

Adsorption Study of Reactive Violet 8 and Congo Red Dyes onto Aloe Vera Micropowder Impregnated with Cu Atoms as a Natural Modified Sorbent and Related Kinetics and Thermodynamics

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In this research, ordinary Aloe Vera micropowder (OAMP) and its impregnated form (IAMP) as the natural sorbents were prepared and then characterized by several techniques such as Fourier transform spectrophotometry (FT-IR), scanning electron microscopy (SEM), elemental analysis (EA), Brunauer-Emmett-Teller and Barrett-Joyner-Halenda (BET/BJH) essays and X-ray powder diffraction (XRD). The removal efficiencies of the prepared adsorbents were assessed upon their capacities for removing reactive violet 8 (RV8) and congo red (CR) dyes as the organic pollutants. Our preliminary adsorption experiments showed that the OAMP ability for removing RV8 and CR is very less than that for the IAMP form, so we focused on the IAMP removal ability and used it as a fairly powerful adsorbent in this study. The effect of several parameters such as initial adsorbate concentration (C_0), adsorbent dosage, contact time, temperature, and solution pH on the adsorption capacity of IAMP adsorbent were investigated and then several isotherm models were examined to fit the experimental results. Consequently, we concluded that the Langmuir and Freundlich models fit reasonably the experimental results. In addition, thermodynamic and kinetic studies of the adsorption process were studied and the corresponding thermodynamic and kinetic parameters were concluded and reported.

Keywords: Adsorption, Aloe Vera, Congo Red, Reactive Violet 8, Sorbate, Sorbent

INTRODUCTION

Industrial wastewaters are one of the most important sources of the environmental pollution, so that sometimes the value of chemical oxygen demand (COD) and biochemical oxygen demand (BOD) or the concentration of the compounds in them reaches tens of thousands of milligrams per liter [1]. Dye-containing wastewater, such as the wastewater of the textile industry, is one of the most important industrial wastewaters created large-scale environmental problems [2]. In the textile industry, a variety of natural and synthetic fibers are used to produce various fabrics. In this industry, various chemical treatments are applied to the materials. Textile industries produce

wastewaters with different qualities and quantities due to a variety of manufacturing methods, colors and chemicals, and therefore, they have particular complexity among the various types of industrial wastewater in the treatment process [3,4]. The most important source of pollution in the wastewater of the textile industry is the entry of dye substances into the sewage [2,5]. In the absence of treatment of textile wastewater, colored materials directly enter the environment and cause undesirable effects. Dyes even in low quantities have interfering effects on the penetrating of sunlight into the water and subsequently photosynthesis process and harm aquatic ecosystem [6]. On the other hand, there is the risk of getting this material into the human food chain.

Dyes are generally divided into three groups of anionic (direct, acid, and reactive dyes), cationic (play, base) and

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non-ionic dyes. One of the most important widely used dyes in the textile industry is Reactive Violet 8 and Congo Red. Due to the presence of aromatic structure, these dyes are potentially carcinogenic and mutagenic and, in addition, they are resistant to biological biodegradation [7]. Reactive Violet 8 is widely used in dyeing paper, wool, and cotton. Reactive Violet 8 is toxic and may be adsorbed through the skin and cause irritation, and it is harmful to inhale and swallow. Variety of treatment methods including biological, physical and chemical methods such as coagulation [8], deposition membrane separation [9], electrochemical oxidation [10], ion exchange [11] and adsorption [10,12] have been used for the purpose of dyes removal from industrial wastewater and aquatic ecosystems.

Among treatment methods, adsorption technique has been given greater consideration due to its advantages such as low cost, simplicity, ease of use, high treatment efficiency and high applicability for the removal of the various types of pollutants [13]. Nowadays, available and inexpensive natural adsorbents such as Aloe Vera, rice husk, rice bran, walnut, pine cones, wheat bran, straw, and sawdust have been applied for removal purposes. Abedi *et al.* generated nano-adsorbents from Aloe Vera leave for removing of heavy metal ions from the aquatic environment [14]. The particles of this adsorbent have been modified using iron oxide magnetic nanoparticles. The appropriate adsorption properties of the modified adsorbent are due to increase the surface oxidation groups by magnetic nanoparticles. Ziane *et al.* examined the adsorption of Reactive Black 5 and Congo Red by modified dolomite [15]. Fabryanty *et al.* studied the removal of purple dye by bentonite-alginate composite [16].

In this research, Aloe Vera powder as a low-cost natural adsorbent was for the first time used for removing Congo Red and Reactive Violet 8, two textile dyes from aqueous media. In order to improve the adsorption capacity, the surfaces of Aloe Vera were effectively processed by copper atoms. No processed and processed Aloe Vera were characterized by SEM, EA and BET/BJH techniques and some other ones. The influence of different experimental parameters on the adsorption capacity of the processed Aloe Vera for CR and RV8 removing were studied. In addition, isotherms, kinetics, and thermodynamics of the adsorption process were investigated and discussed in details. CR and

RV8 dyes have some interesting specifications.

EXPERIMENTAL

RV8 and CR with high purity were purchased from Sigma Aldrich and used without further purification. Magnesium powder, copper chloride (CuCl_2), hydrochloric acid (HCl) and the other necessary reagents were obtained from Merck (Germany). Ordinary Aloe Vera micropowder and its impregnated form were prepared from the Aloe Vera plant cultivated in Bushehr province of Iran.

