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Intraparticle diffusion processes during acid dye adsorption onto chitosan

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Abstract

The adsorption of five acid dyes onto chitosan was studied. The equilibrium capacities based on the Langmuir analysis were 1.54, 2.66, 1.11, 1.25 and 1.03 mmol/g chitosan for Orange 10 (AO10), Acid Orange 12 (AO12), Acid Red 18 (AR18), Acid Red 73 (AR73) and Acid Green 25 (AG25) respectively. The batch adsorption rate for the five systems based on an intraparticle diffusion rate parameter derived from the plots of dye adsorbed versus the square root of time indicated that the adsorption mechanism was predominantly intraparticle diffusion but there was also a dependence on pore size as the dye diffuses through macropore, mesopore and micropore respectively.
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1. Introduction

The waste water from industry has always been a potential threat to the environment. Over $4.4 \times 10^6 \, \text{m}^3$ of aqueous waste and dye effluent were discharged per day in China (Marc, 1996) and this effluent has high BOD loading and long lasting colour that is aesthetically and environmentally unacceptable (Annadurai and Krishnan, 1997). These dyes may even be toxic and even carcinogenic (Vandevivere et al., 1998). The printing and textile industry mainly contribute to the discharge of dye effluent and the governments of different countries have enacted strict rules controlling the discharge of waste. In order to minimize the pollution, manufacturers and government officials are seeking for solutions to tackle the problem in an efficient way.

Existing effluent treatment processes can only remove half of the dyestuff lost in the residual liquors. People are looking for a system which can remove most of the colour and generate reusable water from the effluent. A range of adsorption systems for dye removal have been investigated extensively, such as trickling filter (Lin and Lin, 1993), activated sludge (Ganesh et al., 1994), chemical coagulation (Vandevivere et al., 1998), carbon adsorption (Walker and Weatherley, 2000) and photodegradation processes (Chu and Ma, 2000; Chu and Tsui, 1999).

Activated carbon is a highly effective adsorbent for water treatment, but it is an expensive adsorbent (Pollard et al., 1992). Cheaper precursors for activated carbon have been developed and tested with varying degrees of success; these include corn cob (Tsai et al., 1998), bagasse (Valix et al., 2004), pecan shells (Ahmedna et al., 2000), waste tire (Mui et al., 2004) among many others. In addition to activated carbons, several other available cheap resources have been studied, including peat (Brown et al., 2001), pith (Ho and McKay, 1999; Namasivayam et al., 2001) and other agricultural by-products (Marshall and Johns, 1996).

A limited number of dye adsorption studies have been carried out on chitin and chitosan (Knorr, 1983). Several

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of these references related to adsorption to treat textile effluents. There is a lack of detailed critical analysis for the adsorption of dyes onto chitosan even though high sorption capacities have been obtained in several cases.

In this work, the adsorption of five Acid Dyes, namely, Acid Orange 10 (AO10), Acid Orange 12 (AO12), Acid Red 18 (AR18), Acid Red 73 (AR73) and Acid Green 25 (AG25) onto chitosan in an agitated batch adsorber was studied and the concentration versus time decay curves were measured. The experimental data were measured and analysed using an intraparticle diffusion adsorption model.

2. Methods

2.1. Adsorbent

The adsorbent used was a powdered form of chitin purchased from Sigma Chemical Company (practical grade, extracted from crab shells). All raw chitin was dried at 75 °C in an oven for 6 h and then was sieved into discrete particle size range from 355–500 μm.

2.2. Absorbates

Five different commercial available textile dyestuffs were used including four azo dyes (AO10, AO12, AR18 and AR73) and one anthraquinone dye (AG25). All dyestuffs were obtained from Aldrich Chemical Co. and used without any further purification process.

2.3. Preparation of chitosan

The sieved chitin was deacetylated to chitosan by using 48% sodium hydroxide solution (w/w) at 100 °C under nitrogen atmosphere for 1 h. Then, the product was washed with deionized water completely, dried at 70 °C

in an oven overnight and sieved again into several particle size ranges. The fractions were further dried in vacuum oven for one day and stored in desiccators. The degree of deacetylation was characterized by ^{1}H-NMR method and was found to be 53%. The surface area and pore-size distribution were determined by N_2 adsorption–desorption isotherm at −196 °C using Quantachrome Autosorb 1-CLP. The BET (Barrett et al., 1951) surface area was 70 m^2/g. The particle size distribution is shown in Fig. 1.

2.4. Concentration measurement and calibration

In order to calculate the concentration of the sample from each experiment, a calibration curve of each dye was first prepared using five different concentrations and the absorbance was measured using a Varian Cary 1E UV/VIS spectrophotometer over a range from 400 nm to 700 nm. The calibration checks were carried out in duplicate. Then, the maximum absorbance of each dye was plotted against a range of dye concentrations. From these results, the concentration of the dye was calculated with Eq. (1) and constant, k_{dye}, for each dye, (Table 1)

Dye Concentration (mmol/L)

$$= \text{Maximum Absorbance}/k_{dye} \qquad (1)$$

2.5. Batch kinetic adsorption study

These experiments were used to investigate the influence of initial dye concentration on the adsorption rate. An adsorption vessel in a batch stirred tank configuration was used in all of the experiments. The design of the standard agitated batch vessel has been described in previous papers (Cheung et al., 2000a; Choy et al., 2001; Furusawa and Smith, 1973). The standard tank configuration was utilized to obtain the relative dimensions of the vessel and its
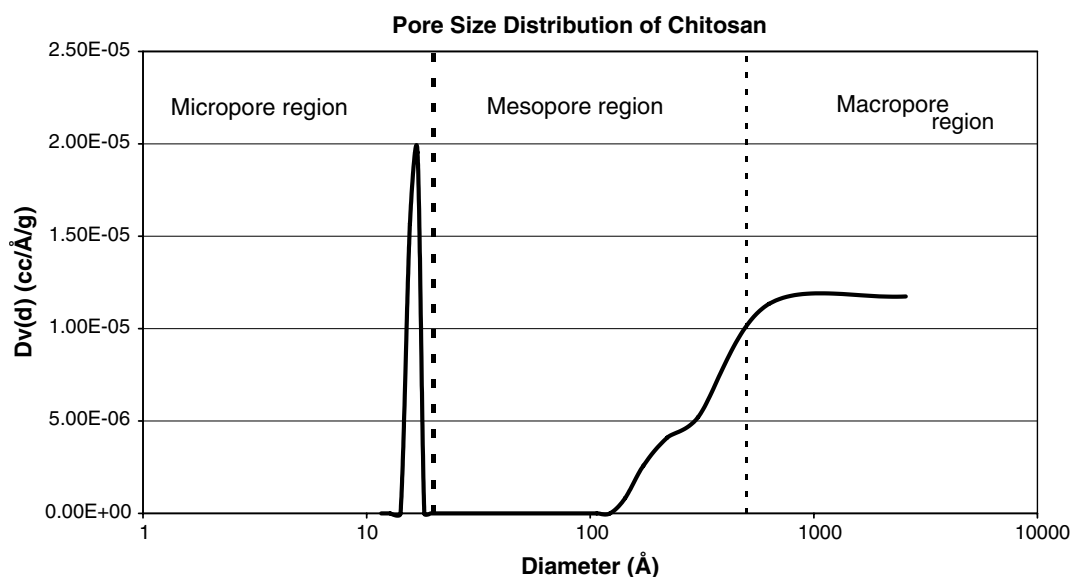

Fig. 1. Pore-size distribution of chitosan.