Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.22658

123 (2018) 348–357
August

The iron modification effect on performance of natural adsorbent scoria for malachite green dye removal from aquatic environments: modeling, optimization, isotherms, and kinetic evaluation

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Received 3 February 2018; Accepted 21 June 2018

ABSTRACT

Malachite green (MG) is a synthetic dye which is widely used as biocide in aquaculture and dyeing agent in textile industries. This dye could be difficult to remove from aquatic environments due to its features and low degradability. According to the effect of ferrous on the physical and chemical characteristics of scoria, this study was to evaluate iron-coated scoria performance in removing MG from aqueous solutions. Adsorption process is carried out in vitro at different pH, adsorbent dosage, contact time, and constant concentration of the dye. Results indicated that all parameters of the model were inaccurate ranges, which confirm the validity of the obtained model to predict the amount of MG removal. Moreover, MG removal rate increased with increasing the pH, the adsorbent dosage, and the contact time. The highest efficiency was 94.2% obtained at pH = 11, adsorbent dose = 1.4 g/L, and contact time = 75 min. Adsorption of MG on iron-coated scoria was found to follow both the Langmuir and Freundlich isotherms and pseudo-second-order kinetic model. The separation factor and adsorption intensity in the iron-modified scoria were obtained lower than the bare scoria. According to the results, it can be concluded that iron via chemical changes of adsorbent structure causes increase in the efficiency of scoria for removal of MG.

Keywords: Iron-modified pumice; Malachite green dye; Regression model; Isotherm; Kinetic

1. Introduction

Most of the dye compound is resistant to biodegradation due to its complex features, it can cause carcinogenic, toxic, and mutagenic effect on human and animals [1–4]. Dye is one of the most important contaminating materials in textile industry wastewater [5,6]. Malachite green (MG) is a cationic dye widely used in textile industries; this dye is also used in the fisheries industry as an antifungal and bacterial to treat parasites and fish diseases. But recent studies indicated that some diseases such as carcinogens, genetic mutation, and abortion have been observed as a result of consuming triphenylmethane dye MG in terms of nitrogen accumulation in animal body [7,8]. Malachite dye is resistant to biodegradation and it is very hard to remove from aqueous solution. Various methods have been used to remove MG, amongst those, the adsorption technique is considered the efficient method due to its high efficiency, easy operation, and low cost [9].

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Several materials have been used by researchers to remove MG from aquatic environments, for example, Khan et al. [10] used novel brown linseed deoiled cake activated carbon as an adsorbent, whose results indicated that the absorbance rate was 213.57 and 136.58 mg/g for acridine orange and azure B 19, respectively, Khan and Nazir utilized magnetic chitosan-bamboo sawdust composite, whose finding showed the adsorption capacity (q_m) of 217.39 mg/g at a contact time of 30 min and an adsorbent dose of 0.5 g/L. In column studies, the data fitted well with the Thomas model in an adsorption capacity of 225.13 mg/g at a flow rate of 20 mL/min and a bed height of 5 cm [11]. Scoria is a mineral which is used for adsorption process due to their abundant availability, lightweight (with a density of 0.5–1 kg/L), and high porosity (the pores volume of 85%). This type of rock with superficial structure and large surface area properties made it easy for adsorption process [12]. It can be stated that, this type of rock involves low permeability because the majority of its inner porosity especially small pore size, are not interconnected, also it contains a high percentage of silica (72%–59% of SiO_2). So, the above-mentioned properties lead to its toughness feature [13,14]. Scoria is used for various environmental purposes, mainly used as an adsorbent to remove organic matter, pesticides, grease and fat, strontium ions, cesium, uranium and thallium, phosphorus, copper, nickel, and zinc. Also, it might be used in slow filtration to remove pathogens from water, and used to irrigate the mud for removal of turbidity under rapid filtration situation, furthermore used to stabilize TiO_2 for photocatalytic degradation of organic pollutants such as 3-nitrobenzene sulfonic acid from aqueous solutions [15]. Response surface methodology (RSM) is a useful set of mathematical and statistical methods, which studies the interactive effect of one or more independent variables on one or more dependent variables [16]. The common method for optimization of multifactorial system deals with one factor at one time. However, this type of method takes more time, also not reveal the alternative effects between ingredients. In this study, the central composite design (CCD) has been used to modeling and optimization the absorptive in removal of MG dye from aqueous solutions to evaluate the interactions between variables along with their direct effects on the process [4,17–19].

According to the effect of dopant metals on scoria structure such as pore size, surface area, chemical composition changes (operating groups), and the intensity of its ion exchange [20], in this study, the scoria characteristics was modified using iron, to improve the ability of this adsorbent to remove MG dye from aquatic environments.

