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Research Article

Adsorptive removal of Acid Red 18 dye (AR18) from aqueous solutions by Red mud: Characteristics, isotherm and kinetic studies

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Abstract: Dyes have many applications in various industries. In addition to Mutagenic and carcinogenic potential to humans, these materials cause the production of toxic byproducts in the aqueous solutions. In the present study, the adsorption potential of Red mud in a batch system for the removal of Acid Red 18 dye (AR18) from aqueous solutions was investigated. The effects of pH, contact time, biomass and Acid Red 18 dye concentrations were studied. Residual concentration of Acid Red 18 dye was read using a spectrophotometer at a wavelength of 508 nm. In optimal conditions of operation including pH=3, contact time=75 minutes, adsorbent dose 4 gr/L and the initial concentration of Acid Red 18 dye= 25 mg/l, removal efficiency of the process was obtained over 98.9%. The adsorption equilibriums were analyzed by Langmuir, Freundlich, Temkin and BET isotherm models. It was found that he data fitted to Langmuir (R^2=0.997) better than isotherm other models. Batch kinetic experiments showed that the adsorption followed pseudo-second-order kinetic model with correlation coefficients greater than 0.997. According to achieved results, it was defined that Red mud not only was an inexpensive absorbent, but also a quite effective factor in removal of Dyes from water and wastewater. The results showed that Red mud was an inexpensive absorbent and quite effective in removal of Dyes from aqueous solutions.
Keywords: Adsorption isotherm, Adsorption kinetic, Red mud, Acid Red 18 dye.

INTRODUCTION

Dyes are colour organic compounds which can colorize other substances [1,2]. These substances are usually present in the effluent water of many industries, such as textiles, leather, paper, printing, and cosmetics [3,4]. The complex aromatic structures of dyes make them more stable and more difficult to remove from the effluents discharged into water bodies [5]. Several physicochemical methods such as photochemical oxidation, ultrafiltration, nanofiltration, Ozone treatment, cation exchange membranes, reverse osmosis, chemical coagulation, electrochemical degradation, biosorption have been used for removal of dyes from wastewater [6,7]. However, these processes are effective and economic only in the case where the solute concentrations are relatively high [8,9]. The adsorption technique has proven to be an effective and attractive process for the treatment of these dye-bearing wastewaters [10,11]. The adsorption characteristics of dyes on various adsorbents have been extensively investigated for many purposes involving separation and purification [12,13]. As an alternative low-cost absorbent material, solid wastes are generally used as adsorbent for the remediation of wastewater [14,15]. One type of solid waste materials, Red mud, is largely produced from the alumina industry [16,17]. The Red mud emerges as a by-product of the caustic leaching of bauxite to produce alumina [18]. This material is principally composed of fine particles of silica, aluminum, iron, calcium and titanium oxides and hydroxides, which are responsible for its high surface reactivity [19,20]. In the present study describes the use of Red mud for removal of AR18 dye from aqueous solutions. The adsorption of AR18 dye has been investigated as a function of contact time, pH, dye concentration and adsorbent dose. Adsorption isotherm and kinetic studies have been performed to describe the adsorption process.

MATERIALS AND METHODS

Acid Red 18 is an anionic dye with molecular weight 604.47 g/mol and Molecular Formula

$C_{20}H_{11}Na_3N_2O_{10}S_3$ which was provided from Alvan Sabet Company of Iran and the other chemicals used in these experiments were the product of the Merck Company (Darmstadt, Germany). Double distilled water (DDW) was used throughout the study. Fig 1 shows the structure of the investigated dye. Stock solutions of dyes were prepared by dissolving the powder in double distilled water. Dye solutions of different initial concentrations were prepared by diluting the stock solution in appropriate proportions.

The specific surface area of Red mud before use was determined by the BET-N2 method using an ASAP 2000 apparatus based on nitrogen adsorption–desorption isotherms at 77K. The morphological features and surface characteristics A. filiculoides before and after use were examined using an environmental scanning electron microscopy (ESEM) instrument (Philips XL30).

Preparation procedure of adsorbent

The first, the red mud was provided from Tabriz-Iran Aluminum Co. Red mud was washed thoroughly with distilled water, dried at 110 o C for 24 hours. The each 10 gr of Red mud was activated by using of 20 ml Nitric acid for 24 h. Then, it was rinsed 3 times by the distilled water. It was dried in 103^{o}C for 6 h. After that the red mud was grinded and sieving by using a 100 mesh sieve [21].

