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Phosphate removal by hydrothermally modified fumed silica and pulverized oyster shell

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ABSTRACT

A calcined and hydrothermally annealed material for phosphate removal was prepared in a hollow cylindrical shape from fumed silica generated by a ferroalloy factory, and pulverized oyster shell. Phosphorus removal from wastewater by this material calcined at a range of temperatures (700–900 °C) and hydrothermally annealed at temperatures from 130 to 180 °C, for 8–16 h, was investigated and the most suitable physicochemical conditions were determined. XRD, SEM, EDS, and XRF techniques were used to characterize the microstructures and compositions of the materials produced, and UV–Vis spectrophotometry using the ammonium phosphomolybdate blue method was used to determine the phosphate concentration in the wastewater. The results indicate that calcium carbonate in oyster shell reacted with SiO_2 in fumed silica and formed hydrated calcium silicate after hydrothermal treatment, and the hydrated calcium silicate reacted with phosphate ions in wastewaters to form hydroxyapatite precipitate. The optimal conditions for material production were calcination at 800 °C, and hydrothermal annealing at 150 °C for 12 h. Materials made under these conditions showed 74% or 92% phosphate removal after 2 or 4 h, respectively.

1. Introduction

Phosphorous is key nutrient for life, which in excess causes eutrophication of bodies of water. The methods for removal of phosphate from wastewaters can be classified as chemical precipitation, biological treatment, and sorption [1,2]. Of these, chemical treatment usually by phosphate precipitation with calcium, aluminum, or iron salts is considered to be the most effective method. However, there are problems of sludge handling and the potentially high cost of coagulating agents, consequently the disposal and neutralization of the effluent can be time-consuming and costly [3,4]. Biological treatments rely on biomass growth or intracellular bacterial polyphosphate accumulation, and are subject to the restrictions of time, temperature, and environment [5,6]. Consequently, in recent years considerable attention has been paid, based on economical and environmental concerns, to the sorption method, which is considered to be more practical and economic than many other methods. Different sorbents, such as fly ash [7,8], blast furnace slag [9], mesoporous structural materials [10], aluminum sludge [11], red mud [12,13], and many others [14–21] have been widely investigated for wastewater treatment, but they all have some restrictions such as relatively low efficiencies, and most sorbents are used in a powder form and will often remain in suspension in the water, making them difficult to recover. In addition, there remain the problems of sludge handling and disposal with sorption technologies, as for chemical precipitation.

Fumed silica powder is an ultrafine amorphous material that is produced in the process of electric furnace smelting of silicon–iron alloys [22], and collected by particulate collectors. This form of silica contains nearly 92% SiO_2 and is often used in concrete manufacture and other industrial processes. Oyster shells are generated in large quantities from the seafood industry in China and many other countries. Oyster shells are a rich source of calcium carbonate and can be used directly as sorbent, but they will decompose and generate sludge in slightly acidic aqueous solutions, which often makes them an unattractive option for phosphate removal. In our previous work [23] we found that to improve the usefulness of oyster shells clay can be added and shaped with the oyster shell powder to make a collectable phosphate-removal material. Unfortunately, the adsorption capacity of the oyster shell powder decreases rapidly and the material consequently has a short service life. This aim of the present work was to produce a high sorption capacity material that is readily collectable and possesses sustained phosphate-removing capacity, using fumed silica powder and pulverized oyster shell as starting materials. In addition, we investigated the effects of different calcining temperatures, hydrothermal annealing temperatures, and annealing times on phosphate removal. The phosphate-removal

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Table 1
Chemical compositions (wt.%) of the principal raw materials.

Material	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	LOI	Total
Oyster shell	1.25	0.64	0.11	54.31	0.01	0.01	0.93	0.11	42.96	100.12
Fumed silica	91.94	2.06	1.65	–	–	0.90	0.30	–	3.15	100.00

