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ORIGINAL ARTICLE

Removal of Reactive Yellow 84 from aqueous solutions by adsorption onto hydroxyapatite

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Abstract The adsorption of a reactive dye, Reactive Yellow 84, from aqueous solution onto synthesized hydroxyapatite was investigated. The experiments were carried out to investigate the factors that influence the dye uptake by the adsorbent, such as the contact time under agitation, absorbent dosage, initial dye concentration, temperature and pH of dye solution. The experimental results show that the amount of dye adsorbed increases with an increase in the amount of hydroxyapatite. The maximum adsorption occurred at the pH value of 5. The equilibrium uptake was increased with an increase in the initial dye concentration in solution. The experimental isotherm data were analyzed using Langmuir isotherm equation. The maximum monolayer adsorption capacity was 50.25 mg/g. The adsorption has a low temperature dependency and was endothermic in nature with an enthalpy of adsorption of 2.17 kJ mol^{-1}.

1. Introduction

Wastewaters from dying and finishing operations in the textile industry are generally high in both color and organic content. Color removal from textile effluents has been the target of great attention in the last few years, not only because of its potential toxicity, but mainly due to its visibility problems (Yu-Li Yeh and Thomas, 1995; Morais et al., 1999). Recent estimates indicate that approximately 12% of synthetic textile dyes used each year is lost during manufacture and processing operations and 20% of these lost dyes enter the environment through effluents that result from the treatment of industrial wastewaters (Hwang and Chen, 1993; Nawar and Doma, 1989).

From an environmental point of view, the removal of synthetic dyes is of great concern. Among several chemical and

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physical methods, sorption has evolved into one of the most effective processes for decolorization of textile wastewaters. The most commonly used adsorbent for color removal is activated carbon, because of its capability for efficiently adsorbing a broad range of different types of adsorbates. At present, there is a growing interest in using low-cost and non conventional alternative materials instead of traditional adsorbents. Several researchers have been studying the use of alternative materials, which, although less efficient, involve lower costs.

Calcium hydroxyapatite (HAP), $Ca_{10}(PO_4)_6(OH)_2$, is an important inorganic material in biology and chemistry (LeGeros, 1991; Elliott, 1994; 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. The interaction between macromolecules and hydroxyapatite has received special attention because of the physicochemical properties of this material, which is similar to bone mineral, as well as its biocompatibility, osteoconduction, and bioresorption properties (Urist et al., 1994; Marcus et al., 1996). Hydroxyapatite is widely used for chromatographic purposes (Kawasaki, 1991; Gorbunoff, 1984) and is suitable for a number of biomedical applications, e.g., artificial bone and roofs of teeth as well as a carrier for drug delivery (Aoki, 1994; Barroug and Glimcher, 2002; Cannon and Bajpai, 1995). In addition, this material can be efficient matrixes of water purification. As of now, this material is very 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 (Bensaoud et al., 1999; Lin et al., 2009; Wei et al., 2010).

In our laboratory, the work is in process to evaluate the possibility of the use of synthetic hydroxyapatite for wastewater pollution management. Our previous study has shown that the synthesized hydroxyapatite can totally remove disperse dye; disperse blue SBL, from aqueous solutions (Barka et al., 2008). The aim of the present study was to determine the optimum conditions for the removal of an azo reactive dye, Reactive Yellow 84 (CI) from aqueous solutions by synthesized hydroxyapatite. The factors that influence the dye uptake by the adsorbent were investigated.

2. Materials and methods

All reagents used in the preparation and the adsorption studies were of analytical grade. Calcium hydroxyapatite HAP was synthesized by double decomposition according to the procedure described by Rey et al. (1989). A solution composed of 35.4 g of $Ca(NO_3)_2{\cdot}4H_2O$ (Scharlau, Spain) in 0.5 l of distilled water was immediately poured at room temperature into a solution composed of 34.8 g of di-ammonium hydrogenphosphate $(NH_4)_2HPO_4$ (Riedel-de Haën, Germany) in 1 l of distilled water. The pH of the solution was adjusted to seven by ammoniac solution. After low agitation for 2 h, the suspension was briefly filtered on a large Büchner funnel, washed with distilled water, dried at 70 °C for 48 h and sieved in particles sizes lower than 63 μm.

