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Removal of acid blue 113 and reactive black 5 dye from aqueous solutions by activated red mud

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ABSTRACT

Removal of acid blue 113 (AB113) and reactive black 5 (RB5) dyes from aqueous solutions by activated red mud was investigated at different reaction parameters. Activated red mud has higher removal efficiency for AB113 than that for RB5. This can be explained by a greater molecular size of RB5 than that of AB113 and by different binding affinity with the surface of the activated red mud. Equilibrium data was fitted well with Freundlich isotherm and the kinetic data followed a pseudo second-order model. Maximum adsorption capacity was 83.33 mg/g and 35.58 mg/g at pH 3 for AB113 and RB5, respectively.

1. Introduction

It has been reported that approximately 20% of whole azo dyes produced in the world might be lost during dyeing processes [1–4]. Azo dyes are known as one of the important pollutants in wastewater [1–4]. Azo group (–N=N–) and aromatic group are contained in chemical structure of the azo dyes. Aromatic rings in the azo dyes are toxic and mostly non-biodegradable. Discharge of colored compounds in water increases biochemical oxygen demand in water and induces an inhibition of light transmission into water, causing reduced concentration of dissolved oxygen in water required for photosynthesis [1,3,4]. Therefore, removal of these species is highly necessary. Various methods such as filtration, adsorption, electrodeposition and membrane systems or even ion exchange process have been used to remove dyes from industrial wastewater [5]. The application of membrane systems for the wastewater treatment has major problems such as membrane scaling, fouling and blocking. The disadvantage of the ion exchange process is high cost of resin while the electrodeposition method requires more intensive energy than other methods [6–9]. Adsorption with activated carbon is regarded as an efficient method for the removal of numerous dyes from water and wastewater, but high cost of the activated carbon inhibits its large scale applications [10]. To solve these problems, in recent years, some investigations have been carried out to treat large quantities of dyes from wastewater using low cost adsorbents [11–14]. Ozcan et al. reported that pH value of 1.5 was favorable for the adsorption of acid blue 193 by Na-bentonite and DTMA-bentonite [11]. They also reported that the isothermal data was well described by the Freundlich equation and dynamical data was fitted well with the pseudo-second-order kinetic model. The adsorption capacity of DTMA-bentonite (740.5 mg/g) was found to be around 11 times higher than that of Na-bentonite (67.1 mg/g). Tsai et al. used activated bleaching earth to treat acid dyes (i.e., acid orange 51, acid blue 9, and acid orange 10) having different molecular sizes from aqueous solution [12]. Removal of dyes by activated bleaching earth followed the order: acid orange 51 > acid blue 9 > acid orange 10, parallel to the molecular weights and molecular sizes of the acid dyes. The adsorption (below 3%) of acid blue 9 and acid orange 10 onto the clay adsorbent were far lower than that (~24%) of acid orange 51. Further, the adsorption kinetic of acid orange 51 can be well described by the pseudo-second-order reaction model. Based on the isotherm data obtained from the fittings of the adsorption

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kinetics, the Langmuir model appears to fit the adsorption better than the Freundlich model. Ozcan et al. [11] studied adsorption of two dyes, acid red 57 and acid blue 294, onto acid-activated bentonite in aqueous solution in a batch system. Acidic pH was favorable for the adsorption of these dyes. The dynamic data was fitted well the pseudo-second-order kinetic model and also followed the intraparticle diffusion model up to 90 min, but diffusion is not the only rate controlling step. The Freundlich model agrees very well with experimental data. Shirzad-Siboni investigated removal of an azo dye (reactive black 5) with scallop as a low-cost and widely available adsorbent [14]. Removal efficiency declined with the increase of solution pH and initial dye concentration but with the decrease in adsorbent dose.

Red mud (RM) is a solid waste residue formed after the caustic absorption of bauxite ores during the production process of alumina. It is a highly alkaline waste material with pH 10–12.5 and is mainly composed of fine particles containing aluminum, iron, silicon, titanium oxides and hydroxides. Due to the alkaline nature of RM, it causes an important impact on the environment. Therefore proper disposal or treatment of waste RM is necessary where alumina industries are installed. It can be economically used for the removal of dyes in wastewater. Hence, research work for the application of RM as an alternative low cost adsorbent has much attention [15–17].

In this work, applicability of activated red mud (ARM) in the removal of dye from aqueous solution was investigated using a batch reactor. Compared to the previous studies, an originality of this work was in the elucidation of different removal capacity between AB113 and RB5 by activated red mud considering molecular size and different functional groups of these two dyes. Effect of various factors such as contact time, pH, initial dye concentrations and adsorbent dosage on the removal of dyes by ARM was also studied.