2. Material and methods

2.1. Preparation of adsorbent and its modification

The raw scoria used in this study was collected from the Ghorveh region mines, in Kurdistan, Iran. Scoria was washed thoroughly with distilled water to remove the impurities, until the water turbidity reached to less than 1 NTU, then 300 g of scoria powder with a size of 50# weighted and washed with distilled water several times and dried in oven at a temperature of 105°C for 1 h. To dope ferrous metal on adsorbent, the prepared scoria sample was kept in hydrochloric acid (37%) for 24 h, and then washed with deionized distilled water for several times. Afterward, scoria was kept in deionized distilled water for 24 h and dried at 105°C for 14 h. The prepared sample was kept in $Fe(NO_3)·3.9H_2O$ (0.5 m) solution at pH = 12 and 25°C (laboratory temperature) for 72 h, then dried at 110°C for 14 h. To remove the extra iron and nitrate from scoria, it was washed again with distilled water, dried at 105°C for 14 h. The structure and composition of the adsorbent was characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), and Fourier transform infrared (FTIR) spectroscopy, and the physical and chemical characteristics of scoria were determined before and after modification [21].

2.2. Adsorbent characteristics

The adsorbent was characterized by FTIR, XRD, and SEM. The FTIR was carried out using a spectrometer (WQF-510) with a resolution of 4 cm^{-1} in the range of 400–4,000 cm^{-1} with KBr pellets technique as shown in Fig. 1. The chemical characteristics were determined by the XRD method (Shimadzu XRD-6000) (Table 1). Surface morphology of the synthesized adsorbent was analyzed using SEM (Philips XL30) technique (Fig. 2).

2.3. Experimental design (determine sample size)

Experiments (the required sample size) were designed using the RSM (Design Expert 8.0, Stat-Ease Inc., Minneapolis, MN, USA). Due to the range of variables as well as applying other required parameters into the above-mentioned software, 20 experiments were obtained as shown in Tables 2 and 3.

Three main independent parameters "contact time" (min) (X_1), "adsorbent dosage" (g/L) (X_2), and "initial pH" (X_3), and the adsorption of MG dye by the Mn-modified pumice (response) were selected for the experimental design via CCD. In the CCD model, the number of experiments (N) was calculated with $N = 2^k + 2k + x_0$, where k is the number of parameters and x_0 is the number of central points. Therefore, the total number of runs was calculated to be 20 considering $k = 3$ and $x_0 = 6$.

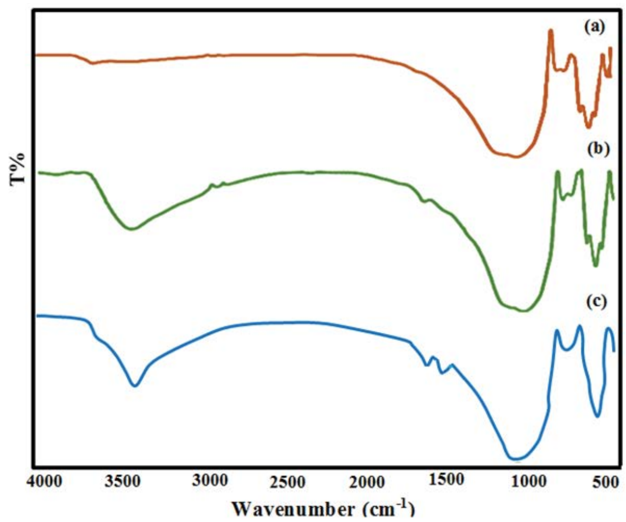

Fig. 1. FTIR of absorbent: (a) raw scoria, (b) iron-modified scoria, and (c) after adsorption of MG on iron-modified scoria.

Table 1
Chemical characteristics of raw and iron-modified scoria

Raw scoria	Percent	Iron-modified scoria	Percent
SiO_2	48.79	SiO_2	59
Al_2O_3	19.6	Al_2O_3	11.4
K_2O	4.4	K_2O	1.97
Fe_2O_3	9.1	Fe_2O_3	10.5
CaO	7.9	CaO	7.43
MgO	8.05	MgO	5.7
P_2O_5	1	P_2O_5	0.9
TiO_2	1	TiO_2	2.4
etc.	0.16	etc.	0.7

Considering that industrial mills neutralize their produced effluents contain MG up to pH = 7, also the color and other pollutants are removed. Moreover, owing to similar previous studies about other variables to determine the runs, the central points (run with the most repeating) of variables range, the pH of 7, the absorbent dosage of 0.8 g/L, and the contact time of 45 min were considered. It should be noted that the initial concentration of MG was 85 mg/L measured in all investigated runs.

