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Adsorption of Acid Blue 158 by porous Polymeric Adsorbent Amberlite XAD-2

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ABSTRACT

The studies have been conducted on the removal of the basic dyes Acid Blue 158 and Acid Orange 74 using porous polymeric Amberlite as an adsorbent. The adsorbent was characterized by measuring their porosities and pore size distributions. The microstructure of the adsorbent was examined by scanning electron microscopy (SEM). The batch adsorption experiments were carried out under various operating parameters like initial dye concentration, contact time, adsorbent dose and pH. The equilibrium data fitted well to the Langmuir and Freundlich isotherm equations. The experimental data fitted very well with pseudo second order kinetic model and Elcovich model suggesting chemisorption which is confirmed by desorption studies.

Keywords : Amberlite XAD-2 , Acid Blue 158, Langmuir Isotherm, Freundlich Isotherm.

I. INTRODUCTION

Adsorption of methylene blue on magnesium silicate: kinetics, equilibria and comparison with other adsorbents have been studied (Franco Ferrero, 2010). Separation of malachite green and methyl green cationic dyes from aqueous medium by adsorption on amberlite xad-2 and xad-4 resins using sodium dodecylsulfate as carrier was investigated intensively (Luís Gustavo et al., 2011). Equilibrium and kinetic studies on the adsorption of surfactant, organic acids and dyes from water onto natural biopolymers have also been studied (Min-Yun Chang, 2005).

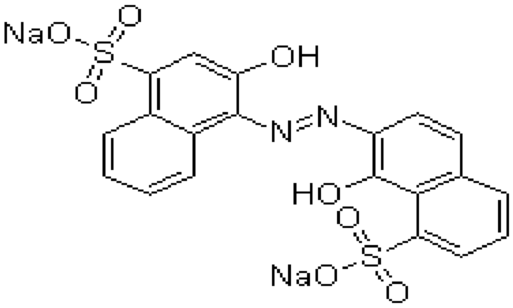
A wide range of technologies and methods like coagulation, oxidation, electrochemical, ion-exchange, biodegradation and ultra-filtration have been discovered and adopted to overcome the excessive discharges of colourants from petrochemical, textile, leather-making, pharmaceutical as well as food and beverage industries. However all these are not comparable to adsorption technique in term of efficiency, operating cost, process flexibility and ease of operation[1-6]. These methods are inefficient and incompetent because of the stability of these dyes towards light, oxidizing agents and aerobic digestion and also of their high solubility in the aqueous media. A comprehensive investigation shows that adsorption technique was the most appropriate and efficient one [7-8].

Basic dyes are cationic and they are used to dye fabrics such as wool, silk, nylon, and acrylics where bright dying is the prime consideration. Auramine is used as a cationic dye for paper, textiles, and leather[9]. It has also been used as an antiseptic and as fungicide. It may be a carcinogen in human since it has been shown to cause liver and lymphatic cancers in animals[10]. It was historically used as a component in brilliantine, a grooming product intended to soften men's hair [11]. It has been detected in a small percentage in food samples as it is used as food colourant in some countries like India and China. Auramine O is a yellow fluorescent dye; soluble in water and in ethanol. Both auramine and auramine O have been used to stain acid-fast bacteria in sputum or in paraffin sections of infected tissue and as a component of the Truant auramine - rhodamine stain for tubercle bacilli[12]. Chemicals similar to auramine can destroy or disturb the ability of the blood to carry oxygen. Therefore it was thought that a method to treat dye wastewater containing auramine yellow and auramine O is highly desirable. Hence in the present study an attempt has been made to explore the feasibility of using the Amberlite for the removal of basic dyes.

II. MATERIAL AND METHODS

The adsorbent used in this study is Amberlite (3g) was allowed to swell in 15 ml of water-free alcohol and stirred for 2 hours at 25 ^{0} C to get a uniform suspension.. A stock solution (1000 mg / L) of dye is prepared using doubly distilled water. Various dye solutions with different initial concentrations are prepared by diluting the stock dye solution. The adsorbate used in this study is Acid Blue 158. [2] Acid Blue 158.