XRD patterns of a sample powered by a XPERT-PRO diffractometer system (Philips, Netherlands) showed reflections characteristic of poorly crystalline apatite similar to bone mineral. No other crystalline phase was detected. The generated IR spectra obtained by using VERTEX 70 spectrophotometer (Bruker Optics, Germany) was dominated mainly by bands characteristic of apatitic phosphates and water molecules. The spectra showed bands assigned to apatitic OH^- and HPO_4^{2-} ions, which indicates the non-stoichiometry of the apatite. These results were confirmed by the chemical analyses which showed that the apatite is calcium deficient, its Ca/P ration was 1.42. This value is lower than that of stoichiometric hydroxyapatite (1.67). The specific surface area of the synthetic apatite determined according to the BET method using N_2 adsorption was 137 m^2/g.

The Reactive Yellow 84 was obtained from a textile firm as a commercial available dye formulation designed as Suncion Yellow H-E4R. The chemical structure of the dye is shown in Fig. 1. Solutions were prepared by dissolving requisite quantity of the dye in distilled water. The volume of colored solution was 500 mL.

Adsorption experiments were carried out by varying the initial concentration from 10 to 40 mg L^{-1}, the amount of hydroxyapatite from 0.4 to 1.6 g L^{-1}, the temperature from 20 to 50 °C and the pH from 2.1 to 10. The pH was adjusted to a given value by the addition of HCl (1 mol L^{-1}) or NaOH (1 mol L^{-1}) and was measured using a Schott titroline (TE96) pH-meter.

The dye solutions were filtered by Millipore membrane filter type 0.45 μm HA, and the concentrations of dyes were determined from its UV-Vis absorbance characteristic with the calibration method. A Jenway 6405 UV/Visible spectrophotometer was used. For this measurement, the wavelength of maximum absorption (λ_{max}) was 226 nm. The quantity adsorbed was calculated by measuring the concentration of the solution before and after adsorption using the following equation:

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

where q (mg g^{-1}) is the quantity of dye adsorbed per unit mass of adsorbent, C_0 (mg L^{-1}) is the initial dye concentration, C (mg L^{-1}) is the dye concentration at any time and R (g L^{-1}) is the mass of adsorbent per litre of aqueous solution.

3. Results and discussion

3.1. Effect of adsorbent mass on the kinetics of adsorption

Kinetics of retention describes speeds of reactions that permit to determine the contact time under agitation put to reach the adsorption equilibrium. The adsorption kinetics of Reactive Yellow 84 on hydroxyapatite was studied by changing the quantity of adsorbent (0.4 to 1.6 g L^{-1}) in the test solution and keeping unchangeable the initial dye concentration

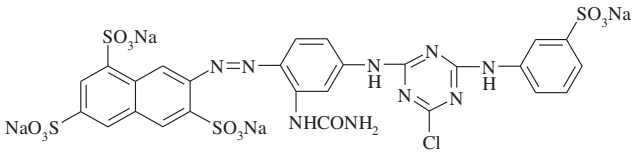

Figure 1 Chemical structure of Reactive Yellow 84.