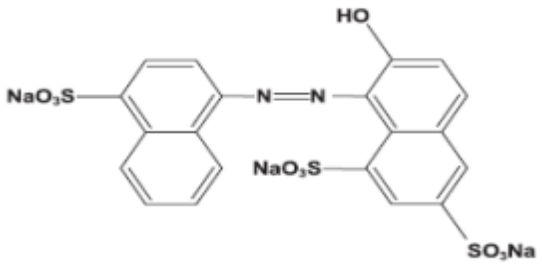

Fig-1: The chemical structures of AR18 [22]

Batch adsorption experiments

The batch adsorption system was employed in present study and the most effective factors for adsorption process including contact time (10-180 min), pH (3-11), adsorbent dose (0.5-8 g L^{-1}) and initial concentration of dye (25- 200 mg/L) were assessed.

The optimum pH was determined by varying the pH in range of 3-11 and keeping constant of other variables (contact time, adsorbent dose and initial dye concentration). The experiments were preformed in 200 milliliter beaker with a constant concentration of dye. Then this mixture was shaked with a shaker device of enforce model with 180 rpm and the room temperature of 20 – 25°C. HCl and NaOH were used to adjust the pH solution. In the next step, the optimum adsorbent dose was estimated by keeping constant of contact time and initial day concentration and also the obtained optimum pH. After determination of the optimum pH and adsorbent dose, the various concentrations of the dye in the specified times of contact was investigated. The final dye concentration in solution was measured by the UV-Visible spectrophotometer at a wavelength of 506 nm and with regarding to standard curve [23]. The equilibrium experiments of adsorption process was occurred after determination of equilibrium time in order to evaluate the effect of adsorbent mass on dye removal to obtain the adsorption isotherms. The amount of adsorption at equilibrium, q_e (mg/g), was calculated by [24]

$$q_e = \frac{(C0 - Ce)V}{W} \quad (1)$$

Where C_0 and C_e (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium, respectively. V (L) is the volume of the solution and W (g) is the mass of dry sorbent used.

The dye removal percentage can be calculated as follows [25]:

$$R = \frac{C0 - Ce}{C0} \times 100$$

Adsorption isotherms

The equilibrium adsorption isotherm is importance in the design of adsorption systems. Although several isotherm equations are available, but four important isotherms including Langmuir, Freundlich, Tekmin and BET isotherms were selected. The Isotherm equations are presented the Table-1.

Table-1: The equations of isotherms [26,27]

Model	Equation
Langmuir	$\frac{ce}{qe} = \frac{1}{q_m K_L} + \frac{ce}{q_m}$
Freundlich	$\text{Log } \frac{x}{m} = \frac{1}{n} \log Ce + \log K_F$
Tekmin	$q_e = B_1 ln (k_t) + B_1 ln (c_e)$
BET	$\frac{c_e}{(C_i - C_e)q} = (\frac{1}{q_m A}) + (\frac{A-1}{q_m A})$

Adsorption kinetics

The study of kinetic models was performed in contact time between 10-150 min with dye concentration of 50 and 100 mg/L and optimum amount of pH and adsorbent dose. To evaluate the differences in the biosorption rates and uptakes, the kinetic data were described with Elovich, Intraparticle diffusion, pseudo first, pseudo second order models. The linearized form of model is shown in Table-2.

Table-3: The equations of kinetics [28,29]

Model	Equation
pseudo first order	$\log (q_e - q) = \log q_e - k_1 t / 2.3$
pseudo second order	$t/q = 1/k_2 q_e^2 + t/q_e$
Elovich	$q_e = (\frac{1}{\beta})\ln(\alpha\beta) + (\frac{1}{\beta}) \ln t$
Intraparticle diffusion	$qt = k_{dif}\, t\, 0.5 + c$

RESULT AND DISCUSSION

The specific surface area is related to the number of active adsorption sites of Red mud. The adsorption was increased with the specific surface area and pore volume of the sorbent. The specific surface area of the Red mud was determined in the size of 30 m^2/g. SEM of Red mud after and before dye adsorbed are shown in Fig-2. It is clear that, Red mud has considerable numbers of pores where, there is a good possibility for dyes to be trapped and adsorbed into these pores. Based on analysis of the images taken by SEM before and after the dye adsorption process, highly heterogeneous pores within Red mud particles were observed. After AR18 dye adsorption, the pores were packed with dyes.