Several instruments and techniques were used for characterization of the prepared sorbents and measuring the adsorption capacities. The commonly used instruments were XRD, SEM, FT-IR, BET/BJH apparatus, pH-meter, spectrophotometer, and the other necessary tools.

To prepare the Aloe Vera powder, a proper amount of Aloe Vera leaves was washed with distilled water and ethanol and then was dried in a suitable oven for 1 h. The dried leaves were thoroughly powdered and sieved via a mesh number 200 (nearly micro size or smaller). This was named ordinary Aloe Vera micropowder (OAMP).

For impregnating Aloe Vera powder with Cu atoms, 5.0 g of prepared Aloe Vera micropowder was mixed with 200 ml of 0.1 M CuCl_2 , and then 2 g of magnesium powder was added to the mixture in a very slowly stepwise manner while the mixture was fully stirred by a magnetic stirrer (the time duration was about 60 min). Then, 100 ml of 1M $\text{HCl}_{(\text{aq})}$ was added, in order to dissolve residual Mg (stirring was continued). Finally, the ultimate mixture was filtered and washed several times with distilled water and ethanol. The resulting impregnated Aloe Vera powder (IAMP) was dried in a proper oven at 50 °C for 1 h. The final product was thoroughly grounded and sieved *via* 200 mesh condition. The ultimate obtained powder was used in the adsorption experiments as a natural efficient adsorbent for removing RV8 and CR dyes from the studied solution phases. $\text{Cu}^{2+}(\text{aq})$ ion has a good tendency to be reduced by Mg atom ($\text{Cu}^{2+}(\text{aq}) + \text{Mg}(\text{s}) \rightarrow \text{Cu}(\text{s}) + \text{Mg}^{2+}(\text{aq})$), and then a fraction of the produced Cu atoms will be deposited on the Aloe Vera powder surfaces. The copper salts have a low cost and readily found in every research laboratory. Some researchers have used the method, but with the other reducing agents and the reduceable species [17].

Table 1. Element Analysis of the OAMP and IAMP

Adsorbent	%C	%O	%Si	%S	%Cl	%K	%Ca	%Mg	%Cu
OAMP	46.85	48.45	0.28	0.44	0.66	1.14	2.17	-	-
IAMP	46.96	48.52	0.61	0.07	0.10	1.04	1.11	0.40	1.09

Table 2. Results from the BET /BJH Analysis

r_p , peak (nm)	Total pore volume ($\text{cm}^3 \text{g}^{-1}$)	Mean pore diameter (nm)	a_s , BET ($\text{m}^2 \text{g}^{-1}$)	Adsorbent type
1.29	0.004	18.16	0.94	Pure Aloe Vera
1.29	0.018	14.02	5.22	Aloe Vera impregnated with copper

Adsorbent Characterization

The element analysis of OAMP and IAMP forms were carried out and the results are shown in Table 1. It is noticeable that the IAMP contains near 1 percent of Cu atoms. As can be seen from the data in Table 1, OAMP and IAMP have fairly different elemental compositions and the deposition of copper atoms onto the surface of the IAMP structure can be confirmed from the obtained results.

In addition, the BET/BJH experiment was done to evaluate the specific surface area of OMPA and IMPA sorbents. The result showed that the obtained BET surface area for IMPA form is noticeably greater than of OMPA form. Therefore, the IMPA powder is a more efficient sorbent than OMPA form.

The SEM images of ordinary micropowder and impregnated form of Aloe Vera powders are shown in Figs. 1a and 1b, respectively. By comparing these images, one can find out the significant characteristic differences between the OAMP and IAMP forms.

The SEM images exhibit a rigid structure for the OAMP form, while respect to the IAMP form, a series of spherical particles are appeared on the surface of it due to the presence of copper atoms. The proper treatment of the OAMP structure with Cu atoms improves its structural

properties and adsorption qualities compared to the OAMP raw structure. Further characterizations are given in the supporting information.

RESULTS AND DISCUSSION

Adsorption Experiment

The procedure of performing a typical adsorption experiment is very important. In general, the common procedure (batch method) is as follow: A suitable dose of sorbent (*e.g.*, 0.10 g) is mixed with the desired volume of sorbate solution with a known concentration (*e.g.*, 50.0 ml with the concentration of 10.0 mg l^{-1}). The temperature and the solution pH are fixed at desired values (*e.g.*, $30.0 \text{ }^\circ\text{C}$ and 5.5, respectively).

The mixture should be stirred during the optimum time (*e.g.* 30.0 min) and under the other optimum conditions. The ultimate mixture should be filtered (using a filter paper with high quality). Finally, the concentration of the filtered solution (the obtained solution upon filtering) must be determined by an effective method, such as spectrophotometric measurement, atomic absorption method, *etc.* In addition, the initial concentrations should also be measured with the same instrument in order to

