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Adsorption of Disperse Blue SBL dye by synthesized poorly crystalline hydroxyapatite

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Abstract

The present study has been undertaken to evaluate the adsorption in batch mode of a disperse dye (Disperse Blue SBL) by poorly crystalline hydroxyapatite synthesized by coprecipitation between $Ca(NO_3)_2$ and $(NH_4)_2HPO_4$ reagents in aqueous solution at room temperature. The adsorption experiments were carried out to investigate the factors that influence the dye uptake by the adsorbent, such as the contact time under agitation, adsorbent dosage, initial dye concentration, solution temperature, and pH. The experimental results show that the percentage of dye removal increases with increasing the amount of adsorbent, until the total discoloration. The adsorption isotherms follow the model of Langmuir with a high adsorption capacity. The adsorption was pH and temperature dependent.

Key words: hydroxyapatite; Disperse Blue SBL; adsorption isotherm; enthalpy of adsorption

Introduction

Color is the first indicator of contamination to be recognized in wastewater. Many industries, such as textile, tanning, printing, food, cosmetics, and so on, use organic compounds as dyes to color their final products. In the dyeing section of a textile industry, about 1,000 L of water are used for every 1,000 kg clothes processed (Garg *et al*., 2004). The presence of these species in wastewater, ever at very low quantities, is highly visible and undesirable; their presence in aquatic systems reduces light penetration, which retard photosynthetic activity and also has a tendency to chelate metal ions producing microtoxicity to fish and other organisms (MacKay *et al*., 1980). To depollute the dyeing wastewater, a number of methods including chemical oxidation and reduction, chemical precipitation and flocculation, photolysis, adsorption, ion pair extraction, electrochemical treatment, and advanced oxidation have been investigated. Most conventional adsorption systems use activated carbon in spite of its higher production cost and regeneration difficulty. Consequently, a number of low cost and easily available materials are being studied for the removal of different dyes from aqueous solutions at different operating condition (Wong and Hu, 2007; Dogan and Alkan, 2003; Chu and Chen, 2002; Annadurai *et al*., 2002; Ghosh and Bhattacharyya, 2002; Oscar and Sengil, 2002). In our laboratory, the work is in process to evaluate the possibility of the use of synthetic phosphates, essentially hydroxyapatite for wastewater pollution management.

Calcium hydroxyapatite (HAP), $Ca_{10}(PO_4)_6(OH)_2$, is an important inorganic material in biology and chemistry (Elliott, 1994; LeGeros, 1991; Arends *et al*., 1987). Their availability structure, ionic exchange property, adsorption affinity, and their characteristic to establish bonds with organic molecules of different sizes have conferred to this material to attract more attention during the last two decades. Calcium phosphates, especially apatites, are widely used for chromatographic purposes (Kawazaki, 1991; Gorbunoff, 1984) and are suitable for a number of biomedical applications, e.g., artificial bone and roofs of teeth, as well as a carrier for drug delivery (Barroug and Glimcher, 2002; Cannon and Rajpai, 1995; Aoki, 1994). In addition, this material can be a matrixes efficient of water purification. As of now, this material is much studied in the removal of rare earths and heavy metals (Gómez del Río *et al*., 2004; Krestou *et al*., 2004; Vega *et al*., 2003; Misra, 1998; Middelburg and Comans, 1991), but limited studies are investigated in the removal of organic molecules (Raîs *et al*., 2001; Bensaoud *et al.*, 1999). The aim of the present study was to determine the optimum conditions for the removal of a disperse dye (Disperse Blue SBL) from aqueous solution by synthesized hydroxyapatite.

