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Synthesis of cationic polymeric adsorbent and dye removal isotherm, kinetic and thermodynamic

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ABSTRACT

Poly(quaternary ammonium salt) (PQAS) as a cationic polymeric adsorbent was synthesized and characterized by FTIR. Isotherm, kinetic and thermodynamic of dye removal from single and binary systems was investigated. Acid Blue 25 (AB25) and Acid Red 18 (AR18) were used. The effect of operational parameters (adsorbent dose, pH, dye concentration and salt) on dye removal was studied. The dye removal followed the Langmuir isotherm and pseudo-first order kinetics. The adsorbent maximum dye adsorption capacity (Q_0) was 2000 and 1667 mg/g for AB25 and AR18, respectively. The thermodynamic data showed that dye adsorption was spontaneous, endothermic, and a physisorption reaction.

1. Introduction

Textile and other industries such as paper, color photography, pharmaceutical, plastics, leather, food, cosmetic, etc. were used dyes. The presence of dyes on natural water resources are aesthetically undesirable and have serious environmental impact. It is estimated 10,000 different commercial dyes and pigments are used and over 7×10^5 t are produced annually world-wide [1–10]. The discharge of highly colored waste affects the nature of water reducing photosynthetic activity by inhibiting sunlight penetration. Most commercial dyes are chemically stable and are difficult to be removed from wastewater. In addition some dyes produce toxic, carcinogenic and mutagenic intermediates by hydrolysis, oxidation, etc. [7,11,12]. Thus, dye removal from wastewaters before their release into the natural environment is very essential [1,13–15]. Many methods such as coagulation/flocculation, biological treatment, ozonation, photocatalysis, filtration, electrochemical, membrane processing, adsorption, etc. have been used to remove dyes from colored wastewaters [16–22].

Adsorption process is a suitable method to remove pollutants from wastewater. It allows flexibility in terms of both design and operation and produces pollutant-free effluents that are suitable for reuse. Adsorption has considerable advantages in comparison to conventional methods, particularly from the technical, economic, and environmental point of views. Thus among other techniques, adsorption process has been shown to be an effective technique with its efficiency, capacity and applicability on a large scale to remove dyes as well as having the potential for regeneration, recovery and recycling of adsorbents [11,23–27]. Several adsorbents have been experienced on the possibility to remove dye from wastewaters. For obtaining high-performance adsorbent, it is crucial to select the more efficient and cheaper adsorbents by higher adsorption ability [27].

In this paper, poly(quaternary ammonium salt) (PQAS) as a cationic polymeric adsorbent was synthesized and characterized by FTIR. Dye removal of PQAS from single and binary systems was investigated. Isotherm, kinetic and thermodynamic of adsorption process was studied. Acid dyes (Acid Blue 25 (AB25) and Acid Red 18 (AR18)) were used as model pollutants. The effect of adsorbent dose, pH, dye concentration and salt on dye removal was studied.

2. Materials and methods

2.1. Chemicals

Acid Blue 25 (AB25) and Acid Red 18 (AR18) were received from Ciba and used without further purification. The chemical

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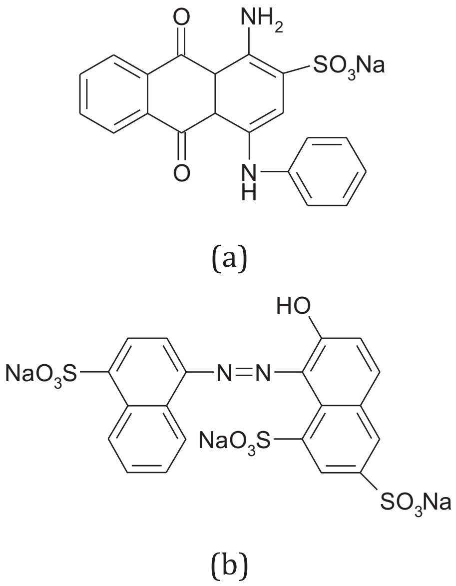

Fig. 1. The chemical structure of dyes (a) AB25 and (b) AR18.

structures of dyes are shown in Fig. 1. Hexamethylene diisocyanate (HDI), hydroxyethyl methacrylate (HEMA), *N*,*N*-dimethylethanolamine (DMEA), 1,6-dibromohexane, dibutyltin dilaurate (DBTDL), *tert*-butyl hydroperoxide (TBHP) (70% solution in water), sodium formaldehydesulfoxylate (SFS) and acetone were obtained from Merck Company and used without any purification.

