

Short communication

Equilibrium studies for the adsorption of Acid dye onto modified hectorite

P. Baskaralingam, M. Pulikesi, V. Ramamurthi, S. Sivanesan*

Department of Chemical Engineering, A.C. College of Technology, Anna University, Chennai 25, Tamilnadu, India

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Abstract

The adsorption of Acid dye, C.I. Acid Red 151 from aqueous solution onto modified hectorite at different concentrations and pH has been studied. Hectorite clay has been modified using two cationic surfactants, cetyldimethylbenzylammonium chloride and cetylpyridinium chloride. Present experimental study shows that acidic pH favours enhanced adsorption. The adsorption isotherms are described by means of Langmuir and Freundlich isotherms. The adsorption capacity has been found to be 208.33 and 169.49 mg g⁻¹ for the modified cetyldimethylbenzylammonium chloride-hectorite (CDBA-hect) and cetylpyridinium chloride (CP-hect), respectively.

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1. Introduction

The main pollution source of textile effluent emerges from the dyeing process. The effluent discharged from the dyeing industries is highly coloured and disposal of this coloured water into the receiving water body not only causes damage to aquatic life, but also to human beings by causing mutagenic and/or carcinogenic effect. Many physical and chemical treatment methods namely adsorption, coagulation, precipitation, filtration, electro-dialysis, membrane separation and oxidation have been used for the treatment of textile effluents [1]. The adsorption process provides an attractive method for the treatment of textile effluent especially if the adsorbent is inexpensive and readily available [2]. Adsorption is a surface phenomenon. The adsorption at a surface or interface is largely as a result of binding forces between atom, molecules and ions of the adsorbate on the surface of the adsorbent. Hectorite, which is 2:1 smectite clay, is composed of units made up of two silica tetrahedral sheets with a central Mg octahedral sheet. It has permanent negative charges that arise due to the isomorphous substitution of Li⁺ for Mg²⁺ [3]. The negative charge is counterbalanced by the presence of inorganic cations on the clay surface. By the ion exchange mechanism, the inorganic cation could be exchanged by the organic cation. Thus

the clay surface becomes hydrophilic to organophilic [4]. Acid dyes are water-soluble anionic dyes with negative charges. The surface of the clay hectorite has to be modified for the adsorption of anionic dyes. It is made possible by the cation exchange mechanism. At present no literature is available on the modified hectorite as adsorbent for the colour removal from aqueous solution.

In this study, two organic cations with different structures have been used, viz. cetyldimethylbenzylammonium chloride and cetylpyridinium chloride. The organic cation has positive charge on the Nitrogen atom and it attracts the opposite negative charge by electrostatic attraction. These types of modified clays have been extensively used for a number of environmental applications [5–8]. The objective of the present work is to examine the effectiveness of the modified hectorite in removing Acid Red 151 (C.I. AR 151), which bears a negatively charged SO₃⁻ group in its aqueous solution.

2. Experimental

2.1. Materials and methods

The smectite clay, hectorite (SHCa-1, hec) was obtained from the Source Clay repository of the Clay Minerals Society, CA, USA. Synthetic textile dye AR 151 was obtained from SHIDIMO, Interaux Pvt., Ltd., India and was used without further purification. The chemical structure of C.I. Acid Red 151

* Corresponding author. Tel.: +91 44 22203525; fax: +91 44 22355373.
E-mail address: sivanesh@yahoo.com (S. Sivanesan).

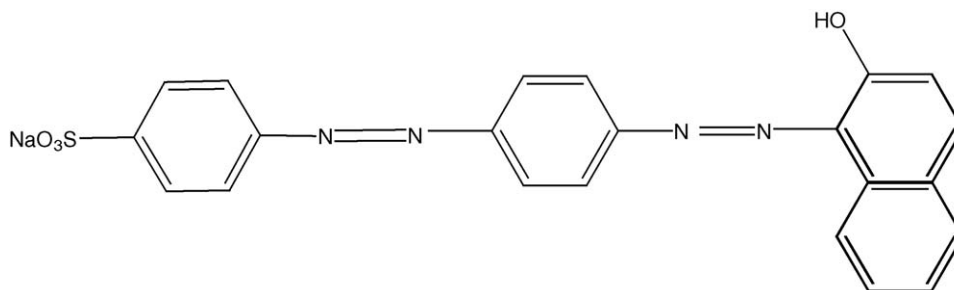


Fig. 1. Structure of C.I. Acid Red 151.

is shown in Fig. 1. The cationic surfactants used for the modification were supplied by SRL, Mumbai, India.

