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Removal of a textile dye by adsorption on synthetic calcium phosphates

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ABSTRACT

The objective of this study was to investigate the ability of synthetic calcium phosphates to remove a textile dye from aqueous solutions. The adsorption of Reactive Yellow 4 (RY4) on apatitic tricalcium phosphate (PTCa) and apatitic octocalcium phosphate (OCPa) from aqueous solutions was investigated. The kinetic study shows that equilibrium is quickly obtained for both phosphates. The kinetic analysis showed that the pseudo-second-order model had the best fit to the experimental data. The adsorption isotherms of the dye by both phosphates were correlated with Langmuir and Freundlich models depending on the phosphate studied. In addition, the maximum adsorption capacity decreased from 35.50 to 31.86 mg/g and 29 to 19.85 mg/g for PTCa and OCPa, respectively, when the temperature was increased from 25 to 45 °C. The thermodynamic evaluation of RY4 adsorption on both phosphates revealed that the adsorption phenomenon was a spontaneous, exothermic and physical process. Accordingly; synthetic calcium phosphates have been shown to be a very efficient and low-cost adsorbent, and a promising alternative for eliminating dyes from industrial wastewaters.

Contents

1. Introduction

The problems of water resources and pollution are increasingly on the agenda. Many industries like textile or cosmetic industry use for their end products of organic compounds in particular colors. In Morocco the textile industry, representing 31% of all Moroccan industries whose reactive dyes are widely used for dyeing wool and nylon. In the textile industry, about 1000 l of water are used per 1000 kg of clothes processed in dyeing [1]. Thus the releases of this industry are loaded dyes [2] and present a real danger to the environment due to the high water consumption and the important wastewater discharges rejected without any treatment. The first step of removal of dyes in the wastewater is a physico-chemical treatment by adding chemical reagents; then a biological step occurs using activated sludge in aeration [3]. Note, however, that dyes are poorly biodegradable where there is a limiting factor of biological treatment.

Other physico-chemical treatments are currently used. They include the adsorption on clay as sepiolite, zeolite, montmorillonite, smectite, bentonite, alunite and perlite [4–7]. All these methods are significantly different in terms of discoloration, process and economic

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balance [8,9]. Recently, calcium phosphates are very much studied in the removal of heavy metal ions [10], fluoride [11], nitrobenzene [12] and protein [13]. Barka et al. [14,15] have reported that the natural phosphate and poorly synthesized crystalline hydroxyapatite were used for the removal of dyes from aqueous solutions. The results showed that both materials were effective to remove dyes.

Hydroxyapatite (Ca10(PO4)6(OH)2, HAP), a bioceramic analogous to the mineral component of bone, has been used extensively in such fields as bone repairs, bone implant and bioactive materials due to its excellent biocompatibility, slow biodegradation, osteoconductivity and mechanical properties [16–19]. Calcium phosphates, especially apatites, present remarkable interest, 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. In addition, this material can be efficient matrixes of water purification.

In this context, we are interested in the possibility of using synthetic calcium phosphate as apatitic tricalcium phosphate, which is a solid with atomic ratio of Ca/P, equal to 1.5, and octocalcium phosphate apatite of Ca/P ratio, equal to 1.33, in order to eliminate the reactive dye; Reactive Yellow 4 (RY4), from aqueous solution. The Langmuir and Freundlich models were used to fit the equilibrium isotherm.

2. Materials and methods

2.1. Materials used

2.1.1. Adsorbents

The adsorption tests were conducted on two calcium phosphates: apatitic tricalcium phosphate (PTCa) and phosphate apatitic octocalcium (OCPa).

The first one (PTCa) was prepared at room temperature by a double decomposition method [20]. The solution A (47 g of calcium nitrate Ca $(NO_3)_2 \cdot 4H_20$ (Scharlau, Spain) in 550 ml of distilled water + 20 ml of ammonia solution) was added quickly at room temperature into the solution B (26 g of di-ammoniumhydrogenphosphate$(NH_4)_2HPO_4$ (Riedel-de Haën, Germany) in 1300 ml of distilled water + 20 ml ammonia solution). The precipitate was filtered, washed, and dried at 80 °C for 24 h.