2.2. Synthesis of PQAS

Urethane acrylate with a tertiary amine terminal group was synthesized by HDI (16.8 g, 0.1 mol), HEMA (13 g, 0.1 mol) and DMEA (8.9 g, 0.1 mol) in the presence of DBTDL (0.15 g) as catalyst and 100 mL acetone as a reaction solvent at 45 °C for 2 h. Then, cationic polymerizable urethane acrylate was synthesized by quaternization of tertiary amine groups of urethane acrylate with 1,6-diboromooctane at 55 °C for 2 h. Finally, PQAS was synthesized by radical polymerization in the presence of *tert*-butyl hydroperoxide (TBHP) (70% solution in water) and sodium formaldehydesulfoxylate (SFS) as redox radical initiator at 75 °C for 2 h (Fig. 2).

2.3. Characterization of PQAS

Fourier transform infrared spectroscopy (FTIR) spectrum of PQAS was obtained by Perkin-Elmer Spectrophotometer Spectrum One within wavelength range of 4000–450 cm^{-1}.

2.4. Batch adsorption experiments

2.4.1. Single system

The adsorption experiments were performed in batch mode. The dye adsorption was done by mixing PQAS in jars containing 200 mL of a dye solution. The liquid and solid phases were separated by centrifuging. UV–vis spectrophotometer CECIL 2021 was employed for absorbance measurements of the samples. The maximum wavelength (λ_{max}) used for determination of residual concentration of AB25 and AR18 in supernatant solution were 600 and 507 nm, respectively.

2.4.2. Binary system

To study dye removal in binary system, several initial concentrations of AB25 (100–175 mg/L) were prepared with the presence of constant initial concentration of 100 mg/L of AR18. The remaining concentrations of both dyes were also analyzed using UV–vis spectrophotometer. The experiments were repeated for other constant initial concentrations of AR18, which are 125, 150 and 175 mg/L. The experiments were repeated over again in order to study the adsorption behavior of AR18 with the presence of different constant initial concentrations of AB25 (100, 125, 150 and 175 mg/L). Dye concentration was calculated as follows: for a binary system of components AB25 and AR18 measured at λ_1 and λ_2, respectively, to give optical densities of d_1 and d_2 [28]:

$$C_A = \frac{(k_{B2}d_l - k_{B1}d_2)}{(k_{A1}k_{B2} - k_{A2}k_{B1})} \qquad (1)$$

$$C_B = \frac{(k_{A1}d_2 - k_{A2}d_1)}{(k_{A1}k_{B2} - k_{A2}k_{B1})} \qquad (2)$$

where k_{A1}, k_{B1}, k_{A2}, and k_{B2} are the calibration constants for components A and B at the two wavelengths λ_1 and λ_2, respectively.

2.5. Adsorption kinetics

Study of adsorption kinetics was carried out in order to investigate the relationship between contact time and dye uptake. The initial concentration influence of the reagent on the adsorption kinetic at constant temperature of 25 °C was investigated. In single dye systems, initial dyes concentrations 100, 125, 150 and 175 mg/L were used and in mixture dyes systems, initial dyes concentrations 100 + 100, 125 + 125, 150 + 150 and 175 + 175 mg/L were used.

2.6. Adsorption thermodynamic

The influence of temperature on the dye adsorption was investigated on the single dyes concentrations 100, 125, 150 and 175 mg/L and binary dyes concentrations 100 + 50, 125 + 125, 150 + 150 and 175 + 175 mg/L at 298, 308, 318 and 328 K. The same experiments were done for binary dyes solutions.

3. Results and discussion

3.1. Characterization of PQAS

Fig. 3 shows FT-IR spectrum of PQAS. The peak at 3290 cm^{-1} is due to N–H stretching vibration of urethane band. The C–H stretching vibration of CH_3 and CH_2 was at 2932 and 2859 cm^{-1}. The peak at 1467 cm^{-1} is attributed to C–H bending vibration of CH_2. The C–H bending vibration of CH_3 can be seen at 1388 and 1373 cm^{-1}. The peaks at 1721, 1534, 1249, 1139 and 1050 cm^{-1} represent the C=O stretching vibrations of urethane band and ester bands, N–H bending vibration of urethane band, C–N stretching vibrations of urethane bands, C–O stretching vibration of urethane band and C–O stretching vibration of ester band, respectively [29].

3.2. Effect of operational parameters on dye removal

3.2.1. Adsorbent dosage effect

Fig. 4 shows the effect of adsorbent dosage on the dye removal from single and binary systems of dyes. The dye removal efficiency increased with the adsorbent dosage up to a certain limit and then it reached a constant value. It can be attributed to increased adsorbent surface and availability of more adsorption sites.