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Central composite methodology for methylene blue removal by *Elaeagnus angustifolia* as a novel biosorbent

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ABSTRACT

In this research, the performance of Persian olive or *Elaeagnus angustifolia* (EA) as a potential biosorbent for the removal of methylene blue (MB) as a cationic dye from contaminated wastewaters was studied. In this regard, the response surface methodology (RSM) was used to investigate the effect of important parameters (time, pH, initial dye concentration and EA dosage) and their interaction on the removal efficiency, to optimize the process, and to model the experimental data. The Fourier transform infrared (FTIR) analysis, field emission electron microscope (FESEM) images, X-ray diffraction (XRD) pattern, Brunauer–Emmett–Teller (BET) surface area analysis, zeta potential and determination of isoelectric pH were employed to characterize the selected biosorbent. The dye removal efficiency of 95.66% was achieved at the predicted optimum conditions. The isotherm (Langmuir, Freundlich and Temkin), kinetic (pseudo-first-order, pseudo-second-order and intraparticle diffusion) and thermodynamic parameters were also investigated at equilibrium. High values of correlation coefficients indicated that experimental data are best fitted to Temkin isotherm and pseudo-second-order kinetic model. The thermodynamic parameters showed that the adsorption of MB onto the surface of EA was an exothermic and spontaneous process. This statistical survey illustrated that EA can be introduced as an effective biosorbent with high adsorption capacity of 185.185 (mg/g) for the removal of MB from colored industrial effluents.

1. Introduction

The subject of trace organic and elements elimination from water streams has become an item of interesting concern for various researchers worldwide. Industries like textile, leather, paper and plastics discharge high amounts of dye material into the environment, which causes severe problems to human lives, animals and plants [1,2].

The organic 3,7-bis(dimethylamino) phenothiazine-5-ium-chloride called methylene blue (MB) is a cationic dye molecule which is extensively used in dyeing processes of textile industry [3–5]. The toxicity and non-biodegradability of MB are well known and there are many reports on harmful side effects relating to the contacting and ingestion of MB such as vomiting, diarrhea, gastritis, eye burns, headache, chest pain, etc. [6,7].

Among the most studied technologies (precipitation, adsorption, ion exchange, filtration, electrochemical and advanced oxidation processes (AOPs)) for water and wastewater treatment and purification [8], adsorption procedure using various types of materials has been widely surveyed for the removal of organic dye molecules, heavy metals and other types of contaminants. Carbon based adsorbents (activated carbon, CNTs, graphene, etc.), hyper branched polymers, dendrimers, mineral compounds, low-cost and natural adsorbents, and also different combination of these adsorbents are being studied by many researchers worldwide [9–14].

Although, achieving high efficiencies for the contaminant abatement is one of the main goals of the adsorption process, the economic aspects of the employed technique and materials are of great importance. Consequently, the natural, low-cost and waste materials obtained from agriculture and various industries have been increasingly employed as inexpensive and available biosorbents [1,15–18]. *Elaeagnus angustifolia* or *E. angustifolia* (EA) is a fruit extensively distributed from the northern regions of Asia to the Himalayas and Europe. EA is also commonly used in Iranian traditional medicine for its therapeutic effects especially in treating rheumatoid arthritis and joint pain. This fruit is widely available in local markets especially Iranian stores [19–21].

Therefore, the objective of the present study is to prepare *E. angustifolia* (EA) as a natural low-cost biosorbent to investigate its dye removal ability from aqueous solutions containing methylene blue (MB) as the dye contaminant. The surface

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morphology, functional groups identification, crystallinity, specific surface area and surface charge determination were analyzed by Field emission electron microscope (FESEM) images, Fourier transform infrared (FTIR) analysis, X-ray diffraction (XRD) pattern, Brunauer–Emmett–Teller (BET) surface area analysis, zeta potential and isoelectric pH (pH_{ZPC}) analysis. After characterization of the biosorbent, the adsorption processes were carried out and the effect of important factors including initial dye concentration, time, pH and biosorbent dosage were examined as input variables on the dye removal efficiency (%) through the response surface methodology (RSM) as a powerful statistical technique which have shown a growing interest among different researchers worldwide [22,23]. RSM can build an analytical model to relate the response function to the selected variables. It also determines the effect of individual factors and their interaction on the response. The central composite design (CCD) is an efficient experimental design and one of the most popular methodologies to build a quadratic (second-order) model between the response function and variables with a minimal amount of experimental data [24]. After modeling the adsorption process by a response surface as a function that approximate the results, the optimization of removal procedure was performed by response optimizer and the results were also compared with other studies in this area. Finally, the equilibrium study of the process by isotherm, kinetic and thermodynamic parameters were conducted at the obtained optimum conditions to illustrate the mechanism, rate and nature of the adsorption of MB dye molecules onto the EA biosorbent.

