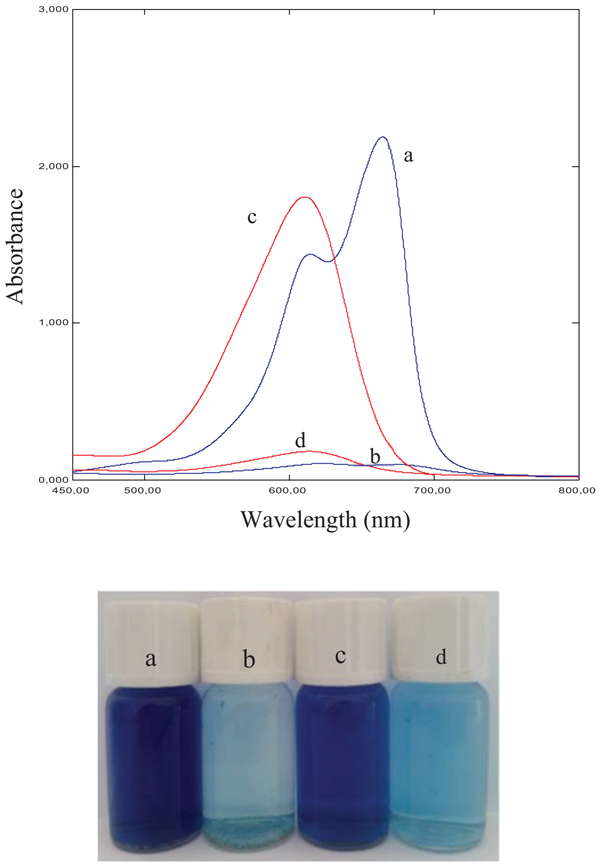

Fig. 5. Photograph of 50 mg L^{-1} MB and IC before and after biosorption, and UV–Vis. spectrum of MB and IC before and after biosorption (a, b, c, and d, respectively) (MB spectrum is diluted five times).

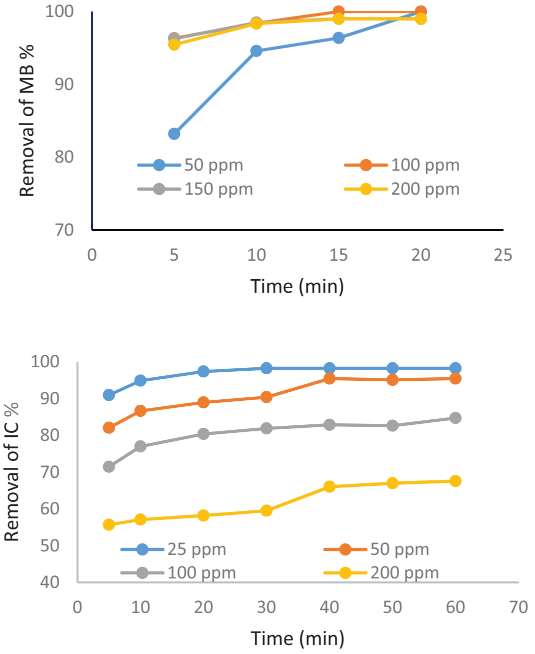

Fig. 6. Effect of the initial dye concentration on biosorption.

Fig. 6 at high initial concentrations for MB, the time required for quantitative biosorption was short, that is, 10 min was enough for quantitative biosorption of 100 and 200 mg L^{-1} and 50 min was for 100 mg L^{-1} IC.

3.6. Effect of the biosorbent amount

The effect of biosorbent dosage on the biosorption capacity of the methylene blue and indigo carmine was investigated, while other experimental parameters were kept constant. The biosorbent dosage was studied from 25 to 200 mg for biosorption studies of both dyes. As can be seen in Fig. 7, the quantitative biosorption of MB was 50 to 200 mg of *E. angustifolia* and the quantitative biosorption of IC was 100 to 200 mg.