In order to prepare the modified hectorite, the natural hectorite was first converted into Na-hectorite for the cation exchange by organic cation. The Na-hectorite was prepared by stirring the clay with 1 N NaCl using a mechanical stirrer for 24 h. This was followed by washing several times with distilled water until the chloride ions were absent in the filtrate. The clay was dried in a hot air oven at 60 °C for further use. The modified hectorites were prepared by dropwise addition of 0.1 M aqueous solutions of cetyldimethylbenzylammonium chloride and cetylpridinium chloride to a 0.5% (w/w) aqueous suspension of the Na-hectorite [9]. It was stirred for 24 h. The complex was centrifuged and washed as beforehand. The modified hectorite was dried in hot air oven and ground to 200 mesh size.

2.2. Characterization of modified hectorites

The chemical composition of hectorite as well as surface area of hectorite and modified hectorite is presented in Table 1. BET surface area of modified hectorite was measured using SmartSorb 92 surface area analyzer and N₂ gas was used as adsorbate. The modification of hectorite by organic cation was confirmed by X-ray powder diffraction using a Rigaku Dmax 2500 diffractometer and Cu K α radiation. The XRD of hectorite and modified hectorite is shown in Fig. 2. The basal spacing value of hectorite, CDDBA-hectorite and CP-hectorite is 12.61, 19.15 and 18.83, respectively. The increase in the basal spacing for the modified hectorite is ascribed to the intercalation of cationic surfactants into the interlayer of hectorite with bimolecular arrangement.

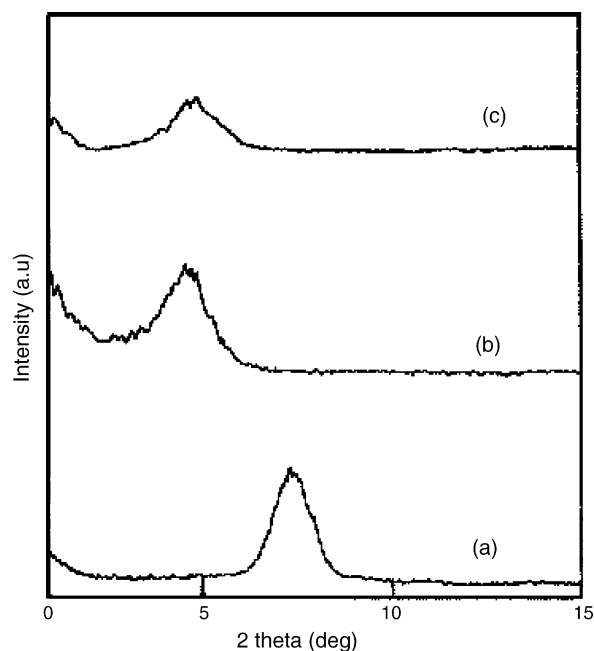


Fig. 2. XRD analysis of hectorite, CDDBA-hectorite and CP-hectorite: (a) hectorite; (b) CDDBA-hectorite; and (c) CP-hectorite.

Adsorption experiment was carried out by agitating 300 mg of adsorbent with 50 ml of different dye concentrations at the solution pH at 200 rpm and 30 °C in a thermostated orbital shaker (NEOLAB, Mumbai). The absorbance of supernatant dye solution was measured by monitoring the absorbance at 549 nm using UV–vis spectrophotometer (HITACHI U 2000 Spectrophotometer). pH was measured using a pH meter (Elico, model LI 120, Hyderabad, India). The amount of dye adsorbed by the modified

Table 1
The chemical characteristics of hectorite and modified hectorites

Constituents (hectorite)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	TiO ₂	CaO	MgO	MnO	K ₂ O	Na ₂ O	Li ₂ O	F	P ₂ O ₅	S	Loss on ignition
Percentage	34.7	0.69	0.02	0.25	0.038	23.4	15.3	0.008	0.13	1.26	2.18	2.60	0.014	0.01	20.6
Adsorbent	Cation exchange capacity (CEC)			Total organic carbon content (%)			Specific surface area N ₂ area (m ² g ⁻¹)								
Hectorite	43.9 mEq/100 g			0.1			63.19								
CDDBA-hectorite	–			12.6			10.83								
CP-hectorite	–			10.6			4.24								

