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Synthesis of hydroxyapatite/clay and hydroxyapatite/pumice composites for tetracycline removal from aqueous solutions

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ABSTRACT

Synthesized hydroxyapatite/clay (HA-C) and hydroxyapatite/pumice (HA-P) composites were used for tetracycline (TC) uptake studies from aqueous solution and their uptake capacities were compared. HA-C and HA-P composites were synthesized by precipitation method and the structures of the synthesized composites were characterized by XRD, SEM and BET analyses. Cation exchange capacities of HA-C and HA-P were found to be 84 meq/100 g and 33 meq/100 g, respectively. The TC adsorption using HA-C and HA-P was studied on batch mode. Various parameters such as contact time, solution pH, initial TC concentration, composite dosage, salinity and temperature were optimized. Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm models were applied to the equilibrium data. The maximum adsorption capacity onto HA-C was found to be 76.02 mg/g and about four times larger than the adsorption capacity of the HA-P (17.87 mg/g). The results indicated that the TC uptake onto HA-C and HA-P composites is mainly by a surface complexation and ion-exchange mechanism which depend on the solution pH. The calculated values of thermodynamic parameters indicated that the TC adsorption is favorable, physicochemical in nature. The sorption process follows pseudo-second-order and intraparticle diffusion kinetic models. The TC adsorption mechanism by HA-C and HA-P has been proposed.

1. Introduction

Antibiotics are extensively used worldwide in human therapy and the farming industry and they are widely produced (Ji et al., 2010a,b; Ke Sun et al., 2011). Only a small portion of antibiotics could be metabolized or absorbed by humans and animals (Bound and Voulvoulis, 2004). Residues of antibiotics are accumulated in soil and environmental waters and they may lead to occurrence of resistant species (Daughton and Ternes, 1999). Tetracycline (TC) is often used in human therapy and veterinary. The low cost and the wide applications of TC have led to fair concerns with regard to unsafe residue in animal-production foods such as milk, meat, egg, cheese, and honey, which could be directly toxic or else provoke allergic response in some hypersensitive individuals. Therefore, efficient and inexpensive treatment methods for the removal of such compounds from the environment were developed (Dai et al., 2012; Ersan et al., 2013). TC antibiotics are a group of broad spectrum antimicrobial activities against a variety of disease-producing bacteria (Chang et al., 2009a,b,c). TC molecule is strongly polar and has three proton-active groups: the tricarbonylamide group (C-1-C-3), a dimethylammonium group (C-4) and phenolic diketone groups (C-10-C-12). It bears different charges on different sites depending on solution pH. TC is a cation (+00), below pH 3.3, a zwitterions (+-0), between pH 3.3 and 7.7 and

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an anion (+– or 0—) above pH 7.7 (Chang et al., 2009a,b,c) (Fig. 1).

Natural and nano materials such as graphene oxide (Gao et al., 2012), titania–silica composite (Brigante and Schulz, 2011), kaolinite (Li et al., 2010a), rectorite (Chang et al., 2009a), smectite (Li et al., 2010a,b); montmorillonite (Parolo et al., 2008), goethite (Zhao et al., 2011) and magnetite nanoparticles (Zhang et al., 2011) composed materials were used in previous studies.

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$; HAp) is a major inorganic constituent of teeth, bones and phosphate mineral rocks (Gupta et al., 2012). HAp has been investigated for the removal of many toxic metal ions, dyes and fluoride ions from aqueous solution (Wang et al., 2011). However, characteristic of HAp existing in the form of white powder therefore isolating the suspended fine solids from aqueous solutions after adsorption is not easy (Choi and Jeong, 2008; Dong et al., 2010). Therefore, HAp based composite materials have been investigated in order to improve its applicability for the water treatment (Dong et al., 2010). For example, the hydroxyapatite/polyacrylamide composite hydrogels (Jang et al., 2008a,b), hydroxyapatite/polyurethane composite foams (Jang et al., 2008a), hydroxyapatite/chitosan composite (Hou et al., 2012) and hydroxyapatite/magnetite composite (Dong et al., 2010) have been used to remove toxic metal and dye from aqueous solutions. Till now there have been no study regarding hydroxyapatite/clay and hydroxyapatite/pumice composite. The reason for choosing clay and pumice as a binding material for HAp is their high abundance in nature, non-toxicity and adsorption properties. In addition, studies for tetracycline removal by such composites have been not reported yet.