3.7. Biosorption isotherms

Biosorption isotherms are necessary to understand the relationship between adsorbate and biosorbent. There are important equilibrium models which can be used for evaluation of the surface properties and the adsorption process. Langmuir, Freundlich, and Temkin isotherms have been widely employed for the clarification of biosorption (or adsorption) process. The Langmuir equation is as follows:

$$Q_e = \frac{Q_{\max} K C_e}{1 + K C_e} \tag{2}$$

where Q_e is the amount of dye per mass of biosorbent (mg g^{-1}); $Q_{\max}$ is the maximum biosorption capacity (mg g^{-1}); C_e is the equilibrium dye concentration (mg L^{-1}); and K is a constant that is related to the biosorption rate [27].

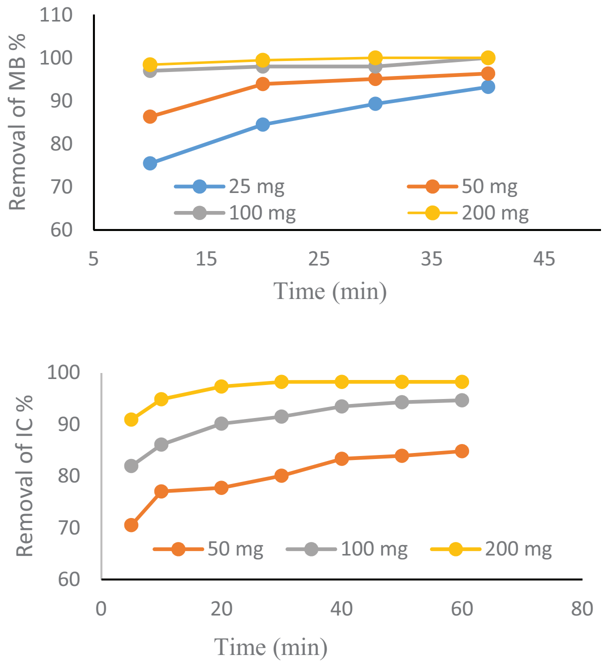

Fig. 7. Amount of biosorbent on the removal of IC and MB solution at different interval times.

Langmuir equation can be given as follows:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{\max}} C_e + \frac{1}{K Q_m} \tag{3}$$

The Freundlich isotherm equation is given as shown below [28,29]:

$$Q_e = K_f C_e^{1/n} \tag{4}$$

where Q_e is the amount of biosorbed dye per mass of biosorbent, K_f is the Freundlich constant, C_e is the equilibrium IC concentration and $1/n$ is a constant related with biosorption intensity [30]. The multilayer biosorption process is thought to be best suited to the Freundlich model rather than the Langmuir model. The Freundlich isotherm can be written in linear form as follows:

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{5}$$

A plot of ln Q_e vs. ln C_e gives a straight line with a slope equal to $1/n$ and intercept equal to ln K_f.

The Temkin isotherm is shown as biosorbent–adsorbate interactions. This isotherm is given by the following equation [31,32]:

$$Q_e = B \ln A_T + B \ln C_e \tag{6}$$

The constant B (J mol^{-1}) is related to the heat of biosorption. A_T (L g^{-1}) is the Temkin isotherm equilibrium binding constant.

The experimental results showed that the biosorption mechanisms for MB and IC were suited to the Langmuir model with a correlation constant of >0.9994 and 0.9933, respectively. The $Q_{\max}$ value was found to be 344.8 mg g^{-1} for MB and 9.72 mg g^{-1} for IC. The n value calculated from the Freundlich isotherm was >1 for both MB and IC dye molecules. The n values (3.4 and 10.9) indicated favorable biosorption of MB and IC on *E. angustifolia*. The heat of the biosorption process for MB and IC was calculated from the Temkin isotherm model to be 47.6 and 1.6 J mol^{-1}, respectively.

The calculated isotherm parameters for each model are summarized in Table 2. The Langmuir adsorption isotherm for MB and IC on *E. angustifolia* is shown in Fig. 8.