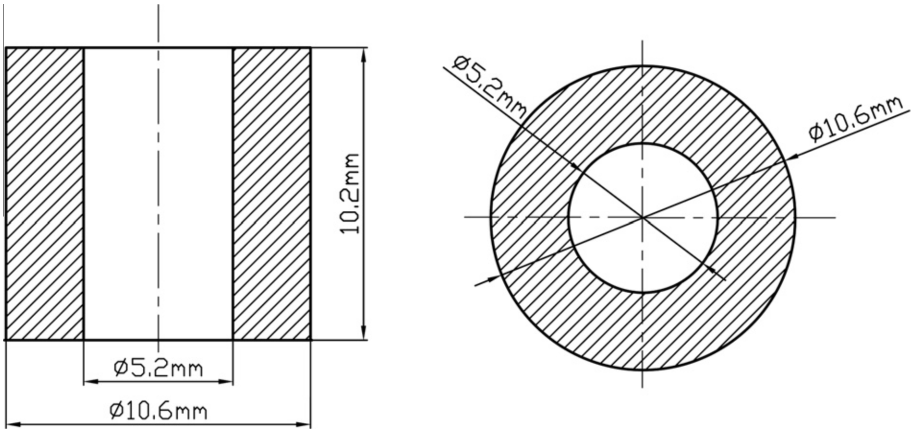

Fig. 1. Cross-sectional and plan view of the oyster shell and fumed silica donuts produced; all dimensions are mm.

mechanism was deduced by microstructure analysis and geochemical analysis of the solid material.

2. Materials and methods

2.1. Materials

Fumed silica powder used in this study was obtained from XIBEI Iron Alloy Company, China. The chemical composition of the fumed silica and oyster shell, determined by XRF, are given in Table 1.

2.2. Sample preparation

The pulverized oyster shell was sieved to <200 mesh particle size and combined with the fumed silica in the mass proportion 58:42, equivalent to a Ca:Si mole ratio of 5:6. Water was added to provide plasticity and the resulting paste was then shaped using donut metal molds. The shape and sizes of the samples that were investigated are shown in Fig. 1, for a dry sample weight of 2.0 g.

Batches of dry donut samples were heat treated at temperatures (700, 750, 800, 850, or 900 °C) for 1 h. After cooling the samples were hydrothermally cured for 8 or 16 h in an autoclave at a temperature between 130 and 180 °C.

2.3. Characterization

The crystalline phase of each sample was determined with a Philips X'pert-MPD X-ray diffractometer (XRD) using Cu Kα1 radiation, with lamp voltage 40 kV and lamp current 40 mA; a scan rate is $4^\circ\,min^{-1}$ was used to allow identification of the peaks. The microstructures of the cured material were examined using a Philips XL30 scanning electron microscope (SEM), and chemical compositions were determined by energy dispersive X-ray spectroscopy (EDS) and X-ray fluorescence analysis (XRF) before and after phosphate removal.

All experiments were carried out using a $5\,mg\,L^{-1}$ phosphate solution prepared from $Na_2HPO_4{\cdot}2H_2O$ in deionized water [24]. Phosphate concentrations and removal efficiencies were determined using the ammonium phosphomolybdate blue method. Absorbance was measured with an SP-721E spectrophotometer.

3. Results

3.1. Calcination and hydrothermal treatment results

The phosphate-removal capacity of all of the samples was evaluated under the same conditions, using an initial phosphate concentration of $5\,mg\,L^{-1}$. The adsorbent dose was fixed at 2.0 g $(100\,mL)^{-1}$ of waste (one donut piece per 100 mL wastewater).

It is apparent from Fig. 2 that phosphate removal for samples calcined at 700 °C increased with increasing hydrothermal temperature and time, but the efficiency was relatively low. The best of this cohort of samples was annealed at a hydrothermal temperature of 160 °C for 12 h, and removed 40% of the phosphate after 2 h contact and 70% after 4 h. When the calcination temperature was increased to 750 °C all of the samples showed greater phosphate removal than those calcined at 700 °C. The best of this cohort of samples was hydrothermally annealed at 150 °C for 12 h, and removed 81% of the phosphate after 4 h contact. Samples calcined at 800 °C showed greater phosphate-removal capacity than samples calcined at either 700 or 750 °C. Hydrothermal annealing at 150 °C for 10–12 h gave the highest phosphate-removal efficiency, namely 74% with 2 h contact time and 92% after 4 h.

However, phosphate-removal capacity decreased with increasing calcining temperature. All of the samples calcined at 850 °C show lower phosphate removal compared to samples calcined at 800 °C. Despite this, the five samples hydrothermally annealed at 150 °C still have the highest phosphate removal for this cohort, ranging from 68% to 70% for 2 h contact. When contact times were extended to 4 h, the samples hydrothermally annealed at 130 °C showed the best phosphate-removal ability. Increase of calcining temperature to 900 °C further decreased phosphate-removal capacity. However, for this cohort of samples hydrothermal annealing at 130 °C provided the best phosphate-removal ability. These data indicate that at calcination temperatures greater than 800 °C a product was produced that during subsequent hydrothermal annealing had a stable crystallographic structure, and low phosphate reactivity.

3.2. XRD analysis results

XRD investigation of the crystalline phases during calcination and hydrothermal annealing indicated that during calcination at