

Adsorption of acid dye onto organobentonite

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Abstract

Removal of Acid Red 151 from aqueous solution at different dye concentrations, adsorbent doses and pH has been studied. The bentonite clay has been modified using cationic surfactants, which has been confirmed using XRD and FT-IR analyses. Experimental result has shown that the acidic pH favours the adsorption. The adsorption isotherms are described by means of Langmuir and Freundlich isotherms. The adsorption capacity has been found to be 357.14 and 416.66 mg g⁻¹ for the cetyldimethylbenzylammonium chloride-bentonite (CDBA-bent) and cetylpyridinium chloride-bentonite (CP-bent), respectively. Kinetic studies show that the adsorption followed second-order kinetics.

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1. Introduction

India is one of the largest producers and end user of dyes and pigments and caters to the needs of various industrial segments, viz. textile, tannery, paper, rubber, plastic and paints, etc. The effluents discharged from dyeing industries have colour and are reported to have low BOD and high COD. Frequent changes of dyestuff used in dyeing processes cause considerable variations in the wastewater characteristics, particularly colour, pH, and COD [1]. Untreated disposal of this coloured water into the receiving water body not only causes damage to aquatic life, but also to human beings by mutagenic and/or carcinogenic effect. It can cause severe damage to the reproductive system, liver, brain and dysfunction of kidneys [2]. Textile effluents are usually treated by physical and chemical processes such as sorption, oxidation, flocculation, etc. Colour removal by activated carbon, H₂O₂, Sodium hyperchlorite and other chemical agents has been widely practiced in the textile industries [3–9]. Naturally occurring clays such as bentonite has shown good results as an adsorbent for the removal of various metals, organic compounds and various basic dyes [10–14].

Bentonite, which is primarily a smectite clay, is composed of units made up of two silica tetrahedral sheets with a cen-

tral Al octahedral sheet. It has permanent negative charges that arise due to the isomorphous substitution of Al³⁺ for Si⁴⁺ in the tetrahedral layer and Mg²⁺ for Al³⁺ in the octahedral layer. This negative charge is balanced by the presence of exchangeable cations (Na⁺, Ca²⁺, etc.) in the lattice structure. By the ion exchange mechanism, the inorganic cation could be exchanged by the organic cation. In aqueous solution, water molecules enter into the lattice structure causing the clays to swell. The introduction of organic cation changes the clay from hydrophilic to hydrophobic form [15]. Acid dyes are water soluble anionic dyes and are used to dye wool, nylon and silk fibres. Since the anionic dyes are negatively charged, the surface of the natural clays has to be modified for the adsorption studies. It is made possible by cation exchange mechanism using cationic surfactants. These surface modified clays were used as adsorbent for the adsorption of phenolic compounds and pesticides [16–21].

In this study, two organic cations with different structures have been used, viz. cetyldimethylbenzylammonium chloride and cetylpyridinium chloride. The modification of bentonite with the organic cation decreases the surface area and it is confirmed by the BET analysis. But the intercalation of organic cation into the lattice structure of the bentonite leads to more surface active sites available for adsorption. The organic cation has positive charges on its surface it would attract the negative charge from the adsorbate dye molecules. This kind of cationic surfactant modified organobentonites have been extensively used for a number of environmental applications. The objective of

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the present work is to examine the effectiveness of the prepared organobentonite in removing AR 151, which has negative SO_3^- anion from aqueous dye solution. The effect of modification by two different organic cations in the adsorption process is also compared.

2. Experimental

2.1. Materials and methods

Synthetic textile dye AR 151 was obtained from SHIDIMO, Interaux Pvt., Ltd., India and was used without further purification. The chemical structure of the dye is shown in Fig. 1. Bentonite was used as an adsorbent and obtained from E.Merck (India) Limited, Mumbai 18, India. The surfactant used for the modification was supplied by SRL, Mumbai 99, India. The cation exchange capacity (CEC) of the clay bentonite was estimated using the ammonium acetate method [22] and it was calculated to be 67 mequiv./100 g.

