



Synthesis of a ferric hydroxide-coated cellulose nanofiber hybrid for effective removal of phosphate from wastewater



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ABSTRACT

Ferric hydroxide-coated cellulose nanofibers (Fe(OH)₃@CNFs) were synthesized for the removal of phosphate from wastewater. The maximum sorption capacity of Fe(OH)₃@CNFs for phosphate was estimated to be 142.86 mg/g, demonstrating a superior adsorption capacity compared with many adsorbents reported in the literature. Batch experiments were performed to investigate various adsorption conditions on the adsorption performance. It was discovered that an increased solution ionic strength would remarkably enhance the adsorption. Additionally, Fe(OH)₃@CNFs achieved a favorable adsorption performance over a wide range of pH conditions, which could result in operation cost savings. The adsorption of phosphate can be described by both the Langmuir isotherm and pseudo-second-order models. The phosphate adsorbed by Fe(OH)₃@CNFs was characterized using XPS, SEM, S_{BET} and EDS. The data obtained revealed that the electrostatic attraction and ligand exchange constituted the major forces in phosphate adsorption. This work suggested that Fe(OH)₃@CNFs are a promising adsorbent for phosphate removal.

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1. Introduction

Phosphorus is an essential nutrient in aquatic ecosystems. However, the extensive use of phosphates inevitably results in large amounts of P-bearing wastewater, which is considered a major element of eutrophication (Xiong & Peng, 2008; Zhang, Liu, Liu, & Qu, 2009). Limiting phosphate can prevent eutrophication (Cooke, Welch, Peterson, & Nichols, 2005). There are various techniques available to remove phosphate from wastewater such as chemical, biological and physical treatment methods (De-Bashan & Bashan, 2004; Lee, Kwon, Jeon, & Koopman, 2009). Among the various techniques, adsorption was found to be the most suitable method for meeting the stringent requirements for phosphate removal and is beneficial to phosphate recycling due to the ease of operation, convenience and economic advantages (Bhatnagar & Sillanpää, 2011; Oladoja, Ahmad, Adesina, & Adelagun, 2012).

Phosphorus resources are finite, and estimates indicate that there is only enough remaining to last for 50–100 years (Cordell, Drangert, & White, 2009). This problem has increased concerns regarding phosphorus recovery and the final disposal after use. A sorbent with eco-friendly characteristics can eliminate the disposal problem of phosphate-loaded adsorbents. Therefore, it is necessary to develop adsorbents that are biodegradable, non-toxic and environmentally friendly. Many adsorbents, such as inorganic sorbents, organic sorbents and industrial by-products (Loganathan, Vigneswaran, Kandasamy, & Bolan, 2014), have been studied in recent years. However, these studies mostly focused on the removal efficiency. It is also necessary to consider the final disposal of phosphate-loaded adsorbents. Therefore, the application of natural polymers in phosphate removal is a potentially valuable solution. Natural cellulose fibers (CNFs) were extracted from softwood pulp and are considered an inexhaustible raw material (Klemm et al., 2011). CNFs are natural polymers that exhibit many well-known advantages, such as biodegradability, non-toxicity, worldwide availability and low cost (Zhang et al., 2011). However, current studies of CNFs in environmental remediation are mainly focused on the removal of organics, heavy metals (Sehaqui, de Larraya, Tingaut, & Zimmermann, 2015) and color dyes (Wang et al., 2014). There are a few reports on the use of CNFs as an adsorbent for the removal of anions pollutants such as PO₄³⁻.

Abbreviations: CNFs, cellulose nanofibers; Fe(OH)₃@CNFs, ferric hydroxide modified cellulose nanofibers; TEMPO, 2,2,6,6-Tetramethyl-1-piperidinyloxy.

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The concentration of phosphate varies widely in wastewater resulting from different processes. In industrial wastewater, the concentration could reach up to several hundreds of milligrams per liter. Recently, many studies on the adsorption of phosphorus focused on relatively highly concentrated phosphorus-containing wastewater. Municipal wastewater, which produces a larger quantity of emissions than industrial wastewater, has a low phosphorus concentration of 4–15 mg/L. With the increasing problems caused by water eutrophication, municipal wastewater should require more stringent phosphate emission standards.

Many adsorbents have achieved the optimum adsorption performance under acidic conditions (Loganathan et al., 2014), while wastewater commonly has a neutral pH (Xie, Wang, Fang, Li, & Wu, 2014). For these adsorbents, extra chemicals need to be added to the wastewater to increase the acidity to achieve better adsorption efficiency. Then, the pH needs to be adjusted back to a neutral condition to meet the emission standards after adsorption, which would greatly increase the operation costs. Thus, it is necessary to develop adsorbents that have a superior adsorption capacity under neutral conditions. Additionally, developing a novel adsorbent that possesses high selectivity is equally important for real wastewater, which contains many coexisting ions.