In this study, a novel and economic hydroxyapatite/clay (HA-C) and hydroxyapatite/pumice (HA-P) composites were synthesized by precipitation method and they were used in tetracycline (TC) removal from aqueous solutions. The effect of solution pH, composite dosage, the effect of presence of salinity and temperature were studied for the determination of optimum experimental conditions.

2. Materials and methods

2.1. Materials

Clay and pumice were supplied from Sivas and Kayseri-Basakpınar in Turkey, respectively. The type of clay mineral is kaolinite and composed from 59% SiO_2, 25% Al_2O_3 and other ions. They were washed with distilled water several times and dried at 50 °C in oven. Later, dried sample was grinded to a particle size below 0.125 mm.

2.2. Synthesis of HA-C and HA-P composites

The HA-C and HA-P composites were synthesized. Firstly, $Ca(NO_3)_2{\cdot}4H_2O$ (1.65×10^{-2} mol) was dissolved in 15 ml of distilled water in a 250 ml Erlenmeyer. 5 ml of concentrated ammonia was added and the solution was diluted with deionized water until the total volume of the solution was 30 ml. 1.0 g of clay was added into the solution with stirring. On the other hand, $(NH_4)_2HPO_4$ (9.9×10^{-3} mol) was dissolved in 30 ml of distilled water in a 250 ml Erlenmeyer and 10 ml of concentrated ammonia was added. The solution was added into the suspension containing clay and the mixture was kept on stirring for 10 min. Then, the mixture was placed in a water bath at 100 °C and stirred continuously for 10 min. The mixture was allowed to stand at room temperature overnight. Then, synthesized HA-C composite was filtered and washed with distilled water for 6–8 times. The HA-C composite was dried at 50 °C in oven (Kanai et al., 2003). The HA-P composite was obtained with the same method.

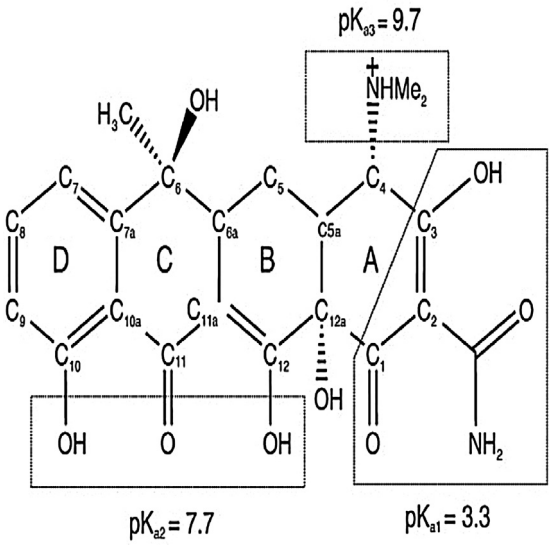

Fig. 1 – Moleculer structure of TC [Chang et al., 2009a,b,c].

2.3. Characterization of HA-C and HA-P composites

The powder X-ray diffraction patterns (XRD) of HA-C and HA-P before and after TC adsorption were recorded on Bruker AXS D8 Advance model powder diffractometer in order to study the structure of the composites. The surface morphology of HA-C and HA-P was observed by a scanning electron microscope (SEM, LEO 440).

2.4. Cation exchange capacity (CEC)

Five gram of sample was placed into Erlenmeyer and 100 ml 2 M NaCl solution was added in order to convert the composites to Na^+ form. Residual NaCl solution on composite surface was washed with distilled water. Then 100 ml 1 M KCl solution was added into Erlenmeyer. Then, Na^+ ion concentration in KCl solution was measured with flame photometer and cation exchange capacity (CEC) was calculated.

$$\mathrm{CEC\,(meq/g)} = \frac{V_{KCl}\,(L) \times \mathrm{Na\,(meq/L)}}{m_{amount}\,(g)} \quad (1)$$

2.5. Batch experiments

The batch experiments were carried out in 250 ml Erlenmeyer containing 100 ml of aqueous solution. Effect of solution pH (2–10), composite dosage (1–10 g/L), contact time (2.5–180 min), initial TC concentration (10–300 mg/L) and temperature (20–50 °C) on adsorption of TC by HA-C and HA-P was investigated. The influence of various parameters such as solution pH, contact time, composite dosage and salinity on removal of TC by HA-C and HA-P was investigated by varying one parameter at a time and keeping the remaining other parameters as constant. The details of the experimental conditions are presented in Table 1. pH was adjusted with HCl and NaOH. The suspension was shaken in temperature controlled shaker at 130 rpm. The residual concentration