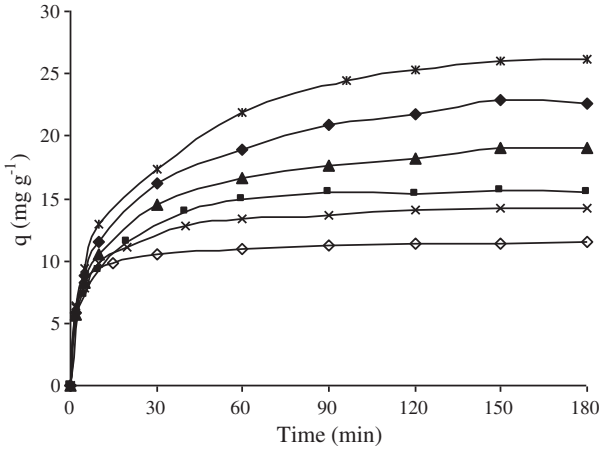

Figure 2 Kinetics of adsorption of Reactive Yellow 84 on HAP at different adsorbent dosages. Adsorbent dosages: * 0.4 g L^{-1}; ♦ 0.6 g L^{-1}; ▲ 0.8 g L^{-1}; ■ 1 g L^{-1}; × 1.2 g L^{-1}; ◇ 1.6 g L^{-1}.

(20 mg L^{-1}), temperature and pH. Fig. 2 shows change of adsorbed quantity per gram of adsorbent, the adsorption was found to be rapid at the initial period of contact time and then to be slower with the increase in contact time. In another case, as adsorbent dose increases, the quantity of dye adsorbed per mass of adsorbent and the equilibrium time decrease consequently. Additionally, the percentage of decoloration increases from 52% to 92% by increasing the amount of hydroxyapatite from 0.4 to 1.6 g L^{-1}, this is due to the surface area available by more adsorbent particles.

3.2. Effect of initial dye concentration on adsorption process

The kinetics of adsorption of Reactive Yellow 84 at different initial concentrations was achieved. Fig. 3 shows the extent of dye adsorption as function of reaction time. It was found that, as the initial concentration increases, the equilibrium time and the amount of dye adsorbed per gram amount of adsorbent increase. It is further noted that the amount of Reactive Yellow 84 increases from 11.48 to 26.19 mg g^{-1} by increasing

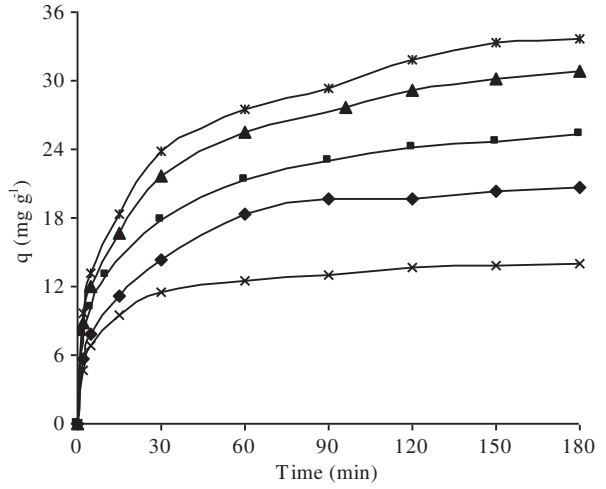

Figure 3 Kinetics of adsorption of Reactive Yellow 84 at different initial concentrations. Initial concentrations: × 10 mg L^{-1}; ♦ 15 mg L^{-1}; ■ 20 mg L^{-1}; ▲ 30 mg L^{-1}; * 40 mg L^{-1}.

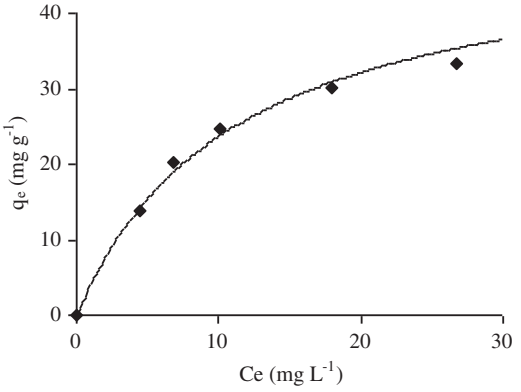

Figure 4 Adsorption isotherm of Reactive Yellow 84 on hydroxyapatite. Continues curve: Langmuir isotherm model.

the initial concentration from 10 to 40 mg L^{-1}. The kinetics adsorption curves are smooth and continuous leading to saturation of hydroxyapatite by Reactive Yellow 84. This result suggests the possibility of mono-layer coverage adsorption of Reactive Yellow 84 on hydroxyapatite (Yadava et al., 1987). From the kinetics curves, the amounts of dye adsorbed after 180 min of contact time are illustrated in Fig. 4. This isotherm belongs to type L of the Giles et al. (1960) classification, which 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 adsorbed molecules are more likely to be adsorbed on monolayer on a surface containing a finite number of identical sites and there is no strong competition from the solvent.