To improve the adsorption performance, suitable modifications are needed. Metal hydroxide has been used to modify different adsorbents to improve their surface and adsorption efficiency (Nguyen et al., 2014). Ferric hydroxide is a low-cost and environmentally friendly substance, demonstrating chemical stability over a wide pH range (Cumbal & SenGupta, 2005). It has been reported that ferric hydroxide plays a major role in phosphate immobilization (Persson, Nilsson, & Sjöberg, 1996) and can be safely used in aquatic environments (Huang, Liao, & Shi, 2009). Ferric hydroxide particles lack mechanical integrity when used in their native form but can be dispersed on a fixed-bed that provides the necessary mechanical strength, extensive surface area and inner pore spaces to accommodate the ferric hydroxide particles (Blaney, Cinar, & SenGupta, 2007). These features indicate that ferric hydroxide-coated CNFs may be an attractive option as a phosphorus adsorbent.

As two eco-friendly and economic materials, CNFs and ferric hydroxide were proposed to synthesize a ferric hydroxide modified CNFs (Fe(OH)₃@CNFs) adsorbent and were first used in phosphate removal. In this study, its adsorption performance and mechanism of adsorption for phosphate removal were investigated in detail. We proposed a new adsorbent to achieve a better adsorption efficiency in neutral conditions when treating simulated municipal wastewater. Furthermore, Fe(OH)₃@CNFs not only exhibited great adsorption performance but also could be disposed of in an eco-friendly manner by applying them to the soil to increase soil fertility.

2. Materials and methods

2.1. Materials

Never-dried moso bamboo pulp was supplied by Yongfeng Paper Co., Ltd. (Sichuan, China). Its cellulose content was higher than 93%, as reported by the supplier. KH₂PO₄ and Fe(NO₃)₃·9H₂O were used for the adsorption studies. All of the chemicals were analytical grade and were obtained from Kelong Company (Chengdu, China). Deionized water was used throughout the experiment.

2.2. Preparation of CNFs

The CNFs were extracted from softwood pulp. First, 30 g of softwood pulp board was cut into small pieces and soaked in 3 L of distilled water. After that, a mechanical disintegrator (BLF-YB20,

China) was used to disperse the softwood pulp in distilled water for 3 min (29000 rpm). Then, 200 mL of an aqueous mixture of TEMPO (0.469 g) and sodium bromide (3.087 g) was added and stirred for another 20 min. The oxidation reaction was initiated by adding 193.6 g of NaClO. The pH decreased as the oxidation proceeded and was adjusted to 10 ± 1 with 1 M NaOH. It was then washed with deionized water. After the sonication treatment (JY99-IIDN, Scientz, China) at 1200 W for 30 min, the cellulose suspension was diluted with distilled water to a concentration of 0.5 wt%. To obtain a fine CNFs product, the suspension was further processed with a high shear homogenizer (T18, IKA, Germany) at a rotation speed of 20,000 rpm for 1 h.

2.3. Preparation of Fe(OH)₃@CNFs

Fe(NO₃)₃·9H₂O was added to the CNFs suspension at room temperature. The NaOH (1 M) was dropwise added into the mixture until the OH⁻/Fe³⁺ molar ratio reached 3 and then stirred at room temperature for 24 h. The mixture was then centrifuged to remove the supernatant and washed with deionized water until free from Cl⁻. The residue was frozen in a freeze drying chamber (LAB-1A-50E, China) at -40 °C for 48 h and then stored at room temperature.

2.4. Material characterization

The CNFs before and after modification were coated with gold using a vacuum sputter coater (Quorum Q150T ES, UK) and then observed with SEM and EDS (LEO 1530, Germany) at 10 kV. XPS (X-ray photoelectron spectroscopy) signals were collected on a VG Micro MK II instrument. The specific surface area, pore diameter and pore volume of the freeze-dried samples were also measured using a V-Sorb 2800P instrument and the Brunauer–Emmett–Teller (BET) method.

2.5. Adsorption experiments

The adsorption performance of Fe(OH)₃@CNFs was tested through batch experiments. The pH-dependent adsorption behaviors were studied in the pH range of 4.5–10.5 with dilute NaOH and HCl. First, 50 mg of Fe(OH)₃@CNFs and 100 mL 10 mg P/L of standard KH₂PO₄ solutions were added to a 150-mL beaker flask. After the supernatant was filtered using a 0.45-μm filter, the concentration of phosphate in the working solution was measured using the molybdenum-blue ascorbic acid method (Apha, 2005). The adsorption capacity was calculated using (Eq. (1)). All of the experiments were performed three times. A salt effect experiment was conducted by mixing 50 mg of Fe(OH)₃@CNFs with a 100-mL solution containing 10 mg P/L and other anions at pH 4.5. After shaking for 8 h, the equilibrium phosphate concentrations were measured. All of the experiments were performed in duplicate.

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

where q_e is the sorption capacity at equilibrium (mg/g), C_0 is the initial concentration of PO₄³⁻ (mg/L), C_e is the equilibrium concentration of PO₄³⁻ (mg/L), V is the volume of PO₄³⁻ solutions and m is the mass of the adsorbent (g).

For the kinetic adsorption, 50 mg of Fe(OH)₃@CNFs was added to a 100 mL solution (initial phosphorus concentration: 10 mg P/L) by varying the adsorption time (0–24 h). After the supernatant was filtered using a 0.45-μm filter, the concentration of phosphate in the working solutions were determined. Each time point was analyzed three times. The obtained data were analyzed using the pseudo-first-order equation (Eq. (2)) and the pseudo-second-order equation (Eq. (3)).

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