



Simultaneous removal of nitrogen and phosphorus by magnesium-modified calcium silicate core-shell material in water

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ABSTRACT

In this study, a new core-shell material (CMCS) is prepared with magnesium oxide (MgO) around calcium silicate hydrate (CSH), and CSH is prepared by SiO₂ from the red mud. The CMCS simultaneously removes ammonia nitrogen (NH₄⁺) and phosphate (PO₄³⁻) by chemical precipitation and it can achieve recovery of nitrogen and phosphorus. The removal process of NH₄⁺ and PO₄³⁻ is as follows. First, the shell of MgO is used to remove NH₄⁺ and a part of the PO₄³⁻ by the assisted adsorption and struvite (MgNH₄PO₄·6H₂O) precipitation method. Then the CSH is used to remove the residual part of PO₄³⁻ by chemical precipitation (Ca₅(PO₄)₃OH, CaHPO₄ and Ca₃(PO₄)₂). Furthermore, the MgO shell of CMCS not only removes NH₄⁺ and PO₄³⁻, but also can control the calcium ions (Ca²⁺) spill from CSH and pH in the process of removing NH₄⁺ and PO₄³⁻. The removal rate of NH₄⁺ and PO₄³⁻ can reach 76.63% and 87.18%, respectively, in the solution in 80 min, but in the actual wastewater the removal rate of NH₄⁺ and PO₄³⁻ is 61.40% and 62.83%, respectively. Finally, CMCS was recycled five times and its removal rates of NH₄⁺ and PO₄³⁻ are 21.01% and 24.99%, respectively. The aim of this article is to present CMCS, which has a good effect on removing the NH₄⁺ and PO₄³⁻ simultaneously.

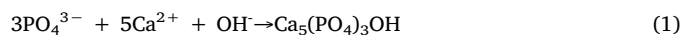
1. Introduction

With the development of animal husbandry, a large amount of untreated livestock wastewater has been put into rivers, leading to eutrophication. Livestock wastewater is one of the refractory wastewaters, containing ammonia nitrogen (NH₄⁺) and phosphate (PO₄³⁻). Nitrogen (N) and phosphorus (P) in wastewater have good recycling value as slow release fertilizers (Okano et al., 2013). With the increasingly serious environmental pollution and waste of resources, it is necessary to remove NH₄⁺ and PO₄³⁻ and recover them in water. For this purpose, it is a good idea to produce insoluble salts by chemical precipitation (Kirinovic et al., 2017; Rouff, 2012).

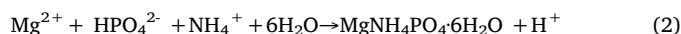
Because of the high content of NH₄⁺ and PO₄³⁻ in livestock wastewater, the effect of biological treatment of NH₄⁺ and PO₄³⁻ is not good. Therefore, the process of reducing the concentration of NH₄⁺ and PO₄³⁻ set up before or after biological treatment is necessary (Kima et al., 2008). Some previous studies mainly focused on the removal of NH₄⁺ and PO₄³⁻, such as with physical adsorption (Gao et al., 2015; Lee et al., 2009), chemical precipitation, and the biological method (Zhang et al., 2016; Wang et al., 2016). The simultaneous removal of NH₄⁺ and PO₄³⁻ is a better research direction in water. Previous articles have reported that the formation of insoluble salt is a NH₄⁺ and PO₄³⁻ removal and

recovery method (Okano et al., 2013; Rouff, 2012), the chemical precipitation method can achieve this. In the present study, the removal of PO₄³⁻ by chemical precipitation is performed so that the element of Ca²⁺, Mg²⁺ is used to generate hydroxyapatite (HAP) and Mg₃(PO₄)₂. NH₄⁺ removal by chemical precipitation causes magnesium ammonium phosphate (MAP) crystallization to form a struvite precipitation, achieving NH₄⁺ and PO₄³⁻ removal at the same time (Song et al., 2007).