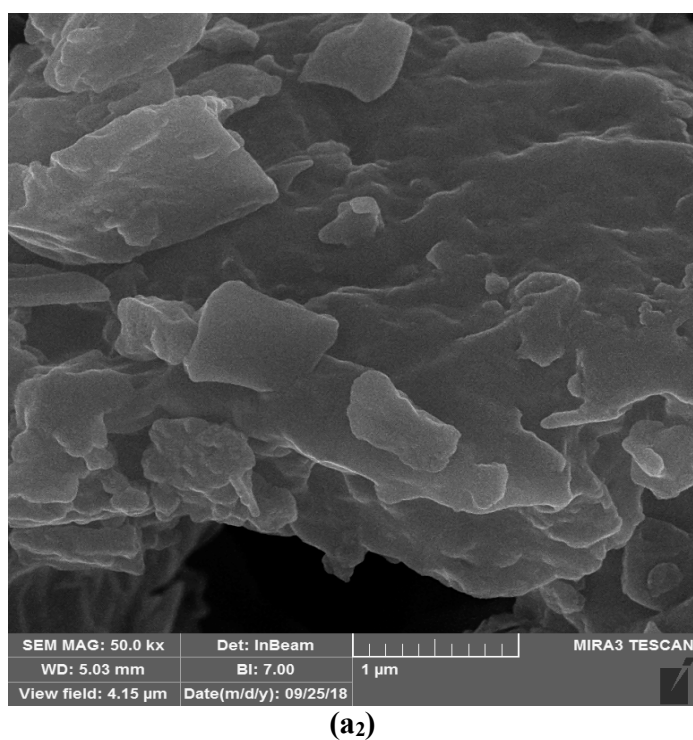
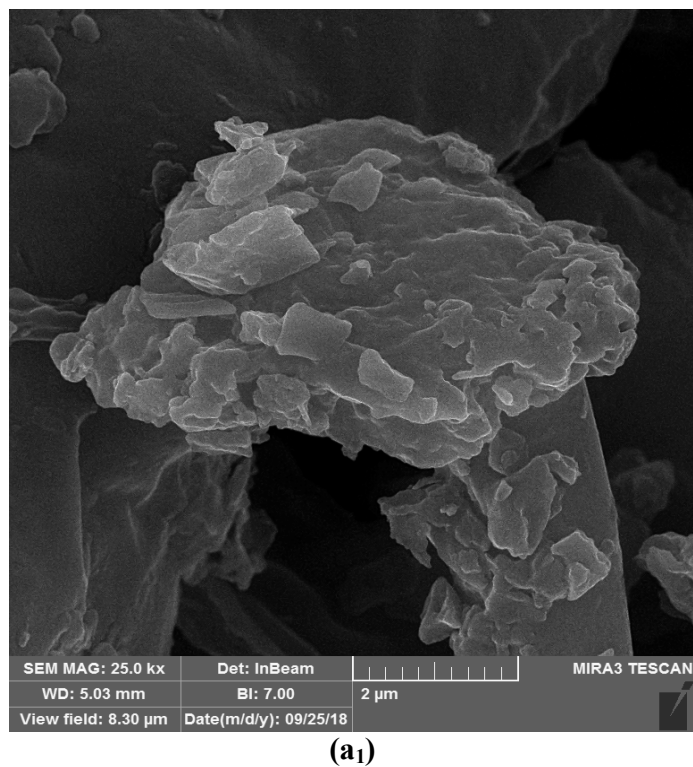
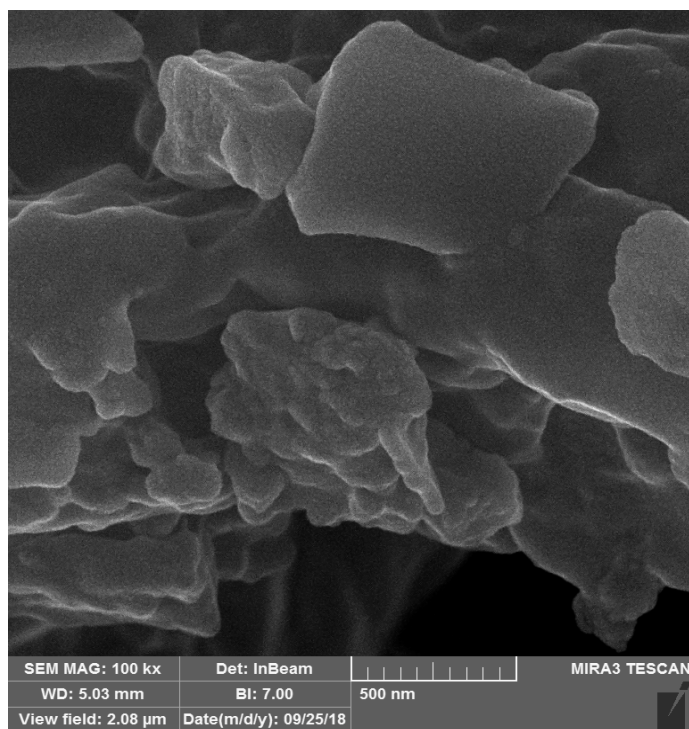
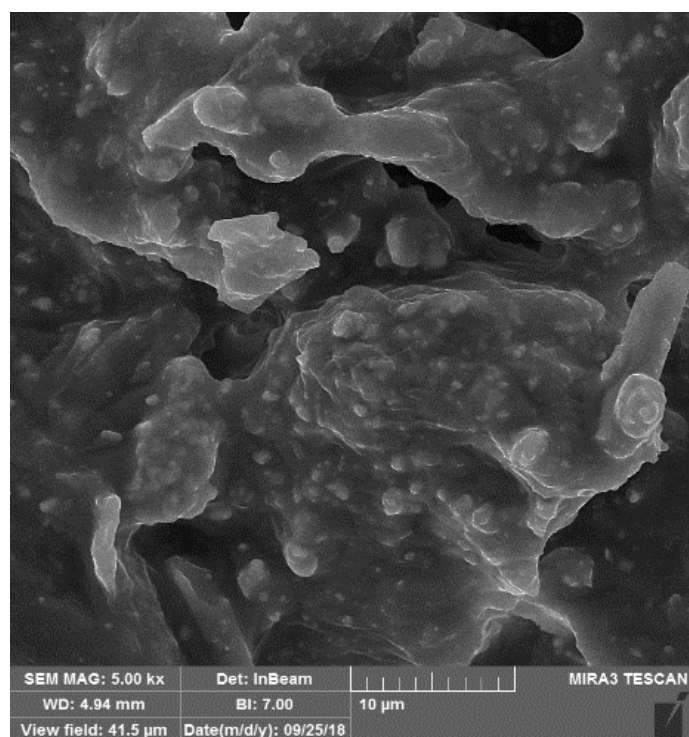


Fig. 1. SEM micrographs of the OAMP form (a₁: 25000×, a₂: 50000× and a₃: 100000×) and the IAMP form (b₁: 5000×, b₂: 25000× and b₃: 50000×).