3.8. Batch kinetic studies

The controlling mechanism of the biosorption process was investigated with kinetic tests. The equilibrium time was 20 min for MB and 40 min for IC. The Lagergren's pseudo-first-order model and pseudo-second-order model were used, which are the most common models used to fit the kinetic sorption experiments [29,33]. The linearized first-order kinetic model is given below:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \tag{7}$$

Table 2
Langmuir, Freundlich, and Temkin isotherm parameters for MB and IC biosorption onto *E. angustifolia*

Dye	Langmuir parameters			Freundlich parameters			Temkin parameters		
	Q_{max} (mg g^{-1})	K (L mg^{-1})	R^2	K_f (L mg^{-1})	n	R^2	B (J mol^{-1})	A_t (L mg^{-1})	R^2
MB	344.8	0.03	0.9994	26.22	3.45	0.9754	47.64	0.94	0.9910
IC	9.7	0.47	0.9933	5.51	10.9	0.9800	1.61	2,031	0.9627

Table 3
Kinetic data for adsorption of MB and IC on *E. angustifolia*

	Pseudo-first-order rate parameter				Pseudo-second-order rate parameter			
	Initial dye concentration (mg L^{-1})	Q_e (mg g^{-1})	k_1 (min^{-1})	R^2	Q_e (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	h (mg g^{-1} min^{-1})	R^2
MB	50	2.37	0.17	0.940	3.28	0.24	2.58	0.999
	100	1.58	0.19	0.949	6.32	0.54	21.48	0.999
	200	3.95	0.21	0.967	12.7	0.22	35.48	0.999
IC	50	0.81	0.024	0.905	6.1	0.16	6.1	0.999
	100	2.24	0.003	0.937	10.69	0.08	9.14	0.999
	200	9.23	0.019	0.936	16.61	0.03	9.04	0.992

where k_1 (min^{-1}) is the rate constant of pseudo-first-order adsorption, Q_e (mg g^{-1}) is the amount of solute adsorbed on the surface at equilibrium and Q_t (mg g^{-1}) is the amount of solute adsorbed at any time.

The linearized second-order kinetic model is given as the equation below:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^{\,2}} + \frac{t}{Q_e} \tag{8}$$

where k_2 (g mg^{-1} min^{-1}) is the second-order rate constant. The Q_e and k_2 can be calculated from the slope and intercept. The constant k_2 is used to calculate the initial sorption rate h (mg g^{-1} min^{-1}). h is calculated from the equation given below:

$$h = k_2 Q_e^{\,2} \tag{9}$$

The parameters of the pseudo-first-order and second-order models are summarized in Table 3. The correlation coefficients for the pseudo-first-order model were found to be low, indicating that the biosorption of MB and IC on *E. angustifolia* does not fit pseudo-first-order kinetics. High correlation coefficients (R^2 > 0.999) demonstrated the biosorption of MB and IC on to *E. angustifolia* agreement in the pseudo-second-order kinetic model. As seen in Table 3, increasing the initial MB and IC concentration resulted in an increase of both Q_e and h. This resulted in faster biosorption of MB and IC onto *E. angustifolia*.

3.9. Desorption and reusability of the E. angustifolia

Different solvents such as ethanol, acetone, and 1 M of acid (HCl and HNO_3) and base (NH_3 and NaOH) were

