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Cadmium sorption characteristics of phosphorylated sago starch-extraction residue

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ABSTRACT

The residue produced by the extraction of sago starch is usually discarded as a waste material. In this study, we phosphorylated the sago starch-extraction residue with phosphoryl chloride and used the phosphorylated residue to remove cadmium from wastewater. The phosphoric ester functionality in the phosphorylated residue was evaluated by means of infrared microspectrometry and solid-state NMR. The dependence of the cadmium sorption behavior on pH, contact time, and electrolyte concentration and the maximum sorption capacity of the phosphorylated residue were also studied. The cadmium sorption varied with pH and electrolyte concentration, and the maximum sorption capacity was 25.2 mg g^{-1}, which is almost half the capacity of commercially available weakly acidic cation exchange resins. The phosphorylated residue could be reused several times, although cadmium sorption gradually decreased as the number of sorption–desorption cycles increased. The phosphorylated residue sorbed cadmium rapidly, which is expected to be favorable for the continuous operation in a column.

1. Introduction

The sago palm, *Metroxylon sagu*, grows in lowland Southeast Asia, within 10° of the Equator. The palm accumulates starch in its trunk, more than 200 kg of dry starch which may be accumulated at about 8–12 years [1]. Sago starch is a staple food in tropical Southeast Asia and it is a promising solution for the food crisis of countries with tropical wetlands and may also further their economical development. In Asia and the Pacific region in 2008, there were approximately 2 million hectares of natural sago palm forests and about 0.14 million hectares of planted sago palms, out of a total swamp area of about 20 million hectares [2]. Sago palm has the potential to yield up to 25 tons of starch per hectare per year, and the sago starch yield per unit area could be about 3–4 times that of rice, corn, and wheat and about 17 times that of cassava [2]. However, the extraction of sago starch produces large amounts of residue for which no suitable method of disposal has been established. Recently, several researchers reported the production of biodegradable plastics using sago starch-extraction residue [3,4], and the development of additional uses for this extraction residue is desirable. For example, if the residue could be treated in some way to make it an effective sorbent, it could be used for the removal of heavy metals in wastewater.

There are many mines and refineries in Southeast Asia, some of which produce copper, zinc, tin, and nickel. Heavy metal-containing wastewater generated by these facilities pollutes the environment and adversely affects human health. For example, the toxicity of cadmium, which is a by-product of the refining of zinc and other materials, is well documented; excess cadmium intake is associated with renal damage, anemia, hypertension, and Itai-itai disease [5]. In Japan, the allowable limit for cadmium in water related to human health is 0.01 mg L^{-1}. Several remediation techniques, such as precipitation on lime [6], ion exchange [7–9], adsorption onto activated carbon [10,11], membrane processes [12], and electrolytic methods [13], have been utilized to reduce the concentration of heavy metal ions in effluents [14]. However, these methods are generally expensive for the application in the environment. Several researchers have investigated phosphorylation techniques to generate efficient, low-cost sorbents for the removal of heavy metal from water [15–22]. Phosphorylation, which is an esterification reaction, can be expected to impart heavy metal sorption capacity to sago starch-extraction residue.

The objectives of this study were to produce phosphorylated sago starch-extraction residue for use as a sorbent for cationic heavy metal ions, especially cadmium ions, in water samples and to evaluate the cadmium sorption characteristics of the phosphorylated residue.

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2. Materials and methods

2.1. Phosphorylation of sago starch-extraction residue

Sago starch-extraction residue obtained from Leyte in the Philippines was used as a raw material. The extraction residue, which is composed of starch (55% by weight), cellulose, hemicellulose, and lignin, was pulverized in a grinder; and the resulting powder was passed through a 0.5-mm sieve. The sieved extraction residue was placed in an extraction thimbles and lipids were removed by refluxing the sieved powder in a Soxhlet extractor for 24 h in a mixture of ethanol and benzene (1:2) [3]. After lipid removal and drying, the extraction residue (5 g) and 80 mL of *N*,*N*-dimethylformamide (C_3H_7NO) were mixed, and the slurry was allowed to stand for 10 min; then phosphoryl chloride ($POCl_3$) was added, along with tributylamine ($[CH_3(CH_2)_3]_3N$; 5 mL) for the removal of hydrochloric acid, which interferes with the phosphorylation reaction. Then the slurry was stirred in an oil bath at 80 °C for 2 h. After the reaction, the product was washed with a mixture of ethanol and hexane (9:1) for the removal of the unreacted reagents. The weight of the product was almost the same as that of the raw material (5 g). The phosphorylated extraction residue produced in this way (powder) was designated as P-SR$_{WA}$ (WA indicates "with amine"). We also prepared phosphorylated extraction residue without tributylamine (P-SR$_{WOA}$) to determine how the esterification reaction was affected by the presence of the amine, which is known to accelerate esterification reactions [23].

2.2. Elemental analysis

2.2.1. Phosphorus analysis

The phosphorus contents of P-SR$_{WA}$, P-SR$_{WOA}$ and the untreated sago starch-extraction residue were determined by the molybdenum blue method [24,25].

