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Natural Clay -An Adsorbent for Basic Dye

Research Article

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Abstract

The adsorption behaviour of Basic Red-12 on Vermiculite and has been investigated to understand the physicochemical process involved and to explore the potential use of low cost materials in textile effluent treatment and management. The adsorption process was found to be pH dependent and optimum pH obtained is 8.0. The equilibrium was established in 2 h and Pseudo first order kinetics was followed. The process obeys Langmuir and Freundlich model. Scanning electron microscopic analysis reveals a conspicuous surface morphology of VC. The results of XRD and FTIR spectroscopy reveal that the process is electrostatic complexation mechanism driven. The thermodynamical measurements suggest that all processes are exothermic accompanied with negative ∆Go, ∆Ho and ∆S o.

Key words: Vermiculite; Basic Red-12; Isotherms; Thermodynamics

Introduction

Dyes constitute the focus of much of environment concern now a days. Dyes are used in many industries like textile, paper, leather, plastics, cosmetics, pharmaceuticals etc. These industries use a considerable amount of water for dyeing and their effluent mainly consist of colored waste water. Color is the first observable parameter for checking the quality of water and according to WHO recommendations the water used for drinking purpose should be colorless. In industrial waste water color is the first apparent pollutant. The presence of very small amount of color hampers the penetration of sunlight and affects aquatic flora and fauna. The presence of dyes impart excess organic load in waste water. Around 10,000 different types of dyes are available worldwide with an annual production of 7×10^5 metric tonnes [1].

This is observed that aerobic biodegradation has very less color removal efficiency. Most of the treatment technologies work on biological treatment processes. Other physical and chemical methods like coagulation [2,3] oxidation, [4] membrane separation, [5] and adsorption are in practice. Adsorption is a procedure of choice due to its simplicity, efficiency and cost efficacy [6]. Activated carbon is the best adsorbent but its higher cost and difficult regeneration has encouraged many workers for the research of new adsorbents. Ionic dyes have been removed by the use of adsorbents like orange and banana peels [7], almond shells [8], corn cob [9], de-oiled soya [10], shale oil ash [11], Sugar cane bagasse [12], coir pith [13], hazelnut shells [14], rice husk [15], wheat husk [16], Baggase [17], bark [18] etc.

Natural clays are abundant on most of the continents of the world. Clay materials possess layered type of structure and they are classified on the basis of their layered structures. These clays are much cheaper than activated carbon. Alkan et.al [19] investigated the removal of reactive blue 221 and acid blue 62 anionic dyes onto sepiolite from aqueous solutions. The adsorption capacity of sepiolite increased with increasing temperature and decreasing pH. The sepiolite sample calcinated at 200 °C has a maximum adsorption capacity. However, calcination at higher temperature caused a decrease in the adsorption capacity. It was found that the Freundlich isotherm appears to fit the isotherm data better than the Langmuir isotherm. Yuan et.al [20] investigated the adsorption of methylene blue and neutral red over ordered mesoporous carbons. Theoretical studies showed that the adsorption kinetics of dyes on ordered mesoporous carbons was well depicted by using pseudo-second-order kinetic model. Wang et.al [21] evaluated the efficiency of natural zeolite for the removal of malachite green in batch system. Kinetic studies indicate that malachite green adsorption on the natural zeolite in a single component system follows the first-order kinetics. Dogan et.al [22] investigated the removal of reactive dyes over surfactant modified zeolite. The adsorption of reactive black 5 and reactive red 239 in aqueous solution on cetyl trimethyl ammonium bromide (CTAB) modified zeolite was studied in a batch system. Experiments were performed at different conditions such as initial dye concentration, contact time, temperature and pH. CTAB modification covered the zeolite surface with positive charges and the adsorption capacity of zeolite increased. The adsorption capacity of reactive red 239 was found to be two times higher than reactive blue 5 due to the hydrophilicity of the dye molecules.

In the present work Natural clay Vermiculite has been used as an Adsorbent for Basic Dye 'Basic Red-12' for study of adsorption parameters and for studying thermodynamics of the adsorption process.