2.4. Preparation of samples and adsorption experiments

MG dye has molecular formula $C_{23}H_{26}N_2CL$ (molecular weight of 364.5 g/mol) was purchased from the Merck Company, Germany. The MG stoke solution (1,000.00 mg/L) was prepared by dissolving 1 g of MG in 1,000 mL distilled water, and the sample with concentration of 85 mg/L was prepared using the above prepared stock solution. All working solutions (200 mL of each sample) used in experiments were prepared by diluting stock solution (85 mg/L) and the adsorption parameters including laboratory temperature, pH of 3, 5, 7, 9, and 11, retention times of 15, 30, 45, 60, and 75 min, adsorbent dosages of 0.2, 0.5, 0.8, 1.1, and 1.4 g/L with a mixing rate of 200 rpm were studied. At the end of each operation, 15 mL of the solution was centrifuged at 2,000 rpm for 15 min. The remaining concentration of the solution was measured by a spectrophotometer (Cary 50 made by Perkin Elmer) at 665 nm [21]. All experiments were repeated three times to achieve the acceptable results, also the calibration curve was calculated due to absorbance rate and dye concentrations to prepare the standard solution.

2.5. Investigation of adsorption isotherms

Adsorption isotherms based on properties and equilibrium adsorption data could evaluate how adsorbents react with absorbent materials, which play an important role in optimizing the adsorption. In this study, the results obeyed the Langmuir and Freundlich adsorption isotherms. The dye absorbance was measured, and equilibrium adsorption capacity by pumice powder was evaluated as follows [22]:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where q_e is the equilibrium adsorption capacity (mg/g); C_0 and C_e are the initial and equilibrium concentration (mg/L) of MG dye solution; V is the volume (L); M is the adsorbent weight (g).

2.5.1. Langmuir isotherm

The Langmuir is an effective isotherm for the adsorption of solute from a liquid solution based on mono layer adsorption on the adsorbent surface containing a limited and uniformed number of adsorption sites. The linear form of the Langmuir isotherm is commonly calculated as follows [23].

$$\frac{1}{q_e} = \frac{1}{Q_m} + \frac{1}{bQ_mC_e} \tag{2}$$

where C_e and b are in order the equilibrium concentration (mg/L) and equilibrium constant (mg/L). q_m is monolayer absorption capacity (mg/g).

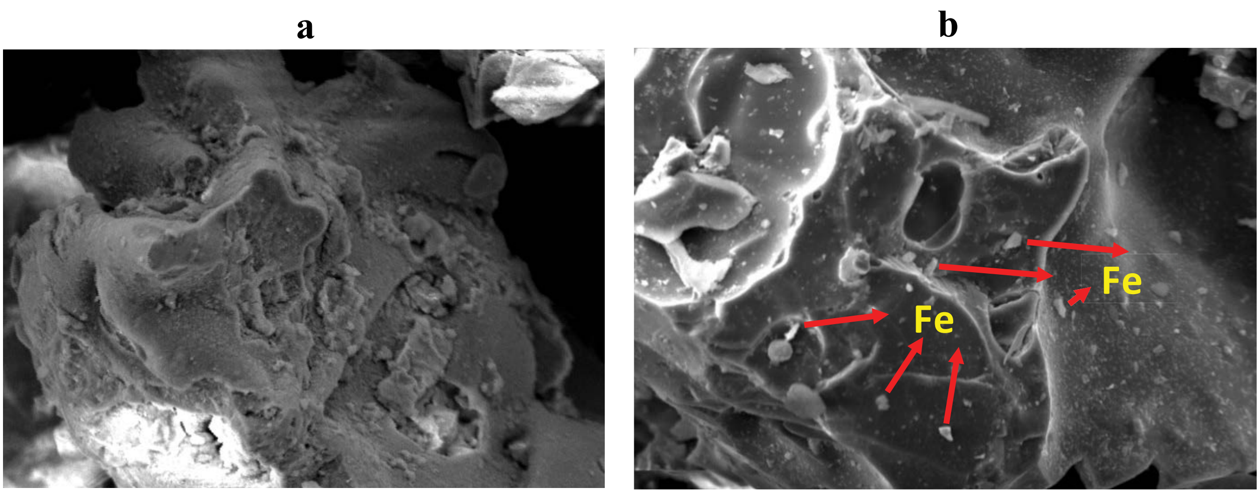

Fig. 2. SEM of absorbents: (a) raw scoria and (b) iron-modified scoria.

Table 2
Experimental range and level of the independent variables

Variables	Range and level				
	–α(–1.5)	–1	0	1	+α(1.5)
Contact time (min)	15	30	45	60	75
Adsorbent dosage (g/L)	0.2	0.5	0.8	1.1	1.4
pH	3	5	7	9	11

The dimensionless constant (separation factor), R_L is the essential characteristic of the Langmuir isotherm, which is defined as follows:

$$R_L = \frac{1}{\left(1 + bC_0\right)} \quad (3)$$

where R_L is the separation factor, C_0 is the initial concentration (mg/L), and b is the Langmuir constant.