2.2. Preparation of organobentonite

The Na-bentonite was prepared by stirring the sample with 1 N NaCl using a mechanical stirrer for 24 h. This was followed by washing several times with distilled water until chloride ions were absent in the filtrate. The clay was dried in a hot air oven at 60 °C for further use. The organobentonites were prepared by dropwise addition of 0.1 M aqueous solutions of CDBA and CPC to a 0.5% (w/w) aqueous suspension of the Na-bentonite [23]. It was stirred for 24 h. The complex was centrifuged and washed several times with distilled water until the absence of chloride ion in the filtrate. The organobentonite was dried in hot air oven and ground to 200 mesh size.

2.3. Adsorption studies

Adsorption studies were carried out for the two modified clays, viz. CDBA-bentonite and CP-bentonite as the Na-bentonite showed little adsorption even with high adsorbent mass. The adsorption experiment was carried out by agitating 100 mg of adsorbent with 50 mL of dye solution at the solution pH of various concentrations at 200 rpm and 30 °C in a thermostated orbital shaker (NEOLAB, Mumbai). Dye concentration was estimated spectrophotometrically by monitoring the absorbance at 549 nm using UV–vis spectro-

photometer (HITACHI U 2000 Spectrophotometer). pH was measured using a pH meter (Elico, model LI 120, Hyderabad). The kinetic studies were carried out in a mechanical stirrer. The samples were withdrawn from the shaker at regular time intervals and the dye solution was centrifuged. The absorbance of supernatant solution was measured. Effect of adsorbent dosage was studied with different adsorbent doses (0.005–0.025 g) and 50 mL of 150 mg L⁻¹ dye concentration solution at equilibrium time. The amount of dye adsorbed by the modified clay, q_e (mg g⁻¹), was calculated by the following mass balance relationship:

$$q_e = (C_0 - C_e)v/w \quad (1)$$

where C_0 and C_e are the initial and equilibrium solution concentrations of dye respectively (mg L⁻¹), v the volume of the solution (L) and w is the mass (g) of the adsorbent used.

3. Results and discussion

3.1. Chemical composition of bentonite

The chemical composition of bentonite as well as surface area of bentonite and modified clays is shown in Table 1. BET surface area of bentonite and organobentonite was measured using SmartSorb 92 surface area analyser and N₂ gas was used as adsorbate. The clay, bentonite and the modified clays were analyzed by X-ray powder diffraction using a Rigaku Dmax 2500 diffractometer and Cu K α radiation. FT-IR spectra have been recorded at room temperature using Shimadzu FT-8300.

3.2. XRD analysis

The XRD of bentonite, CDBA-bentonite and CP-bentonite is shown in Fig. 2. The basal spacing value of bentonite, CDBA-bentonite and CP-bentonite is 14.38, 24.65 and 22.63 Å, respectively. The increase in the basal spacing for the modified clay is attributed to the intercalation of cationic surfactants into the interlayer of bentonite with a monolayer arrangement.

3.3. FT-IR analysis

The FT-IR spectrum of bentonite and modified bentonites is shown in Fig. 3. The strong adsorption bands at 2921 and 2854 cm⁻¹ in both the modified bentonites correspond to $-\text{CH}_3$

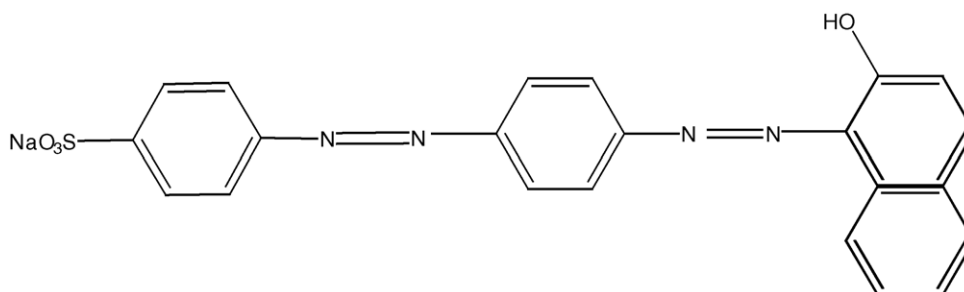


Fig. 1. Chemical structure of Acid Red 151.

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