- Name : Acid Blue 158
- Synonyms : Disodium 3-hydroxy-4-[(1-hydroxy-8-sulpho-2-naphthyl) azo]naphthalene-1-Sulphonate
- Molecular Structure :



- Molecular Formula: $C_{20}H_{12}N_2O_8S_2{\cdot}2Na$
- Molecular Weight : 518.43

III. RESULTS AND DISCUSSION

3.1 Characterization of Adsorbent

Physico-chemical characteristics of the adsorbents were studied as per the standard testing methods. The surface morphology of the adsorbent was visualized via scanning electron microscopy (SEM) (Fig.1,2). The diameter of the composite range was 50µm.

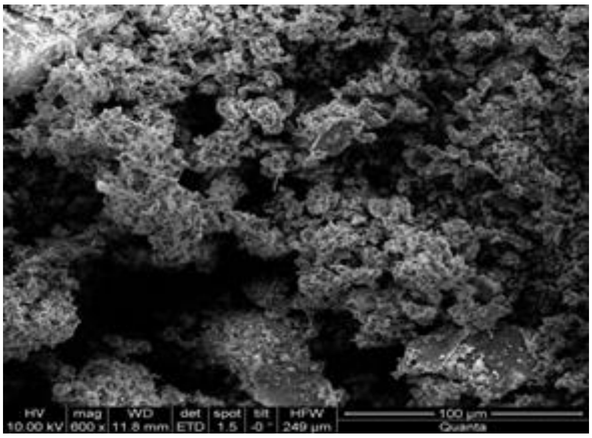


Fig.1: SEM of pure Amberlite

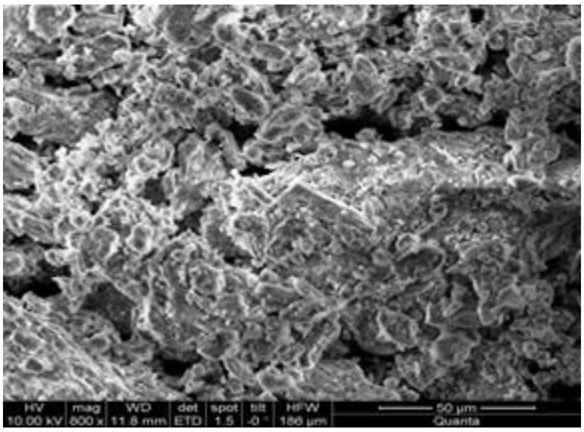


Fig.2: SEM of Amberlite

3.2 Batch Adsorption Method

Entire batch mode experiments were carried out by taking 50 ml of the respective dye solution and a known amount of the adsorbent in a100 ml conical flask. The flasks were agitated for pre-determined time intervals in a thermostat attached with a shaker at the desired temperatures (303K to 311K) and then the adsorbent and adsorbate were separated by filtration. Studies on the effects of agitation time, pH, initial dye concentration, adsorbent dose were carried out by using known amount of adsorbent and 50ml of dye solution of different concentrations. Dye solution (50 ml) with different amounts of adsorbent was taken to study the effect of adsorbent dosage on the removal of dye.

3.3 Effect of Initial Dye Concentration

The effect of initial dye concentration and contact time on the removal of Acid Blue 158 is shown in Fig.3. For this study 50 ml of 10 to 100 mg/L of dye solution was agitated with 100 mg of adsorbent. The absorbance of the agitated solution was measured by uv/vis spectrophotometer

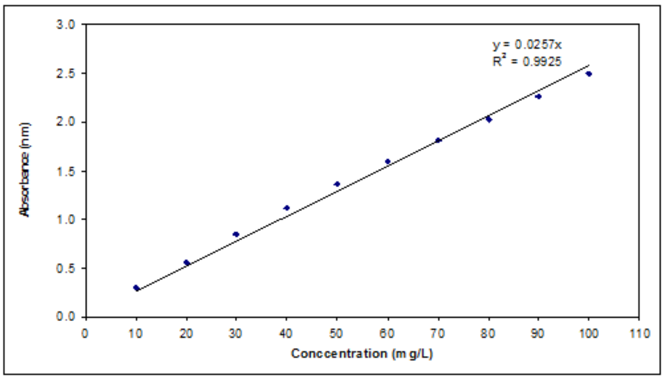


Fig 3 : Effect of initial concentration on sorption capacity of Acid Blue 158

3.4 Effect of Agitation Time

The effect of agitation time on the removal of Acid Blue 158 and Acid Orange 74 are shown in Fig. 5, 6. For this study 50 ml of 10 to 100 mg/L of dye solution was agitated with 100 mg of adsorbent. The absorbance of the agitated solution was measured by uv/vis spectrophotometer. The extent of removal of dye was faster in initial stages, then showed decreasing pattern and finally became constant showing the attainment of equilibrium. The extent of removal was found to be 94% and 95% for Acid Blue 158 and Acid Orange 74 respectively. Fig. 3,4 show that the curves are single, smooth, indicating monolayer coverage of the adsorbent surface.