The HAP crystallization on crystal seed can be described as the following reaction: (Okano et al., 2015)



The MAP crystallization on crystal seed can be described as the following reaction: (Huang et al., 2011)



MAP crystallization is used to remove NH₄⁺ and PO₄³⁻, which have many restrictions, for example, pH values (Gunay et al., 2008), interfering ions (Huang et al., 2011; Sen, 2014), and the mole ratio of NH₄⁺ and PO₄³⁻ in water. The maximum limiting condition of NH₄⁺ and PO₄³⁻ removal is the pH value in water. In recent years, some problems have required attention during the removal process of using MAP to

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remove NH_4^+ and PO_4^{3-} , there is the difficulty of solid-liquid separation, and the pH in wastewater must be adjusted. Calcium silicate hydrate (CSH) has good sedimentation effect and influences pH in water, so a material can have the characteristics of CSH in the process of simultaneous removal of NH_4^+ and PO_4^{3-} . Therefore, we design a material of reasonable structure to implement this idea.

Over the past several years, the increasing efforts have been devoted to the design and controlled preparation of advanced nanostructured materials with multifunctional properties. Nanostructured materials have attracted considerable attention and have become an increasingly important interdisciplinary research field in chemistry, materials science, biology, and engineering (Li et al., 2013). For example, they have been used to make electrodes in electrochemistry (Xiong et al., 2010), TiO_2 core-shell nanospheres, and nanowires to enhance charge separation and hole transportation (Wu et al., 2017). As a catalyst, the trade-off between selectivity and activity is well understood (Song et al., 2017), as well as CO exchange to CO_2 (Wang et al., 2014), drug delivery (Wang and Gu, 2015), energy storage and dielectric applications (Huang and Jiang, 2015), and adsorption and release functions (Li et al., 2013). The core-shell structure has spawned many new structures, hollow spheres (Xia and Mokaya, 2005), coaxial hollow nanospheres, tubes (Xiong et al., 2010; Zhou et al., 2017) and multi-layer coaxial hollow spheres (Zhou et al., 2017). These structures are also used for physical, chemical and biological applications. Carbon is commonly used as hard template that is convenient for preparing materials and its surface has some holes. These pores are beneficial for preparing core-shell structures.

In the study, the core-shell structure is used to design a new material (CMCS) for a new application. As a nontoxic, economical, and environmental friendly material, magnesium oxide (MgO) has already been widely used to treat wastewater (Liu et al., 2011; Cao et al., 2012; Nguyen et al., 2013). Therefore, MgO is used as the shell of CMCS to remove NH_4^+ and PO_4^{3-} simultaneously. CSH as a core can provide variable pH and a good settlement effect in the removal process. CMCS can not only remove NH_4^+ and PO_4^{3-} but also provide removal conditions for itself. The core-shell structure of CMCS and the possible mechanism for the new material formation were investigated using X-ray diffraction (XRD), Fourier Transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), and EDX, BET, TG, and X-ray photoelectron spectroscopy (XPS). The experiment of removing NH_4^+ and PO_4^{3-} at the same time will also be investigated.

2. Materials and methods

2.1. Materials

Raw red mud was obtained from China Shandong Aluminum Industry Company. The CaO was obtained from Shanghai Fengxian Fengcheng Reagent Co. The $\text{C}_6\text{H}_{12}\text{O}_6$ was obtained from Tianjin Kermel Chemical Reagent Co., Ltd. $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was obtained from Tianjin Tianli Chemical Reagent Co., Ltd. The citric acid was obtained from Tianjin Zhiyuan Reagent Co. Ltd. All the above reagents were of analytical grade. All solutions were prepared with the deionized water.

2.2. Preparation of calcium silicate hydrate

Fig. 1a shows the process for extracting SiO_2 from red mud, the chemical composition of red mud is shown in Table S1. SiO_2 was extracted from red mud (Man et al., 2017) to prepare the CSH with CaO. Next, 1.254 g of CaO and 0.746 g of SiO_2 were mixed in 60 mL of deionized water and then stirred for 30 min. The molar ratio (n) of Ca/Si is 1.8 and the ratio of solid to liquid is 1:30. The suspensions were transferred to a 100 mL hydrothermal reactor at 220 °C for 16 h. Afterwards, the sample was washed with deionized water several times. The resulting product was dried at 120 °C for 10 h and approximately 1.4 g of CSH was obtained.