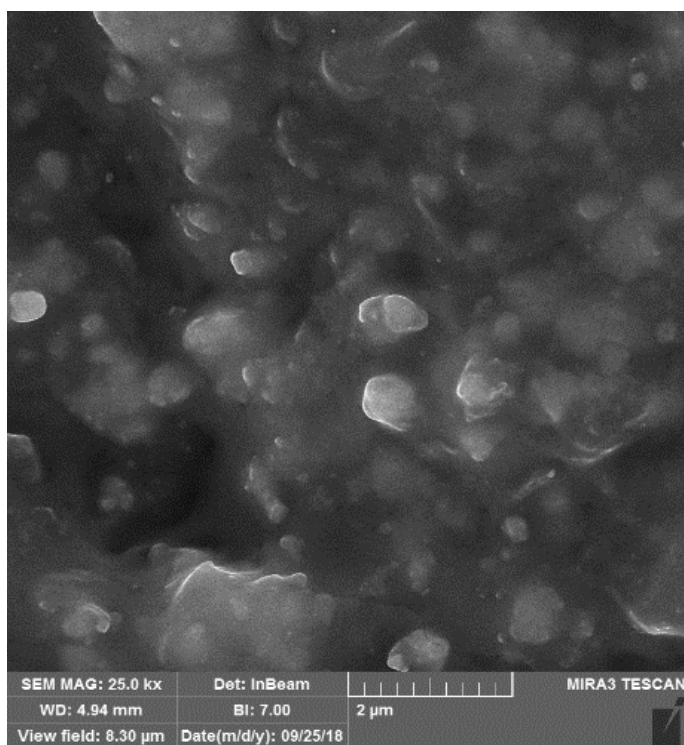


(a3)

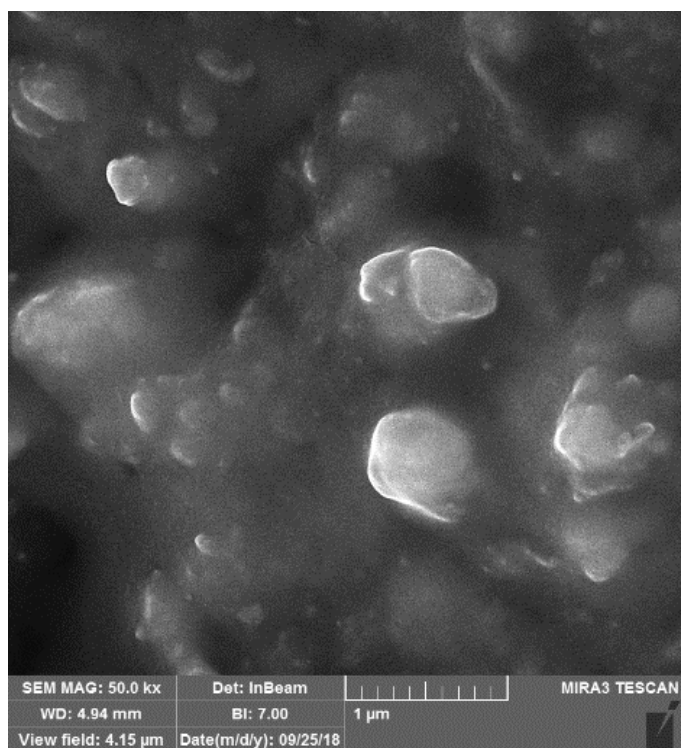


(b1)

Fig. 1. Continued.



(b₂)



(b₃)

Fig. 1. Continued.

achieve a high reliable precision.

Using the obtained results of such measurement, we can determine the removal percent (or %Ad), adsorption capacity (q : the amount of sorbate (in mg) per g of sorbent), and the other related parameters.

$$(\%Ad) = \left(\frac{C_0 - C_e}{C_0} \right) \times 100 \quad (1)$$

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (2)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (3)$$

where C_0 , C_t and C_e (in mg l^{-1}) represent the initial concentration of the sorbate, the concentration of the sorbate at time t , and the respect concentration at equilibrium, respectively, V is the volume of the test solution containing the sorbate in terms of liter, m is the dosage mass of the sorbent in gram. It is necessary to notice that the large value of the removal percent or q_e is a reliable indication of the efficiency of the studied adsorption process.

Here, it should be noted that determining the optimum conditions, such as the initial concentration of the sorbate, the dosage of the sorbent, the contact time, the solution pH and the temperature are very important for carrying out the adsorption experiments and then selecting a suitable isotherm model to fit the experimental data and also concluding a reasonable rate law for the adsorption kinetics. Therefore, we investigated the mentioned optimum conditions respect to the considered adsorption process, in order to construct the reasonable isotherm models and kinetic rate law for representing the experimental data.