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

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K \cdot qm} \cdot \frac{1}{C_e} \tag{2}$$

where q_m (mg g^{-1}) is the mono-layer coverage of the adsorbent particle in terms of mg dye/g of adsorbent, q_e (mg g^{-1}) is the amount of dye adsorbed at equilibrium, K (L mg^{-1}) is the Langmuir equilibrium constant and C_e (mg L^{-1}) is 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 K estimated are respectively 50.25 mg g^{-1} and 0.089 L mg^{-1}. The Langmuir maximum adsorption capacity of hydroxyapatite for Reactive Yellow 84 was lower than that of Disperse Blue SBL (243.90 mg g^{-1}) obtained in our previous work (Barka et al., 2008). This result can be due to the difference of molecular structure and the interactions between each dye and the surface of hydrodyapatite.

Although the affinity of hydroxyapatite for the removal of dyes from aqueous solution was less than that of activated carbon cited in previous works (Al-Degs et al., 2000; Barka et al., 2006), it can take a good place between low-cost adsorbents investigated in the removal of dyes (Barka et al., 2009; Akkaya et al., 2007; Ceyhan and Baybas, 2001; Yener et al., 2006).

3.3. Effect of temperature on adsorption process

The temperature has two major effects on the adsorption process. Increasing the temperature is known to increase the rate

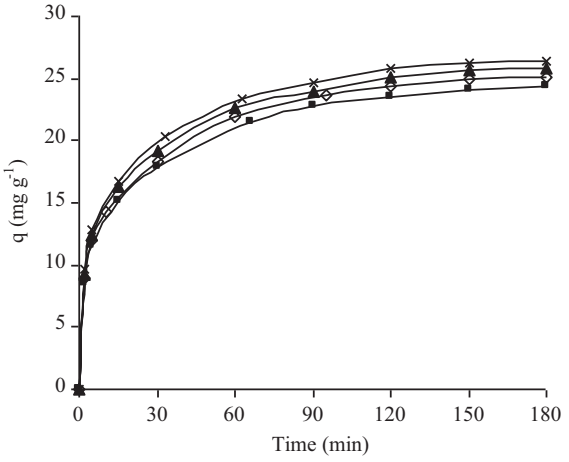

Figure 5 Effect of temperature on the kinetics of adsorption of Reactive Yellow 84 on HAP. Temperature: ■ 20 °C; ◇ 30 °C; ▲ 30 °C; ×50 °C.

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 et al., 2000). Fig. 5 shows the results of experiments carried out at different solution temperatures. The removal of Reactive Yellow 84 increases from 24.31 to 26.45 mg g^{-1} by increasing the temperature of the solution from 20 to 50 °C, indicating that the process to be endothermic. This kind of temperature dependence of the amount of the dye adsorbed may be due to the fact that a possible mechanism of interaction is the reaction between the sulfonyl groups of Reactive Yellow 84 and the cationic sites of hydroxyapatite such a reaction could be favoured at higher temperatures.

The enthalpy of adsorption (ΔH) has been calculated using the following equation:

$$q_e = q_0 \exp\left[-\left(\frac{\Delta H}{RT}\right)\right] \quad (3)$$

where q_e (mg g^{-1}) is the amount of dye adsorbed at equilibrium, q_0 is the temperature independent factor (mg g^{-1}), ΔH is the enthalpy of adsorption (J mol^{-1}), R is the gas constant (8.31 J K^{-1} mol^{-1}). The linear transformation of this equation expressed by ln (q_e) as function of $1/T$ gives a straight line whose slope is equal to $-\Delta H/R$; the result was shown in Fig. 6. The slope of the linear curve was −262.6, which correspond to an enthalpy of adsorption of 2.17 kJ mol^{-1}. The enthalpy of adsorption was very lower and positive indicating that the process is endothermic, and hence it can be concluded that the process is governed by interactions of physical nature (Netpradit et al., 2004).

