Adsorption of phosphorus by calcium-flour biochar: Isotherm, kinetic and transformation studies

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HIGHLIGHTS

- Ca-decorated biochar was synthesized.
- Excellent sorption capacity of 314.22 mg g^{-1} for P was observed.
- Langmuir and pseudo-second-order models fit the sorption process adequately.
- Formation of Ca$_5$(PO$_4$)$_3$(OH) crystal contributes to P sorption.

ARTICLE INFO

ABSTRACT

Discharging phosphorus (P)-contaminated water directly into the aquatic environment leads to resource loss and eutrophication. Thus, removing P from waste streams is imperative. In this study, calcium-decorated biochar (Ca-BC) in different mass ratios of Ca to BC was designed to effectively adsorb P from solution. Ca-BC was characterized through X-ray diffraction (XRD) analysis, followed by isotherm and kinetic adsorption experiments. The decorated Ca on the BC surface was found to have preferred P adsorption ability. A design of calcium hydroxide (Ca(OH)$_2$) to flour in a mass ratio of 2:1 was found to have a maximum adsorption capacity of 314.22 mg g^{-1} for P. The Langmuir and pseudo-second-order models fit the sorption process adequately. XRD analysis indicated that the preferable adsorption ability to P was due to the reaction of Ca(OH)$_2$ and PO$_4^{3-}$, forming the hydroxylapatite (Ca$_5$(PO$_4$)$_3$(OH)) crystal. The P in solution was transformed to the crystal. Thus, Ca-BC is an environmental friendly and low-cost sorbent for P removal.

1. Introduction

Phosphorus (P) is an essential nutrient, but it is a non-renewable resource (Cordell et al., 2009). A phosphate rock deposit is estimated to last for only 100 years (Cooper et al., 2011). However, high levels of P in fluvial water, carried by rain and by domestic and industrial sewers, are discharged into surface bodies such as lakes and rivers. The severe runoff of the P resource may lead to pollution, because the European Union has limited the total concentration for effluent to 1–2 mg L^{-1} depending on the sensitiveness of the receiving water body (Triantafyllidis et al., 2010). Thus, the discharge of excessive P can trigger severe environmental pollution such as eutrophication (Carvalho et al., 2011) and resource loss. Hence, to comply with "Circular Economy" principles, designing a strategy for removing and capturing P from aqueous solution is imperative.

In the past decades, various biological (Nancharaiah et al., 2016) and physiochemical (Barbosa et al., 2016; Nguyen et al., 2016) methods have been developed for removing P. Among them, adsorption is one of the physical processes, in which various sorbents from carbon to minerals, including hydrous zirconium (Lin

et al., 2017), iron and iron-rich substrate (Baken et al., 2015; Triantafyllidis et al., 2010), fibers (Yamazaki et al., 2016), zeolite (Zhang et al., 2014), lanthanum/aluminum (Xu et al., 2017), and metal-modified carbon (Cui et al., 2016; Michalekova-Richveisova et al., 2017; Li et al., 2016a,b; Xiong et al., 2017), have been tested. Clearly, metal ion-modified carbons have received maximum attention among these sorbents due to their merits of low cost and environmental friendliness (Liu et al., 2013). The most used metals, including lanthanum (Dai et al., 2014; Koilraj and Sasaki, 2017), aluminum (Wan et al., 2017), magnesium (Jung et al., 2017; Li et al., 2016a,b), and ferric (Chen et al., 2011) play a major role in enhancing the adsorption ability for removing and recovering P from aqueous solution. The main mechanisms contributing to the adsorption process is the chemisorption between the metals and phosphate. In addition, calcium (Ca), due to its nontoxicity and wide availability, is considered another prospective metal for modifying biochar for enhancing the adsorption ability to remove other pollutants, and not just P (Jiang et al., 2017). For example, in the past decade, Ca has been supported on activated carbon for preferable SO_2 removal (Muñoz-Guillena et al., 1997; Macías-Pérez et al., 2007). Furthermore, powdered zeolite has been activated in the presence of Ca for enhancing the P adsorption capacity from 57 to 203 mg $P-PO_4^{3-}$. The mechanism is ascribed to the formation of brushite (Hermassi et al., 2016) and a high pH value (Rietra et al., 2001). Moreover, the presence of Ca^{2+} can enhance the adsorption ability of P onto zirconium oxide (Lin et al., 2017). The pretreatment of natural clinoptilolite by calcium hydroxide ($Ca(OH)_2$) can enhance Ca-P surface precipitation (Mitrogiannis et al., 2017).