The absorption process could be determined using the R_L parameter:

Type of absorption process	Factor R_L
Undesirable	$R_L > 1$
Linear	$R_L = 1$
Desirable	$0 < R_L < 1$
Irreversible	$R_L = 0$

2.5.2. Freundlich isotherm

The Freundlich equation based on multilayer adsorption on heterogeneous adsorbent sites with unequal and non-uniform energy was used for the adsorption of MG dye on the adsorbent. The linear form of Freundlich isotherm was calculated as follows [24]:

$$q_e = \log K_f + \frac{1}{n}\log C_e \quad (4)$$

where q_e is the amount of dye adsorbed (mg/g), C_e is the equilibrium concentration of dye (mg/L), and K_f and n are constants incorporating the factor affecting the capacity ((mg/g)(g/L)$^{(1/n)}$) and intensity of absorption, respectively [25].

2.6. Reaction kinetics

The reaction kinetics is essential to find the information about the factors affecting the reaction rate [24].The reaction kinetic constants were calculated using the following Lagergrens pseudo-first-order and Hu pseudo-second-order equation [26].

2.6.1. First-order kinetic equation

The linear form of first-order kinetic equation was shown as follows [27]:

$$\log\left(1 - \frac{q_t}{q_e}\right) = -\frac{K_1}{2.302} \quad (5)$$

Table 3
Real and predicted average removal percentage of malachite green dye on iron-modified scoria

Run	Variables			Responses (removal of dye, %)			
	Factor 1	Factor 2	Factor 3	Iron-modified scoria		Raw scoria	
	A: Contact time (min)	B: Adsorbent dosage (g/L)	C: pH	Actual	Predicted	Actual	Predicted
1	15	0.2	3	23.6	23.3	20.5	16.70
2	75	0.2	3	32.5	35.2	22.2	24.40
3	45	0.8	7	61.2	61.1	54.0	51.60
4	45	0.8	7	62.2	61.1	54.0	51.60
5	45	0.8	7	60.2	61.1	54.0	51.60
6	75	1.4	11	94.2	98.9	82.5	86.50
7	75	1.4	3	61.1	66.3	45.5	49.50
8	45	0.8	7	59.2	61.1	54.0	51.60
9	15	0.2	11	50.0	56.0	47.6	53.70
10	45	0.8	7	63.2	61.1	54.0	51.60
11	75	0.2	11	68.5	67.9	65.8	61.40
12	45	0.8	9	80.8	69.3	66.1	60.80
13	60	0.8	7	69.1	64.1	57.4	53.50
14	15	1.4	3	54.3	54.4	34.7	41.80
15	45	1.1	7	75.8	68.9	70.6	57.90
16	30	0.8	7	56.5	58.2	46.8	49.60
17	45	0.8	5	53.9	53.0	38.6	42.30
18	15	1.4	11	84.2	87.1	78.2	78.80
19	45	0.5	7	50.4	53.4	41.8	45.30
20	45	0.8	7	61.9	61.1	54.0	51.60

where q_t and q_e are the amount of adsorbed dye at time t and equilibrium (mg/g), respectively, K_1 is the pseudo-first-order kinetic rate constant (min^{-1}).

2.6.2. Pseudo–second-order kinetics

The linear pseudo-second-order model can be revealed in the following equations:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} \quad (6)$$

$$h = kq_e^2 \quad (7)$$

where h is the primary absorption rate when $t \rightarrow 0$ (mg/g/min), k is the pseudo-second-order kinetic adsorption constant) g/mg/min).

3. Results

Table 3 shows the real and predicted removal percentage of MG dye by the iron-modified and bare score. The MG dye removal by the iron-modified scoria and the validity of analyzed parameters is given in Table 4. Table 5 represents the constant of the Langmuir and Freundlich isotherms and kinetic constants of pseudo-first-order and pseudo-second-order equations. Table 6 depicted maximum adsorption

Table 4
The removal model of malachite green dye by iron-modified scoria and validity investigation parameters from central composite design after elimination of insignificant model terms

Type of scoria	Modified equations with significant terms	Type of model	F-Value	Prob > F	Mean	SD	R^2	Adj. R^2	Pred. R^2	AP	PRESS	PLF
Raw scoria	Removal (%) = + 70.76 + 3.93A + 13.45B + 19.83C	Linear	39.85	0.001>	56.76	6.47	0.8820	0.8598	0.7859	25.70	1,216.17	0.124
Iron-modified scoria	Removal (%) = + 61.14 + 5.94A + 15.53B + 16.33C	Linear	74.58	0.001>	61.14	4.54	0.9333	0.9207	0.8881	37.212	553.31	0.098

SD: standard deviation, R^2: determination coefficient, Adj. R^2: adjusted R^2, Pred. R^2: predicted R^2, AP: adequate precision, PRESS: predicated residual error sum of squares, PLF: probability for lack of fit.

