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Competitive removal of cationic dye (BR 46) and heavy metal (copper II) from synthetic textile effluent using adsorbent of *Melia azedarach* sawdust

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ABSTRACT

Sawdust of *Melia azedarach* wood was investigated for removal of BR46 dye and Cu^{2+} from a binary-solute system. A central composite design was used to determine the effect of various variables including the initial concentration of dye (x_1) and Cu^{2+} (x_2), solution pH (x_3), contact time (x_4), and adsorbent dose (x_5) in the process. Fourier transform infrared spectroscopy (FTIR) was utilized to characterize the surface chemistry of pristine- and solute-loaded sawdust. The results of FTIR showed that the functional groups, especially OH groups, on the sorbent surface are capable of adsorbing cationic dye and heavy metal. The mean removal efficiency of BR46 and Cu^{2+} was obtained as 92.07% and 92.72%, respectively. The experiments indicated the antagonistic adsorption of the cationic dye and heavy metal in a binary system. Adsorbent dose and contact time had the highest and lowest impacts on the decolorization efficiency, respectively, while solution pH and adsorbent dose were the most and the least influential variables on the copper removal, respectively. Adsorption isotherm studies revealed that the experimental data were better fitted to the Langmuir isotherm model. According to the study, adsorption process onto sawdust of *M. azedarach* can be considered as a choice for economical treatment of polluted effluents of the textile industry.

Keywords: Adsorption; Cationic dye; Copper ion; Sawdust

1. Introduction

Demand for textile products experiences a dramatic growth globally as a result of population explosion along with changed lifestyle and appearance of new fashions [1]. Textile industries use various chemicals and more than 10,000 types of dyestuffs [2]. Synthetic dyes have a widespread application in industrial scale, as they are more resistant and more brightened in comparison with natural dyes. Moreover, their production does not impose such cost and they can be easily applied [3]. Synthetic dyes are classified into some categories based on the structure. They may be acidic, basic, disperse, azo, diazo, anthraquinone-based, or metal complex-based [4]. Basic dyes, also known as cationic dyes, have been widely used in the dyeing of different fabrics from acrylic to nylon, silk, and wool in textile industries [5]. Some heavy metals especially lead, chromium, cadmium, and copper make a big contribution to the production processes of dye pigments [6].

Among different activities of textile industry, dyeing and finishing sectors may release 10%–50% of unfixed dyes

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to the effluent [7]. Various textile processes such as sizing of fibers, scouring, bleaching, mercerizing, dyeing, printing, and finishing generate huge amounts of wastewater [8]. The enormous volume of wastewaters containing many contaminants including heavy metals and dyes will finally find their way into water bodies. Toxicity and mobility have imposed heavy metals on priority pollutants. Heavy metals are a serious threat to the public health and they have very harmful effects on the aquatic life and environment [9]. The color is an indicator of pollution and it can be seen more than any other pollutant in the receiving water bodies [10]. The presence of dyes in the effluents even in low concentrations may act as a barrier and prevents light penetration into the water; thus, it puts negative effects on the aquatic life [11].

Selection of successful wastewater purification technologies for effluents polluted by dyes and heavy metals is affected by the characteristics of the pollutants. For example, many synthetic dyes are too chemically stable to be removed by traditional treatment methods [12]. Both dyes and heavy metals are resistant to biological degradation. Biological treatment of synthetic dyes seems difficult as they have a complex aromatic molecular structure [13], high molecular weight, and high solubility [14]. Although anaerobic biological treatment has achieved some successes in the textile wastewater treatment, it is not suggested because of the aromatic amines formation as a result of azo dyes breakdown [15]. Excessive use of chemicals, production of secondary pollutions in the form of sludge generation, and operation expenses are considered as the main drawbacks of some physicochemical treatment methods including coagulation–flocculation and electrochemical techniques [16].

Adsorption process as an alternate method has been successfully applied to treating multipollutants mixtures and improving water quality [17]. It can be easily designed with a low space requirement and little investment cost [18]. Activated carbon is known as the most applied adsorbent; however, its large-scale application has faced limitations regarding heavy regeneration expenses and hard recovery [19]. Nowadays, there is a special interest in using low-cost adsorbents prepared from copious resources [20]. Sawdust is one of the appealing adsorbents in the removal of various pollutants such as dyes and heavy metals from polluted streams and effluents [21]. In structure, it contains lignin and cellulose that donate negative charges on the surface and make it an adsorbent of choice for removal of cationic species [22].

In this context, the inexpensive and local abundant sawdust of *Melia azedarach* wood has received a special interest. The aim of this study was to quantify the dye and heavy metal removal efficiencies using *M. azedarach* sawdust adsorbent and determine the effect of operating variables such as initial concentration of pollutants, solution pH, contact time, and adsorbent dose on the adsorption rate.

2. Materials and methods

2.1. Chemicals

The model dye (BR46 ≥ 98% purity) was supplied by Shadiloon Textile, a local industrial factory. The selected dye has a wide application in textile dyeing processes. It has been introduced in different classifications as basic, azo, and reactive dye [23]. Other chemicals such as $CuSO_4·5H_2O$, HCl, NaOH, and KNO_3 were purchased from Merck. Preparation of stock solutions (1,000 mg L^{-1}) was conducted through diluting 1.00 g BR46 and 3.93 g $CuSO_4·5H_2O$ in 1,000 mL of doubled distilled water (DDW).

2.2. Preparation of adsorbent

In this study, sawdust of *M. azedarach* wood was prepared from a local garden and used as the adsorbent. Deadwood of Pollard *M. azedarach* trees is available in all seasons. The collected deadwood was crushed, grounded, and passed through 50 mesh sieves (300 μm). The obtained sawdust was completely washed by DDW and then dried at 105°C in an oven to reach a stable weight. The dehydrated material was soaked with 10% HCl solution and heated at the boiling point for 30 min. After cooling at room temperature, the product was sieved and washed again to eliminate remained chemicals. After 24 h drying at 60°C–80°C, the prepared adsorbent was sieved to get 50 mesh size particles. To prevent the contamination of the final product, it was preserved in an airtight container for use at subsequent sorption experiments [24,25].