1 Materials and methods

All reagents used in the preparation and the adsorption

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studies were of analytical grade. HAP was synthesized by coprecipitation according to the procedure described by Rey *et al*. (1989). A calcium nitrate solution $Ca(NO_3)_2{\cdot}4H_2O$ (Scharlau, Spain) (35.4 g in 0.5 L of distilled water) was immediately poured at room temperature into a di-ammoniumhydrogenphosphate $(NH_4)_2HPO_4$ (Riedel-de Haën, Germany) solution (34.8 g in 1 L of distilled water), and the pH of the solution was adjusted to 7 by ammoniac solution. After low agitation for 2 h, the suspension was filtered on a large Buchner funnel, washed with distilled water, dried at 70°C for 48 h, and sieved such as the size of the particles are lower than 63 μm.

A specimen was characterized by X-ray diffraction using a XPERT-PRO diffractometer system (Philips, the Netherlands), Infrared spectroscopy IR using VERTEX 70 spectrophotometer (Bruker Optics, Germany). The Scanning Electron Microscopy (SEM) was achieved using a DSM 950 electronic microscope (Carl Zeiss Optical, USA). The specific surface area was determined according to the BET method using N_2 adsorption. The calcium content of the solid was determined by complexometry with EDTA and the phosphate ion concentration was obtained by spectrophotometry of phospho-vanado-molybdic acid.

The Disperse Blue SBL was obtained from a textile firm as a commercially available dye formulation and was used without further purification. The chemical structure of Disperse Blue SBL is shown in Fig.1.

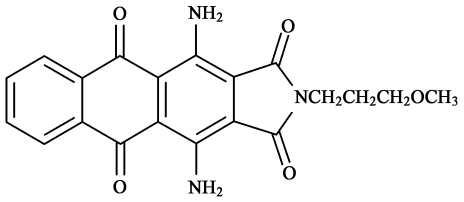

Fig. 1 Chemical structure of Disperse Blue SBL.

The solutions were prepared by dissolving requisite quantity of the dye in distilled water. The effect of adsorbent dosage on the adsorption kinetic was obtained in 500 ml by varying the amount of hydroxyapatite from 0.05 to 1 g/L. Adsorption isotherms have been obtained with different initial concentrations of dye with 0.1 g/L of poorly crystalline apatite at different solution temperatures. The effect of pH on the adsorption was carried out by varying pH from 4 to 10 by addition of HCl (1 mol/L) or NaOH (1 mol/L). The mass of poorly crystalline was 0.1 g/L.

The dye solutions were filtered through a 0.45 μm Millipore HA membrane filter, and the concentrations of dyes were determined from its UV-Vis absorbance characteristic with the calibration method. A Jenway 6405 UV/Visible spectrophotometer (Jenway, England) was used. For this measurement, the wavelength of maximum absorption ($\lambda_{max.}$) was 585 nm. The quantity adsorbed was calculated by measuring the concentration of the solution before and after adsorption using Eq.(1):

$$q = \frac{(C_0 - C)}{R} \tag{1}$$

where, q (mg/g) is the quantity of dye adsorbed per unit mass of adsorbent, C_0 (mg/L) is the initial dye concentration, C (mg/L) is the dye concentration at any time, and R (g/L) is the ratio of the mass of adsorbent per litre of aqueous solution.

2 Results and discussion

2.1 Characterization of the absorbent

X-ray diffraction patterns of the absorbent (Fig.2a) showed reflections characteristic of poorly crystalline apatite similar to bone mineral, no other crystalline phase was detected. The sample yielded broad and overlapping reflections, indicating its low crystallinity. The generated IR spectra dominated mainly by bands characteristic of apatitic phosphates and water molecules (Fig.2b). The spectra showed bands located at 3,564 cm^{-1} and at 635 cm^{-1}, both assigned to apatitic OH^- ions, and bands at 960 cm^{-1} and 1,142–1,209 cm^{-1} representative of apatitic HPO_4^{2-}, which indicates the nonstoichiometry of the ap-