On the basis of the preceding descriptions, this study decorated Ca adequately on the surface of carbon, because carbon is a stable and advantageous sorbent and supporter material. The decoration of Ca could provide several active sites for binding phosphates considering the potential of crystallization with P. In this study, flour as a carbon source, and $Ca(OH)_2$, evolved as a Ca source, were mixed with water to form gels for synthesizing Ca-doped carbon for removing P from wastewater and used as a potential fertilizer. Batch isotherm and kinetic adsorption experiments were conducted to investigate the adsorption behaviors of P from aqueous solution, whereas Fourier transform infrared (FT-IR) and X-ray diffraction (XRD) analysis were conducted to investigate the reaction between P and Ca as well as the fate of P during the removal process, further evaluating the production phase.

2. Materials and methods

2.1. Materials

Flour, produced by Guangzhou LingNan SuiLiang Grain Company, was purchased from a market in Guangzhou University, China. Each 100 g of the flour contained 14.6 g of protein, 1.7 g of fat, 72 g of carbohydrates, and 6 mg of sodium. The flour was dried at 105 °C to remove water. $Ca(OH)_2$, potassium phosphate (K_3PO_4), dipotassium hydrogen phosphate (K_2HPO_4), monopotassium phosphate (KH_2PO_4), and other analytical chemical reagents were of chemical grades and purchased from Aladdin Industrial Corporation, Shanghai, China.

2.2. Preparation of adsorbent

Ca-decorated biochar (Ca-BC) was prepared by carbonization in a programmable tube furnace at 800 °C. Firstly, predetermined weight of $Ca(OH)_2$ and flour were mixed in varied mass ratio of 1:4, 1:2, 1:1 and 2:1. Subsequently, deionized water was added to form dilute gels and stirred by a magnetic stirrer overnight. The gel

mixture in each mass ratio was placed in an oven set at 105 °C to remove water. Next, the dried mixture was placed in a ceramic ark inside a tube furnace (SKF-210, Hangzhou Lantian Instrument Co., China) and then heated at a rate of 10 °C min-1 to 600 °C in the presence of N_2 holding for 2 h. After being carbonized at 800 °C for 2 h in nitrogen atmosphere, the samples were further washed with deionized water to remove the residual ions. The washed biochar was dried and conserved in a desiccator and named Ca-BC (1:1), Ca-BC (1:2), Ca-BC (1:4) and Ca-BC (2:1) according to the dried mass ratio of $Ca(OH)_2$ to flour, where the values in the parentheses represent the ratios. The carbon in the absence of Ca was named flour-derived biochar (BC).

2.3. Adsorption experiments

A stock solution containing 1000 mg L^{-1} P was prepared by dissolving K_3PO_4, K_2HPO_4, and KH_2PO_4 in deionized water, and the desired solutions were prepared by diluting the stock solution. In the adsorption experiments, the adsorbent dose was 1 g L^{-1}, all concentrations are expressed in $P-PO_4^{3-}$. All batch adsorption experiments were performed in conical flasks with a plug on a shaker equipped with a thermostat at 200 rpm and at 25 °C.

Adsorption isotherm characteristics were investigated by varying the initial P concentrations (100, 200, 300, 400, 500 and 600 mg L^{-1}). For each test, the suspension was filtrated through a 0.45 μm cellulose acetate membrane, and the residual P concentration in the filtrate was measured using an ultraviolet spectrophotometer at 700 nm (HITACHI U-2910, Japan). The adsorption amount was calculated as the difference between the initial and residual concentrations. Adsorption kinetic experiments were conducted with an initial P concentration of 300 mg L^{-1}, and the residual sample at each determined time interval was drawn and analyzed. K_3PO_4, K_2HPO_4 and KH_2PO_4 were also used as adsorbates for comparing their adsorption characteristics with those of various P sources.

All experiments were repeated thrice, and the average value was calculated. The equilibrium adsorption capacity (q_e, mg g^{-1}) and the adsorption capacity at different time t (q_t, mg g^{-1}) were calculated as follows:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{2}$$

where C_0 (mg L^{-1}), C_e (mg L^{-1}), and C_t (mg L^{-1}) represent the initial P concentration, the P concentration at equilibrium, and the P concentration at time t, respectively; V (L) represents the volume of the solution; and m (g) represents the adsorbent mass.

2.4. Isotherm models and kinetics models

To further understand the adsorption behavior of P on the different Ca-BC adsorbents, two widely used isotherm models, namely the Langmuir and Freundlich models, were adopted to fit the experimental data.

To clearly investigate the adsorption of P on the Ca-BC adsorbents, the pseudo-first-order and pseudo-second-order kinetic models were applied to describe adsorption kinetics (Wang et al., 2016).

2.5. Analytical method

The Ca-BC samples before and after adsorption were