The Effect of the Initial Concentration

To investigate the effect of the initial concentration on the equilibrium adsorption capacity, q_e , or (% Ad), the experiments were carried out in the concentration range of 5.0-40.0 mg l^{-1} respect to the sorbates (RV8 or CR), while the other parameters were constant (dosage = 0.10 g, contact time = 30.0 min, pH = 5.5 and temperature =

30.0 °C).

The procedure for performing each experiment was as explained previously. The results are shown in Fig. 2a. As seen, by increasing the initial concentration, q_e (or % Ad) decreases and then the direction alters. Regarding the above results, one can conclude that the optimum initial concentration for both of RV8 and CR sorbates may be chosen as 10.0 mg l^{-1} .

The Effect of the Sorbent Dosage

The dosage of the sorbent (IAMP) was changed in the range of 0.010-0.150 g where the other conditions were constant and the experimental procedure was as previous. Because of increasing the active adsorption sites with increasing the amount of the sorbent, the adsorption efficiencies will be increased. Figure 2b shows the related results of this study. We may choose 0.10 g as the optimum dosage.

The Effect of pH

The solution pH influences the adsorbent surface binding sites and the adsorbate state, so the adsorption process is mostly influenced by this factor. At low pH, H^+ (aq) ions and at high pH, OH^- (aq) ions may be adsorbed on a portion of the free adsorption sites of the adsorbent and therefore compete with the main adsorbate in the adsorption process. At the same time, the pH solution may affect seriously the chemical state of the adsorbate and causes a considerable change in the adsorption capacity. So, in any adsorption study, finding the optimum pH is of a great importance. At the present study, the solution pH was changed in the range of 2.0-9.0. Figure 2c shows the results. The experiments were done as explained previously. Upon the experimental results, pH = 5.5 was selected as the optimum value.

The Effect of Contact Time

We carried out the adsorption experiments at the range of 5.0, 10.0, 20.0, 30.0, 40.0 and 50.0 min. The experimental procedure was as before (constant parameters: $C_0 = 10.0$ mg l^{-1} , sorbent dose = 0.10 g, pH = 5.5, $t = 30.0$ °C). The results are shown in Fig. 2d. As can be seen, there is a significant improvement in the amount of the adsorbed dyes with increasing the contact time and the

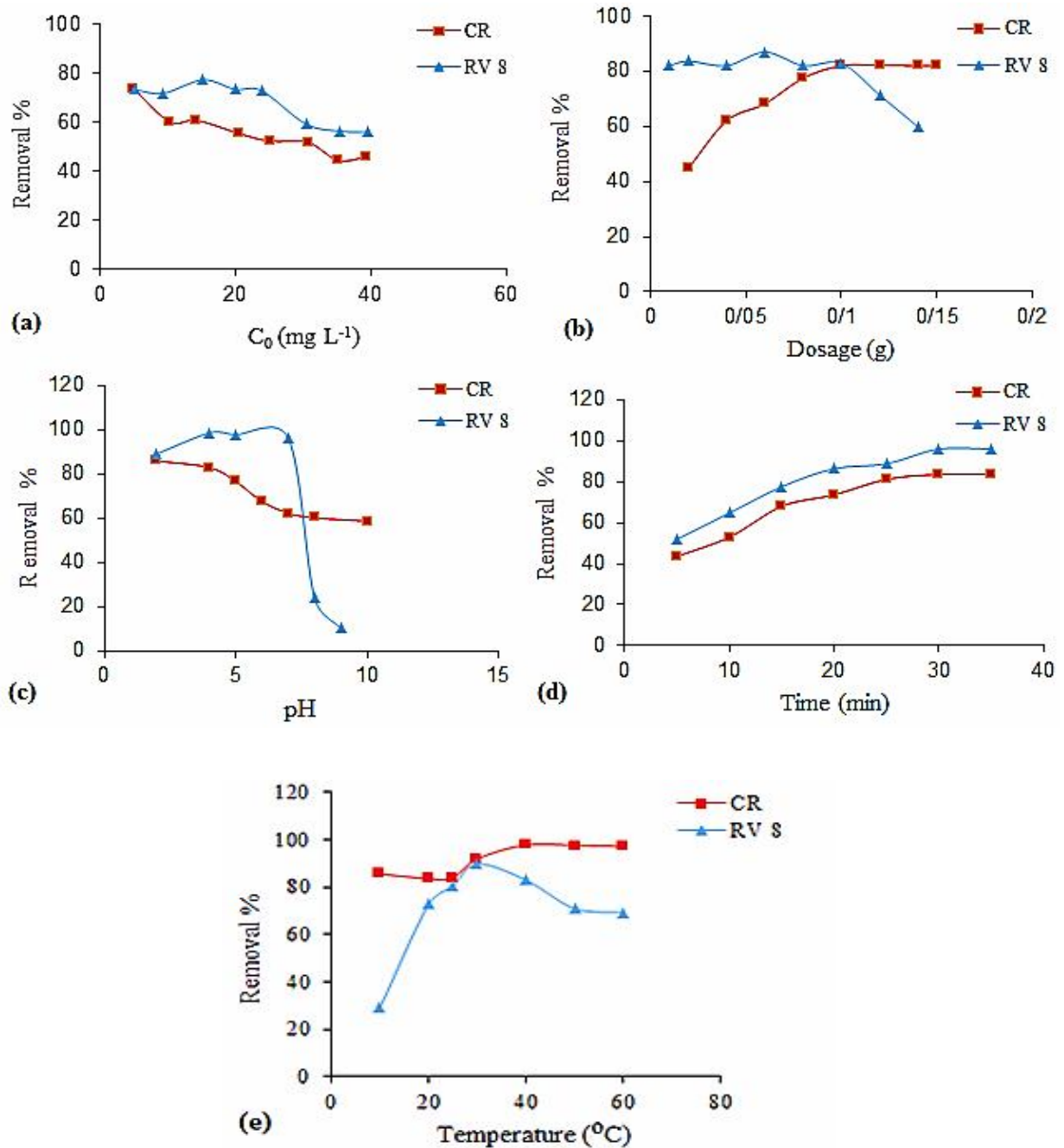


Fig. 2. The effect of (a) initial concentration, (b) dosage, (c) pH, (d) contact time, and (e) temperature on the %Ad for CR and RV8 adsorption onto the IAMP adsorbent.