2.3. Specification of adsorbent

To specify the functional groups of the adsorbent, Fourier transform infrared spectroscopy (FTIR spectrometer, avatar 370, Thermo Nicolet) was employed within the range of 500–4,000 cm^{-1}. The point of zero charges (pzc) of the adsorbent was determined according to Mall et al. [20]. For this purpose, six flasks containing 50 mL of 0.01 MKNO_3 solutions were prepared. Then, 0.1 M NaOH or HCl was added to the solutions for adjusting pH values at 2–12. After adding 0.1 g sawdust to each container, the solutions were shaken for 48 h and their final pH was recorded. On the plot of final pH versus initial pH, pzc refers to the point in which the initial and final values of pH are equal.

2.4. Design of experiments

A central composite design (CCD) was used to design the experiments under response surface methodology (RSM) of Design-Expert 7.0 program. Five variables (including the initial concentration of dye, the initial concentration of metal ion, solution pH, adsorbent dose, and contact time) each at five levels (coded as $-\alpha$, −1, 0, +1, and $+\alpha$) suggested a total number of 50 experiments based on $2^k + 2k + c$ formula in which k represents the number of numeric variables and c refers to the number of replications at the center point. Table 1 shows the variables at actual and coded levels. To evaluate the efficacy of the process, two responses were considered: BR46 removal percentage and copper removal percentage. A quadratic model was used to find a relation between responses and variables as follows [26,27]:

$$Y = b_0 + \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n}\sum_{j=1}^{n} b_{ij} x_i x_j + \sum_{i=1}^{n} b_{ii} x_i^2 \quad (1)$$

Table 1
Independent variables and coded levels

Coded variables	Variables	Actual and coded levels				
		$-\alpha$	–1	0	+1	α+
A: x_1	Initial dye concentration (mg L^{-1})	5.00	18.04	27.50	36.96	50.00
B: x_2	Initial metal concentration (mg L^{-1})	1.00	3.60	5.50	7.39	10.00
C: x_3	Solution pH	2.00	4.30	6.00	7.68	10.00
D: x_4	Contact time (min)	5.00	29.63	47.50	65.36	90.00
E: x_5	Adsorbent dose (g L^{-1})	1.00	3.03	4.50	5.97	8.00

where Y is the response, x_i and x_j are the coded values of variables, b_0 is the constant coefficient, b_i is the linear coefficients, and b_{ij} and b_{ii} are the interaction and second-order coefficients.

Analysis of variance (ANOVA) in the Design-Expert 7.0 program was used for statistical analysis of developed models. The statistical significance of models and terms involved in the models was checked using F-value and p-value, while the quality of fit for the selected model was examined using the coefficient of determination (R^2), adjusted R^2 (Adj. R^2), and predicted R^2 (Pred. R^2) [28].

2.5. Adsorption experiments and analytical methods

Solutions containing both BR46 dye and copper metal ion were prepared in predetermined concentrations. After adjusting pH of the solution, the adsorbent was added in the specified dose and time-course was spent on a magnetic stirrer. Samples were centrifuged for 10 min at 3,000 rpm and analyzed for residual concentrations of dye using a spectrophotometer apparatus (Shimadzu UV/VIS T80/T80+) at λ_{max} = 530 nm. The remained metal ion was determined using atomic adsorption spectroscopy (Varian-AA240). A syringe filter (0.22 μm) was used for separation of adsorbent particles from the solution before chemical analysis. The following equation was used to calculate the removal percentage of target pollutant:

$$\text{Pollutant removal percentage} = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

where C_0 represents the initial pollutant concentration (mg L^{-1}) and C_e the equilibrium pollutant concentration (mg L^{-1}). The amount of adsorbate loaded on the adsorbent at equilibrium state was calculated using the following equation:

$$q_e = \frac{\left(C_0 - C_e\right) \times V}{m} \tag{3}$$

In Eq. (3), V shows the volume of the sample (L) and m accounts for the adsorbent mass (g).

3. Results and discussion

3.1. Sorbent characteristics

Figs. 1(a) and (b) show the FTIR spectra of adsorbent before and after adsorption, respectively. The major bands for sawdust before adsorption include 336.44 cm^{-1} assigning to OH groups stretching vibration and 2,905.28 cm^{-1} indicating asymmetrical stretching vibration of C–H. In the FTIR spectrum of adsorbent after simultaneous removal of dye and heavy metal demonstrates new peaks at 3,419 and 3,362 cm^{-1} corresponding to $-NH_2$ and –OH, respectively, and a band identified at 2,913 cm^{-1} indicating asymmetrical stretching vibration of C–H. The new peak at 2,553.46 cm^{-1} may indicate the presence of N=C groups [29], and the band at 1,425 and 1,459 cm^{-1} confirms the blending vibration CH_3 and scissor vibration CH_2. This finding is in accordance with the results of a previous study dealing with the adsorption of BR46 cationic dye onto sawdust adsorbent [30]. The appearance of peaks between 1,000 and 1,500 cm^{-1} is thought to belong to stretching vibration of C–O. It is remarkable to mention that sulfates (in the composition of $CuSO_4$) have an absorbance at 1,140–1,200 cm^{-1}. Carboxylic groups C=O appear in the region of 1,650–1,900 cm^{-1}. Some new peaks at a wavelength of 400–650 have appeared after adsorption implying the formation of M–O (heavy metal coupled with oxygen). This indicates that the metal ion adsorbed at sawdust surface could activate the functional groups. Yang and Cui [31] also recognized acidic groups such as hydroxyl and carboxyl as the main contributors to the uptake of heavy metal ions. The fundamental changes in the bands of 3,200–3,600 cm^{-1} show that the –OH group has been effective in the adsorption process.