Table 5
Calculated constants of the Langmuir and Freundlich isotherms and kinetic constants of pseudo-first-order and pseudo-second-order equations

Isotherms constants	Q_m (mg/g)		b (L/mg)	R_L	R^2
Langmuir	Iron-modified scoria	3.6	0.138	0.078	0.926
	Raw scoria	2.4	0.0856	0.12	0.946
Freundlich	K_f (mg/g)		$1/n$	R^2	
	Iron-modified scoria	0.73	0.34	0.972	
	Raw scoria	0.88	0.31	0.948	
Kinetic constants	K_1 (min^{-1})			R^2	
Pseudo-first-order	Iron-modified scoria	0.0644		0.961	
	Raw scoria	0.191		0.953	
Pseudo-second-order	K_2 (g/mg/min)			R^2	
	Iron-modified scoria	0.013		0.991	
	Raw scoria	0.0103		0.96	

Table 6
Maximum adsorption capacities (Q_m) of malachite green on the scoria and other adsorbents documented in the literature

Adsorbent	Adsorbate	Q_m (mg/g)	Ref.
Fly ash	Malachite green	0.814	[28]
Tamarind fruit shell	Malachite green	1.95	[29]
Polylactide/spent brewery grains films	Malachite green	0.572	[30]
Iron-modified scoria	Malachite green	3.6	Present study
Raw scoria	Malachite green	2.4	Present study

capacities (Q_m) of MG on the scoria and other adsorbents documented in the literature. Also, the effect of contact time and absorbent dosage on pH = 7 are shown in Fig. 3. Moreover, Fig. 4 represents the effect of contact time and pH on the adsorbent dosage of 0.8 g/L. Defining the effect of adsorbent dosages, contact time, and pH parameters on MG dye removal is denoted in Fig. 5. Fig. 6 reveals the contrast between the real and the predicted values of MG dye removal by the iron-modified scoria. Fig. 7 indicates the optimum efficiency region more than 75%. The results showed that the adsorbent removal efficiency increases with increase in the adsorbent dosage and pH, so the highest removal rate (84.5%) was found at contact time of 75 min, adsorbent dosage of 1.4 g, and pH = 11. Dye absorption obeyed both the Langmuir and Freundlich isotherms and the absorption kinetics was more consistent with the pseudo-second-order equation.

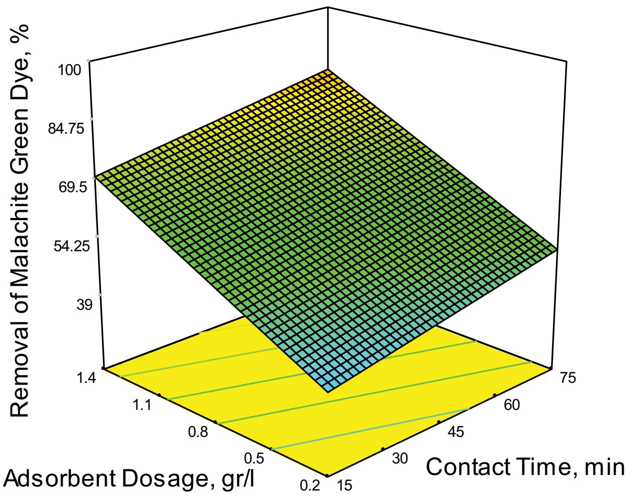

Fig. 3. Effect of contact time and absorbent dose on pH = 7 by iron-modified scoria.

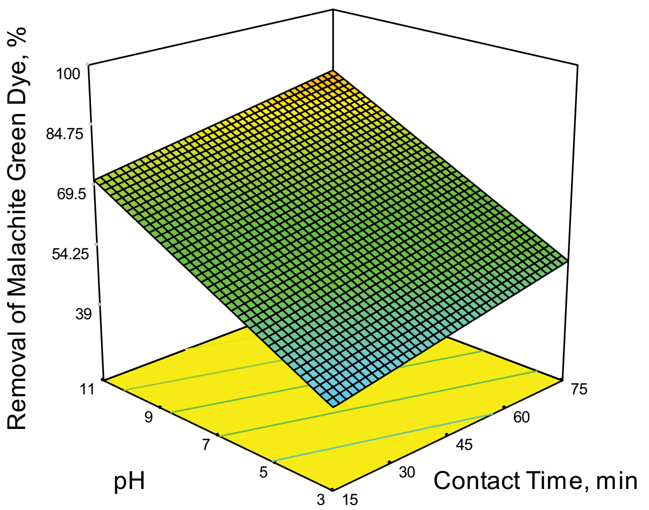

Fig. 4. Effect of contact time and pH = 7 on absorbent dose of 0.8 g/L by iron-modified scoria.