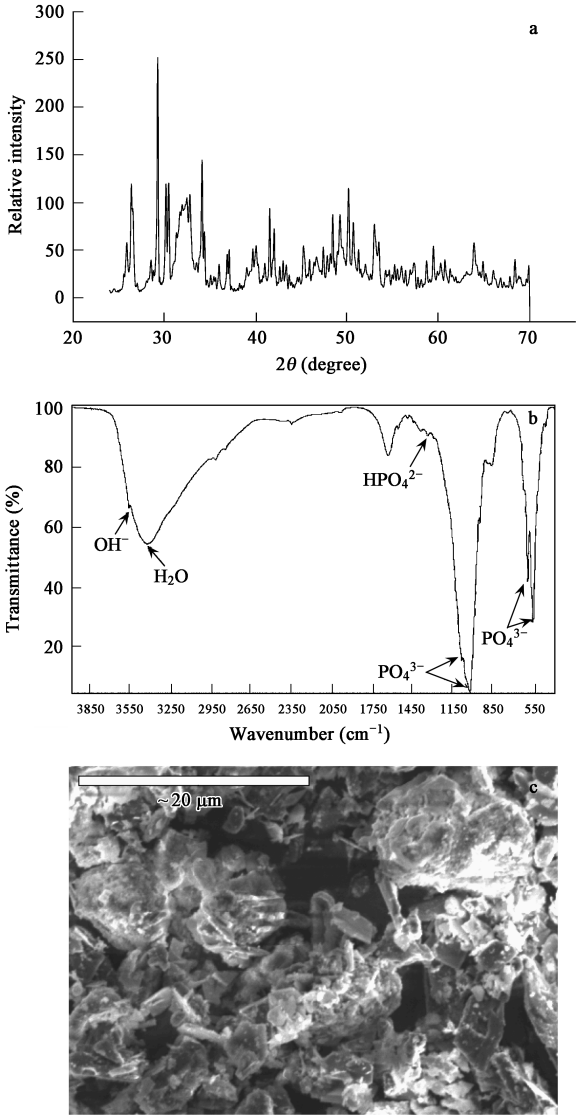

Fig. 2 XRD patterns (a), IR spectra (b), and SEM (c) of poorly crystalline apatite.

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atite. The Scanning Electron Micrograph (Fig.2c) shows phosphatic particles in irregular forms and at different sizes.

Chemical analyses showed that the apatite is calcium deficient. Its Ca/P ratio was 1.42, which is lower than that of stoichiometric hydroxyapatite (1.67). This finding is in agreement with the presence of hydrogenophosphate groups as observed in the IR spectra. The specific surface area of the synthetic apatite was 137 m^2/g.

2.2 Effect of adsorbent mass on the kinetics of adsorption

Kinetics of retention describes the rates of reactions that permit to determine the contact time under agitation put to reach the equilibrium of adsorption. Fig.3 shows the changes of adsorbed quantities of Disperse Blue SBL per gram of adsorbent. The adsorption was found to be rapid at the initial period of contact time and then to be slow and stagnates with the increase in contact time. In addition, the percentage of dye removal was increased and equilibrium time was decreased with the increase in adsorbent dose. The adsorption was 100% at adsorbent dose of 0.5 g/L within 30 min. The increase in the adsorption with adsorbent dose can be attributed to the availability of more adsorbent sites. But the quantity adsorbent per unit of adsorbent dose after 3 h of agitation decreases from 175 to 63.7 mg/g as the adsorbent dose increases from 0.05 to 0.3 g/L. This may be attributed to overlapping or aggregation of adsorption sites resulting in decrease in the total adsorbent surface area available to the dye molecules and an increase in diffusion path length.

2.3 Effect of temperature on adsorption

2.3.1 Adsorption isotherm

The temperature has two major effects on the adsorption process. Increasing the temperature is known to increase the rate of diffusion of the adsorbed molecules across the external boundary layer and the internal pores of the adsorbent particles, owing to the decrease in the viscosity of the solution. In addition, changing temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate (Al-qodah, 2000). The adsorption isotherms of Disperse Blue SBL by hydroxyapatite are depicted in Fig.4. The figure indicates that the adsorbed quantity increases with the increase in the equilibrium concentration according to L-shape in the classification of Giles *et al*. (1974). This result indicates that as more sites in the substrate are filled, it becomes increasingly difficult for the solute molecules to find an available vacant site. This could be either because the dye molecules are more likely to be adsorbed on monolayer on a surface containing a finite number of identical sites or because there is no strong competition with the solvent.