The second one, OCPa was also developed by a fast coprecipitation in a rural hydroalcoholic solution (50% ethanol by volume) between a calcium solution [A'] and a basic phosphate solution [B'] [21]. The solution A'(30 mmol of nitrate calcium Ca $(NO_3)_2 \cdot 4H_20$ (Scharlau, Spain) in 100 ml of distilled water and 100 ml of ethanol) was immediately poured at 37 °C into a solution B'(30 mmol of di-ammoniumhydrogenphosphate$(NH_4)_2HPO_4$ (Riedel-de Haën, Germany) in 250 ml of distilled water, 45 ml of a solution of ammonia and 295 ml of ethanol). The coprecipitate was filtered and then dried in an oven at 80 °C for 24 h.

Both phosphates were characterized by chemical and physical analysis. The calcium content in the solid was determined by complexometry with EDTA and the phosphate ion content by spectrophotometry of phospho-vanado-molybdic acid. The specific surface area was determined according to the BET method using N_2 adsorption (Table 1). Infrared spectroscopy IR was carried out after dispersion of anhydrous KBr (about 2 mg product to 200 mg of KBr) using TENSOR 27 spectrophotometer (Bruker Optics, Germany) (Figs. 1 and 2).

Table 1
Characteristics of phosphates used.

Name	Ca/P	Specific surface (m^2/g)
PTCa	1.50	62
OCPa	1.33	58

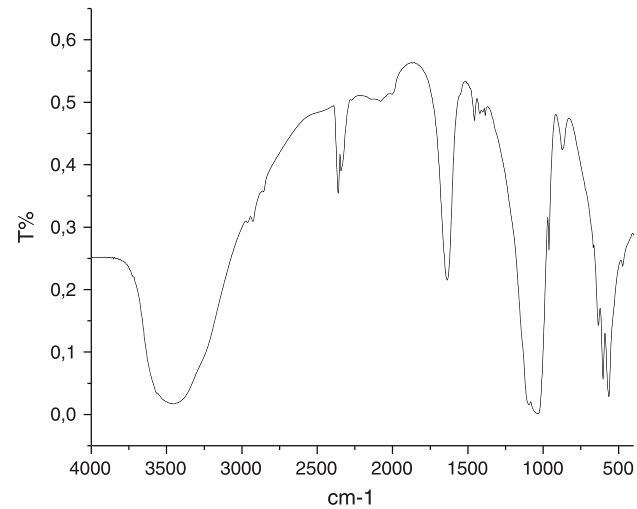


Fig. 1. Infrared absorption spectrum of PTCa of Ca/P = 1.5.

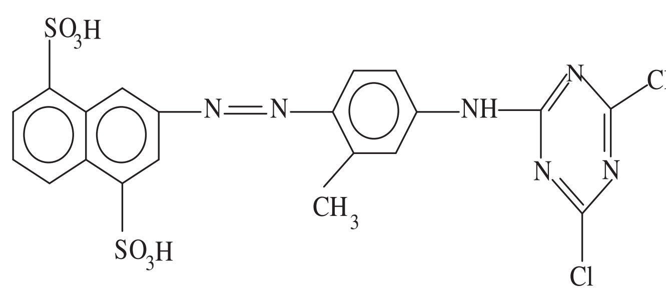
These spectra correspond with the two phosphate apatitic compounds

$Ca9\square(PO_4)5(HPO_4)(OH)\square$ PTCa

$Ca8\square2(PO4)3.5(HPO4)2,5(OH)0,5\square1.5$ OCPa.

2.2. Adsorbate

The Reactive Yellow 4 (C.I) was obtained from a textile firm as a commercially available dye formulation and was used without further purification. It is a soluble dye in water due to the presence of two solubilizing groups (SO_3H).



Chemical structure of dye (C.I. Reactive Yellow 4).

The yellow color is due to the grouping diphenylparaazolonique. The grouping dichlorotriazinique ensures reactivity of the molecule with the textile fiber. The solutions ware prepared by dissolving the required amount of dye in distilled water .The concentration of the dye was determined at 385 nm, using UV spectrophotometer ("UV-2005", Selecta, Spain).

2.3. Experimental protocol

The effect of solid quantity on removal of Reactive Yellow 4 (RY4) was investigated in batch experiments by adding various amounts of adsorbent in the range of 0.05–0.4 g powder into a test tube containing 10 ml of the dye solution. The initial dye concentrations of the solutions were fixed at 100 mg/l, for all batch experiments. The suspension was then stirred for 1 min, after which time the solution was coagulated and settled and the supernatant was analyzed for the remaining dye.

To study the kinetics of adsorption of the dye at 25 °C, a volume of 10 ml of the dye at concentration 100 mg/l was placed in contact with 200 mg of the adsorbent in a test tube. The mixture was stirred at constant speed (500 rpm) for one minute and then placed in a water