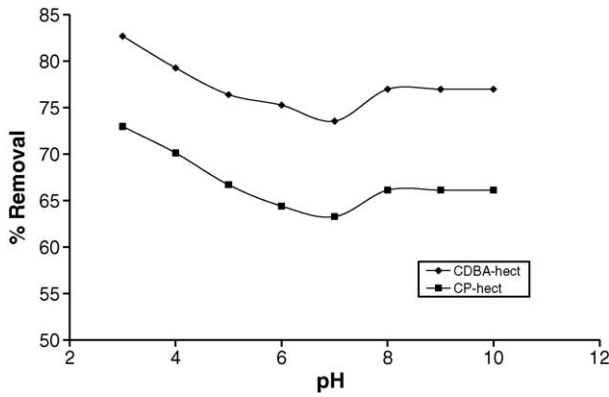


Fig. 3. Effect of pH.

clay, q_e (mg g^{-1}), was calculated by the following mass balance relationship:

$$q_e = (C_0 - C_e) \frac{v}{w} \quad (1)$$

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. Effect of pH

The experimental results of the adsorption of AR 151 onto CDDBA-hect and CP-hect at different initial pH are shown in Fig. 3. Maximum colour removal took place at pH 3 and minimum at pH 7. At lower pH, more protons will be available which increases the electrostatic attraction between the negatively charged SO_3^- anion and the positively charged adsorbent. As the pH of the solution increases, the positive charge on the surface decreases and the number of negatively charged sites increases thereby decreasing the adsorption. In alkaline medium also, small amount of colour removal takes place. This can be explained by formation of covalent bond between the external surface $-\text{OH}$ groups of Si and Al atoms of adsorbent and negatively charged dye molecules.

3.2. Adsorption isotherms

Fig. 4 shows the adsorption isotherms for the adsorption of AR 151 onto modified hectorite. The Langmuir and Freundlich models are commonly used for describing the adsorption isotherm.

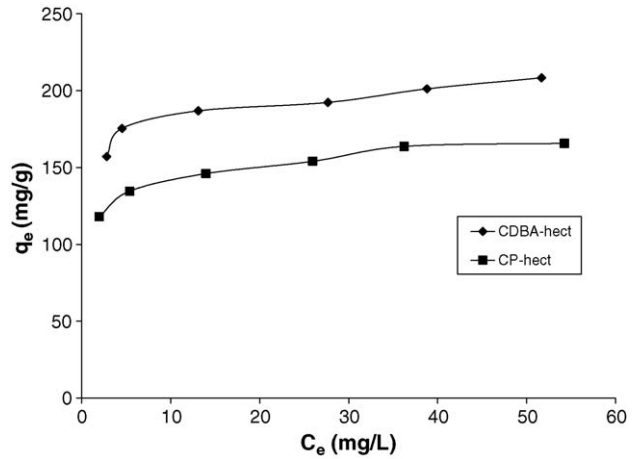


Fig. 4. Adsorption isotherm for the adsorption AR 151 onto CDDBA-hectorite and CP-hectorite.

The basic assumption of the Langmuir model [10] is that adsorption takes place at specific homogeneous sites within the adsorbent. It is further assumed that once a dye molecule occupies a site, no further adsorption can take place at that site.

According to the Langmuir model,

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (2)$$

where C_e is the concentration of dye solution (mg/l) at equilibrium. The constant Q_0 signifies the adsorption capacity (mg/g) and b is related to the energy of adsorption (l/mg).

An essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter [11,12].

$$R_L = \frac{1}{1 + b} C_0 \quad (3)$$

Where b is the Langmuir constant and C_0 the highest initial dye concentration (mg/l). The value of R_L indicates the type of the isotherm to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

The Freundlich equation [13] is basically empirical equation and employed to describe heterogeneous systems. The isotherm assumes that adsorbent surface sites have a spectrum of different binding energies.