adsorption process reached nearly the equilibrium at 30.0 min. According to the results, it may choose 30.0 min as the optimum time.

The Effect of Temperature

To investigate the effect of temperature on the removal percent of RV8 or CR onto the IAMP sorbent, we carried

out the adsorption experiments, at 20.0, 30.0, 40.0, 50.0 and 60.0 °C where the other parameters were constant. Figure 2e shows the results. As seen, the adsorption capacity is increased with increasing the temperature. This trend shows that the adsorption of RV8 or CR onto IAPM is endothermic. From the experimental facilities point of view, we chose 30.0 °C as a suitable temperature.

Adsorption Isotherms

In order to deduce a reasonable isotherm [19-21], we carried out the adsorption experiments with the initial concentrations of 5.0, 10.0, 15.0, 20.0, 25.0, 30.0, 35.0 and 40.0 mg l⁻¹ respectively, while the other optimum factors were constant (dosage mass = 0.10 g, contact time = 30.0 min, pH = 5.5 and temperature = 30.0 °C). The results are shown in Fig. 2a. The equilibrium adsorption capacity, q_e , was calculated for each initial concentration as follow:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (4)$$

where C_0 and C_e are in mg l⁻¹, V is in liter, and m in gram. V is the volume of the test solution and m is the adsorbent mass.

Now, on the basis of q_e s and C_e s, deducing a reasonable isotherm model is quite straightforward. At first, we tried to examine the experimental results by the following linear Langmuir model:

$$\frac{1}{q_e} = \frac{1}{K_L q_m} \left(\frac{1}{C_e} \right) + \frac{1}{q_m} \quad (5)$$

The plot of this linear equation is shown in Fig. 3a. From the slope and the intercept of the plot, we can estimate the values of K_L and q_m (Table 3). This model was fairly suitable to fit the experimental data for CR and RV8 dyes removing ($R^2 = 0.983$ for RV8 and $R^2 = 0.957$ for CR) indicating that the selected model is fairly more favorable for RV8 and less favorable for CR dye. The values of K_L and q_m are 0.18 l mg⁻¹ and 36.90 mg g⁻¹ for CR and 2.22 l mg⁻¹ and 25.19 mg g⁻¹ for RV8, respectively (see Table 3).

The experimental results were also examined upon the linear Freundlich model (Fig. 3b)

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_f \quad (6)$$

where K_f is the empirical freundlich isotherm constant which is related to the surface heterogeneity and its activity, and n is another constant of the model. The values of $1/n$ and K_f can be estimated from the slope and the intercept of the plot, respectively (Table 3). This model was more suitable to fit the experimental data of CR dye adsorption ($R^2 = 0.985$). The values of n and K_f are 1.72 and 6.07 g⁻¹ l^{0.58} mg^{0.42} at 30 °C for CR and 2.19 and 14.87 g⁻¹ l^{0.47} mg^{0.53} for RV8 (see Table 3).

Thermodynamics of the Studied Adsorption

In general, it is customary to define a conditional equilibrium constant, $K(T)$ as:

$$K_{(T)} = \frac{q_e}{C_e} \quad (7)$$

Although this definition is not so rigorous from the thermodynamic point of view, but, it is commonly used in the most research papers dealing with the adsorption studies. To consider the above Eq. (7) and Fig. 2e, we can calculate the value of $K(T)$ at each temperature and using them for calculating the corresponding thermodynamic functions of the studied adsorption.

On the basis of the thermodynamic argument, the relation between the standard Gibbs energy change, ΔG° , and the equilibrium constant, $K(T)$, is:

$$\Delta G^\circ = -RT \ln K_{(T)} \quad (8)$$

and the dependence of $K(T)$ on the temperature (in Kelvin) is:

$$\ln K_{(T)} = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^\circ}{R} \quad (9)$$

where ΔH° and ΔS° are the enthalpy and the standard entropy changes, respectively.

In Fig. 4, the plot of $\ln K(T)$ against $(1/T)$ is shown. According to the Eq. (9) and Fig. 4:

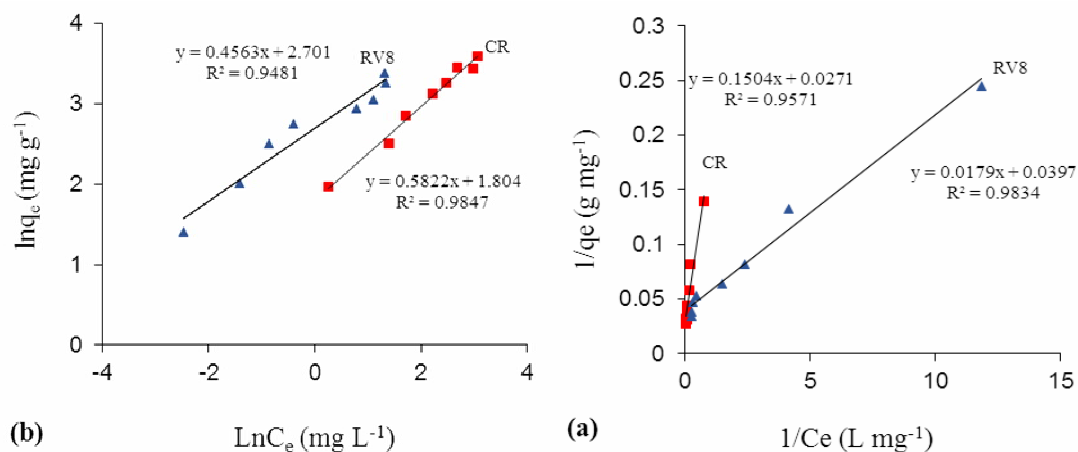


Fig. 3. Isotherm models of the adsorption of CR and RV8 onto the IAMP (a) Langmuir and (b) Freundlich.

Table 3. Isotherm Parameters of the Models Considered for the CR and RV8 Adsorption onto the IAMP Adsorbent

Isotherms	Parameters	Dye	
		CR	RV8
Langmuir	q_m (mg g ⁻¹)	36.90	25.19
	K_L (l mg ⁻¹)	0.18	2.22
	R^2	0.957	0.983
Freundlich	n	1.72	2.19
	$1/n$	0.58	0.47
	K_F (g ⁻¹ l ^{1/n} mg ^(1-1/n))	6.07 (g ⁻¹ l ^{0.58} mg ^{0.42})	14.87 (g ⁻¹ l ^{0.47} mg ^{0.53})
	R^2	0.985	0.948

$$\text{The slope} = -\frac{\Delta H^{\circ}_{add}}{R} \quad (10)$$

and

$$\text{The intercept} = \frac{\Delta S^{\circ}_{add}}{R}$$

Consequently, we obtained: $\Delta H^{\circ}_{add} = +102$ and $+88$ kJ mol⁻¹ and $\Delta S^{\circ}_{add} = +370$ and $+308$ J mol⁻¹ k⁻¹, for CR and RV8 adsorption onto the IAMP adsorbent, respectively. Once, ΔH°_{add} and ΔS°_{add} were known, the values of ΔG°_{add}

at each temperature, may be calculated from the equation $\Delta G^{\circ}_{add} = \Delta H^{\circ}_{add} - T\Delta S^{\circ}_{add}$ or by the Eq. (8). Table 4 summarizes ΔG°_{add} , ΔH°_{add} and ΔS°_{add} values of the studied adsorption at 298 K.

Kinetic Study

In order to investigate the kinetics of RV8 and CR dyes adsorption onto the IAMP sorbent, we carried out some related kinetic experiments at the contact times of 5.0, 10.0, 15.0, 20.0, 25.0, 30.0, 35.0 and 40.0 min, while the other

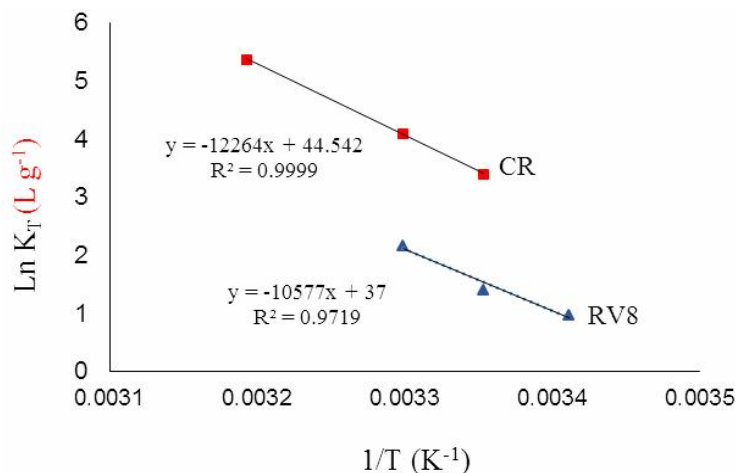


Fig. 4. The van't Hoff plot for CR and RV8 adsorption onto the IAMP sorbent.

Table 4. Thermodynamic Parameters for the Adsorption of CR and RV8 Sorbates onto the IAMP Adsorbent at 298 K

	ΔS° (J mol ⁻¹ K ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔG° (kJ mol ⁻¹)
CR	+370	+102	-8.3
RV8	+308	+88	-3.8

related parameters were constant ($C_o = 10.0 \text{ mg l}^{-1}$, dosage mass 0.10 g, temperature = 30.0 °C and pH = 5.5).

On the basis of the results of these experiments and the equations mentioned in Table 5, the corresponding plots were drawn (Fig. 5) and the values of the related kinetic parameters were concluded (Table 5). The kinetics of CR and RV8 adsorption onto the IAMP sorbent were better coincided with the pseudo-second order reaction.

CONCLUSIONS

Characterization results of the synthesized adsorbents showed the significant differences between the ordinary Aloe Vera micropowder and the impregnated Aloe Vera micropowder. The experimental results revealed that the IAMP form is a good candidate for removing CR and RV8 dyes from the solution phases. Some preliminary adsorption

experiments showed that the OAMP form is considerably less effective as an adsorbent for removing CR and RV8 sorbates from the solution phases than the IAMP form.