Zero electrical charges on the adsorbent surface are defined as pH_{pzc}. pH_{pzc} of sawdust adsorbent was examined in this study. pH_{pzc} in physical chemistry is a concept relating to the phenomenon of adsorption, and it describes the condition under which the electrical charge density on a surface is zero. When pH is lower than pH_{pzc}, the acidic water donates more protons than hydroxide groups, and the adsorbent surface is positively charged. Conversely, above pH_{pzc}, the surface is negatively charged [32]. The results show that the adsorbent is characterized by pH_{pzc} of 2.8, implying that the net surface charge is positive at pH medium below 2.8, neutral at pH 2.8, and negative at pH medium above 2.8 [20].

3.2. Influence of operation variables

3.2.1. Data fitting and modeling

The actual values of responses as a function of experimental matrix designed by RSM are presented in Table 2. A modified quadratic model gave an acceptable fit between

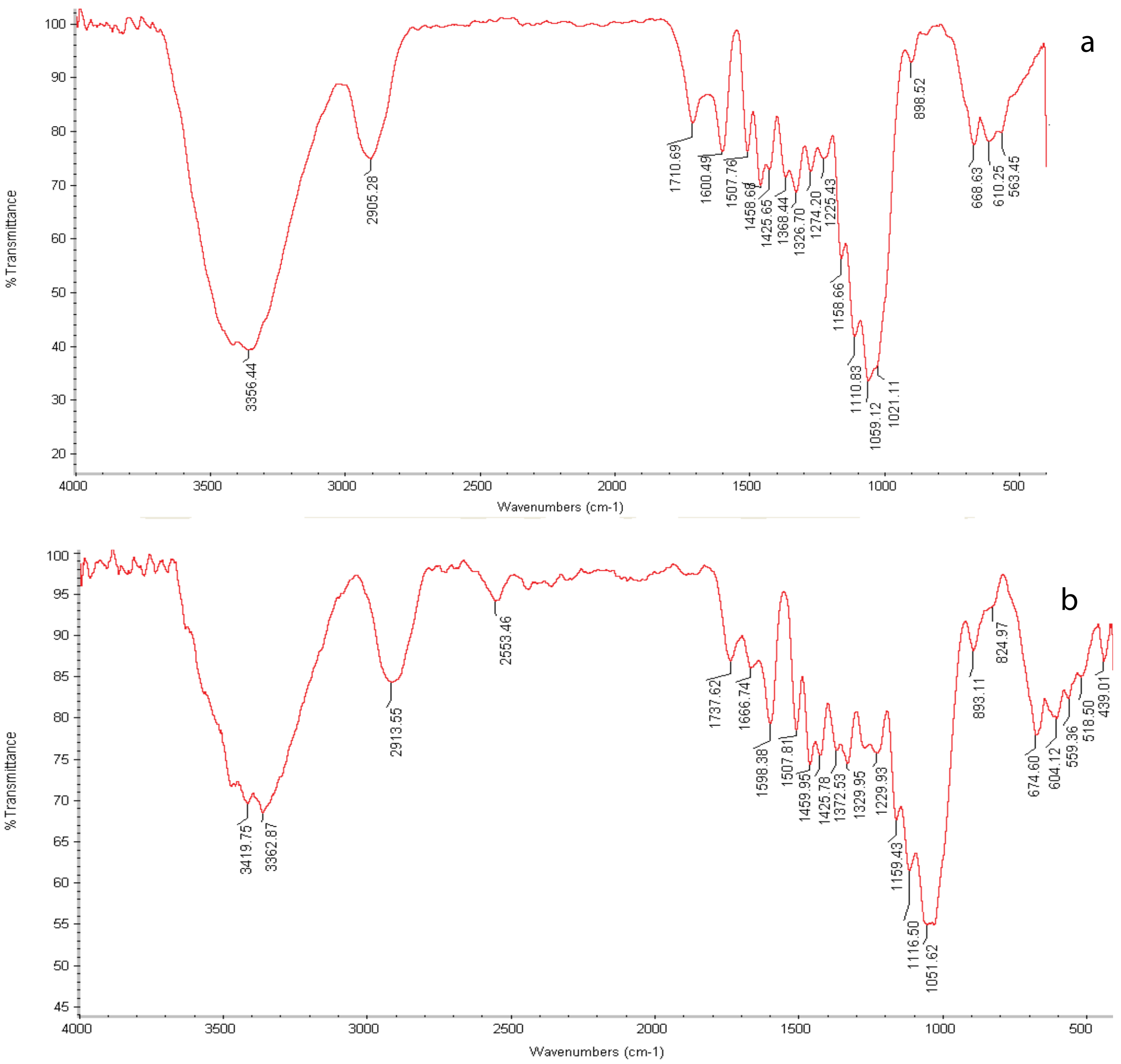

Fig. 1. FTIR spectra of adsorbent before (a) and after (b) the simultaneous adsorption of BR46 and Cu(II).

predicted and experimental results for both responses. The ANOVA results in Table 3 support the significance of developed models by giving F-value of 33.54 and 57.62, respectively, for BR46 and Cu removal percentage models and p-values less than 0.0001 for both models. The p-values less than 0.05 coupled with high F ratios of Fisher distribution test indicate model terms are significant [33]. The p-values of 0.078 and 0.56 imply the insignificant lack of fit, which is also favorable for model credibility. The normal probability and studentized residual graphs indicate a normal distribution of data because they yielded almost straight lines (data not shown). The quality of fit of models was proven through high R^2 values of 0.906 and 0.918 for BR46 and Cu removal models, respectively. The Adj. R^2 values were also close enough to the Pred. R^2 values for both responses (Adj. R^2 of 0.87 and Pred. R^2 of 0.81 for BR46 removal response; Adj. R^2 of 0.90 and Pred. R^2 of 0.87 for Cu removal response).

