



Immobilization of powdery calcium silicate hydrate via PVA covalent cross-linking process for phosphorus removal

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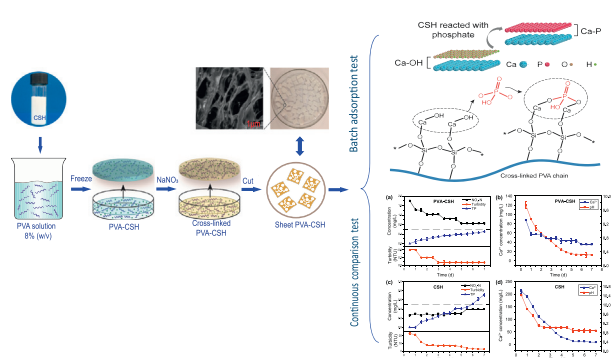
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HIGHLIGHTS

- A novel immobilized sheet material was prepared for phosphorous removal.
- The immobilized material reduced the loss of CSH powder during continuous operation.
- The PVA-CSH performance was evaluated by the turbidity and phosphorous concentration.
- The reaction process of phosphorous adsorbed by PVA-CSH was proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

Calcium silicate hydrate (CSH) is a popular material used for phosphorus removal in recent years. In this work, a novel immobilized material, polyvinyl alcohol-CSH (PVA-CSH), was prepared using a 1:10 weight ratio of CSH powder to 8% PVA solution and then used for phosphorus removal. Samples were characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The adsorption mechanism and practical application properties of phosphorus wastewater were studied by sequential batch and continuous flow experiment. The results showed PVA-CSH possessed a porous network structure and an average pore diameter of 24.94 ± 0.11 nm. Furthermore, the CSH functional groups were unaffected by PVA immobilization. Compared with CSH, PVA-CSH did not easily lose CSH after being immobilized by PVA, and the duration of efficient phosphorus removal stage was approximately 20 h longer than that of CSH. In addition, the effluent turbidity of PVA-CSH was 0.11 ± 0.03 NTU during the continuous operation period, which was significantly lower than CSH. In summary, this research study demonstrated the significant potential of PVA-CSH for practical phosphorus removal.

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1. Introduction

Wastewater from municipal, industrial and agricultural activities contains superfluous phosphorus (Zhou et al., 2012). Excessive phosphorus (P) discharged into water bodies may lead to severe

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eutrophication, which results in the degradation of the water ecosystem and destruction of self-purification capacity (Xiao et al., 2017). Therefore, the removal of phosphorus from wastewater is necessary to meet the discharge limit in controlling eutrophication. In the past several decades, several categories of phosphorus removal methods have been proposed, primarily including biological removal (Geng et al., 2018), chemical precipitation (Qiu et al., 2015) and chemical adsorption (Golder et al., 2006). Among these methods, biological removal methods are advantageous because of their low cost, but the phosphorus concentration of the effluent is easily affected by microbial growth conditions. In light of increasingly stringent phosphorus removal standards, chemical precipitation is a very efficient method. However, chemical precipitation methods usually involve the excess addition of chemicals, which can lead to ecological pollution. Electrochemical induced phosphate precipitation has been proven as an efficient method for phosphorus removal (Lei et al., 2017). Besides, chemical adsorption has become a popular phosphorus removal method because of its simple operation and possible phosphate recovery (Sun et al., 2015; Zheng et al., 2011). Various chemisorption materials have been studied as phosphate adsorbents and include layered double hydroxide (LDH) (Novillo et al., 2014), metal-modified carbon (Cui et al., 2016; Yin et al., 2018) and calcium-based materials (Wang et al., 2018), etc. Particularly, calcium-based materials are advantageous for chemical phosphorus removal because of their simple synthesis, rapid reaction speed and environmental friendliness (Bellier et al., 2006). Previous studies of Ca-based materials mainly focused on apatite (Yagi and Fukushi, 2012), monohydrocalcite (Karageorgiou et al., 2007), calcite (Rejmak et al., 2012) and calcium silicate hydrate (CSH) (Renman and Renman, 2010). Studies have reported that calcium silicate materials could remove phosphate from water via chemisorption processes (Chen et al., 2009). CSH, a common synthetic silicate adsorbent, has been widely used because of its large specific surface area and the unique release capability of Ca^{2+} and OH^- . CSH is synthesized using calcium oxide and silicon oxide materials (Guan et al., 2013). Okano et al. (2013) prepared amorphous CSH to treat anaerobic sludge digestion solution and determined the phosphate adsorption capacity was approximately 40 mg/g for this use. Kuwahara and Yamashita (2017) demonstrated that CSH synthesized from blast furnace slag (BF slag) could be used as a phosphorus removal adsorbent, with a maximum phosphorus adsorption capacity 73-fold greater than that of BF slag.