2. Experimental

2.1. Materials and methods

All chemicals were analytical grade and solutions were prepared with deionized water (18 MΩ cm) from a Hydro-Service reverse osmosis/ion exchange apparatus. The AB113 and RB5 used in this study were obtained from Alvan Sabet company in Iran. Fig. 1 shows the chemical structure and absorption spectrum of the AB113 and RB5. Stock solutions (1000 mg/L) of AB113 and RB5 were prepared by dissolving 1 g of AB113 (M_w = 681.7 g/mol) and RB5 (M_w = 991.8 g/mol) in 1 L of deionized water. It was stored in darkness to avoid ambient light.

2.2. Preparation of activated red mud (ARM)

RM obtained from a bauxite mill in Iran was initially washed with deionized water and dried in an oven at 103 °C for 24 h. Then the RM was soaked in 1 N HNO_3 solution at the 1:2 ratio of RM and nitric acid (w/v) for 24 h [15]. The obtained material was activated in an oven for 4 h at 150 °C in order to produce activated red mud (ARM). Finally the ARM was sieved in the size range of 100 mesh ASTM. The specific surface area of the ARM was known as 32 m^2/g by Research Institute of Petroleum Industry (RIPI). The microstructure and component of the ARM were analyzed by using a scanning electron microscope (SEM, SERON-ATS-2100) and energy dispersive X-ray spectroscopy (EDX, Model 525, 15 kV; Philips, Eindhoven), respectively. Fig. 2 shows typical (a) EDX patterns and (b) SEM image of the ARM. The size of ARM was 5 μm in average. Table 1 shows the major compositions of ARM used in this work. It is noted that iron and calcium are the major components.

Table 2
Calculated kinetic parameters for pseudo first-order and pseudo second-order models for removal of AB113 and RB5 by activated red mud.

	Pseudo first-order model			Pseudo second-order model		
	k_1 (1/min)	q_e (mg/g)	R^2	k_2 (g/mg/min)	q_e (mg/g)	R^2
$AB113_0$ (mg/L)						
20	0.0523	1.95	0.9956	1.77	1.95	0.9999
40	0.0595	3.87	0.9409	0.56	3.86	0.9999
60	0.0691	5.61	0.9917	0.47	5.62	0.9999
$RB5_0$ (mg/L)						
20	0.0637	1.05 0	9575	0.32	1.07	0.9953
40	0.0423	1.70 0	9566	0.14	1.60	0.9882
60	0.0532	1.77 0	9973	0.15	1.80	0.9932

2.3. Adsorption experiments

The equilibrium time (60 min) was determined from adsorption kinetic experiments performed with 6 g/L of ARM and 40 mg/L of initial dye concentration at pH 3. In each adsorption experiment, 0.6 g of ARM was added into Erlenmeyer flaks containing 100 mL of dye solution previously adjusted concentration and pH. The suspension in Erlenmeyer flaks was mixed in a rotator (H1-190 M) at 160 rpm for 60 min. The suspension samples were centrifuged (Sigma-301) at 4000 rpm for 10 min to remove adsorbent. And then remaining concentration of AB113 and RB5 dye in solution was analyzed by UV/VIS spectrophotometer (Shimadzu UV-160A) at a wavelength of 566 nm and 598 nm, respectively [18]. For investigation of competitive adsorption of AB113 and RB5 onto the ARM, same concentration of the two species (each 40 mg/L) was used. This competitive adsorption experiment was performed with 6 g/L of ARM at pH 3 up to 60 min. Adsorption experiments were also conducted at various amounts of adsorbent (2–10 g/L), at various initial dye concentrations (20–100 mg/L) and at various initial pH (3–11). All experiments were carried out at room temperature (25 ± 2 °C).

3. Results and discussion

3.1. Adsorption kinetics

Removal of dyes with variation of time is shown in Fig. 3. At all concentrations, adsorption of AB113 onto the ARM was above 85% within 10 min, while adsorption of RB5 onto the ARM was approximately 45% even after 60 min. This result indicates that ARM has greater removal efficiency for AB113 than that for RB5. This trend can be explained by a greater molecular size of RB5 than that of AB113, causing difficulty in approaching on the surface of the ARM, as well as by different binding affinity with the surface of the ARM between two dyes due to having different functional group such as $-NH_2$, SO_3^-, –OH [19,20]. In order to elucidate competitive adsorption, adsorption of AB113 and RB5 (each 40 mg/L) onto the ARM was also investigated. As shown in Fig. 4, removed amount of AB113 was greater than that of RB5 over the entire reaction time. The removed amount of AB113 and RB5 onto the ARM after 60 min was 3871 mg/kg and 2406 mg/kg, respectively. Experiments were repeated three times and average values including error percents were reported.

The adsorption kinetic for the removal of dyes onto the ARM was analyzed by a pseudo first-order (Eq. (1)) and a pseudo second-order model (Eq. (2)) at various initial dye concentrations [6,7,21–23].

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$