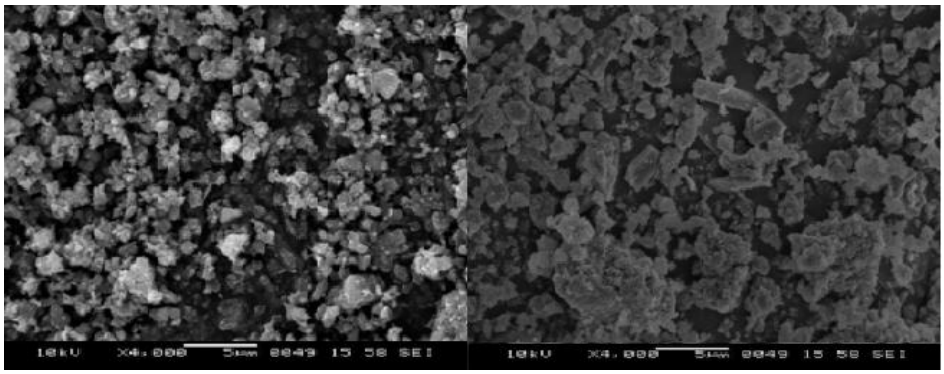

Fig-2: SEM image of Red mud before and after dye adsorbed

Effect of contact time

To investigate the influence of contact time on AR18 removal efficiency, the experiments were conducted by varying the time between 10-180 min using the adsorbent dose of 4 g/L and initial AR18 concentration of 25 mg/L. The effect of contact time on fluoride removal efficiency is shown in Fig-3. The removal efficiency increases by an increase in contact time up to 75 min and this time is known as equilibrium time. As it observed the removal rate in early times of process is faster which it consistent with several studies. This probably is due to large surface area of adsorbent which it is available in beginning of the adsorption process [30,31]. The AR18 removal efficiency in equilibrium time was 98.9%.

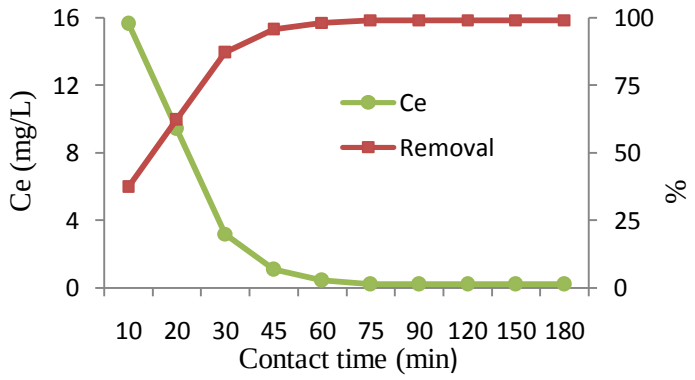

Fig-3: Effect of contact time for AR18 adsorption (Con = 25 mg/L, pH = 3, dose: 4 g/L)

Effect of pH

The effect of pH on dye uptake in the batch process was studied by varying the pH from 3 to 11(Fig-4). The biosorption of AR18 on Red mud decreased significantly with increasing solution pH from 3 to 11. Dye biosorption is a pH dependent process. The pH of the solution influences the properties of biomass materials, affects the adsorption mechanisms and dissociation of the dye molecules. At lower pH, the biosorbent surface turned out to be positively charged and electrostatic attraction developed between positively charged adsorbent and negatively charged anionic dyes. However, at basic pH, adsorption decreased due to presence of hydroxyl ions which showed competition with dye anions for binding sites [11].

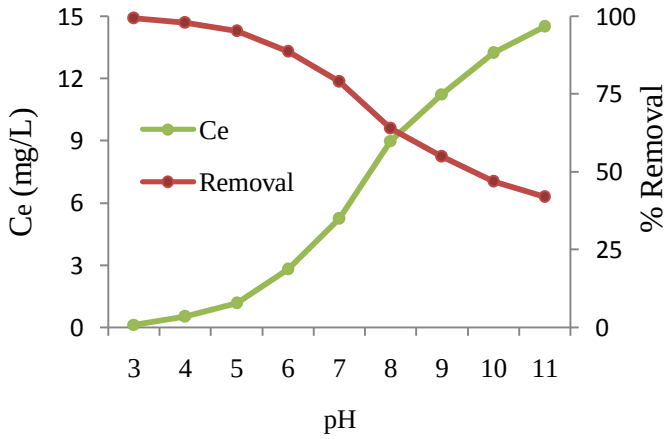

Fig-4: Effect of pH on adsorption of AR18 Dye (Con = 25 mg/L, Contact time = 75 min, Biomass dose: 4 g/L)

Effect of dye initial concentration

The effect of initial AR18 concentration was investigated by varying the concentration in range between 25-200 mg/L. The relation between initial AR18 concentration and removal efficiency is presented in Fig-5.The removal efficiency decreases by increasing the AR18 concentration. It is attributed that it occurs because there is not enough available active site on adsorbent surface in compare with large active sites which it is required to high concentration of AR18 [32].

