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Single and binary adsorption of reactive dyes from aqueous solutions onto clinoptilolite

Tuba Sismanoglu*, Yasemin Kismir, Selcan Karakus

Istanbul University, Engineering Faculty, Department of Chemistry, Avcilar, 34850 Istanbul, Turkey

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ABSTRACT

The adsorption of Reactive Blue 21 (RB21) and Reactive Red 195 (RR195) onto clinoptilolite type natural zeolite (ZEC) has been investigated at 298.15 K. The uptake of single and binary reactive dyes from aqueous solutions has been determined by UV–vis spectroscopy. Two mono-component (RB21 and RR195) and binary component (RB21 with RR195, and RR195 with RB21), isotherms were determined. The mono-component Langmuir isotherm model was applied to experimental data and the isotherm constants were calculated for RB21 and RR195 dyes. The monolayer coverage capacities of clinoptilolite for RB21 and RR195 dyes in single solution system were found as 9.652 and 3.186 mg/g, respectively. Equilibrium adsorption for binary systems was analyzed by using the extended Langmuir models. The rate of kinetic processes of single and binary dye systems onto clinoptilolite was described by using two kinetics adsorption models. The pseudo-second-order model was the best choice among the kinetic models to describe the adsorption behaviour of single and binary dyes onto clinoptilolite.

1. Introduction

Synthetic dyes and pigments released into the environment mainly in the form of wastewater effluents by textile, leather and printing industries cause severe ecological problems. Wastewater from the textile industry is a complex mixture of many polluting substances ranging from organochlorine-based pesticides to heavy metals associated with dyes or the dyeing process. The reactive dyes, which represent the largest class of dyes used in textile processing industries, are almost azo compounds, i.e. molecules with one or several azo bridges (N=N) linking substituted aromatic structures. These dyes are designed to be chemically and photolytically stable, they exhibit a high resistance to microbial degradation and are highly persistent in natural environment. The release of these compounds into the environment is undesirable, not only for aesthetic reasons, but also because many azo dyes and their breakdown products are toxic and/or mutagenic for life.

Various physicochemical and biological techniques can be employed to remove dyes from wastewaters. They include the membrane coagulation/flocculation [1], ion exchange [2], advanced oxidation (chlorination, ozonation) [3], decolourisation and metabolism of the commercially used Remazol dye by a strain of P. Chrysosporium [4], and biological treatment (bacterial and fungal biosorption), biodegradation in aerobic or anaerobic conditions [5].

In comparation with other techniques adsorption is superior in simplicity of design, initial cost, ease of operation and insensitivity to toxic substances. Adsorption is one of the most effective physical processes for colour removal. This technique uses a large number of suitable sorbents as activated carbon [6,7].

Activated carbon is normally employed for this purpose, however, due to its high price it has not enjoyed wide-scale application. Therefore, other inexpensive and effective adsorbents have been tested for example; biopolymer [8,9] and various low-cost adsorbents as clays and zeolites material, etc. [10]. Natural zeolite adsorption is used in the chemical process industries and is playing important role in cleaning up plant effluent and municipal wastewater. Especially, clinoptilolite is probably the most abundant zeolite in nature because of its wide geographic distribution and large size of deposits. The presence of 4.5 million tons of natural zeolites of high quality, mainly those of clinoptilolite in Turkey, created an impetus for the utilization of clinoptilolite in wastewater treatment.

This study was performed to investigate adsorption of single and binary reactive dyes aqueous solutions on clinoptilolite. The constants parameters obtained from single (RB21 and RR195) adsorption equilibrium data were used to predict the binary adsorption behaviour of reactive blue21 and reactive red195 [11].

* Corresponding author.
E-mail address: tusase@istanbul.edu.tr (T. Sismanoglu).

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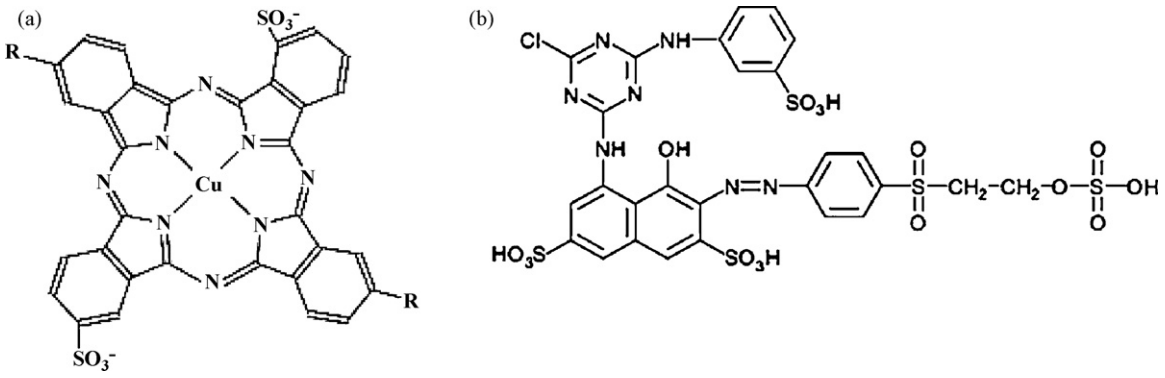

Scheme 1. (a) Possible structure of the reactive blue21. R – reactive linker arms, (b) reactive red195.

The kinetics and isotherms for dyes adsorption onto clinoptilolite (ZEC) were studied in single and binary dye solutions.