As can be seen in Figs. 2 and 3 , most of the adsorption of the dye takes place in the first 30 and 50 minutes of contact time for adsorbents, respectively. Equilibrium is reached within 170 minutes for Duelite 171 and 150 minutes for Amberlite xad 2 adsorbent. Beyond equilibrium time, adsorption is found to be nearly constant. This is mainly because of the fact that at the initial stage of adsorption, vacant surface sites are available, once equilibrium is attained; the remaining vacant sites are difficult to be occupied, probably caused by the repulsive forces between the molecules on the adsorbents the bulk phase (Iscen, Kiran, Ilhan, 2007, Rajoriya et al. 2007 and Wu, 2007).

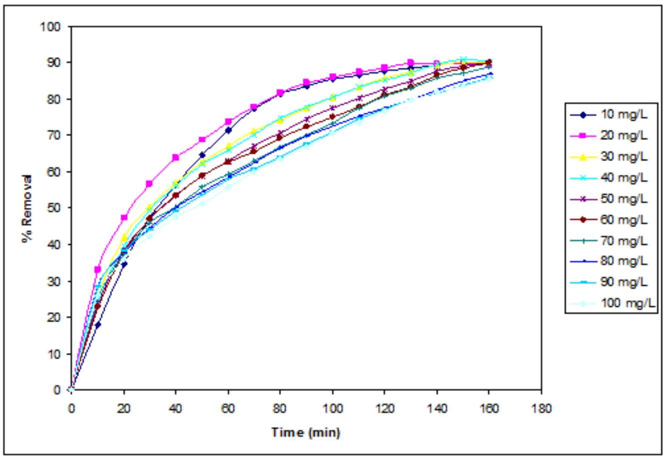


Fig 4 : Effect of agitation time on sorption capacity of Acid Blue 158

3.5 Effect of Adsorbent Dosage

The effect of adsorbent dosage on basic dye removal was studied by keeping all other experimental conditions constant except that of adsorption dosage. The results showed that as the adsorbent concentration increased from 1 g to 3 g, the amount adsorbed per unit mass of the adsorbent increased, then showed decreasing pattern and finally became constant showing the attainment of equilibrium (Fig.7, 8). The decrease in unit adsorption with increasing dose of adsorbent may be basically due to adsorption sites remaining unsaturated during the adsorption process.

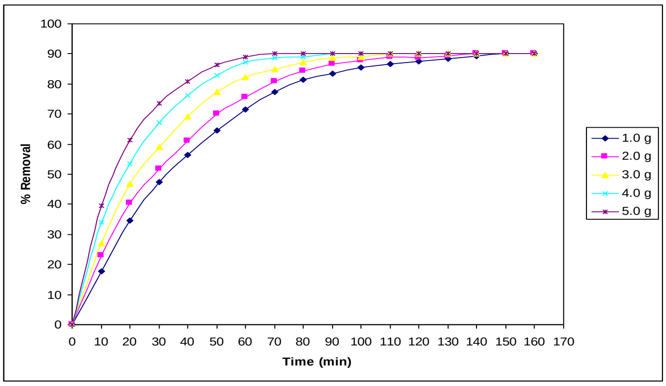


Fig 5 : The effect of adsorbent dosage on sorption capacity of Acid Blue 158.

3.6 Effect of pH

Adsorption pH experiments were carried out at various pH values in the range 3 to 11, maintaining the pH by adding required amount of dilute hydrochloric acid and sodium hydroxide solutions. A pH meter calibrated with 4.0 and 9.0 buffers was used.Fig.9, 10 indicate that maximum dye removal had occurred in basic medium. As the pH increases the sorption capacity also increases. The pH for the adsorbent is determined as 8.0.