3.4. Effect of pH on the adsorption process

The pH is one of the most important factors controlling the adsorption of dyes onto suspended particles, because both adsorbed molecules and adsorbent particles may have functional groups which are affected by the concentration of hydrogen ions (H^+) in the solution and which are involved in the molecular adsorption process at the active sites of adsorbent. Fig. 7

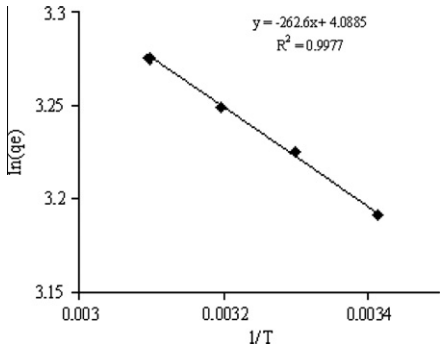

Figure 6 Plot of ln(q_e) versus $1/T$.

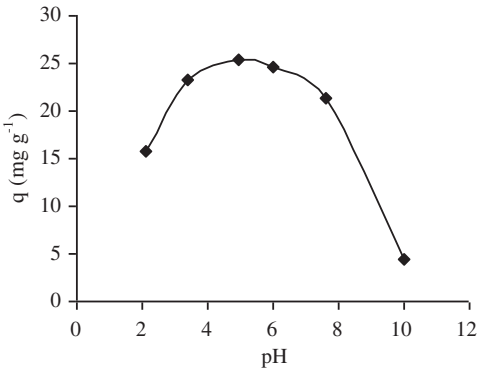

Figure 7 Effect of pH on the adsorption of Reactive Yellow 84 onto hydroxyapatite.

shows the amount of Reactive Yellow 84 adsorbed for different pHs. It was found that above pH = 7 and below pH = 3 the adsorption of the dye decreases.

The pH of the zero charge pH_{zc} of the hydroxyapatite is known to be 7.4 (Corami et al., 2008), for pH values higher than 7.4, the surface of the hydroxyapatite becomes negatively charged and this is the opposite for pH < 7.4. Moreover, the dye is a weak acid, it dissociate less towards an acid pH and is found consequently in neutral electrical form.

From the figure, it can be seen that the amount of dye adsorbed on the hydroxyapatite is high for pH between 3 and 7.5, which indicates that the positive form of hydroxyapatite is responsible for adsorption in this range. For basic pH, the decrease of the amount of adsorbed dye molecules is prevented by the repulsive electrostatic forces existing between the negative charged surface of hydroxyapatite and ϕ-SO_3^- groups of the dye predominant in this range of pH.

The decrease of the amount of adsorption below pH = 3 can be due to the ionization of the amine and amide groups of the dye with H^+, which leads the molecules of the dye to be positively charged. The repulsive electrostatic forces of dye molecules positively charged with the positively charged surface of the adsorbent increase. Consequently, adsorption decreases.

4. Conclusion

Hydroxyapatite is efficiently utilized as an adsorbent for the removal of Reactive Yellow 84 dye from the aqueous

solutions. It has been found that, the adsorbed quantity of dye increases with an increase in the amount of hydroxyapatite. The amount of dye adsorbed was high with high initial dye concentration according to Langmuir model. The Langmuir adsorption capacity was 50.25 mg g^{-1}. The adsorption has a low temperature dependency and was endothermic with an enthalpy of adsorption of 2.17 kJ mol^{-1}. The pH of solution affects both the surface of hydroxyapatite and dye molecule charge. It was found that adsorption was disfavoured in acidic and basic ranges. The interactions between Reactive Yellow 84 molecules and hydroxyapatite particles are essentially of physical nature. Finally, the use of hydroxyapatite shows a greater potential for the removal of reactive textile dyes, as no costly equipment is required.

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