Simultaneous removal of phosphate and nitrite ions from aqueous solutions using modified soybean waste

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ABSTRACT

We investigated the simultaneous removal of phosphate and nitrite ions from aqueous solutions by a combination treatment that used both PG-Ca (poly-γ-glutamic acid combined with flocculating agents) and SB600 (soybeans treated with calcium chloride, hydrochloric acid and calcined at 600 °C). Phosphate ions and nitrite ions were selectivity adsorbed by PG-Ca and SB600, respectively. The removal mechanism of phosphate ions from aqueous solution was related to the presence of calcium hydroxide (derived from PG-Ca), and that of nitrite ions was related to the presence of chloride ions at the surface of SB600.

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Introduction

Phosphorus is an essential element and is an important nutrient for the growth of organisms and the normal functioning of ecosystems [1]. Phosphate containing wastewater is a global problem [2]. Excess phosphorus discharged into water bodies causes eutrophication, which can, in turn, pose a threat to human health and the ecological balance [3,4]. At the same time, phosphorus resources in the world may only last for a further 50 to 100 years [5]. The US Environmental Protection Agency (USEPA) has set the maximum permissible level and the stringent discharge limit of phosphate ions to 0.1 mg/L and less than 0.05 mg/L, respectively [1,6,7]. Therefore, it is necessary to develop efficient methods for the removal of phosphate ions from water and wastewater [1].

Similarly, nitrogen-containing compounds released into environment can create serious problems; such as eutrophication in rivers, the deterioration of water quality, and can pose hazards to human health [8]. Therefore, the USEPA has set a maximum concentration level of 10 mg/L of nitrate-nitrogen in drinking water [9]. It is well known that the nitrite ion can interfere with oxygen transport in the body and may result in a condition known as methemoglobinemia, in which the ability of hemoglobin to exchange oxygen is seriously reduced [10]. Furthermore, the nitrite ion can produce nitrosamine, a carcinogenic compound that is formed on contact with the acidic conditions of the stomach. Nitrosamine has been implicated in the pathology of gastric cancer [11,12]. Because of the risks associated with phosphorous and nitrite (nitrate) contaminated water, there are several existing methods of phosphate and nitrite (nitrate) removal from wastewater. These methods include chemical precipitation, ion exchange, biological treatment, and adsorption [13–17,2,18], ion exchange, reverse osmosis, electrodialysis, and distillation [2,19–25]. Of these, the adsorption method is considered to be the most promising technique due to its simplicity, flexibility of design, ease of operation, and cost-effectiveness [1,26].

Poly-γ-glutamic acid (PGA) is a viscous component of fermented soybeans. It is biodegradable and has a great ability to absorb water. These properties mean that it has applications in a wide range of fields. PGA has been shown to be an effective adsorbent for the removal of various dyes and metals from aqueous solutions [27,28]. In addition, PGA treated by γ-irradiation, or by the addition of flocculants, agglutinates and sediments, and has proved useful for the removal of substances in wastewater. In 2013, the amount of soybean waste generated was 1.45 million t. The majority of this waste was not recycled, and

effective recycling techniques for this material are necessary. Therefore, there are many merits to the concept of using waste biomass (soybean) to produce useful and effective adsorbents for the purification of water, both for society and the global environment. Yokoyama et al. [29] reported on the nitrate ion adsorption properties of Ca-containing charcoal. They suggested that a useful adsorbent for the adsorption of nitrate ions could be produced by soaking wood (waste biomass), which was treated with calcium chloride and hydrochloric acid, in the contaminated solutions. However, Yokoyama et al. did not investigate the adsorption capability of soybean waste for nitrite ion removal in complex solution systems.

In our previous studies [30,31], we focused on the adsorption and removal of phosphate and nitrite ions using PG-Ca (poly-γ-glutamic acid and flocculants) and carbonaceous material produced from soybeans (SB600) in a single-ion solution system. The results showed that phosphate and nitrite ions were selectively adsorbed by PG-Ca and SB600, respectively. However, in order for these materials to be used in real-life situations, we must identify the removal mechanisms for phosphate and nitrate by PG-Ca and SB600. Therefore, the object of this study is to investigate the adsorption–removal mechanism of phosphate and nitrite ions from a binary-ion solution using treated waste biomass derived from soybeans. The effects of the amount of adsorbent, contact time, and the solvent volume on the adsorption–removal of phosphate and nitrite ions were also investigated.