4. Discussion

4.1. Effect of iron modification on studied adsorbent

The results showed that the maximum removal efficiency of MG (94%) was obtained by the iron-modified scoria. Since the structure of scoria such as significant increases in the surface area, the pore size, and its three-dimensional

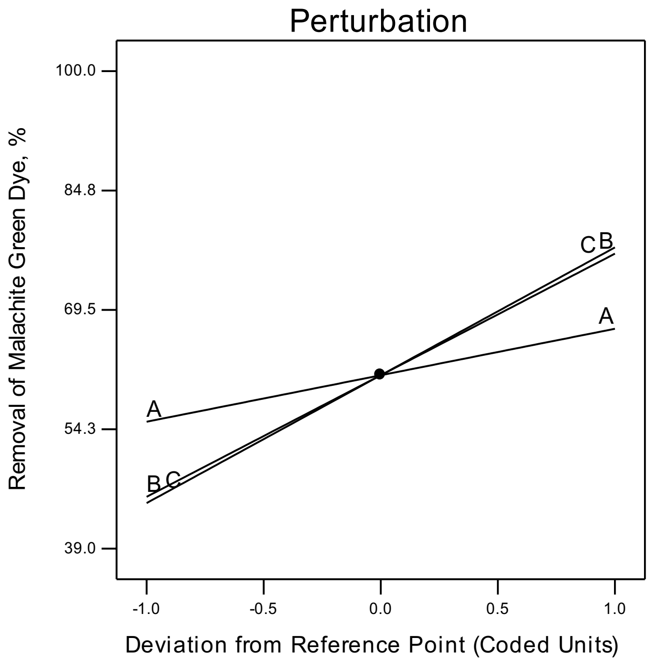

Fig. 5. Determine the effect of adsorbent dosage, contact time, and pH on MG removal by iron-modified scoria.

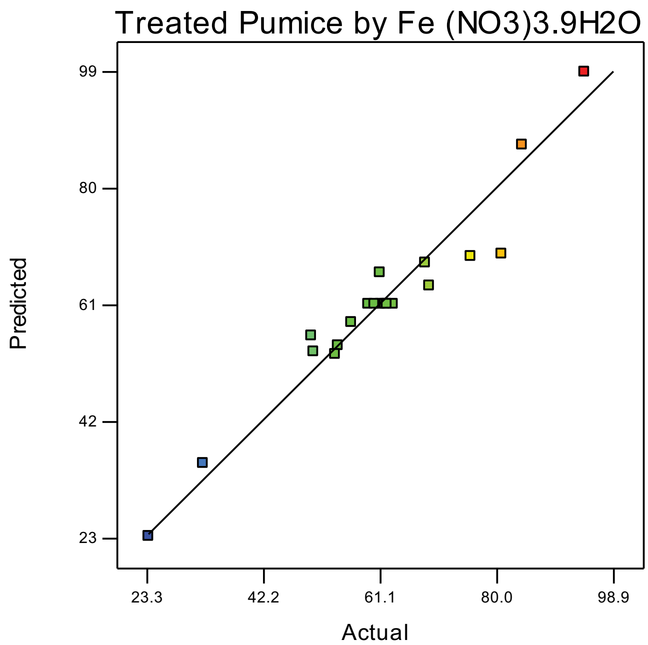

Fig. 6. Determine the confrontation between real and predicted values of removing MG dye by iron-modified scoria.

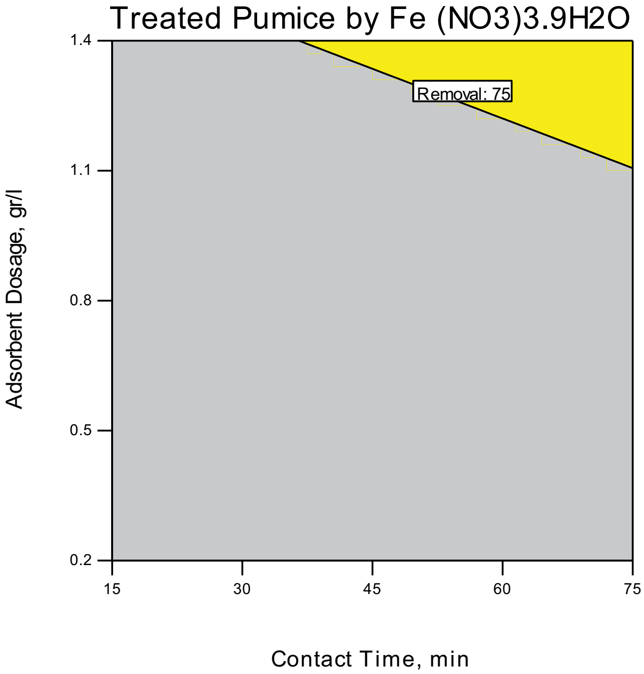

Fig. 7. The optimum efficiency region more than 75% on iron-modified scoria.

