ORGINAL ARTICLE

Adsorption/desorption of Direct Yellow 28 on apatitic phosphate: Mechanism, kinetic and thermodynamic studies

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Abstract   In this study, the adsorption potential of apatitic tricalcium phosphate for the removal of Direct Yellow 28 (DY28) from aqueous solution has been investigated by using batch mode experiments. The effects of different parameters such as pH, adsorbent dosage, initial dye concentration, contact time, addition of ions and temperature have been studied to understand the adsorption behavior of the adsorbent under various conditions. The adsorbent has been characterized by pHzpc measurement, chemical analyses, FTIR, XRD and TEM. The Langmuir and Freundlich models are found to be the best to describe the equilibrium isotherm data, with a maximum monolayer adsorption capacity of $67.02 \, \text{mg g}^{-1}$. Thermodynamic parameters including the Gibbs free energy ΔG, enthalpy ΔH, and entropy ΔS have revealed that the adsorption of DY28 on the apatitic tricalcium phosphate is feasible, spontaneous and endothermic. Among the kinetic models tested for apatitic tricalcium phosphate, the pseudo-second-order model fits the kinetic data well. The introduction of orthophosphate ions in the medium causes a decrease of adsorption. The addition of Ca^{2+} ions favors the adsorption. The results of this study have demonstrated the effectiveness and feasibility of the apatitic tricalcium phosphate for the removal of DY28 from aqueous solution.

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1. Introduction

In Morocco the textile industry, represents 31% of all Moroccan industries whose reactive dyes are widely used for dyeing wool and nylon. The textile industry is one of the greatest generators of liquid effluent pollutants, due to the high quantities of water used in the dyeing processes. Textile wastewater is a complex and highly variable mixture of many polluting substances including dye (Robinson et al., 2001). Many dyes and pigments contain aromatic rings in their structures, which make them toxic, non-biodegradable, carcinogenic and mutagenic for aquatic systems and human health (Lian et al., 2009).

A variety of methods have been employed for removing dyes from colored effluents, such as membrane filtration, oxidation, coagulation–flocculation, biological treatment, electrochemical process and adsorption (Zhang et al., 2013; Maezawa et al., 2007; Szygula et al., 2009; Khataee and Dehghan, 2011; Del Río et al., 2011; Dogan et al., 2007). Among these tech-

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Peer review under responsibility of University of Bahrain.

niques, adsorption is a common technique used for dye removal from aqueous solution, mainly because it is relatively low in cost, robust, environmentally friendly and simple. A starting point in the development of an adsorption unit is the choice of an adsorbent among the various adsorbents.

Different kinds of adsorbents to remove dyes from aqueous solutions have been reported in the literature, such as untreated Coffee residues (Kyzas et al., 2012), activated palm ash (Hameed et al., 2007), Pine Cone (Mahmoodi et al., 2011), bamboo charcoal (Liao et al., 2012), peanut hull (Tanyildizi, 2011), chitosan (Iqbal et al., 2011), agricultural solid wastes (Mohd Salleh et al., 2011), sepiolite (Dogan et al., 2007), animal bone meal (El Haddad et al., 2012) and others.

Recently many researchers have proved the capability of calcium phosphate as adsorbents to remove many types of pollutants (Mourabet et al., 2011, 2012; El Boujaady et al., 2011; El Haddad et al., 2012, 2013). However, there is a lack of literature dealing with the possible application of apatitic tricalcium phosphate as adsorbents for dyes.

Nanocrystalline hydroxyapatite $[Ca_{10}(PO_4)_6(OH)_2,$ HAP] exhibits excellent biocompatibility and adsorption properties, and has been widely used as adsorbents for the adsorption and separation of biomolecules (Wei et al., 2009; Takagi et al., 2004), and for the removal of heavy metals, and phenol (Mobasherpour et al., 2012; Wei et al., 2010). The environmental risk of nanocrystalline HAP itself can be neglected because it has displayed good cytocompatibility (Lin et al., 2005). Moreover, calcium phosphate has also been used for the adsorption of amino acids (El Rhilassi et al., 2011, 2012). The present study was intended to remove Direct Yellow 28 (DY28) from aqueous solutions using apatitic prepared phosphate as a new cost adsorbent. The effect of various parameters like, adsorbent amount, dye concentration, contact time, pH and temperature, kinetics, equilibrium and thermodynamic studies was investigated. Furthermore the characterizations of PTCa have been donned by using XRD analysis, Transmission electron microscopy (TEM) and energy dispersive X-ray (EDX) analysis, and FTIR spectroscopy.

2. Materials and methods

2.1. Adsorbent

Apatitic tricalcium phosphate (PTCa) was prepared at room temperature by a double decomposition method (Heughebaert, 1977). The solution A (47 g of calcium nitrate $Ca(NO_3)_2 4H_2O$ (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 353 K for 24 h.

2.2. Adsorbate

The Direct Yellow 28 (DY28) 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 solubilizing groups (SO_3Na). The structure and characteristics of this dye are illustrated in Table 1.

The dye (DY28) is a large molecule symmetrical consisting of an azo group, two groups benzothiazols and two solubilizing groups (SO_3Na). The solutions were prepared by dissolving the required amount of dye in distilled water. The concentration of the dye was determined at 396 nm, using UV spectrophotometer ("UV-2005", Selecta, Spain).

2.3. Experimental protocol

To study the kinetics of adsorption of the dye at 298 K, a volume of 10 ml of solution concentration 100 mg/L of dye was placed in contact with 200 mg of adsorbent in a test tube. The mixture was stirred at a constant speed (500 rpm) for one minute and then placed in a water bath at 298 K. Later, the solid was separated from the mother solution by filtration through a sintered glass and the dye concentration was determined using the UV–vis spectrophotometer.

The quantity of dye per which was fixed gram of adsorbent was given by the following equation:

$$Q_t = (C_0 - C_t)V/m \tag{1}$$

where Q_t is the quantity of dye in mg per gram of adsorbent, C_0 and C_t are respectively the initial concentrations and time t of the dye (mg/L), V: volume of solution (L), m: mass of adsorbent used (g). The percentage of dye removal was calculated from the relationship:

$$\% \text{ of dye removal} = (C_0 - C_t)/C_0 \tag{2}$$

C_0 and C_t are respectively the initial concentrations and at the time t of the dye (mg/L).

The effect of solid quantity on removal of Direct yellow 28 (DY28) was investigated in batch experiments by adding various amounts of adsorbent in the range of 50–400 mg powder into a test tube containing 10 ml of 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.

2.4. Characterization of the adsorbent

Calcium phosphate was characterized by chemical and physical analyses. 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 (Brunauer–Emmett–Teller) method using N_2 adsorption. Infrared spectroscopy IR was carried out after dispersion of anhydrous KBr (about 1 mg product to 100 mg of KBr) using VERTEX 70 spectrophotometer (Bruker Optics, Germany). Particle size and morphology of as-dried powders were determined by TEM Tecnai G^2 (Philips CM120, USA) observations. An X-ray Powder diffraction (XRD) pattern was analyzed using X'Pert PRO (Germany) X-ray diffractometer with Cu K radiation.

The pH of the zero point charge (pH ZPC) has been determined by placing 0.2 g of adsorbent in glass stopper bottle containing 20 ml of 0.01 M NaCl solutions. The initial pH of these solutions has been adjusted by either adding 0.1 M NaOH or 0.1 M HCl. The bottles have been placed in an