2. Materials and methods

2.1. Chemicals and materials

The clinoptilolite was obtained from the rhyolitic tuff level of the Neogene volcano sedimentary sequence in Gördes, West Anatolia, Turkey. Clinoptilolite (ZEC) was used as adsorbents for removal of RB21 and RR195 from aqueous solutions in this study. This adsorbent was used directly for adsorption experiments without any treatments. Clinoptilolite is a species of zeolite group minerals. The typical unit cell formula of natural zeolite mineral, clinoptilolite, is (Ca, Na, K)$_6$[(AlO$_2$)$_6$(SiO$_2$)$_{30}$]·24H$_2$O. It contained about 91% clinoptilolite with the chemical composition of 67.83–66.70% SiO_2, 11.63–12.04% Al_2O_3, 2.35–2.10% CaO, 1.59–0.48% MgO, 0.95% Fe_2O_3, 0.28–0.29% Na_2O, 1.59–4.97% K_2O, % 0.05 SO_3, loss on ignition 11.81% as reported by Esenli [12]. The clinoptilolite (ZEC) was sieved to obtain a particle size smaller than 125 μm. The dyes reactive blue21 (RB21) and reactive red195 (RR195) were purchased from a textile industry in the company (Turkey) region. Colour index name of Türkisblau G133 is reactive blue21 (RB21). This dye is vinyl sulfone dyes and it has chemical class copper-phtalocyanin ($C_{32}H_{16}CuN_8$ molecular weight 576.10 g mol^{-1}) and reactive linker arms of the following structure R: $SO_2NHC_6H_4SO_2CH_2CH_2OSO_3H$ (molecular weight of single R = 550 g mol^{-1}) [13–16]. Colour index name of Synozol Red HF-6BN 150% is reactive red195 and this dye has a chemical class monoazo and molecular weight 1136.30 g mol^{-1}. Stock solutions of 300 mg L^{-1} were prepared with double-distilled water. The values pH of RB21 and RR195 were measured 7.60 and 6.60, respectively. The molecular structures of the two dyes are illustrated in Scheme 1.

2.2. Single adsorption studies

Stock solutions 300 mg L^{-1} of RB21 and RR195 were used in this study. These stock solutions were diluted to give standard solutions from 10 to 250 mg L^{-1}. 0.1 g ZEC and 10 mL single-component solution were shaken using a shaker with a water bath to control temperature at 25.0 °C. The liquid and solid phases were separated by centrifuging at 3950 rpm for 5 min. The change of adsorbate concentration in each of the solutions was determined spectrophotometrically. All the spectrophotometric measurements were made with a CHE-BIOS Optimum UV–vis spectrophotometer. The maximum absorbance value of RB21 and RR195 was measured at 660 and 540 nm, respectively as shown in Fig. 1. The calibration graph of absorbance versus concentration obeyed a linear Lambert–Beer relationship [16].

The color removal efficiency of the dye was calculated as follows

$$\text{Removal efficiency } (\%) = \frac{(C_o - C_e)}{C_o} \times 100 \quad (1)$$

where C_o and C_e are the initial concentration and concentrations of the dye at equilibrium (mg L^{-1}), respectively.

The mass of reactive dyes adsorbed per unit mass of the adsorbents (q) at any time ($C = C_t$) and at equilibrium ($C = C_e$) was calculated from the Eq. (2).

$$q = (C_o - C)\frac{V}{W} \quad (2)$$

q is the adsorbed amount of reactive dyes in the solid phase at equilibrium ($q = q_e$) and time t (min) ($q = q_t$), respectively. V indicates the volume of dye solution (L) and W is the weight of the adsorbent (g).

2.3. Binary adsorption studies

For binary adsorption system, several initial concentrations of RR195 (10–250 mg L^{-1}) were prepared in 8 different glass-stoppered conical flasks with the presence of constant initial concentration of 50 mg L^{-1} of RB21 in each flask. Then, the experiment was carried out following the steps as for single system adsorption process. The remaining concentrations of both solutions were also analyzed using UV–vis spectrophotometer through the multi-component determination option. The experiments were repeated for other constant initial concentrations of RB21, which are 100 and 150 mg L^{-1}. The tests were repeated over again in

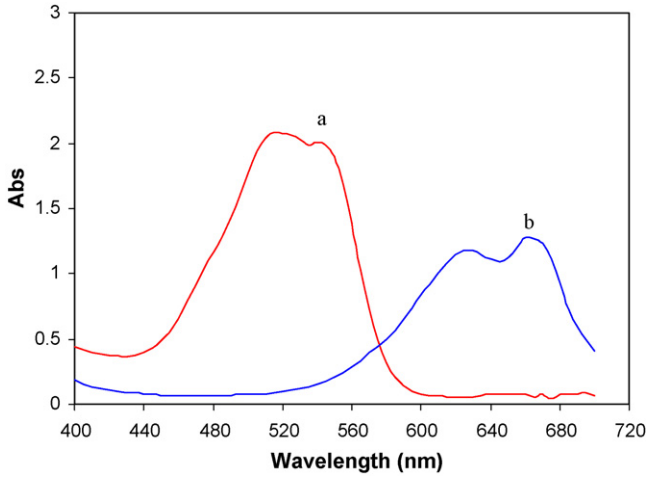

Fig. 1. Typical spectrum of the single dye (a) RR195 (b) RB21.