The coefficients of effects for the selected models were calculated by design expert software and the approximating functions of BR46 and Cu removal percentages are given in Eqs. (4) and (5) as follows:

$$Y_1 = +92.07 - 2.86x_1 - 2.08x_2 + 2.27x_3 + 2.07x_4 + 3.51x_5 - 0.89x_1x_2 + 1.29x_1x_3 + 1.11x_1x_5 - 1.05x_3x_5 - 1.48x_3^2 - 1.01x_5^2 \quad (4)$$

$$Y_2 = +92.72 - 3.71x_1 - 2.97x_2 + 3.54x_3 + 1.83x_4 + 1.21x_5 + 2.22x_1x_3 + 1.83x_2x_3 - 3.84x_3^2 \quad (5)$$

where Y_1 represents the removal rate of BR46 (%), Y_2 the removal rate of Cu(II), and x_1 to x_5 are defined in Table 1. In the above models, only the significant terms, that is, the terms with p-values greater than 0.05, were included. Eqs. (4) and (5) show the average removal values of 92.07% and 92.72%, respectively, for BR46 and Cu responses in spite of variables and interaction of variables. The magnitude of coefficients in front of terms indicates the degree of significance of that term in the model. For better understanding and interpretation of the significance of coefficients, the

Table 2
The experimental matrix of CCD along with the observed results

Run order	Experiment design					BR46 removal %	Cu^{2+} removal %
	x_1	x_2	x_3	x_4	x_5		
1	36.96	7.39	4.30	65.37	5.97	90.31	74.31
2	18.00	3.60	4.30	65.37	5.97	96.54	96.98
3	18.00	7.39	7.68	29.60	5.97	94.35	92.38
4	5.00	5.50	6.00	47.50	4.50	98.02	98.42
5	50.00	5.50	6.00	47.50	4.50	87.12	82.08
6	27.50	5.50	6.00	90.00	4.50	96.24	98.35
7	18.00	3.60	7.68	29.60	5.97	95.54	95.41
8	18.00	3.60	7.68	65.37	5.97	97.53	96.58
9	18.00	7.39	4.30	65.37	5.97	95.05	93.36
10	36.96	3.60	7.68	65.37	3.00	89.78	92.23
11	18.00	7.39	4.30	65.37	3.00	92.06	89.72
12	18.00	7.39	7.68	65.37	5.97	95.05	94.28
13	27.50	5.50	2.00	47.50	4.50	75.76	60.42
14	27.50	5.50	6.00	47.50	4.50	91.76	93.02
15	18.00	3.60	7.68	65.37	3.00	94.55	96.41
16	36.96	3.60	4.30	65.37	3.00	85.39	89.25
17	27.50	5.50	6.00	47.50	4.50	91.08	93.95
18	27.50	5.50	6.00	47.50	4.50	91.76	93.48
19	36.96	3.60	4.30	29.60	3.00	81.21	81.92
20	27.50	5.50	6.00	5.00	4.50	82.76	84.90
21	36.96	7.39	4.30	29.60	5.97	83.66	73.25
22	18.00	3.60	7.68	29.60	3.00	93.55	96.23
23	18.00	7.39	4.30	29.60	3.00	85.10	87.15
24	36.96	7.39	4.30	65.37	3.00	77.01	74.81
25	36.96	7.39	7.68	65.37	5.97	93.27	93.20
26	36.96	3.60	7.68	65.37	5.97	96.06	93.79
27	27.50	5.50	6.00	47.50	8.00	95.03	96.42
28	27.50	5.50	6.00	47.50	4.50	90.73	92.55
29	36.96	7.39	7.68	29.60	5.97	90.03	90.29
30	27.50	5.50	6.00	47.50	4.50	92.11	93.05
31	27.50	5.50	6.00	47.50	4.50	90.73	92.55
32	18.00	3.60	4.30	65.37	3.00	92.56	95.87
33	36.96	3.60	7.68	29.60	3.00	89.28	88.25
34	18.00	7.39	7.68	65.37	3.00	92.84	93.33
35	18.00	7.39	4.30	29.60	5.97	93.39	87.46
36	18.00	3.60	4.30	29.60	5.97	94.55	96.82
37	18.00	7.39	7.68	29.60	3.00	87.58	92.33
38	36.96	7.39	7.68	29.60	3.00	84.41	89.52
39	36.96	7.39	4.30	29.60	3.00	66.49	71.37
40	36.96	3.60	4.30	29.60	5.97	90.49	84.44
41	36.96	3.60	7.68	29.60	5.97	92.78	92.85
42	27.50	1.00	6.00	47.50	4.50	95.71	99.90
43	27.50	5.50	6.00	47.50	4.50	91.42	92.55
44	18.00	3.60	4.30	29.60	3.00	89.07	89.15
45	36.96	7.39	7.68	65.37	3.00	86.96	91.35
46	27.50	5.50	6.00	47.50	1.00	75.14	85.80
47	27.50	10.00	6.00	47.50	4.50	85.27	83.12
48	27.50	5.50	6.00	47.50	4.50	95.08	86.10
49	27.50	5.50	10.00	47.50	4.50	89.15	77.83
50	36.96	3.60	4.30	65.37	5.97	94.13	90.78

Table 3
ANOVA results for the modified quadratic model of BR46 and Cu removal

Response	source	Analysis of variance				
		Sum of squares	df	Mean square	*F*-Value	*p*-Value
BR46 removal	Model	1,811.56	11	164.69	33.54	<0.0001
	Residual	186.58	38	4.91	–	–
	Lack of fit	172.82	31	5.57	2.83	0.078
	Pure error	13.77	7	1.97	–	–
Copper removal	Model	2,859.18	8	357.40	57.62	<0.0001
	Residual	254.30	41	6.20	–	–
	Lack of fit	210.63	34	6.20	0.99	0.56
	Pure error	43.66	7	6.24	–	–

Pareto analysis was utilized and the results are illustrated in Fig. 2. This analysis gives an estimate of contribution percentage of effects. As can be seen, among the main variables, the most significant effect on dye adsorption is allocated to adsorbent dose (x_5 variable), followed by initial dye concentration (x_1 variable), solution pH (x_3 variable), initial metal concentration (x_2 variable), and contact time (x_4 variable). For Cu adsorption, the significance of main variables affecting the process decreased in the following order: initial dye concentration (x_1 variable), solution pH (x_3 variable), initial metal concentration (x_2 variable), contact time (x_4 variable), and adsorbent dose (x_5 variable).

