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$La(OH)_3$-modified magnetic pineapple biochar as novel adsorbents for efficient phosphate removal

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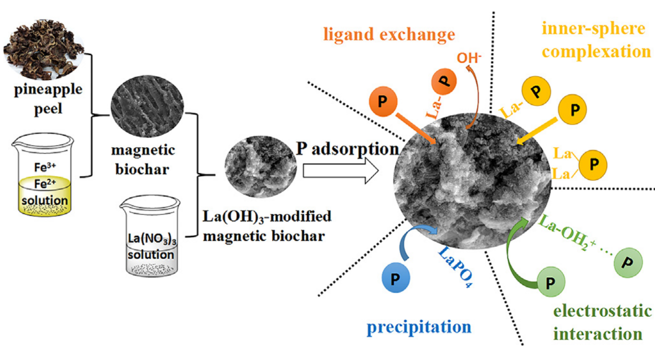
GRAPHICAL ABSTRACT



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ABSTRACT

A series of $La(OH)_3$-modified magnetic pineapple biochar (La*x*-MC) with different contents of $La(OH)_3$ were prepared and used as phosphate adsorbents for the first time. With the increase of $La(OH)_3$ content, the adsorption capacity for phosphate increased while the magnetic property decreased. La10-MC exhibited excellent magnetic property for easy recovery and high adsorption capacity up to 101.16 mg P/g, which was 27 times that of pineapple biochar and much higher than most phosphate adsorbents. Adsorption isotherm and adsorption kinetics were better fitted by Langmuir model and pseudo second-order model, respectively. The removal efficiency > 96.04% in coexisting ions indicated its high selectivity to phosphate. Little decrease in removal efficiency after three adsorption-desorption cycles suggested its excellent stability and cyclic utilization. Leaching study demonstrated the negligible risk of La^{3+} and Fe^{3+} leakage during adsorption process. Mechanism study revealed that the adsorption mechanism involved precipitation, electrostatic interaction, ligand exchange and inner-sphere complexation.

1. Introduction

Phosphate is a basic nutrient which is vital for the growth of aquatic organisms. But excessive emission of phosphate to the runoff system is confirmed to lead to eutrophication, which causes water quality deterioration, aquatic ecosystem collapse and even algal bloom. Therefore, it is very urgent to remove phosphate from wastewater before it is released into the ecosystem. At present, there are many techniques for the removal of phosphate, such as electrolysis method, biological treatment, membrane technology, chemical precipitation and

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adsorption methods (Pan et al., 2017). In particular, adsorption is considered as a promising technology to remove phosphate, due to its advantages such as cost-effectiveness, high selectivity and easy operation (Li et al., 2016; Jiang et al., 2017). Most adsorbent materials include natural materials, waste materials and synthetic materials. For example, natural clays, natural waste materials (such as nutshell) (Vaghetti et al., 2009), industrial waste materials (such as fly ash and furnace slag) (Can and Yildiz, 2006; Johansson and Gustafsson, 2000), synthetic metal oxides and hydroxides (such as activated aluminum oxide and granulated ferric hydroxide) (Genz et al., 2004) and functionalized inorganic materials (mesoporous materials) (Chouyyok et al., 2010) were sequentially reported. However, most of the adsorbents have various drawbacks, such as high cost, low adsorption rate, low adsorption capacity, poor renewability and unstable performance. Therefore, it is essential to develop a low-cost and highly efficient adsorbent with excellent renewability for phosphate removal.

Recently, biochar has been investigated as a potential adsorbent in the treatment of pollutants in wastewater. It has attracted a wide range of concerns, which exhibits a variety of advantages, such as a wide variety of sources, low cost, environmental friendliness and facile fabrication (Yang et al., 2018). Thus, the unique features make it greatly promising in adsorbing inorganic and organic pollutants from waterbodies (Wang et al., 2016), and many researchers have begun to explore the use of biochar in pollutants removal. However, the performance of virgin biochar in phosphate removal is unsatisfactory, especially, the phosphate adsorption capacity of virgin biochar was still low. For example, biochar from corn cobs, gardenwood waste and wood chips exhibited 0.036, 0.132 and 0.296 mg P/g adsorption capacity, respectively (Michalekova-Richveisova et al., 2017). It was reported that decorating biochar with metal oxides or hydroxides could significantly improve the adsorption capacities of biochar towards phosphate. For example, porous MgO-biochar nanocomposites (Zhang et al., 2012b) and biochar/AlOOH nanocomposite (Zhang and Gao, 2013) have been synthesized to increase its adsorption capacity for phosphate. Recently, lanthanum-containing materials have been extensively investigated, and exhibited a variety of advantage in the removal of phosphate, such as a superior adsorption capacity, excellent adsorption selectivity, wide operating pH range and high removal rate (Huang et al., 2014). For example, La-decorated silica spheres (Huang et al., 2015), $La(OH)_3$-modified exfoliated vermiculites (Huang et al., 2014), La-based metal-organic frameworks (Liu et al., 2016) and Lanthanum-decorated hydrochar were prepared as phosphate adsorbents (Dai et al., 2014) and had a superior performance in phosphate removal. Therefore, it has a deep significance to modify biochar with lanthanum oxides or hydroxides which can make full use of both advantages in phosphate removal. However, there are only two reports to date, in which lanthanum loaded biochar was prepared and exhibited adsorption capacity up to 46.37 mg P/g (Wang et al., 2016), and La_2O_3 grafted oak was synthesized with the highest adsorption capacity at about 142.70 mg P/g (Wang et al., 2015). However, there is a distinct disadvantage of biochar for phosphate removal is the difficulty to separate it from solution, which is a common problem for powder adsorbent. Magnetic separation, compared with traditional methods for powder recovery from water, shows various advantages of high efficiency, low cost and easy operation. Thus, magnetic media were added to the powder biochar to form magnetic composites, which could easily be separated from solution by magnetic field (Zhang and Gao, 2013). For example, a novel magnetic biochar containing iron oxide as magnetic media which efficiently adsorbed organic pollutants and phosphate was reported and it could be easily recycled from the suspension through magnetic field (Wang et al., 2015). Magnesium oxide-decorated Fe_3O_4 magnetic biochar was reported to show high adsorption capacity and easy to be recovered from aqueous solution (Li et al., 2016). Thus, the combined decorating of lanthanum oxides or hydroxides and magnetic media into materials, not only can greatly improve the adsorption performance in phosphate removal but also make the materials easily recovered from the water. However, lanthanum oxides or hydroxides-decorated iron oxides magnetic biochar has never been reported.