Materials and Methods

Materials and Chemicals

Vermiculite (VC) a 2:1 type aluminosilicate clay mineral was obtained from Tamil Nadu Minerals limited, Dharampuri. This was crushed and finally powdered and particle size <0.5mm was separated for adsorption study. This was activated by washing with DDW and filtration using vacuum pump and drying at 353 K for 24h and stored in air tight container for further study. The dye Basic red 12(C.I. Basic Red 12) (molecular weight 357.51), molecular formula$C_{25}H_{29}N_2Cl$ (1, 3, 3-Trimethyl-2-[3-(1, 3, 3-trimethyl-2-indolinylidene) propenyl]-3-indoliumchloride was purchased from Thomas Baker company and was used without further purification. The FTIR of VC and surface derivatives was carried out with Perkin Elmer spectrophotometer in the range 400-4000 cm^{-1} using perkin elmer spectrophotometer. The pH of dye solutions and pH_{zpc} were determined by using pH meter by Toshvin (TMP-85). The weighing were carried out on a digital weighing balance of accuracy up to 0.1 mg by citizen Co. Shimadzu 2101 PC UV –Visible spectrophotometer was used for the determination of residual dye concentration in the medium. The sample was also characterized by X-ray diffractometry using an X'PERT PRO PANalytical with Cu-K_α radiation.

Adsorption Studies

The series of experiments were conducted by placing 50 ml of dye solution in an Erlenmeyer flask and adding the required amount of adsorbent to that in an incubator shaker. The pH of different solutions was adjusted with 0.1 N HCl and 0.1 N NaOH. After attainment of equilibrium the aqueous phase was analyzed for residual dye concentration using UV visible spectrophotometer. From the absorbance data q_e (mg g^{-1}) was determined using eq 1.

$$q_e = \frac{(C_0 - C_e)V}{W} \qquad (1)$$

Where C_0 is initial dye concentration, C_e is final dye concentration and V is volume of dye in liters and W is mass of adsorbent in g. The isotherms were studied by using 50 ml of dye solution within concentration range of 200 ppm to 500 ppm for VC at 303 K, 313 K and 323 K.

Results and Discussions

Structure of VC

The SEM of VC suggests a compact and less porous arrangement of ions in the adsorbent (Figure 1). Surface chemistry of the adsorbents such as specific surface area, pore volume distribution and pore diameter were measured. Pore volume was determined by the technique. The zero point charge of the adsorbents and derivatives was determined by solid addition technique. The results of the surface area analysis, pore volume, bulk density and pH_{zpc} reveals that the surface area of VC is 65.213 m^2/g, with pore volume 4.160 cm^3/g, bulk density 2.46 g/ml and pH_{zpc} 2.5. Generally, larger the surface area, higher is the adsorbent's capacity. However, the surface area must be available in certain pore sizes. The pores on adsorbents are classified by IUPAC as micropores, macropores, and transitional pores. The micropores have diameters of 10-100 A°, pores larger than 1,000 A° are considered as macropores and pores with diameters in the range of 100 to 1,000 A° are defined as transitional. The large pores serve mainly as passageways to the smaller pores where the adsorption forces are stronger.

The FTIR spectra of VC suggests the main bands at 1020 cm^{-1} and 1080 cm^{-1}due to Al-O bond stretching, the bands are also observed at 3500 and 3400 cm^{-1} due to O-H bonds in VC (Fig. not shown here) .

The XRD spectra confirm crystalline structure of VC. (Figure 2).

Effect of adsorbent dose

To investigate the effect of adsorbent dose on adsorption of dye on VC, the experiments were conducted with adsorbent dose between 2.5 g/100 ml to 20.0 g/100 ml at 303 K and it was found that with an

Figure 1: SEM of Vermiculite at magnification 1800x (15kV).

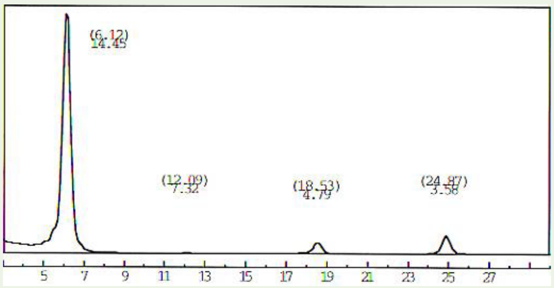

Figure 2: XRD Spectra of VC.