3.2.2. Explanation of main effects

As Eqs. (4) and (5) show, an increase in the initial concentration of dye (x_1 variable) from –1 level to +1 level results in the reduction of removal percentage of BR46 from 94.93% to 89.21%. The same trend is also observed for Cu^{2+} as its removal percentage reaches from 95.69% to 89.75% by increasing the initial metal concentration (x_2 variable) from –1 level to +1 level. The lower pollutant uptake at higher initial concentrations can be due to the less available active sites on the sorbent surface for adsorption of more ions [34]. The negative coefficient of the x_2 variable in Eq. (4) and x_1 variable in Eq. (5) indicates that increasing initial Cu^{2+} concentration leads to the reduction of BR46 removal percentage and increasing initial dye concentration results in the reduction of metal removal percentage. In other words, the removal efficiency of a species is negatively affected by the applied concentration of the other species. This phenomenon demonstrates the competitive behavior of the two cationic pollutants for adsorption onto the anionic adsorbent. Simultaneous removal of pollutants from multicomponent solutions has been examined by other researchers and controversial results have been gained. For example, Ghorbel-Abid and Trabelsi-Ayadi [35] showed that in a binary-element system, chromium(III) adsorption increases while cadmium(II) uptake decreases. Tovar-Gómez et al. [36] examining the simultaneous adsorption of AB25 dye and heavy metal ions of Zn^{2+}, Ni^{2+}, and Cd^{2+} indicated the synergistic effect of AB25 on the removal of metallic species. The competition among four

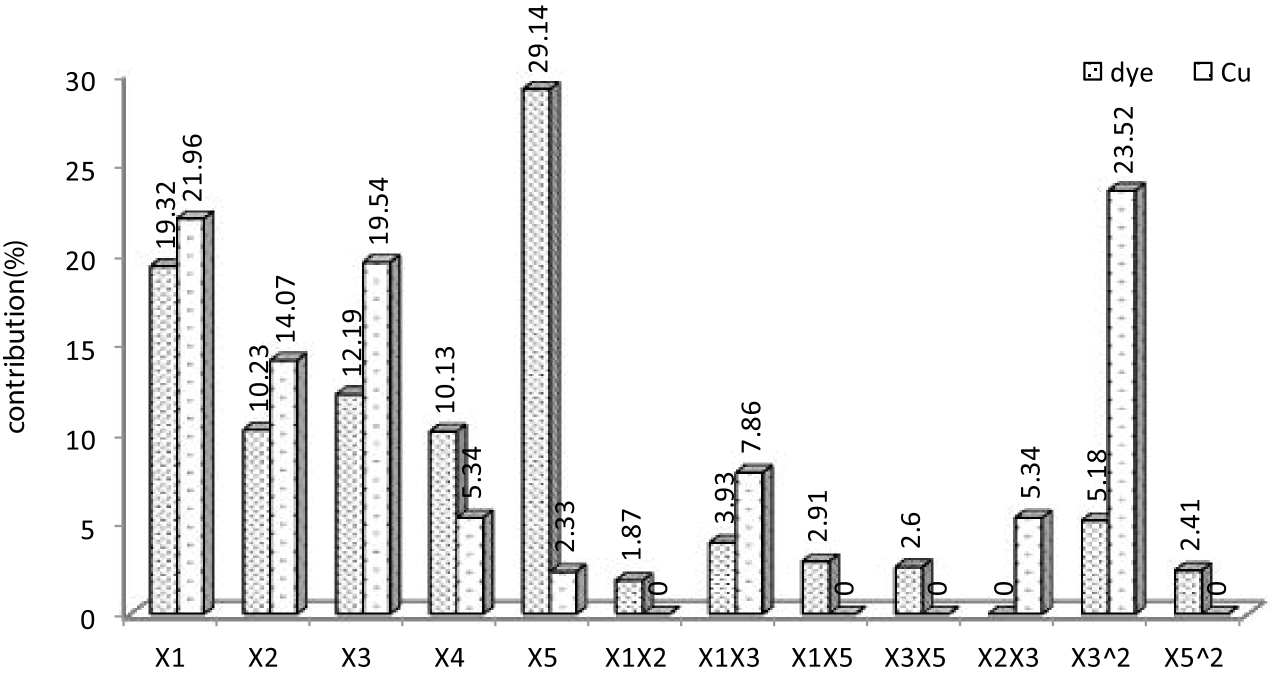

Fig. 2. Graphical Pareto analysis of the effects in the models.

heavy metals has also been reported by Srivastava et al. [37] for adsorption onto kaolinite.

Solution pH can affect the adsorbent surface charge, the ionization of various contaminants, and the functional groups of adsorbent active sites. In fact, it influences the chemical bonds of the adsorbent surface. Therefore, the effect of pH values was investigated on the adsorption process. In this study, increasing solution pH from 4.32 to 7.68 enhanced the removal rate from 89.8% to 94.34% for dye and 89.18% to 96.26% for Cu ions. In the explanation of the results, it should be noted that BR46 has amino groups with positive charges in its structure, which makes it more activated at pH values between 6 and 10. Considering that OH functional groups are prevailing groups on the surface of sawdust at pH values higher than 2.8, an electrostatic attraction has led to the adsorption of dye on sawdust surface. In addition, copper metal as a cation experienced its highest removal at pH values from 6 to 7. This observation can be explained by a reduction in the number of rival H^+ ions at higher values of pH. The positive effect of solution pH on the removal rate of cationic species using negatively charged adsorbents has been reported by Doltabadi et al. [30] for Basic Red 46 sorption onto Sawdust and by Arshadi et al. [38] for Co(II), Cu(II), Ni(II), and Cd(II) ions adsorption onto barley straw ash.