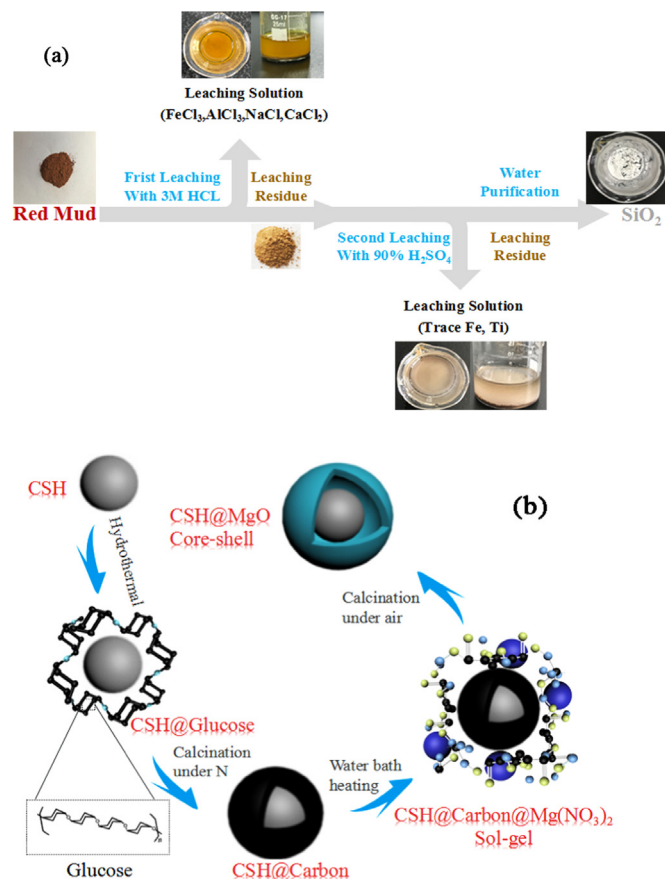


Fig. 1. Schematics of extracting SiO_2 from red mud (a) and the formation of CSH, CSH@C and CMCS spheres (b).

2.3. Preparation of calcium silicate hydrate @ carbon

Afterward, glucose-derived carbon material was coated on CSH using a simple hydrothermal process. Then, 0.6 g of as-prepared core/shell CSH@C nanospheres were easily dispersed by ultrasonication using a KQ-400B ultrasonic cleaner (ultrasonic frequency is 40 kHz, capacity is 15 L) in 40 mL of 0.5 M aqueous glucose solution. The suspension was transferred to a 100 mL Teflon-lined autoclave, which was then heated in an air-flow electric oven (101-OES, the temperature range was room temperature +10–250 °C) at 180 °C for 9 h. The product was harvested by centrifugation and washed with deionized water and ethanol at least five times. After drying at 50 °C, the resulting brown powder was carbonized at 500 °C for 4 h under inert atmosphere by a resistance-heated tube furnace (SK-3-12K, the temperature of work is 1100 °C, and furnace size is $\Phi 60 \times 600$).

2.4. Preparation of the core-shell structure of CMCS

According to $n(\text{H}_2\text{O}):n(\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}):n(\text{citric acid}):n(\text{ethanol}) = 100:9:9:2.1$, a stable gel was formed to generate MgO on the CSH@C surface. Then, 0.5 g CSH@C, 3.6 g $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 2.925 g citric acid were dissolved in the solution of 10 g H_2O and 0.32 g ethanol (99.7%). The mix solution was stirred at 80 °C in the water bath and was heated for 6 h. The suspension was dried at 80 °C for 12 h until it became a dry gel. After that, the dry gel was placed in a muffle furnace and preheated at 200 °C for a duration of 60 min and later sintered at 500 °C for 8 h. During the preheating process, the heating rate was 2 °C min^{-1} . The heating rate was 3 °C min^{-1} in the second heat process. Finally, the obtained sample was CMCS, the CMCS was cooled down to room temperature and sealed for preservation after the grind.

The growth model of CMCS spheres involving four steps was

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