deformation will be changed in modifying scoria. Therefore, these structural alterations lead to increasing the absorption by the adsorbent material in terms of increase in the surface area and adsorption sites [31,32]. The results of this study are consistent with other researcher's studies. As Kim [33] and Vaughan [34] studied on aluminum- and iron-modified zeolite and activated carbon to remove arsenic, respectively.

4.2. Characterization of adsorbent

XRD of the adsorbent shows that there are significant changes between the natural and modified scoria, but these wide changes seem not to be only due to the increases in manganese oxide in the modified scoria resulting the effects of modifying adsorbent with manganese, but it could be occurred due to the chemical changes in different samples of the mine scoria during its formation. The FTIR spectra show a broad band between 500 and 1,000 cm^{-1} for adsorbent which indicates the presence of Si–O–Si and Si–O–Al bonds [32]. However, strong and sharp peaks can be observed in modified scoria due to more silica content. The change was observed at 1,570 cm^{-1} which illustrated aromatic C=C stretching vibration of MG adsorbed on modified scoria [35].

4.3. Validity of the model

Consequently, to obtain the predicted value presented a model is required, and the proposed model should be valid. The validity of the models is expressed by parameters such as R^2, R^2-Adj, Prob > F, AP, and PLF. The results indicated that all above-mentioned parameters were inaccurate ranges (Prob > F and PLF < 0.5 and AP > 4), that imply the validity of the obtained models to predict the amount of dye removal. It can be also stated that the difference between the actual and the anticipated value of MG dye removal by iron-modified scoria decreases rather than raw scoria. So distribution of the available sites on the iron-modified adsorbent indicated that the actual removal rate on the predicted value line increased.

4.4. Effect of variables on response

Comparing the effect of contact time, adsorbent dosage, and pH in MG dye removal efficiency by the modified and raw scoria showed that the dye removal rate increases with increase in the contact time, the adsorbent dose, and the pH [36]. Also, the main effective parameters were in order related to pH, adsorbent dosage, and contact time. However, the results of the study showed that the pH gradient (C) was more than the adsorbent dosage (B) and contact time (A) gradients, which shows the more effective of this parameter in dye removal efficiency.

The more effective of pH rather than other factors (adsorbent dosage and contact time) could be due to the more effect of pH on the physicochemical characteristics of the adsorbents and absorbent. With increase in the solution pH value, the adsorbent net surface is negatively charged, which adsorb cationic species. MG is a cationic dye and involves two nitrogen atoms and methyl ions [37] hence, this dye removal increases in alkaline environments due to electrostatic gravity, where the negative charge of adsorbent surface increases [10]. Also, the MG dye changes more chemically in pH higher than 9, and absorbed significantly [9]. The results indicated that dye absorption decreases with decrease in pH, which could be due to electrostatic repulsion in terms of produced ion proton (H^+) in an acidic environment. Therefore, the cationic dye removal decreases. Considering that the SiO_2 is the main composition of scoria, SiO_2 content converts to Si^{+3} ions due to decrease in pH, which cause the electrostatic repulsion and decreases the cationic dye. Therefore, the slight dye absorption in acidic environments is due to dye penetration in the adsorbent pores [38,39]. Furthermore, maximum degradation of investigated dye in acidic condition has occurred using the iron-modified scoria rather than using raw scoria. Although, modifying scoria with iron cause increase positively charged on the adsorbent surface, in fact the absorption of cationic dye might be decreased due to existing a high electrostatic repulsion, and the absorption may be occurred due to increase the specific surface area of the catalyst. Since modification of scoria cause increases the specific absorbent surface area, which increases the efficiency of iron-modified scoria compared with raw scoria despite of electrostatic refraction [31]. It can be stated that the scoria-modified function creates an irregular structure in scoria as a result increases the absorption rate [32]. This result is in consistent with other studies, as Kim (2004) and Vaughan (2005) showed that the aluminum and iron-modified zeolite and activated carbon, respectively, contain a high specific surface area rather than their nonmodified catalyst [33,34]. The found results indicated that the adsorption changes are noticeable in terms of contact time, because with increases the adsorbent dose, the more sites will be available for absorption [40]. Accordingly, a high amount of absorption rate occurred in early time, and the absorption rate has gradually reached in stable situation. Afterward decreased to occupy the absorption sites, this results are in consistent with Santhi, Sharma, and Seey studies, whose results showed that the pH effects on MG dye absorption by activated carbon significantly, as well causes extensive physical and chemical changes on the absorbent surface [9,41,42]. The Santhi study showed that the maximum removal of MG by activated carbon occurs at pH of 7, because the adsorbent level is negative at this pH, so more cationic malachite dye absorption took place. Whereas, in low pH to overcome the hydrogen ion, the charge level of adsorbent was positive, therefore electrostatic repulsion reduces the absorption of cationic dye. Also, this study indicated that the adsorbent surface is more positive in pH < 4. The adsorbent surface is heterogeneous and combination of negative and positive charge in pH of 4–6, but in pH more than 6 the absorbent surface will be charged negatively due to hydroxyl ion. This result indicated that more than 50% of dye removals by adsorbent occur at the first 30 min. Consequently the absorption rate decreases with increase in contact time. It could be mentioned that the maximum dye absorption was recorded at pH of 7 and early contact time due to negative adsorbent surface charge [42]. The other researches results, for example, Sharma and Seey revealed that the MG dye removal increases with increase in pH [9,38].