The uptake of dye and metal ion on the adsorbent as a function of contact time was nearly similar for both the solutes. At contact time of 29.63 and 65.37 min, a removal efficiency of 90.00% and 94.14% for dye and 90.89% and 94.55% for Cu was obtained, respectively. Evidently, more contact time provides more chance for collision among pollutants and adsorbent, which reduces the pollution load and raises the adsorption capacity.

To assess the effect of adsorbent dose on the removal efficiency, a range of sawdust doses from 3 to 6 g L^{-1} was employed. It was found that higher doses of adsorbent increase the removal efficiency as a result of more adsorption areas [21], as the removal of 87.5%–94.5% for BR46 and 91.50%–93.90% for Cu was calculated by increasing adsorbent dose from 3 to 6 g L^{-1}.

3.2.3. Explanation the combined effects of variables

In the quadratic models, it should be noted that the effect of variables on responses depends on other variables. Three-dimensional graphs presented in Figs. 3 and 4 can be helpful to better interpret the combined effects of variables. As given in Fig. 3(a), conducting the adsorption process at lower dye concentrations and higher pH can cause more uptake of dye. As can be observed, the experiments under pH 4.3 and the initial dye concentration of 18 mg L^{-1} yielded 92.46% of dye removal, while at the same concentration of dye and applied pH of 7.68, a removal of 94.42% was obtained. In addition, a dye concentration of 36 mg L^{-1} led to 84.2% and 91.3% of dye removal under pH values of 4.3 and 7.68, respectively. Fig. 3(b) illustrates the interaction effect of initial concentration of dye and sawdust on the dye removal. The removal rates of 96.3% and 91.5% for dye removal (at a dye concentration of 18 mg L^{-1}) were gained using 6 and 3 g L^{-1} of sawdust, respectively. In the presence of 36.96 mg L^{-1} dye concentration in the solution, adding 3 and 6 g L^{-1} of adsorbent yielded removal efficiencies of 83.7% and 92.8%, respectively. According to Fig. 4(a), the maximum efficiencies for Cu removal were achieved when pH values changed between 6.5 and 7. It can be seen that 95% of Cu removal occurred at 3.6 mg L^{-1} metal concentration after performing the treatment at pH 6.5, while the other operating variables had been set at their central points. Fig. 4(b) refers to the Cu adsorption as a function of the rival pollutant concentration

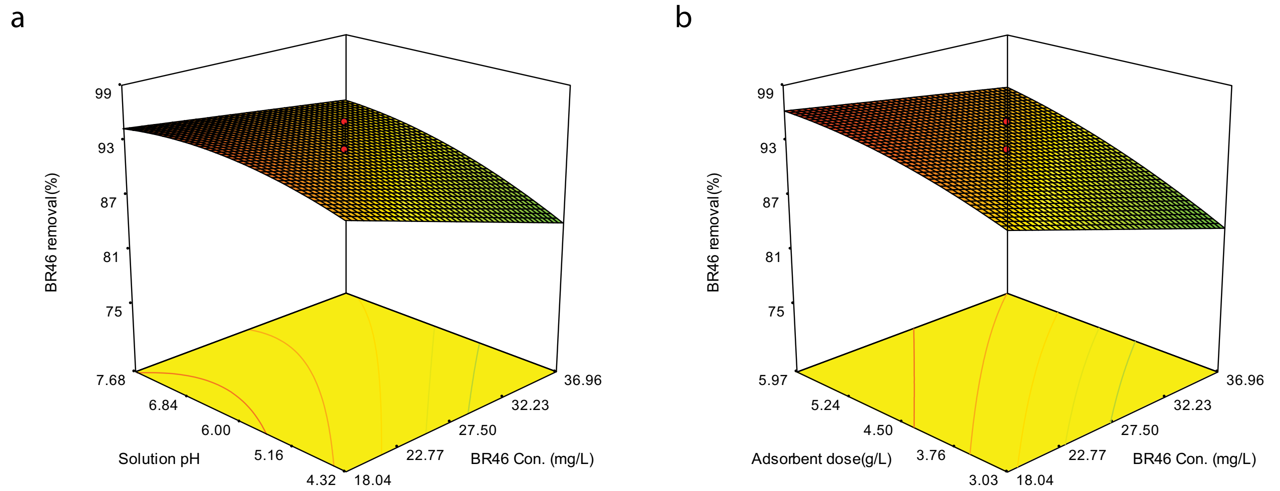

Fig. 3. 3D surface plots of most important interaction effects: dye removal as a function of dye initial concentration–solution pH (a) and dye initial concentration–adsorbent dose (b).

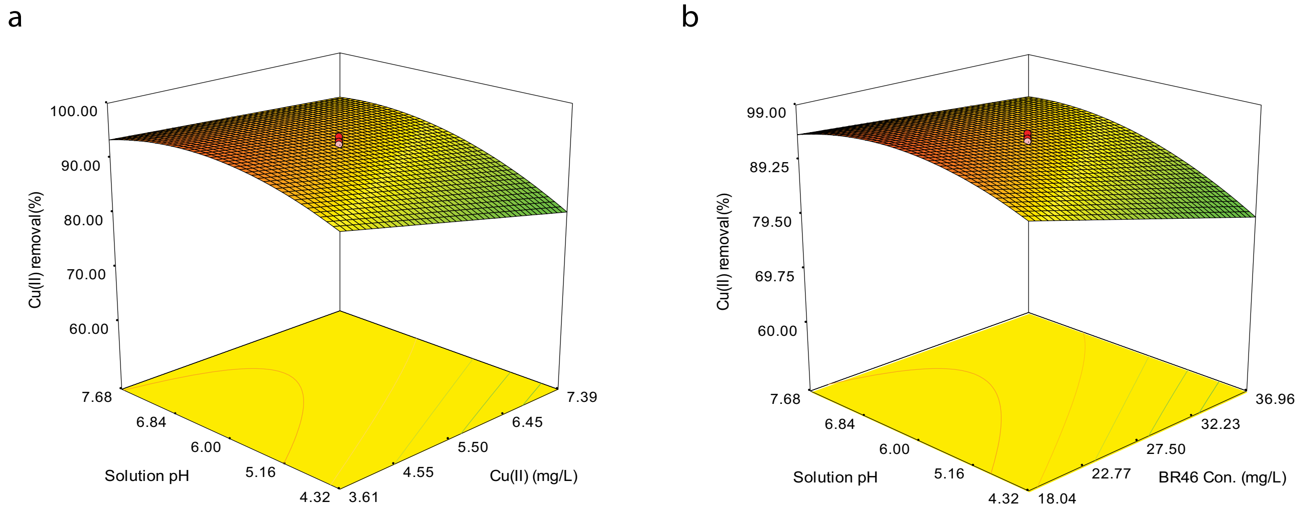

Fig. 4. 3D surface plots of most important interaction effects: Cu removal as a function of Cu initial concentration–solution pH (a) and dye initial concentration–solution pH (b).