In this study, it is the first time to use pineapple peel waste to prepare biochar, which was decorated by both magnetic Fe_2O_3 and lanthanum hydroxides. The performances in phosphate adsorption of the resulting adsorbent were studied. The characteristics of the adsorbent were investigated. The influences of phosphate initial concentration, contact time, solution pH, co-existing ions on the adsorption process were examined. The studies of adsorption isotherms and kinetics were also conducted, and the adsorption mechanism was revealed. Finally, the desorption-adsorption recycle of the adsorbent were inspected.

2. Materials and methods

2.1. Materials

Pineapple peels were collected from a fruit market in Guangdong province of China. Lanthanum (III) nitrate (Aladdin), potassium dihydrogen phosphate (Aladdin), isopropanol, sodium hydrate, hydrochloric acid, ferrous chloride tetrahydrate, ferric choride hexahydrate, trisodium citrate, potassium chloride, sodium carbonate, sodium bicarbonate, sodium sulfate and sodium nitrate were purchased from Guangzhou Chemical Reagent Factory. All of the chemicals and reagents were of analytical grade. All chemical solutions were prepared with distilled water.

2.2. Preparation of adsorbent

2.2.1. Biochar (C) production

Pineapple peel biochar derived from the pyrolysis of pineapple peel at 300 °C, which was used as the base material for Fe_2O_3 and $La(OH)_3$. In brief, raw pineapple peel was dried at 105 °C for 24 h, then screened through an 80 mesh and chopped by a rotary cutting machine. The dry pineapple peel powders were washed with deionized water and absolute ethyl alcohol twice, which was then dried at 80 °C overnight. Dried pineapple peel powders were moved into a porcelain crucible and heated in a muffle furnace at 300 °C for 1 h. The resulting powders were washed using distilled water and absolute ethyl alcohol, which was dried finally.

2.2.2. Synthesis of magnetic biochar (MC)

A certain amount of dried pineapple biochar powder was added into 250 mL solution containing 1:1 M ratio of ferrous chloride tetrahydrate and ferric chloride hexahydrate (Chen et al., 2011). Under vigorous magnetic stirring at 60 °C in water bath for 0.5 h, 1 mol/L NaOH solution was added dropwise into the above suspension until its pH increased up to 11. 0.25 g of trisodium citrate was subsequently added and continuously stirred for 1 h at 80 °C. Finally, the product was washed with deionized water and absolute ethyl alcohol repeatedly and then dried at 80 °C overnight.

2.2.3. Synthesis of $La(OH)_3$-modified magnetic biochar (Lax-MC)

Briefly, 1.0 g of MC was dispersed in 25 mL of deionized water and stirred for 0.5 h to obtain a uniformly dispersed magnetic biochar suspension. Subsequently, a defined amount of Lanthanum (III) nitrate was dissolved in 25 mL isopropanol, which was then added to the above magnetic biochar suspension. The acquired suspension was continuously stirred for 18.5 h before adjusting the suspension pH value to 9.0. After being magnetically stirred for 5 h, the suspension was settled down for 24 h. Then, the powders were separated, washed with deionized water and ethyl alcohol and dried at 80 °C overnight. Finally, a batch of La*x*-MC adsorbents were prepared and named as La0.63-MC, La1.25-MC, La2.5-MC, La5-MC, La10-MC and La15-MC, corresponding to the ratios between La and MC of 0.63, 1.25, 2.50, 5.00, 10.00 and 15.00 mmol/g in the suspension, respectively.