



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.

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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% perchloric 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. ³¹P and ¹³C solid-state NMR analysis

³¹P and ¹³C 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 ¹³C and ³¹P solid-state NMR analysis. The ³¹P 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 ¹³C 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 HNO₃ 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:

cadmium sorption percentage

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

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 NaNO₃ 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).

Table 1
Phosphorus content of P-SR sample.

Sample	Phosphorus mg P g ⁻¹ DW	Total carbon g g ⁻¹ DW	Total nitrogen g g ⁻¹ DW
P-SR _{WA} ^a	32.0	0.40	0.01
P-SR _{WOA} ^b	8.5	0.40	0.00
Untreated ^c	0.0	0.41	0.00

DW: dry weight.

^a Phosphorylated sago starch-extraction residue produced with amine.

^b Phosphorylated sago starch-extraction residue produced without amine.

^c The untreated sago starch-extraction residue.

2.5.5. Sorption–desorption cycling

P-SR_{WA} (0.2 g) was stirred with 25 mL of aqueous cadmium (50 mg L⁻¹) at pH 4.0 for 1 h (in duplicate). The amount of sorbed cadmium on P-SR_{WA} was determined according to the method described in Section 2.5.1. After air drying for 12 h, the cadmium-containing P-SR_{WA} (0.2 g) was stirred in aqueous HNO₃ (0.1 mol L⁻¹, 25 mL) at 25 °C for 1 h. The amount of desorbed cadmium (as indicated by the amount of cadmium released from P-SR_{WA}) in the HNO₃ solution was determined with an atomic absorption spectrophotometer (Z-5010, Hitachi Co.). P-SR_{WA} was recovered from the HNO₃ solution, air dried, and then reused for cadmium sorption. The cycle of cadmium sorption and desorption was carried out three times. The percentage of cadmium desorption was calculated as follows:

cadmium desorption percentage

$$= 100 \times \frac{\text{amount of desorbed cadmium (mg)}}{\text{amount of sorbed cadmium (mg)}}$$

3. Results and discussion

3.1. Elemental characteristics of P-SR_{WA}

Table 1 shows the phosphorus content of the untreated extraction residue and the phosphorylated residues which was produced with and without tributylamine (P-SR_{WA} and P-SR_{WOA} respectively). The untreated extraction residue did not contain phosphorus, and the phosphorus content of P-SR_{WA} (32.0 mg P g⁻¹) was clearly higher than that of P-SR_{WOA} (8.5 mg P g⁻¹). The hydrogen chloride produced by the reaction of phosphoryl chloride and compound which has OH group catalyzes hydrolysis of the phosphoric ester [27,28]. The extraction residue also contains the compound which has OH group such as glucose and cellulose, therefore, the presence of a tertiary amine is necessary to remove the hydrogen chloride. Sakakura et al. [23] reported that tributylamine markedly accelerates the esterification reaction. The total carbon and total nitrogen contents of the untreated extraction residue and the P-SR_{WA} and P-SR_{WOA} samples were nearly identical.

P-SR_{WA} was used for subsequent analyses because it had the highest phosphorus contents and thus could be expected to show superior cadmium sorption behavior.

3.2. Infrared microspectrometric characteristics of P-SR_{WA}

The FT-IR spectra of P-SR_{WA} and the untreated extraction residue (Fig. 1) showed large adsorption bands at 3400 cm⁻¹ (O–H stretching), 2900–2980 cm⁻¹ (C–H stretching), and 1150 and 1070 cm⁻¹ (C–O stretching) [29]. P-SR_{WA} showed new bands at 1200 and 980 cm⁻¹. There was a band at 1200 cm⁻¹ corresponding to the P=O bonds [30] and a shoulder at 980 cm⁻¹ attributed to C–O–P stretching [31]. The intensities of the bands at 1200 and 980 cm⁻¹ were compared to those of the untreated extraction residue using the relative absorbance method described by Nada et al. [32]. The relative absorbance (band intensity of any group/band

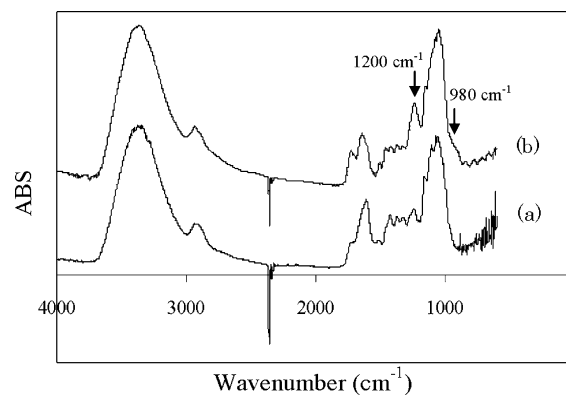


Fig. 1. FT-IR spectra of P-SR_{WA}. (a) Untreated: the untreated sago starch-extraction residue. (b) P-SR_{WA}: phosphorylated sago starch-extraction residue produced with amine.