and solution pH. As can be seen, the effect of solution pH on Cu removal efficiency is strengthened at higher dye concentrations because by applying solution pH in the range of 4.32 to 7.68, the removal efficiency varied from 79.53% to 90.94% at a dye concentration of 36.96 mg L^{-1} and from 91.28% to 93.94% at 18.04 mg L^{-1}. This behavior explains why the interaction effect of initial dye concentration and solution pH is significant in the Cu removal model (Eq. (5)).

3.3. Adsorption kinetics

Kinetic experiments provide valuable information for better understanding of rate, pathways, and mechanisms of adsorption reaction [19]. The pseudo-first-order equation is described as follows:

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{6}$$

where q_t (mg g^{-1}) and q_e (mg g^{-1}) are the amount of target loaded on sawdust at time t and at equilibrium, respectively. k_1 is the rate constant (min^{-1}) of pseudo-first-order kinetics which can be determined by the plot of ln $q_e - q_t$ against t [39]. This equation suggests that changing the adsorption rate of the analyte is proportional to the fluctuations of saturation concentration and the amount of analyte uptake at time t [19]. The pseudo-second-order model is given as follows:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{7}$$

where k_2 (g adsorbent (mg adsorbate min)$^{-1}$) is the equilibrium rate constant of pseudo-second-order model and is taken from the intercept value in the plot of t/q_t versus t [39]. The pseudo-second-order kinetics normally is able to describe adsorption system at reaction times higher than 20 min. This model in the present study created a remarkable fit with the experimental data and generated the excellent values of R^2 for both target pollutants (see Fig. 5 and Table 4). Therefore, it can be concluded that the adsorption of BR46 and Cu(II) onto the surface of sawdust is governed by chemical binding between these cationic species and the negative surface sites of the adsorbent induced by lignin and cellulose. The correlation coefficients equal to 0.9998 verify the agreement between observed and calculated values.

The equilibrium time in the work was observed to be 40 min. A same equilibrium time has been reported by Wang et al. [34] in the removal of heavy metals and dyes from wastewater by coal ash. Table 4 also represents the other kinetic variables. The rate constants of pseudo-second-order kinetics for BR46 and Cu(II) on sawdust adsorbent were 6.06 and 2.72 g (mg min)$^{-1}$, respectively, while 4.36 mg of dye and 0.66 mg of metal were removed per 1 g of adsorbent at equilibrium. The equilibrium uptake value was determined as 3.31 mg g^{-1} for adsorption of Zn^{2+} on $Ca(PO_3)_2$-modified carbon in Tovar-Gomez et al. study with the rate constant of 2.67 g (mg min)$^{-1}$. In Rosales et al. study [19], the pseudo-second-order kinetic model provided better description compared with pseudo-first-order kinetic model for adsorption of Azure B on Nay zeolite and gave k and q_e values of 8.72 g (mg min)$^{-1}$ and 1.418 mg g^{-1}, respectively.

3.4. Adsorption isotherms

Adsorption isotherms are calculated to describe the distribution behavior of adsorbate molecules in the equilibrium state of the adsorption process. In this study, Langmuir and Freundlich models were chosen. The Langmuir isotherm reflects a homogeneous surface adsorption, while in the Freundlich model, the adsorption sites are assumed heterogeneous [19]. The following equation gives the Langmuir isotherm:

$$\frac{1}{q_e} = \frac{1}{q_{\max} b C_e} + \frac{1}{q_{\max}} \tag{8}$$

where $q_{\max}$ refers to the maximum probable uptake of the pollutant on adsorbent surface and b shows the adsorbate tendency to be attracted by the adsorbent sites. A favorable adsorption achieves under high values of $q_{\max}$ and steep line of variable b [40]. Another way to express the desirability of the model is calculating the equilibrium dimensionless coefficient R_L:

$$R_L = \frac{1}{1 + bC_0} \tag{9}$$

where b is the Langmuir constant and C_0 shows the initial concentration of pollutant. R_L value equal to 0 implies irreversible adsorption, $0 < R_L < 1$ reflects favorable adsorption, R_L equal to 1 shows a linear adsorption, and R_L above 1 is an undesirable state of adsorption [41]. Freundlich isotherm has been created tentatively [42]. It is believed that stronger binding sites are occupied primarily, and along with the increase of site occupation, the bond strength decreases [19]. The Freundlich isotherm is a function of binding capacity (K_f) and constant coefficient (n), which is represented as follows [43]:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{10}$$

The value of $1/n$ represents the adsorption intensity. In most cases, a value between 1 and 10 demonstrates a good sorption. The n values close to 1 show less surface heterogeneity, while more heterogeneity of the surface appears in the case of n values approached 10. The values of $n > 1$ represent an optimal adsorption. The values of K_f and n can be determined by Freundlich graph [44].