4.5. Adsorption kinetics and isotherm

The adsorption isotherms study showed that the dye absorption obeyed the Freundlich isotherm. Khairia [42] evaluated the efficiency of palm seed in the removal of MG dye who showed that the dye removal fitted with the Freundlich isotherm. Also, Heidari et al. [31] investigated the efficiency of aluminum-modified scoria to remove arsenic whose results obeyed the Freundlich isotherm. This indicated that the absorption sites on the absorbent surface are multilayer and heterogeneous. The absorption fits with the Langmuir isotherm, the separation coefficient (R_L) is the important parameter, which showed the ability of adsorbent in removing and separating of dye. The results of the Langmuir isotherm indicated that the R_L was in the optimal range (0–1). On the other hand, the iron-modified scoria was a suitable absorbent to remove MG dye in the study, in which the results are inconsistent with Moraci et al.'s investigation [43]. Actually, the amount of R_L in the iron-modified scoria was closer to zero than raw scoria, which indicated that the modified absorbent is more effective [32]. "As" shown in Fig. 5 the surface area beyond 75% in iron-modified scoria was higher than the raw scoria. According to the Freundlich isotherm result, the calculated absorbance intensity ($1/n$) for iron-modified scoria was within the optimal range (0–0). In fact, the amount of $1/n$ in the iron-modified scoria was lower than bare scoria.

However, with modified scoria, despite the further removal of dye by the iron-modified scoria (due to the physical removal and increases the surface area), the intensity of absorption rate between cationic dye and adsorbent reduces due to electrostatic repulsion in terms of positive charge resulting doped iron on the adsorbent. Given that the $1/n$ value in the Freundlich isotherm represents the interaction between adsorbent and absorbance, as l/n value tends to zero, this interaction was the strongest and powerful [44].

Therefore, the absorption coefficient (K_f) for iron-modified scoria of 0.73 was obtained less than the raw scoria (0.88). An investigation of the adsorption reaction kinetics on the scoria showed that the adsorption process for all adsorbent forms obeyed the pseudo-second-order kinetic model. Some researchers such as Akbal [45] and Visa et al. [46], Doğan et al. [47] and Al-Ghouti et al. [48] studied on scoria and similar absorbents, whose results showed that the kinetic absorption of cationic dye obeyed the pseudo-second-order. Following the quadratic equations implies that the adsorption process depends on the absorption, concentration, as the pseudo-second-order equation for absorption is generally based on the adsorption capacity [49].

5. Conclusion

According to obtained results, MG dye removal increased with increase of pH, adsorbent dosage, and contact time. The highest removal efficiency (94.2%) was obtained in pH = 11, adsorbent doses = 1.4 g/L, and contact time = 75 min. All parameters of the model were of inaccurate ranges (Prob > F and PLF < 0.5 and AP > 4), that imply the validity of the obtained models to predict the amount of dye removal. Also, difference between the actual and the anticipated value of MG removal by iron-modified scoria decreases rather than raw scoria. Adsorption data obeyed both the Langmuir isotherm and Freundlich adsorption and pseudo-second-order kinetic. According to the results, it can be concluded that the MG dye adsorption on the iron-modified scoria occurs as both multi and mono layer. The separation factor and adsorption intensity for iron-modified scoria was obtained lower than raw scoria. According to the results, it can be concluded that iron via chemical changes of adsorbent structure causes increase in the efficiency of scoria, which leads to more removal of MG.

Acknowledgment

The authors gratefully acknowledge the Research Council of Kermanshah University of Medical Sciences (Grant no. 93054) for the financial support.

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