Many research studies have demonstrated CSH possesses excellent adsorption properties. However, most synthetic phosphorus removal adsorbents, including CSH, are used as a powder with a particle size $\leq 100 \mu\text{m}$ (Bai et al., 2009); CSH can be lost to the effluent because of their small particle size, which decreased the utilization efficiency of adsorbent materials and polluted the environment (Mohan and Pittman Jr, 2007; Okano et al., 2015). Therefore, the development of a method for the suitable immobilization of phosphorus-removing powders is an urgent need. Polyvinyl alcohol (PVA) has been considered a promising immobilization carrier in recent years because of its chemical stability, high mechanical strength and non-toxicity (Takei et al., 2011; Zain et al., 2011).

Chemical cross-linking is the most commonly used method in PVA immobilization, which involves generating a covalent bond between the hydroxyl group of PVA and the functional groups of cross-linking agents (Derwinska et al., 2008; Yujian et al., 2006). Kumar et al. (2009) prepared cross-linked chitosan/PVA beads using an aqueous suspension of chitosan-PVA. Subsequently, the immobilized material was effectively utilized for the removal of Cd (II) ions. Lai et al. (2016) synthesized PVA-alginate granules using boric acid and calcium chloride as cross-linking agents to immobilize Prussian blue nanoparticles for the removal of cesium. Saturated boric acid is one of the most commonly used cross-linking agents. Unfortunately, it still possesses several deficiencies, including its toxicity and swelling properties (Hsia et al., 2008; Zhang et al., 2007). In addition to saturated boric acid, sodium nitrate (NaNO_3) has also been developed as a cross-linking agent due to

its rapid cross-linking rate and non-toxicity (Hu and Yang, 2014). Materials prepared with NaNO_3 exhibited excellent mechanical strength and chemical stability (Chang and Tseng, 1998). The effective immobilization of CSH powder by PVA may reduce the loss of CSH powder during phosphorus removal. However, to our knowledge, no research has been conducted on the use of PVA to immobilize CSH powder.

In the present paper, we immobilized CSH powder with PVA using NaNO_3 as the cross-linking agent. Combined with the characterization of PVA-CSH and the recovered product, a possible phosphate removal process by the PVA-CSH was proposed. The focus of this study was to evaluate the phosphorus removal performance of an immobilized material (PVA-CSH) by monitoring effluent turbidity and phosphorus concentration.

2. Materials and methods

2.1. Raw materials

In this study, all materials used were at least analytical purity. CSH powder (80–100 mesh) and PVA (nominal degree of polymerization, 1750 ± 50) were obtained from Shanghai Chemical Reagent Co., Ltd. NaNO_3 and KH_2PO_4 were purchased from Chongqing Boyi Chemical Reagent Co., Ltd. These materials and chemicals were stored in sealed bottles. The phosphate solution was prepared by adding KH_2PO_4 into the solution with initial phosphate concentration of 400 mg/L.

2.2. Preparation of PVA-CSH

The preparation of PVA-CSH was performed using four major steps, which are outlined in Fig. 1 (a). Step 1: Firstly, an 8% (w/w) aqueous PVA solution was prepared. Secondly, CSH powder was added to the solution using a 1:10 weight ratio of CSH powder to PVA solution. Thirdly, the suspension was subjected to agitation for 15 min. Step 2: Firstly, the evenly dispersed mixture was plated onto a Petri dish. Secondly, the mixture was incubated at -20°C for 1 h to freeze the mixture into a molded thin sheet with a resulting thickness of 0.5–1.5 mm. Step 3: A 25% (w/v) NaNO_3 solution was added to the frozen PVA-CSH sheet. In the next 2 h, the PVA cross-linking reaction will occur via N—O covalent bonds. The proposed PVA cross-linking reaction process using NaNO_3 is shown in Fig. 1 (b). Step 4: Firstly, the cross-linked sheet material (PVA-CSH) was washed three times with ultrapure water to remove NaNO_3 and unbound CSH powder. Secondly, the cross-linked PVA-CSH sheet was trimmed into smaller irregular sheets, which were approximately 1 cm \times 1 cm in size. Additionally, the reaction process of PVA and CSH is shown in Fig. 1 (c).

2.3. Characterization of PVA-CSH

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) analyses of the prepared material (PVA-CSH) were performed with a JSM-7800F SEM (Electronics JEOL Corp., Japan). Nitrogen adsorption-desorption isotherms were measured by a nitrogen adsorption apparatus (ASAP2020, Micromeritics Corp., USA). Specific surface areas were calculated using the Brunauer-Emmett-Teller (BET) method, and pore sizes were obtained from the adsorption branch of nitrogen isotherms using the Barrett-Joyner-Halenda (BJH) method. The phase composition of PVA-CSH and CSH before and after reacting with phosphate was examined by X-ray diffraction (XRD, Thermo Fisher Scientific, China). The chemical bonds present in samples were determined by Fourier transform infrared spectroscopy (FTIR, Shimadzu, Japan) over a range of 400–4000 cm^{-1} .

2.4. Solubility experiments

The release of Ca^{2+} from PVA-CSH and CSH was investigated via a series of batch experiments. For each experiment, 0.68 g of PVS-CSH

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