The results of data fitting to the models are demonstrated in Fig. 6. In addition, the isotherm constants and correlation coefficients are presented in Table 5. Regarding the obtained R^2 values, all the values were greater than 0.95, but better determination coefficients of Langmuir isotherm were observed for both pollutants. Therefore, the adsorption process of dye and metal ion followed the Langmuir model. It implies that the sawdust adsorbent is rather homogenous on the surface and the solutes (BR46 and Cu(II)) are adsorbed

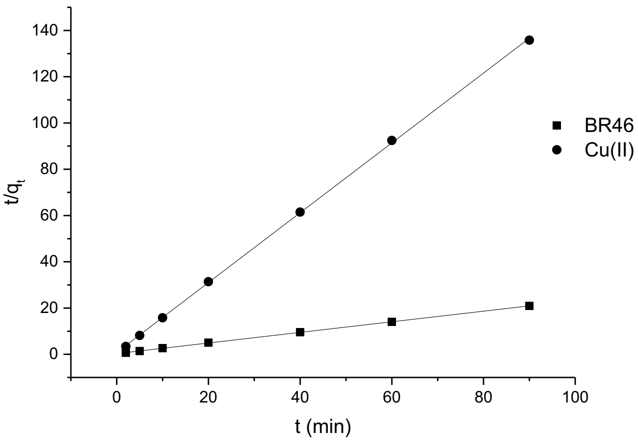

Fig. 5. The pseudo-second-order kinetics for adsorption of BR46 and Cu^{2+} onto *Melia azedarach* sawdust.

Table 4
The kinetic variables of the removal of target pollutants

Pollutant	Pseudo-second-order kinetic			pseudo-first-order kinetic		
	R^2	q_e (mg g^{-1})	k_2 (g (mg min)$^{-1}$)	R^2	q_e (mg g^{-1})	k_1 (min^{-1})
BR46	0.9998	4.36	6.06	0.5126	2.34	0.012
Cu^{2+}	0.9998	0.66	2.73	0.1633	0.74	–0.005

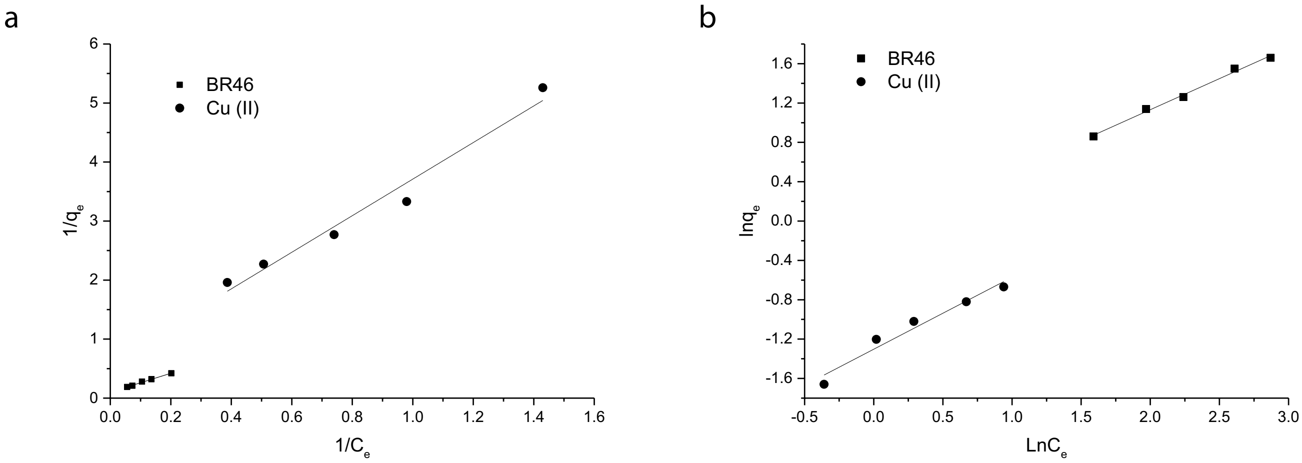

Fig. 6. Langmuir (a) and Freundlich (b) isotherms for BR46 and Cu(II) adsorption onto *Melia azedarach* sawdust.

Table 5
The isotherm constants and correlation coefficients of the fitted models

Pollutant	Langmuir isotherm				Freundlich isotherm		
	q_m (mg g^{-1})	b (mg^{-1})	R_L	R^2	n	K_f (mg g^{-1})	R^2
BR46	16.26	0.099	0.242	0.9940	0.636	1.257	0.9929
Cu^{2+}	5.94	0.537	0.290	0.9712	0.763	5.881	0.9587

by chemical binding. Other investigations also introduced Langmuir isotherm as a better model for describing simultaneous adsorption of dyes and heavy metals onto fly ash [45] and zeolite structures [46], and also for the removal of Cu(II) ions using activated poplar sawdust [47] and maple wood sawdust [48]. According to Table 5, high *b* values obtained for both BR46 (0.099 mg^{-1}) and copper (0.537 mg^{-1}) show their considerable positive effects on the sorption process. The maximum capacity for adsorption of dye and metal ion was found to be 16.26 and 5.94 mg g^{-1}, respectively. A favorable adsorption can also be deduced from the R_L values that are between 0 and 1 (dye R_L = 0.242, copper R_L = 0.29). Similar findings were reported by Karim et al. [49] in the adsorption study of BR46 dye using Moroccan clay. Overall, the observations of this work confirm the homogeneous mode of adsorption under the experiments of the present study.

4. Conclusions

In this work, the efficacy of local plentiful sawdust adsorbent prepared from *M. azedarach* wood was determined for the removal of cationic dye (BR46) and heavy metal (Cu^{2+}) from the simulated textile effluent. According to the results of infrared spectroscopy, functional groups on the sorbent surface were proven to participate in the adsorption of the cationic dye and heavy metal. Based on RSM outputs, the average removal efficiency of BR46 and Cu^{2+} was 92.07% and 92.72%, respectively. Adsorbent dose and contact time had the highest and lowest impacts on decolorization efficiency, respectively, while solution pH and adsorbent dose were the most and the least influential variables on the copper removal percentages, respectively. Adsorption isotherm studies revealed that the experimental data were better fitted to the Langmuir isotherm model. The data also were correlated well with the pseudo-second-order kinetic model. According to the study, adsorption process using sawdust of *M. azedarach* can be considered as a proper choice for economic treatment of polluted effluent of the textile industry.

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