To study the effect of pH on the adsorption capacity of the Acid Orange 74, experiments were carried out using different initial pH values, varying from 2,4,6,7,8 for the Duelite 171 and Amberlite xad 2 adsorbents, respectively. For any adsorption system, pH of the system affects the nature of surface charge of adsorbent. In acidic medium, the oxide surface of adsorbent develops a net positive charge. This in turn renders a strong electrostatic attraction towards anionic dyes than in basic medium (Mahony, Guibal, Tobin, 2002, and Namasivayam et al., 1997).

For Duelite 171 adsorbent when initial dye solution pH is 2, the percent removal of the dye is 80.36% and when dye solution pH is 8, the percent removal of dye is 83.36% (Fig.8). This result indicates that a significantly high electrostatic attraction exists between the surface of adsorbent and the dye; this is possibly due to the increase in positively charged sites on the adsorbent surface as pH increased (Netpradist et al., 2007).

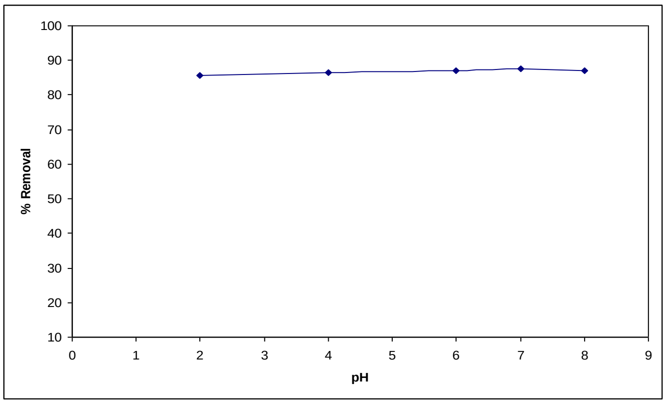


Fig 6 : Effect of initial concentration on sorption capacity of Acid Blue 158

3.7 Adsorption isotherm

Langmuir and Freundlich are the most frequently used models among the several models available in the literature to describe experimental data on adsorption. In this study, also both models were employed to analyze the relationship between the amount of dye adsorbed and its equilibrium concentration

3.8 Langmuir isotherm

The Langmuir adsorption isotherm which assumes that adsorption takes place at specific homogeneous sites within the adsorbent, has been used successfully for many adsorption processes of monolayer adsorption. The linearized Langmuir equation can be represented as

$$\frac{c_e}{q_e} = \frac{i}{bq_0} + \frac{c_e}{q_0} \qquad \text{(Eq. 1)}$$

Where C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of dye adsorbed per unit mass of adsorbent (mg/L) and q_0 and b are Langmuir constants related to adsorption capacity and rate of adsorption respectively. As required by equation (1), plotting C_e/q_e against C_e gave a straight line, indicating that the adsorption of basic dyes on nanocomposite follow the Langmuir isotherm. The Langmuir constants b and q_0 were evaluated from the slope and intercept of the graph.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter R_L which is defined by,

$$R_L = \frac{1}{(1+bc_0)} \qquad \text{(Eq.2)}$$

Where, C_0 is the initial solute concentration, 'b' the Langmuir adsorption constant (L/mg).R_L value less than one indicates favourable adsorption[14].

The R_L values shown in Table1 (all<1) indicate that the adsorption of basic dyes follow Langmuir isotherm.

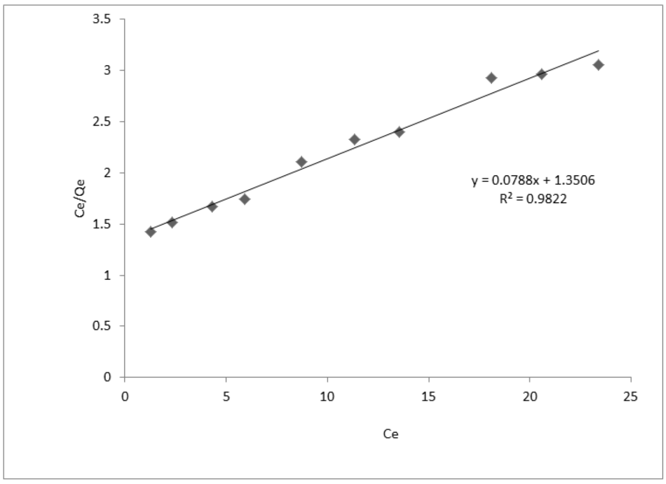


Fig 7 : Plot of Langmuir adsorption isotherm of Acid Blue 158 on Amberlite

Table 1: The values of Langmuir constant Q^0 and b in addition to R_L.