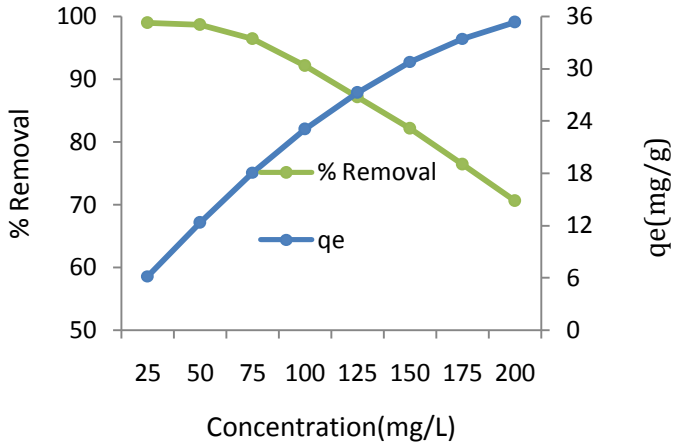

Fig-5: Effect of dye initial concentration (Contact time = 75 min, dose:4 gr/L, pH = 3)

Effects of Adsorbent Dose

The effect of adsorbent dose on dye removal efficiency was studied by varying of adsorbent dose (0.5-4 g/L). The Fig.6 shows that the removal efficiency increases with an increase in adsorbent dose. The adsorption rate increases with increasing of adsorbent dose which it occurs because of increasing the active surface of adsorbent to certain amount of pollutant [33]. The results indicated that although the adsorption efficiency increases by increasing the adsorbent dose, however the amount of adsorbed dye per unit mass (g) adsorbent decreases which it is related to lack of saturation of active site in pollutant adsorption.

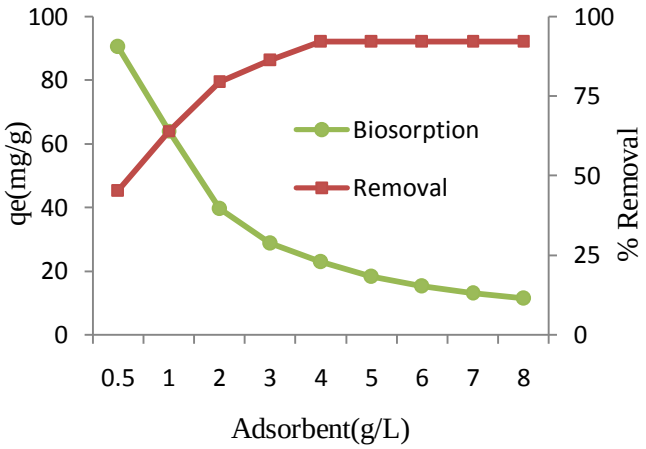

Fig-6: Effect of adsorbent dose (Contact time = 75 min, pH = 3, Con: 100 mg/L)

Adsorption kinetics and isotherms

The results obtained by the adsorption of dye were analyzed by the well- known models of Langmuir, Freundlich and Tekmin and BET. The results showed that AR18 dye on Red mud fitted according to Langmuir Model isotherm model (R^2=0.999). Furthermore it agreed with BET isotherm (R^2=0.965) that better than Freundlich (R^2=0.924) and Temkin model (R^2=0.931). The isothermal models and adsorption kinetics in Table-3 and 4. The R^2 of kinetic models suggested that the pseudo second-order model mechanism is predominant which means the uptake process follows the pseudo second order expression with Correlation coefficients were always greater of 0.995.

Table-4: The adsorption isotherms constants for the removal AR18

Langmuir Model			Freundlich model			Temkin Model			BET Model		
q_m	K_L	**R^2**	n	K_F	**R^2**	B	k_t	**R^2**	**A**	**q_m**	**R^2**
7.14	0.48	0.999	1.84	2.17	0.924	18.9	1.45	0.965	36.4	1.17	0.931

Table-4: The adsorption kinetic model constants for the removal AR18

Pseudo Second-order model				Pseudo First-order model			Elovich			Intraparticle diffusion		
C_o	k_2	R^2	q	K_1	R^2	q	α	β	R^2	K_{dif}	C	R^2
50	0.017	0.998	14.1	0.121	0.884	9.81	1.74	0.35	0.841	0.95	4.45	0.798
100	0.021	0.999	24.2	0.194	0.905	17.4	3.29	0.58	0.826	1.17	2.83	0.814

CONCLUSION

This investigation examined the equilibrium and the kinetic adsorption of AR18 onto Red mud. The results suggested the adsorption capacity increased with increasing contact time and adsorbent dose. The equilibrium data were analyzed using the Langmuir, Freundlich and Tekmin and BET isotherm models. Equilibrium data fitted very well with Langmuir isotherm equation. Adsorption data were modeled using the first and second-order kinetic equations, Elovich and intraparticle diffusion models. The second-order kinetic equation could best describe the sorption kinetics.

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