The Freundlich equation is given by

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

The magnitude of the component n gives an indication of the favourability and K_F the capacity of the adsorbent/adsorbate sys-

Table 2
Langmuir and Freundlich constants for the adsorption of AR 151 onto CDDBA-hectorite and CP-hectorite

Adsorbent	Langmuir constants				Freundlich constants		
	Q_0 (mg g^{-1})	b (l mg^{-1})	R_L	r_L^2	K_F (mg g^{-1})	n	r_F^2
CBDA-hectorite	208.33	0.7384	0.0051	0.9985	149.04	12.30	0.9394
CP-hectorite	169.49	0.6276	0.0071	0.9989	111.43	9.75	0.9889

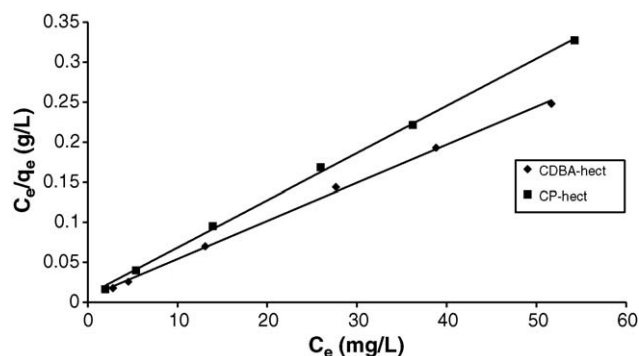


Fig. 5. Langmuir isotherm for the adsorption of AR 151 onto CDDBA-hectorite and CP-hectorite.

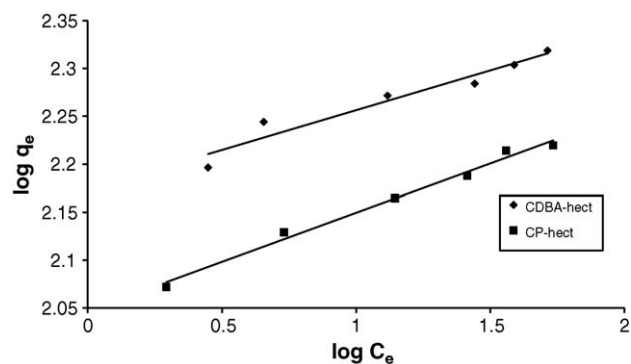


Fig. 6. Freundlich isotherm for the adsorption of AR 151 onto CDDBA-hectorite and CP-hectorite.

tem. The n value between 1 and 10 indicate beneficial adsorption [9].

The values of Langmuir and Freundlich equation constants can be determined from linear Eqs. (2) and (4) and the values of the constants are given in Table 2.

The adsorption data of AR 151 onto modified hectorites were fitted to both Langmuir (Fig. 5) and Freundlich (Fig. 6) models. The correlation coefficient r_L^2 is higher than r_F^2 in both the modified hectorites. Moreover, the dimensionless constant, R_L lies within the favourable limit. It indicates that the Langmuir model is the best fit model for the adsorption of AR 151 onto CDDBA-hect and CP-hect. Since the unmodified did not show any adsorption on the removal of AR 151 even for high dose of hectorite, adsorption studies were carried out only for the two modified hectorites. These modified hectorite show high adsorption capacity and may be used for the removal of anionic dyes in the dyeing effluent. The adsorption mechanism could be explained by:

- (i) There is an electrostatic attraction between the organic cationic groups and the anionic SO_3^- group in the dye molecule.

- (ii) The Van der Waals interaction may occur between the phenyl ring of dye molecule and $-\text{CH}_2$ group of benzyl ring through H-bonding.
- (iii) The organic cations in the interlayers may serve as pillars, which give rise to enough space for dye molecules entry into the interlayer.

4. Conclusion

The intercalation of hectorite by the two cationic surfactants changes the clay from hydrophilic to organophilic. These modified clays become more suitable adsorbent for the removal of negatively charged anionic dyes. Adsorption studies on these modified clays were carried out in terms of different initial dye concentrations and pH. Acidic pH favours the adsorption. Langmuir and Freundlich models were used to describe the adsorption data. The adsorption isotherms were well-fitted by Langmuir model. The kinetic experimental result shows that it followed pseudo second-order kinetic model. The higher adsorption capacity of CDDBA-hect (208.22 mg/g) and CP-hect (169.49 mg/g) show that this modified hectorite could be used as an adsorbent for the colour removal of anionic dyes.

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