Concentration of dye (mg/L)	Acid blue 158				Acid Orange 74			
	R_L	B	Q^o mg/g	R^2	R_L	b	Q^o mg/g	R^2
20	0.9951				0.9995			
40	0.9902				0.9970			
60	0.9854	0.000246	64.102	0.9916	0.9985	0.0000205	22.0	0.9954
80	0.9806				0.9998			
100	0.9759				0.9975			
120	0.9713				0.9970			

3.9 Freundlich Model

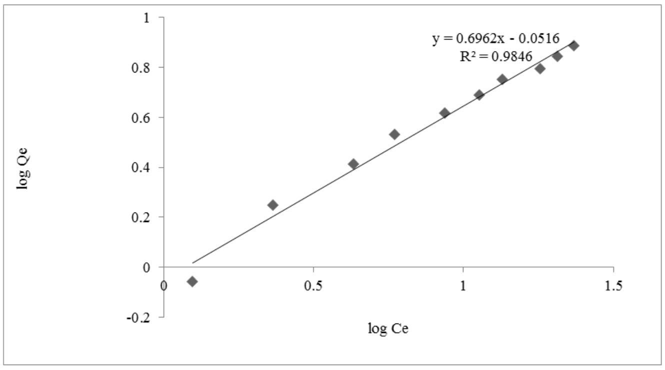


Fig 8. Plot of Freundlich adsorption isotherm of Acid Blue 158 on Amberlite

The Freundlich isotherm, an empirical equation used to describe heterogeneous systems can be expressed in its logarithmic form as

$$\log q_e = \log k_f + \frac{1}{n} \log c_e \qquad \text{(Eq.3)}$$

Where K_f and 1/n are Freundlich constants related to adsorption capacity and adsorption intensity of the sorbent respectively. q_e is the amount adsorbed at equilibrium (mg/g); C_e is the equilibrium concentration of the adsorbate. The plot of log q_e versus log C_e gave a straight lines (Fig.15,16) with good regression coefficients indicating that the adsorption of these dyes follow the Freundlich isotherm. The values of K_f and 1/n calculated from the intercept and slope respectively are recorded in Table 2.

Table 2: The values of Freundlich constant K_f and n.

Dye	K_f L/mg	n mg/g	R^2
Acid Blue 158	6.918	0.9523	0.9906
Acid Orange 74	6.309	0.7407	0.9927

3.10 Kinetics of adsorption

Many kinetic models have been proposed to elucidate the mechanism of solute adsorption. Factors like physical and /or chemical properties of adsorbent, ambient temperature, solution pH and nature of adsorbate, influence the rate and mechanism of adsorption. In order to investigate the mechanism of adsorption of Acid Blue 158 and Acid Orange 74 by the nanocomposite the following three kinetic models were considered.

3.11 Pseudo first order kinetic model

The integrated linear form of this model proposed by lagergren is,

$$log(q_e - q_t) = log\, q_e - (k_1 / 2.303)t \qquad \text{(Eq.4)}$$

Where q_e is the amount of dye adsorbed at equilibrium (mg/g), and q_t is the amount of dye adsorbed (mg/g) at time t, k_1 is the first order rate constant (min^{-1}) and t is time (m). Hence a linear trace is expected between the two parameters log (q_e-q_t) and t, provided the adsorption follows first order kinetics. It is observed that the data does not fit in to first order equation

3.12 Desorption studies

Desorption studies with acetic acid revealed that the regeneration of adsorbent was not satisfactory, which confirms the chemisorptive nature of adsorption.

IV.CONCLUSION

The present investigation showed that Amberlite can be used as adsorbent for removal of Acid Blue 158 and Acid Orange 74. The amount of dye adsorbed varied with initial dye concentration, adsorbent dose, pH and temperature. Removal of dyes by Amberlite was found to obey both Langmuir and Freundlich adsorption models. The adsorption process followed pseudo second order kinetics. This has been further supported by Elovich chemisorptive kinetic model. Desorption studies reveal that no satisfactory desorption taking place confirming chemisorptive nature of adsorption.

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