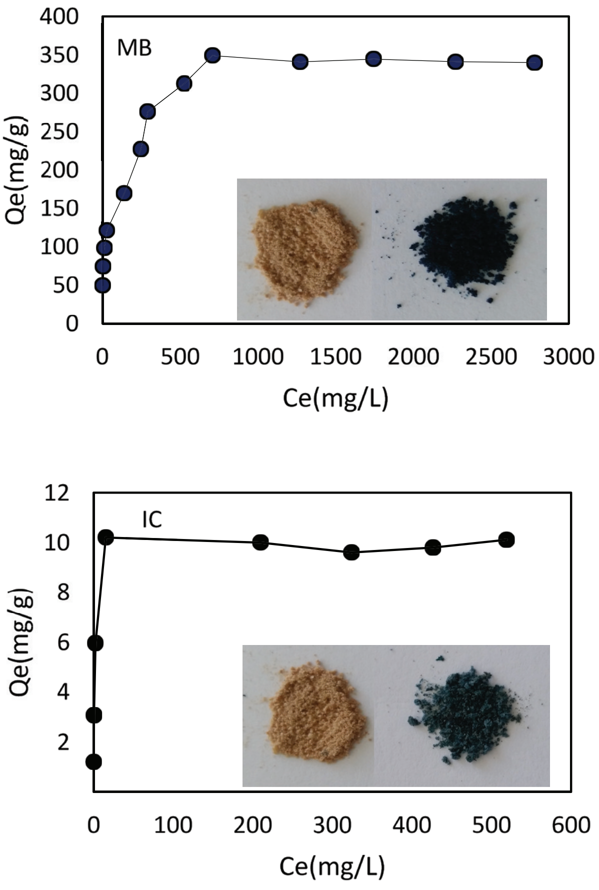

Fig. 8. Langmuir isotherm for of MB and IC biosorption onto *E. angustifolia*.

investigated for desorption of *E. angustifolia*. Desorption with acid and base and organic solvent was unsuccessful. However 1 M NH_3 in methanol, ethanol or acetone were the most suitable and almost complete desorption was achieved. The biosorbent was separated from the solution with decantation and washing with deionized water. Then the biosorbent was re-used in the next biosorption process. After biosorption, the absorbance of the supernatant was monitored spectrophotometrically as described in the biosorption procedure. The desorbed *E. angustifolia* was employed for further biosorption and quantitative biosorption (95≥) was achieved after several cycles (>50).

3.10. Comparison of E. angustifolia with literature data

In the present study, *E. angustifolia* was employed for the effective removal of a cationic and anionic organic dye. There are many reports in literature about the removal of dyes from aqueous solutions with adsorbents. However, most of these adsorbents are suitable for removal of only cationic or anionic dye. Very few studies in literature have used the same adsorbent/biosorbent for both anionic and cationic dyes. Therefore, an important feature of this study is the removal of anionic dyes and cationic dyes by the same biosorbent. Compared with different studies in the literature, the removal of MB and IC from aqueous media with *E. angustifolia* fruits was satisfactory (Table 4).

From the results of the present study, it can be concluded that *E. angustifolia* fruits have relatively high removal capacities, for example, 344 mg g^{-1} for MB (within only 10 min) and 10.2 mg g^{-1} for IC (within 30 min). In addition, *E. angustifolia* is a cost-effective, reusable and environmentally friendly biosorbent and it may be used for the removal of other toxic anionic or cationic species.

Table 4
Comparison of the method with some existing literature data

Biosorbent	q_{max} (mg g^{-1}) MB	q_{max} (mg g^{-1}) IC	Reference
Wheat bran (RY145)	196.1	–	[6]
Tea waste	85.16	–	[13]
Peanut shells	108.6	–	[14]
Garlic peel	82.64	–	[15]
Rice husk ash	–	29.27	[31]
Brazil nut shells	7.81	1.09	[33]
Diplotaxis harra	185.89		[32]
Glebionis coronaria L.	258.76		[32]
Watermelon rind	231.48		[34]
Eichhornia crassipes	35.37		[35]
Papaya leaf	512.55	–	[36]
Magnetic cellulose–poly 4-hydroxybenzoic acid	7.5	–	[37]
Streptomyces fradiae	59.63	–	[38]
Grape-peel	215.7	–	[39]
Compost of olive tree pruning waste	250.0		[40]
Corn stigmata	106.3	63.79	[41]
E. angustifolia fruit	344.8	10.7	This work

4. Conclusions

The results of the present study demonstrated that the powdered *E. angustifolia* fruits are effective, low cost and fast in the removal of anionic and cationic dyes from aqueous solutions. MB was more efficiently removed by the biosorption on *E. angustifolia* fruits than IC. As can be seen from the SEM image, *E. angustifolia* fruits have a highly porous structure with many layers. *E. angustifolia* has good surface area and biosorption capacity for MB and IC. Therefore, *E. angustifolia*-based material can provide a promising alternative as a natural biosorbent for the removal of both anionic and cationic dyes from wastewater produced in textile and cosmetic industries, and in aquaculture activities.

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