The description of the adsorption isotherms has been achieved by applying the linear form of Langmuir equation proposed by Stumm and Morgan (1981):

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K \times q_m} \times \frac{1}{C_e} \quad (2)$$

where, q_e (mg/g) is the amount of dye adsorbed at equilibrium, q_m (mg/g) is the monolayer coverage of the adsorbent particle in terms of mg dye/g adsorbent, K (L/mg) is the Langmuir equilibrium constant, and C_e (mg/L) is the equilibrium concentration.

A plot of $1/q_e$ versus $1/C_e$ yields q_m and K. From the data obtained, the maximum adsorption capacity q_m and the constant of adsorption K estimated are listed in Table 1.

Table 1 Langmuir isotherm constants q_m and K for the adsorption of Disperse Blue SBL by poorly crystalline apatite at different temperatures

T (°C)	q_m (mg/g)	K (L/g)	r^2
30	243.90	0.240	0.98
40	312.50	0.087	0.95
50	434.78	0.037	0.99
60	357.14	0.017	0.97

Table 1 shows that except for 60°C, the maximum capacity of adsorption of Disperse Blue SBL increases from 243.90 to 434.78 mg/g by increasing the temperature from 30 to 60°C. Meanwhile the Langmuir equilibrium constant (K) decreases from 0.240 to 0.017 L/g.

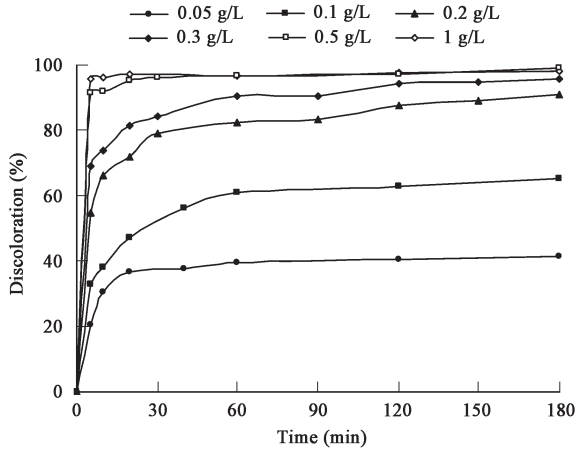

Fig. 3 Kinetics of adsorption of Disperse Blue SBL onto poorly crystalline apatite at different adsorbent dosages.

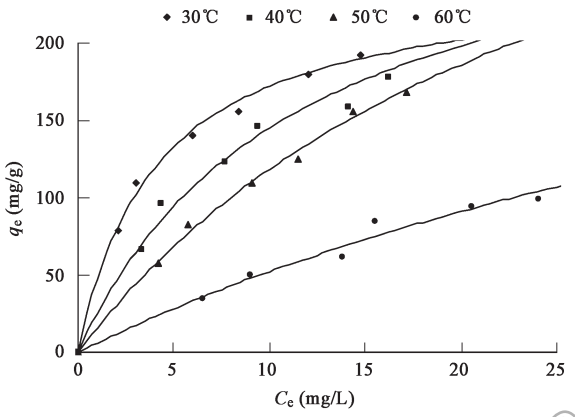

Fig. 4 Adsorption isotherms of Disperse Blue SBL by poorly crystalline apatite at different temperatures.

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2.3.2 Activation parameter

The enthalpy of adsorption was calculated from the linear form of Van't Hoff equation (Banerjee *et al*., 1997):

$$\ln K = \ln K_0 - \frac{\Delta H}{RT} \quad (3)$$

where, K is the Langmuir equilibrium constant of adsorption at the temperature T, K_0 (L/g) is the temperature independent factor, H (J/mol) is the enthalpy of adsorption, R (8.31 J/(K·mol) is the gas constant, and T (K) is the solution temperature. A plot of ln$K$ versus the reciprocal of absolute temperature ($1/T$) gives straight line as shown in Fig.5, and the corresponding enthalpy of adsorption was determined from the slope of linear plot. The enthalpy of adsorption obtained is –73.5 kJ/mol. This value of the change in enthalpy indicates that the adsorption process is exothermic and is chemical in nature involving strong forces of attraction (Eren and Afsin, 2008).