Materials and methods

Materials

PGα21Ca (PG-Ca, poly-γ-glutamic acid and flocculants), and soybeans (virgin SB) were purchased from Nippon Poly-Glu Co., Ltd., and Akamatsushubyou Co., Ltd., Japan, respectively. Solutions of phosphate, nitrite, and chloride ions were prepared using potassium dihydrogenphosphate, sodium nitrite, and potassium chloride, respectively (Wako Pure Chemical Industries, Co., Ltd., Japan). Soybean carbonaceous material (SB600) was produced from virgin soybeans (SB) treated with calcium chloride, hydrochloric acid, and calcined at 600 °C, according to the method reported by Yokoyama et al. [29,31]. Virgin SB added to 1 mol/L calcium chloride solution (500 mL, Wako Pure Chemical Industries, Co., Ltd., Japan) and stirred for 24 h at room temperature. The suspensions were filtered using a 0.45 μm membrane filter (Advantec MFS, Inc., Japan) and then the SB residues were dried for 5 h at 110 °C. The SB samples were then carbonized in a muffle furnace by heating for 2 h at 600 °C under a nitrogen gas flow. Following carbonization, they were decomposed by hydrochloric acid treatment, in which the carbonized SB samples were added to 6 mol/L hydrochloric acid solution (100 mL). The suspensions were filtered and subsequently dried for 5 h at 110 °C to obtain the sample, which is hereafter referred to as SB600, where the numeral indicates the carbonization temperature. Scanning electron microscopy (SEM) was carried out with a JSM-5500LV instrument (JEOL, Japan). The concentration of calcium, aluminum, silica, and oxygen on PG-Ca was measured with an electron probe micro analyzer (EPMA, JXA-8530F, JEOL, Japan) with an accelerating voltage of 15.0 kV and a beam diameter of 5 μm. The surface functional groups of SB600 were measured by titration [31,32].

Measurement of the phosphate and nitrite ion concentration after treatment with PG-Ca and SB600

The adsorbent (0.05 g) was added to a solution of phosphate and nitrite ions (0.5 mmol/L, 300 mL). Adsorbents were added according to four strategies: (1) PG-Ca only, (2) SB600 only, (3)
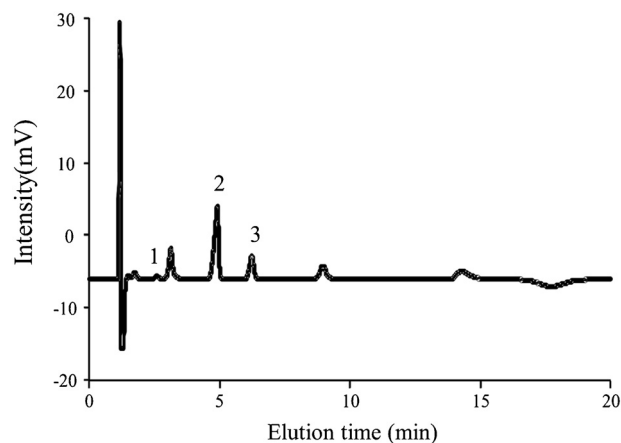

Fig. 1. Chromatograph of anions. (1) Phosphate ion, (2) chloride ion, (3) nitrite ion.

both PG-Ca and SB600 at the same time, and (4) PG-Ca was added 1 h after SB600. The suspensions were stirred at 60 rpm for between 2 min and 5 h at room temperature. Each sample was then filtered through a 0.45 μm membrane filter. The concentrations of phosphate, nitrite, and chloride ions were measured using an ion chromatograph (Fig. 1, Prominence HIC-NS, Shimadzu, Japan). The measurements were performed using a Shim-pack IC-A3 (Shimadzu, Japan) column. The mobile phase comprised p-hydroxylbenzoic acid (8.0 mmol/L), bis–tris (3.2 mmol/L), and 50 mmol/L boric acid (1:1:1). The flow rate was 1.2 mL/min at a temperature of 40 °C. The detector was a CDD-6A conductivity detector (Shimadzu, Japan), and the sample volume was 50 μL. The residual percentage was calculated using in the following equation:

$$R = \left(\frac{C}{C_0}\right) \times 100 \tag{1}$$

where R is the residual percentage (%), C_0 is the initial concentration (mmol/L), and C is the equilibrium concentration (mmol/L).

Effect of hydroxide ions on the adsorption of nitrite ion onto SB600

SB600 (0.5 g) was added to a solution of nitrite ions (10 mg/L, 300 mL). Then, one hour after mixing, calcium hydroxide (0.01–0.5 g) was added to the sample solution. The suspension was mixed at 60 rpm for 5 h at room temperature. After that, the sample was filtered through a 0.45 μm membrane filter. The concentration of nitrite ion was measured using an ion chromatograph. The residual percentage was calculated using Eq. (1).

Effect of the amount of PG-Ca on the adsorption of phosphate and nitrite ions

Both SB600 (0.5 g) and PG-Ca (0.1, 0.3, and 0.5 g) were added at the same time to solutions of phosphate and nitrite ions (0.5 mmol/L, 300 mL), and the suspensions were stirred at 60 rpm for 5 h at room temperature. After that, the samples were filtered through a 0.45 μm membrane filter. The concentrations of phosphate and nitrite ions were measured using an ion chromatograph. The residual percentages were calculated using Eq. (1).

Effect of the contact time on the adsorption of phosphate and nitrate ions

SB600 (0.5 g) was added to a solution of phosphate and nitrite ions (0.5 mmol/L, 300 mL), and then, after mixing for between