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Preparation of adsorbent for phosphate recovery from aqueous solutions based on condensed tannin gel

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ABSTRACT

We have synthesized an iron-loaded tannin gel as an adsorbent for phosphate recovery in aqueous solutions. The use of the tannin gel prepared from condensed tannin, which is a ubiquitous and inexpensive natural polymer, is not only cost effective and environment-friendly, but interesting because the phosphate-adsorbed gel can be expected to use directly as a fertilizer. The amount of iron loaded into the tannin gel oxidized by nitric acid was much larger than that into the non-oxidized tannin gel. This increase in the amount of the loaded iron resulted in the significant increase in the adsorption amount of phosphate onto the gel. Mössbauer spectroscopy indicated that the morphology of iron in the gel is a mono-type complex, which is formed as a result of the reaction between Fe(III) and the oxidized tannin gel with carbonyl groups. The iron-loaded tannin gel showed the adsorption selectivity for phosphate over other anions and the pH independence of phosphate adsorption in the wide range of initial pH 3–12. The phosphate adsorption isotherm for the iron-loaded tannin gel followed the Freundlich equation with constants of $K_F = 2.66$ and $1/n = 0.31$, rather than the Langmuir equation. The adsorption amount of phosphate on iron weight basis for the iron-loaded tannin gel is 31.3 mg-P/g-Fe, which indicates that iron in the gel was efficiently used for the phosphate adsorption compared with other phosphate adsorbents, such as iron hydroxides.

1. Introduction

Although phosphorus is essential for plant growth and necessary for modern agricultural techniques, the shortage of phosphate rock has become increasingly serious [1,2]. Also, phosphate has a potential to cause eutrophication in surface waters. For these reasons, it is of value to recover phosphate from environmental and waste water to overcome the resource scarcity problem as well as to avoid pollution of water environment.

A biological method [3] and a coagulation method [4] are widely utilized for the phosphate removal at industrial level [5]. Under these methods, however, it is difficult to recycle the removed phosphate. A crystallization method [6,7] could be used for the phosphate recovery, but requires complicated and precise control of the operating conditions. In contrast, an adsorption method requires the simple operating conditions and produces little sludge compared with the other methods. This indicates that the adsorption method is promising for the phosphate recovery [8].

The conventional adsorbents such as zirconia and titania are difficult to use in a practical wastewater treatment because their adsorption capacities are insufficient, and the regeneration of the used adsorbent is quite difficult in spite that these adsorbents are rather expensive. In recent years, considerable attention has been paid to the investigation of low-cost adsorbents, such as waste materials [9], by-products [10], aluminum oxide hydroxide [11], and calcined alunite [12], based on economical and environmental concerns. Iron-based compounds are remarkable as inexpensive and environment-friendly adsorbents [13–17]. Borggaard [18] reported that the phosphate adsorption capacities of the iron oxides are proportional to their specific surface areas, because phosphate is adsorbed on the hydroxy groups on their surface. In practical processes, however, the fine particles of the iron oxides with large specific surface area are difficult to handle, indicating that it is necessary to load the iron oxides into some support media to improve the handling. Recent research has thus focused on creating cheap and stable iron-loaded support media [19,20].

Tannins are one of the biomass materials that are inexpensive and ubiquitous natural polymers extracted from leaves or barks of plants and have many hydroxy groups, as shown in Fig. 1 [21]. A tannin gel, which is prepared from the tannins by cross-linking, has a significant ability to adsorb and reduce various metal ions [22–30]. Furthermore, the tannins have a potential for improving soil fertility and productivity [31–33]. Therefore, the application of the tannin gel as the support media of the iron oxides is not only

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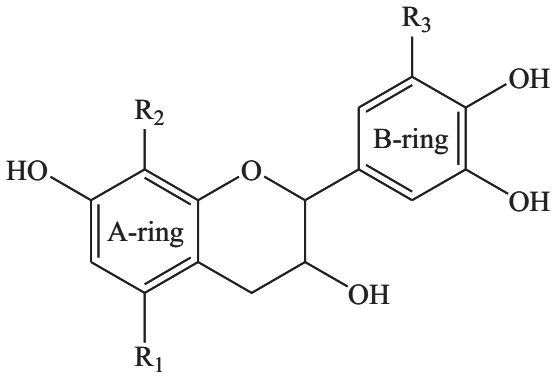

Fig. 1. Estimated chemical structure of condensed tannin molecule. (A-ring: R_1=OH, R_2=H, phloroglucinolic; R_1=R_2=H, resorcinolic; R_1=H, R_2=OH, pyrogallolic. B-ring: R_3=H, catecholic; R_3=OH, pyrogallolic) [21].

a cost effective and environment-friendly, but interesting because the phosphate-adsorbed gel can be expected to use directly as a fertilizer.

In the present study, we have developed the adsorbent for phosphate recovery utilizing the tannin gel as the support media of iron. The optimization of the iron-loaded tannin gel has been carried out in terms of the amount of iron loaded into the gel. Using the obtained iron-loaded tannin gel, the phosphate adsorption experiments have been performed at various solution conditions to investigate the effects of pH and other anionic species. Also, the adsorption isotherm has been obtained and then compared with those of other phosphate adsorbents.