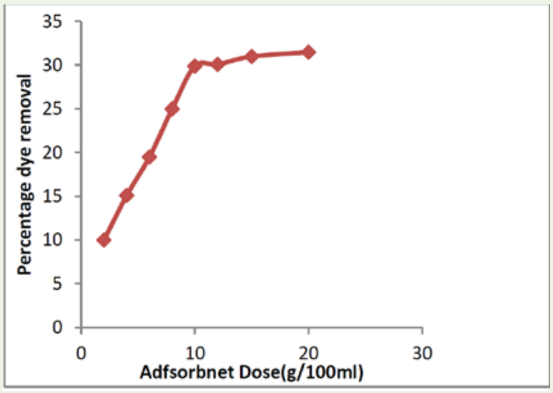

Figure 3: Effect of Adsorbent dose.

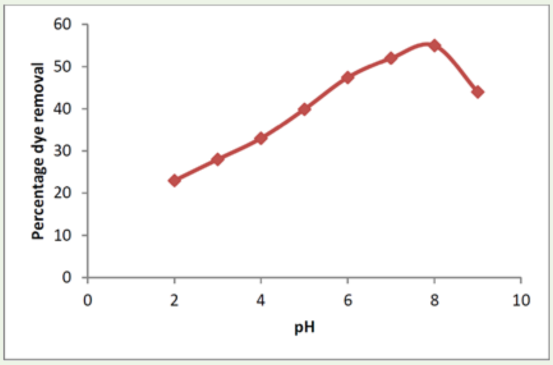

Figure 4: Effect of pH on Dye Removal.

increase in the dose, the adsorption increases. A significant increase is observed at optimum adsorbent dose i.e. 10g/100 ml. The results have been shown in Figure 3.

Effect of pH

Surface change is the most important parameter for ionic dye adsorption. The dye adsorption is affected by solution pH and in the present study the effect of pH is studied in the range of 2-9 while initial concentration (500 ppm), adsorbent dose (7.5 g/100 ml) and temperature (303 K) were kept constant. The adsorption capacity increases when the pH increases for VC. The maximum adsorption of basic dyes occurs at pH 8 due to negative charge on surface in alkaline medium (Figure 4).

Adsorption isotherms

The Freundlich [23] and Langmuir [24] isotherm models have been successfully applied to adsorption processes at temperatures 303 K, 313 K and 323 K and thermodynamic parameters calculated accordingly. For the equilibrium concentration of adsorbate (C_e) and amount of dye adsorbed at equilibrium (q_e), the following linear forms of Langmuir and Freundlich isotherms were studied.

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0C_e} \qquad (2)$$

$$\log\left(q_e - q_t\right) = \log q_e - \left(\frac{k_1}{2.303}\right)t \qquad (3)$$

Where Q_o and b are Langmuir constants and K_F and n are Freundlich constants. The Freundlich and Langmuir isotherms gave straight lines and intercepts and slopes were used to determine the values of Freundlich and Langmuir parameters as given in Table 1 and Table 2. The isotherms are shown in Figure 5.

$$\Delta G^\circ = -RT\ln b \qquad (4)$$

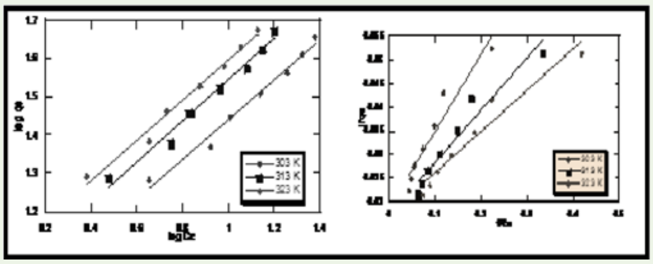

Figure 5: Freundlich adsorption Isotherm and Langmuir adsorption isotherm for adsorption of BR-12 on VC.

Table 1: Freundlich Parameters for Adsorption of BR-12 over VC.

Adsorbent	Temperature(K)	Kf(	n	R	SEE	RSS
VC	303	8.3217	1.9264	0.9901	0.0200	0.002
VC	313	10.316	1.8878	0.9908	0.0204	0.002
V	323	11.771	1.9029	0.9925	0.01850	0.002

Table 2: Langmuir Parameters of Adsorption of dye on VC.