The P-SR$_{WA}$ (0.1 g) was placed in a 300-mL conical beaker and digested with 10 mL of concentrated nitric acid (Wako Co., special grade) and 5 mL of 60% perchloride acid (Wako Co., special grade) on a hot plate (AHS, Asahi-Rika Seisakusho Co.). After digestion, 30 mL of 2 mol L^{-1} nitric acid was added, and the mixture was filtered through filter paper (Advantec No. 5C). The volume of the filtrate was brought to 200 mL with deionized water, and the phosphorus content of the resulting solution was determined. The P-SR$_{WOA}$ and the untreated sago starch-extraction residue were also subjected to the same procedure. The phosphorus contents of P-SR$_{WA}$, P-SR$_{WOA}$ and the untreated sago starch-extraction residue were determined with a spectrophotometer (BioSpec-1600, Shimadzu Co.) by means of colorimetric method.

2.2.2. Total carbon and total nitrogen analysis

The total carbon and total nitrogen contents of the P-SR$_{WA}$, P-SR$_{WOA}$ and the untreated sago starch-extraction residue were determined with a CN coder (MT-700, Yanaco Co.) [26]. The P-SR$_{WA}$ (0.2 g) was mixed with 5 g of copper oxide (Wako Co., chemical grade), and the mixture was placed in the nickel sample holder and combusted in the oxidation furnace of the CN coder. The P-SR$_{WOA}$ and the untreated sago starch-extraction residue were also subjected to the same procedure. The carbon and nitrogen signals were used for the calculation of total carbon and nitrogen contents. Hippuric acid ($C_6H_5CONHCH_2COOH$; Kishida Chemical, for the CN coder) was used as a standard for carbon and nitrogen. Hippuric acid has a constant amount of carbon (60.33%) and nitrogen (7.82%) that is suitable for the standard material for total carbon and nitrogen analyses.

2.3. Infrared microspectrometric analysis

Fourier transform infrared (FT-IR) analysis of P-SR$_{WA}$ was carried out with an IR microspectrometer (FT/IR-4100 type A and IRT-3000, JASCO Co.) and a KBr disk (1 cm in diameter) with an aliquot of P-SR$_{WA}$. The wavenumber range was 600–4000 cm^{-1}.

2.4. ^{31}P and ^{13}C solid-state NMR analysis

^{31}P and ^{13}C solid-state CP/MS NMR analyses of P-SR$_{WA}$ and the untreated sago starch-extraction residue were carried out with a solid-state NMR spectrometer (NM-ECX, JEOL Co.). P-SR$_{WA}$ powder was placed in a zirconia sample tube (4 mm in diameter, 22 mm length, JEOL Co.) to a height of 17 mm. The prepared sample tube was used for both ^{13}C and ^{31}P solid-state NMR analysis. The ^{31}P NMR conditions were as follows: resonance frequency 400 MHz, spinning rate 10 kHz, number of points 2048, and number of scans 512 at 25 °C. Ammonium phosphate dibasic ($(NH_4)_2HPO_4$) was used as a standard. The ^{13}C NMR conditions were as follows: resonance frequency 400 MHz, spinning rate 10 kHz, number of points 2048, and number of scans 1024 at 25 °C. Adamantine ($C_{10}H_{16}$) was used as the standard.

2.5. Cadmium sorption on P-SR$_{WA}$

2.5.1. Effect of pH

P-SR$_{WA}$ (0.2 g) was stirred with 25 mL of aqueous cadmium (50 mg L^{-1}) at pH 2, 3, 3.5, 4, 5, and 6 for 1 h. 0.1 mol L^{-1} of HNO_3 and NaOH solutions was prepared and added dropwise during the pH adjustment to minimize the increase in the solution volume. The supernatant was filtered, and the concentration of cadmium ions in the filtrate was determined with an atomic absorption spectrophotometer (Z-5010, HITACHI Co.). The amount of sorbed cadmium on P-SR$_{WA}$ was calculated from the amount of remaining cadmium ions in the filtrate. The percentage of cadmium sorption was also calculated as follows:

$$\text{cadmium sorption percentage} = 100 \times \frac{\text{amount of sorbed cadmium (mg)}}{\text{total amount of cadmium in the solutuon (mg)}}$$

2.5.2. Effect of contact time

P-SR$_{WA}$ (0.1 g) was stirred with 25 mL of aqueous cadmium (50 mg L^{-1}) at pH 4.0 and contact times of 0.5, 1, 2, and 24 h. The amount of sorbed cadmium on P-SR$_{WA}$ was determined according to the method described in Section 2.5.1.

2.5.3. Effect of the electrolyte concentration

P-SR$_{WA}$ (0.1 g) was stirred with 25 mL of aqueous cadmium (50 mg L^{-1}) at $NaNO_3$ concentrations of 0.01, 0.1, and 1.0 mol L^{-1} at pH 4.0 for 1 h. The amount of sorbed cadmium on P-SR$_{WA}$ was determined according to the method described in Section 2.5.1.

2.5.4. Maximum sorption capacity for cadmium

The different doses of P-SR$_{WA}$ and P-SR$_{WOA}$ (0.05–0.20 g) were stirred individually with 25 mL of aqueous cadmium (50 mg L^{-1}) at pH 4 for 1 h. The sorption data were fitted to a Langmuir isotherm:

$$\frac{C_e}{q_e} = \frac{1}{bQ_{\max}} + \frac{C_e}{Q_{\max}}$$

where C_e is the concentration of the cadmium at equilibrium (mg L^{-1}), q_e is the amount of sorbed cadmium at equilibrium (mg g^{-1}), b is a constant related to the energy of sorption, and $Q_{\max}$ is the maximum sorption capacity for cadmium (mg g^{-1}).