The optimum adsorption parameters were determined as following ($C_o = 10.0 \text{ mg l}^{-1}$, dosage mass = 0.10 g, contact time = 30.0 min, pH = 5.5, temperature = 30.0 °C). Several isotherm models were used to fit our experimental data, but the equilibrium experimental data were fitted approximately with the Freundlich and Langmuir isotherms.

The thermodynamic study showed that the studied adsorption process is spontaneous ($\Delta G^\circ_{\text{add}} < 0$) and endothermic, ($\Delta H^\circ_{\text{add}} > 0$). On the basis of the $\Delta H^\circ_{\text{add}}$ magnitude, we may conclude that the two studied adsorptions (CR adsorption and RV8 adsorption) may be considered as a physical adsorption. In turn, the kinetic study showed that the pseudo second order kinetic model fits better the kinetic data than the other intended models for

Table 5. The Kinetic Models and the Values of the Obtained Kinetic Parameters for RV8 and CR Dyes Adsorption onto the IAMP Adsorbent at 30.0 °C

Model	Parameters	Dyes	
		CR	RV8
Pseudo-first-order $\log(q_e - q_t) = \log q_e - k_1 t / 2.303$	q_e (mg g ⁻¹)	3.21	2.19
	k_1 (min ⁻¹)	0.17	0.10
	R^2	0.629	0.674
Pseudo-second-order $t/q_t = 1/k_2 q_e^2 + t/q_e$	q_e (mg g ⁻¹)	4.44	8.60
	k_2 (g mg ⁻¹ min ⁻¹)	0.15	0.05
	R^2	0.995	0.997
Intraparticle diffusion $q_t = k_{dif} t^{0.5} + C$	C (mg g ⁻¹)	3.46	4.73
	k_{dif} (mg g ⁻¹ min ^{-0.5})	0.13	0.60
	R^2	0.815	0.724
Elovich $q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln(t)$	α (mg g ⁻¹ min ⁻¹)	0.260	22.05
	β (g mg ⁻¹)	4.14	0.77
	R^2	0.717	0.844

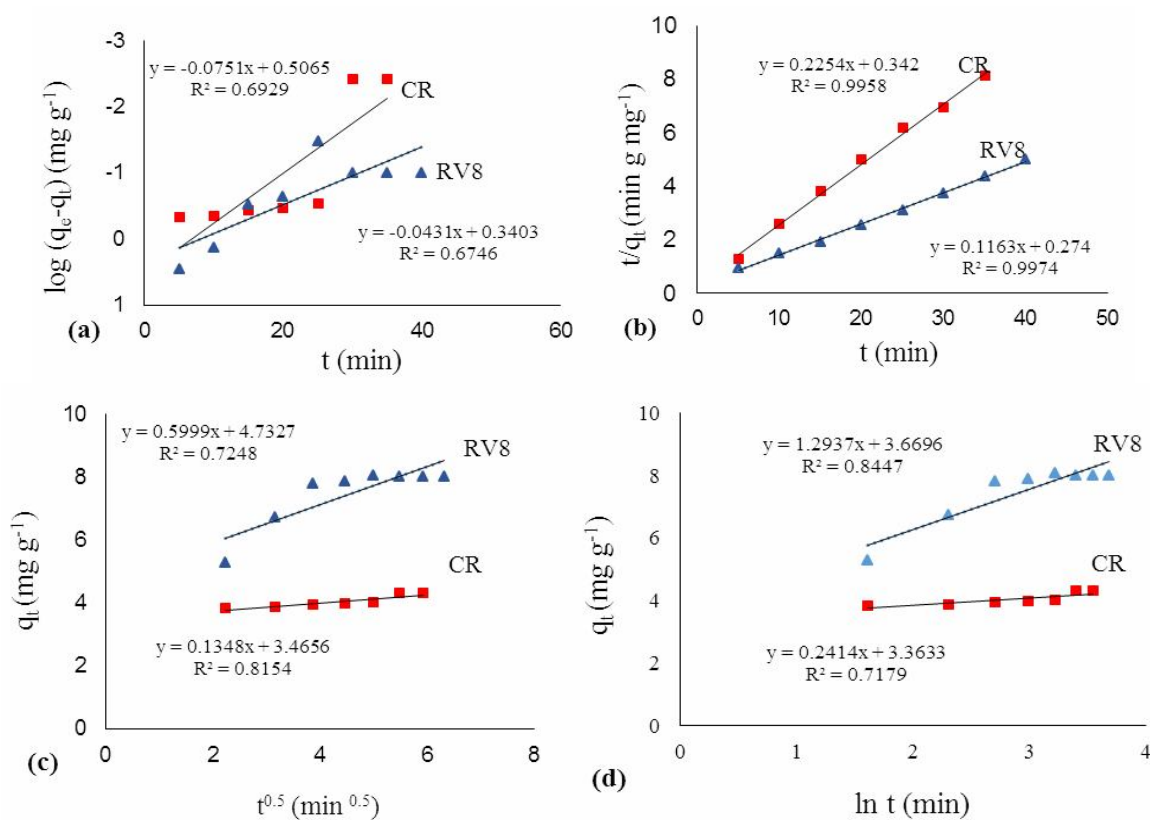


Fig. 5. Kinetic plots of CR and RV8 adsorption onto the IAMP adsorbent at 30.0 °C.

CR removal ($R^2 = 0.995$) and RV8 removal ($R^2 = 0.997$). In summary, the impregnated Aloe Vera micropowder as a natural and low cost adsorbent has a good quality and effectivity for removing CR and RV8 dyes from the solution phases.

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