2. Materials and methods

2.1. Materials

Wattle tannin powder was kindly supplied by Mitsubishi Nuclear Fuel Co., Ltd., and all other reagents were of analytical grade. The stock solutions of iron and phosphate were prepared from iron(III) nitrate nonahydrate and disodium hydrogen phosphate, respectively. Deionized and distilled water was used in all procedure, and all reagents were used as received in the present study.

2.2. Preparation of tannin gel

The tannin gel (TG) was prepared according to the previous paper [29]. Wattle tannin powder (28 g) was dissolved in 50 mL of 0.225 M sodium hydroxide solution at room temperature, and 6 mL of 37 wt% formaldehyde solution was successively added as a cross-linker. After gelation at 353 K for 12 h, the gel obtained was grinded into small particles and then washed with water and 0.05 M nitric acid solution to remove the unreacted substances, and finally rinsed with water again. The gel particles were dried by the freeze drying method.

2.3. Oxidization of tannin gel

The TG particles were oxidized using nitric acid. The TG particles (0.5 g on a dry basis) were added into 50 mL of nitric acid (1, 2, and 5 M), and then the samples were shaken in a water bath at 333 K up to 240 min. The oxidized tannin gel (OxTG) was washed with water to remove the residual nitric acid, and then dried by the freeze drying method. The attenuated total reflectance Fourier transform infrared (ATR FT-IR) spectra of the TG and the OxTG were measured by a Fourier transform infrared spectrophotometer (FT/IR 660 Plus, JASCO). To examine the optimum conditions of the oxidization treatment, the iron adsorption tests were carried out. The OxTG particles (0.05 g on a dry basis) were added into 10 mL of 0.018 mM iron(III) solution at pH 2.0, and the solution was then shaken in a water bath at 298 K for more than 5 days. The concentrations of the iron ions in the solutions were determined using an inductively coupled plasma spectrometer (ICPS) (ICPS-8100, Shimadzu), and the amounts of iron adsorbed onto the gel were calculated from the mass balance.

2.4. Preparation of iron-loaded tannin gel

The OxTG particles (2 g on a dry basis) were added into 100 mL of 1 M iron(III) solution, and the mixture was then shaken in a water bath at 298 K for more than 5 days. The iron-loaded tannin gel (FeOxTG) was separated from the solution and washed with water for a week. The gel was then filtered and freeze-dried. The iron-loaded gel using the non-oxidized TG, FeTG, was synthesized in a similar manner for comparison.

2.5. Characterization of iron-loaded tannin gel

All gels were sieved by the screens with mesh sizes of 125 and 250 μm, and the gel particles in the fraction of 125–250 μm were used in the following characterizations of the gels as well as in the phosphate adsorption experimetns. Krypton sorption measurements of the TG, the OxTG, and the FeOxTG were conducted using an Omnisorp 100CX (Beckman Coulter) at 77 K. Prior to Kr physisorption, the samples were outgassed for 1000 min at 333 K under vacuum. The specific surface areas were calculated from the Brunauer–Emmett–Teller equation over the relative pressure range $P/P_0 = 0.05 - 0.2$, where a linear relationship was maintained. Scanning electron microscope (SEM) images were obtained with a VE-7800 (Keyence) operating at an accelerating voltage in the range 1.7–2.0 kV. The electronic configuration of the FeOxTG was examined by the Mössbauer analysis. The ^{57}Fe Mössbauer spectrum for the FeOxTG was recorded at room temperature by a Mössbauer spectrometer (Topologic Systems) using ^{57}Co source (1.85 GBq).

2.6. Phosphate adsorption experiments

All phosphate adsorption experiments were carried out in a batch system. In the time-course experiments, 0.05 g (on a dry basis) of the TG, the OxTG, the FeTG, or the FeOxTG was added into 10 mL of phosphate solution (100 mg-P/L), and the mixtures were shaken in a water bath at 298 K for the specified times. In the adsorption isotherm measurements, the FeOxTG (0.05 g on a dry basis) was soaked in 10 mL of phosphate solution (10–200 mg-P/L), and the sample solutions were shaken in a water bath at 298 K for more than 5 days. To investigate the effects of pH and other anionic species on the phosphate adsorption behavior, the adsorption experiments were carried out in a manner similar to the adsorption isotherm measurements at an initial phosphate concentration of 100 mg-P/L, where initial pH and ionic strength of the solutions were adjusted using HCl, NaOH, NaCl, $NaNO_3$, and Na_2SO_4. The phosphorus concentrations of the sample solutions after filtration of the gel particles were determined by ICPS, and the amounts of phosphorus adsorbed onto the gel were calculated from the mass balance.

3. Results and discussions

3.1. Loading of iron into tannin gel

The phosphate adsorption amount of the gel is expected to increase with an increase in the amount of iron introduced, because