2.4 Effect of pH

Both adsorbate and adsorbent may have functional groups, which are affected by the concentration of hydrogen ions (H^+) in the solution, which are involved in the molecular adsorption process at the active sites of the adsorbent. Fig.6 shows the effect of pH on Langmuir saturated adsorption capabilities of Disperse Blue SBL by poorly crystalline apatite, with an initial concentration of 20 mg/L and a mass of poorly crystalline apatite of 0.1 g/L. The concentration of the dye solutions was determined taking holding amount the effect of the pH on the calibration curves.

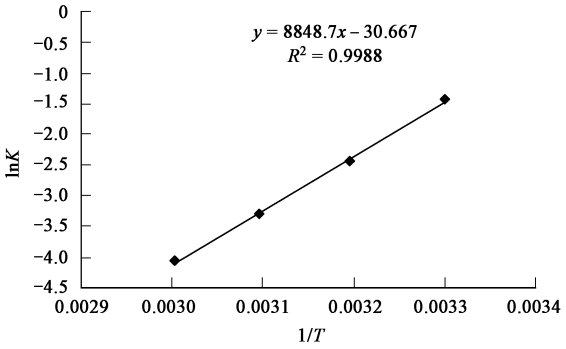

Fig. 5 Van't Hoff plot for adsorption of Disperse Blue SBL by poorly crystalline apatite.

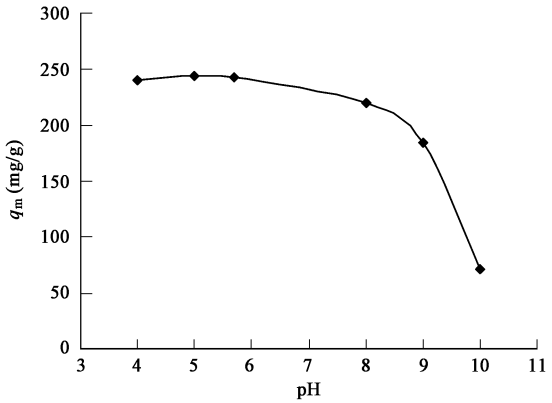

Fig. 6 Effect of pH on Langmuir saturated adsorption capabilities of Disperse Blue SBL onto poorly crystalline apatite.

It was found that the adsorption capability of Disperse Blue SBL decreases when the pH is above 7. These results can be interpreted on the following manner; the pH of the zero charge pH_{zc} of the hydroxyapatite is known to be 7.2. Hence, for pH values higher than 7.2, the surface of the hydroxyapatite becomes negatively charged and the opposite for pH < 7.2. Moreover, the dye is an anionic molecule; the electrostatic repulsion forces with hydroxyapatite were more significant for pH more than 7.2, which lead to the decrease of the adsorption quantities. Similar behavior has been observed by Yin *et al*. (2002) for the adsorption of BSA protein on hydroxyapatite.

3 Conclusions

This study shows that the synthesized poorly crystalline hydroxyapatite can remove Disperse Blue SBL dye from aqueous solutions. It has been found that the initial rate of adsorption was high. The adsorption isotherms follow the model of Langmuir with high adsorption capacities and high temperature dependency. The enthalpy of adsorption shows that the process was exothermic. The adsorption was greatly pH dependent, with a high uptake of dye at low pH and low uptake at high pH. These results show that the interactions between Disperse Blue SBL molecules and hydroxyapatite particles are essentially of an electrostatic nature. Finally, the use of calcium hydroxyapatite shows a greater potential for the removal of textile disperse dyes.

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