Temperature	**Q_ox10^{-3}**	***b***	**R**	**SEE**	**RSS**
(K)	***(mg/g)***	***(L/mg)***			
303	0.0003	38682	0.9667	0.0030	0.000
313	0.0002	55512	0.9686	0.0029	0.000
323	0.0001	69115	0.9701	0.0028	0.000

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Table 3: Thermodynamics of the adsorption process.

Adsorbent	Dye	*ΔH°*	*ΔG°*	*ΔS°*
VC	BR-12	-70.069	-28.321	-0.133

Table 4: Lagergren Pseudo first order kinetics data for dye interactions on VC.

Adsorbent	Dye	q_e	k_1	R	SEE	RSS
		(mg/g)	*(min⁻¹)*			
VC	BR-12	20.351	0.0153	0.9926	0.0547	0.015

$$\Delta H^0 = -R\left(\frac{T_2 T_1}{T_2 - T_1}\right)\ln\left(\frac{b_2}{b_1}\right) \qquad (5)$$

$$\Delta H^0 = -R\left(\frac{T_2 T_1}{T_2 - T_1}\right)\ln\left(\frac{b_2}{b_1}\right) \qquad (6)$$

Where b, b_1, b_2 are Langmuir constants at 303 K, 313 K and 323 K respectively.

To check the validity of isotherms on adsorption data regression coefficient 'R', Standard Estimated error 'SEE' and Random sum of squares 'RSS' are also calculated by using SPSS software.

The value of K_f is increasing with the rise of temperature for BR-12, The value of *n* is in the range 1.00-2.00. The adsorption of dye ions on micro crystals of VC reveals different adsorption mechanisms. This seems that the increase of concentration of dye ions causes increased diffusivity with the rise of temperature, thus the values of intercepts and slopes are also increasing with the rise of temperature. The self diffusion and transport diffusion steps are operating and this leads to molecular redistribution of dye ions on VC after binding with ionic dyes.

The Langmuir adsorption isotherm fits well on the adsorption of ionic dye on VC. The values of R, SEE and RSS suggest that this isotherm model fits on the adsorption of BR-12 on VC. The applicability of Langmuir adsorption model reveals these ionic dyes binds with the aluminosilicate materials to form a chemical bond. The interlayer spacing between the silicate sheets makes possibility of binding of ionic dyes with alumiosilicate minerals

The Thermodynamics of adsorption of BR-12 on VC has been determined (Table 3). The adsorption of BR-12 on VC specify that the process is energetically favourable. The adsorption process is enthalpy driven as the entropy of the process decreases after incorporation of dye ion in inter layers of aluminosilcate structure of VC.

Adsorption Kinetics

Adsorption kinetics depends upon the adsorbent-adsorbate interface and system condition, the adsorption kinetics has been investigated for their suitability and application in water pollution control. Two vital appraisal elements for adsorption process operation unit are the mechanism of adsorption and the reaction rate. Dye uptake rate determines the dwelling time required for completing the adsorption process till attainment of equilibrium, which can be catalogued from kinetic analysis. The first order rate expression of Lagergren based on the solid adsorption capacity is generally expressed by equation 7.

$$\frac{dq}{dt} = k_1(q_e - q_t) \qquad (7)$$

The integrated form of above equation can be expressed by equation 8.

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \qquad (9)$$

Where q_e and q_t are the amount of dye adsorbed at equilibrium and time *t* (min) respectively, k_1, the rate constant of pseudo-first order rate constant (min⁻¹). The kinetic parameters have been shown in Table 4. The adsorption of dye on VC fitted the Lagergren equation well with high regression coefficient and less standard estimated error.

Conclusion

VC is natural clay and has been used as an adsorbent for the removal of basic dye and it has been found that Clays can be used without much chemical modification for the removal of basic dyes from effluent. The Increase in adsorbent dose increases the adsorption efficiency due to increase in active sites on the surface of adsorbent. The pH and temperature are important factors for deciding the adsorption efficiency of material. The zero point charge of VC is below 7.0, thus it acts as an efficient adsorbent at that pH. The Freundlich isotherm fits better than Langmuir suggesting physisorption as a mode of adsorption. Thermodynamic parameters indicate exothermic nature of the process.

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