2. Materials and methods

2.1. Preparation of EA

EA fruit was obtained from a local market in Tehran, Iran. The preparation of EA for adsorption process involved no chemicals. In this regard, EA was first separated from its seed, medulla and pericarp. Then, EA (10 g) was washed with distilled water (1000 mL) for 4 times and then dried in oven at 30 °C for 12 h. The obtained product was milled with a mortar and sieved to particle sizes < 250 μm.

2.2. Adsorption procedure by response surface methodology (RSM)

C.I. Basic Blue 9 (methylene blue (MB), $C_{16}H_{18}ClN_3S$ and M_w: 319.85 g/mol) purchased from Ciba was selected as the synthetic model dye. Other chemicals were of analytical grade purchased from Merck. A four-factor five-level central composite design (CCD) with a total number of 31 experimental runs was conducted to evaluate the effect of four independent variables (x_1: time (min), x_2: $[MB]_0$ (mg/L), x_3: pH and x_4: $[EA]_0$ (g/L)) on the performance of adsorption process. The response function (dye removal efficiency (%)) was further optimized to reach a desired value by Response Optimizer. Data analysis and optimization procedure were performed using the statistical software "Minitab" version 16.1.0.0.

Different volumes of MB solution (500 mg/L) was added to distilled water to prepare the synthetic dye solutions (250 mL). H_2SO_4 (0.1 M) or NaOH (0.1 M) were used for pH adjustments. Adsorption experiments were performed on a magnetic stirrer with the constant stirring rate of 200 rpm in batch mode. The variables and their levels considered in this study are presented in Table 1. According to CCD experiments, the adsorption processes were conducted, the samples were taken from the solution at the determined time intervals (2.5, 5, 7.5, 10, and 12.5 min) and then centrifuged by Hettich EBA20 at 5000 rpm for 10 min. The dye removal efficiency (%) is defined by Eq. (1):

$$\text{Dye removal efficiency}(\%) = \left(\frac{C_0 - C_0}{C_0}\right) \times 100 \tag{1}$$

Table 1
Independent variables in CCD matrix and the response values for MB removal by EA.

Run order	Time (x_1, min)	C_0 (x_2, mg/L)	pH (x_3)	EA (x_4, g/L)	Experimental removal (%)	Predicted removal (%)
1	7.5	30	9	0.3	93.72	93.72
2	10	20	10	0.4	95.9	95.26
3	7.5	50	9	0.3	88.53	86.14
4	7.5	30	11	0.3	93.16	93.91
5	10	40	8	0.4	95.85	96.32
6	10	40	8	0.2	77.16	78.47
7	7.5	30	7	0.3	88.37	87.16
8	5	20	8	0.4	91.71	92.73
9	2.5	30	9	0.3	82.77	82.06
10	7.5	30	9	0.5	97.28	95.07
11	5	20	8	0.2	76.40	7550
12	10	40	10	0.2	85.8	84.77
13	7.5	30	9	0.3	93.72	93.72
14	7.5	10	9	0.3	90.77	92.70
15	7.5	30	9	0.3	93.72	93.72
16	7.5	30	9	0.3	93.72	93.72
17	10	20	10	0.2	91.07	90.35
18	5	40	8	0.4	90.56	91.75
19	5	40	10	0.4	93.53	95.09
20	5	40	8	0.2	65.67	66.29
21	7.5	30	9	0.1	62.95	64.70
22	10	40	10	0.4	96.53	97.91
23	7.5	30	9	0.3	93.72	93.72
24	7.5	30	9	0.3	93.72	93.72
25	10	20	8	0.2	88.52	86.95
26	5	20	10	0.4	94.02	93.18
27	10	20	8	0.4	95.83	96.57
28	5	40	10	0.2	74.61	74.34
29	12.5	30	9	0.3	96.07	96.33
30	7.5	30	9	0.3	93.72	93.72
31	5	20	10	0.2	81.15	80.66