Table 2
Relative absorbance of C–O–P bonds for P-SR_{WA}.

Sample	Relative absorbance ^a	
	1200 cm ⁻¹ /1325 cm ⁻¹	980 cm ⁻¹ /1325 cm ⁻¹
P-SR _{WA} ^b	2.09	0.88
Untreated ^c	1.16	0.52

^a Band intensity of C–O–P group/band intensity at 1325 cm⁻¹.

^b Phosphorylated sago starch-extraction residue produced with amine.

^c The untreated sago starch-extraction residue.

intensity at 1325 cm⁻¹, which corresponds to C–H rocking for a cellulose ring [33,34]) of the bands at 1200 and 980 cm⁻¹ for P-SR_{WA} were higher than those of the untreated extraction residue (Table 2). This result confirmed the presence of the phosphate group on P-SR_{WA}.

3.3. ³¹P and ¹³C solid-state NMR spectra of P-SR_{WA}

The ³¹P solid-state NMR spectrum of the untreated extraction residue did not show any clear peaks, whereas the spectrum of P-SR_{WA} showed a clear peak in the range of 0–1.0 ppm (Fig. 2). This chemical shift is typical for phosphoric di- and triesters [35] and thus confirmed the presence of the phosphoric ester in P-SR_{WA}. (Note that the symmetrical side bands at ±60 ppm are rotational side bands resulting from powder anisotropy [31].)

The ¹³C solid-state NMR spectrum of the untreated extraction residue showed four major peaks, at 62, 72, 83, and 99–103 ppm (Fig. 3). Because the untreated extraction residue consists of sago starch, cellulose, and hemicellulose, the NMR spectrum of the untreated residue was similar to that of sago starch and cellulose, and the four major peaks were assigned to C6 (62.3 ppm); C2, C3, and C5 (72.6 ppm); C4 (83.1 ppm); and C1 (99.8, 103.1 ppm) [31,36]. The chemical shifts of carbons bearing hydroxyl groups available for substitution (C2, C3, and C6) moved to a lower resonance region after the esterification reaction (Table 3), and this is β-effect as substitution effect [31,37]. The peaks for C1 and C4 of P-SR_{WA} appeared at a higher resonance region than the corresponding peaks for the

Table 3
Chemical shifts of ¹³C solid-state NMR spectra for P-SR_{WA}.

Sample	Chemical shift (ppm)			
	C1	C2, 3, and 5	C4	C6
Untreated ^a	103.1, 99.8	72.6	83.1	62.3
P-SR _{WA} ^b	102.8, 99.6	75.6, 72.6	82.2	62.4

^a The untreated sago starch-extraction residue.

^b Phosphorylated sago starch-extraction residue produced with amine.

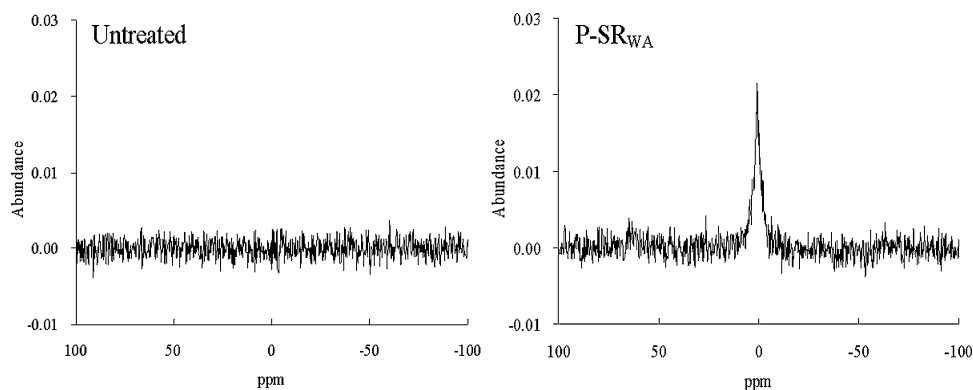


Fig. 2. ^{31}P solid-state NMR spectra for P-SR_{WA}. Untreated: the untreated sago starch-extraction residue. P-SR_{WA}: phosphorylated sago starch-extraction residue produced with amine. Standard material of the phosphate: ammonium phosphate dibasic ((NH₄)₂HPO₄).

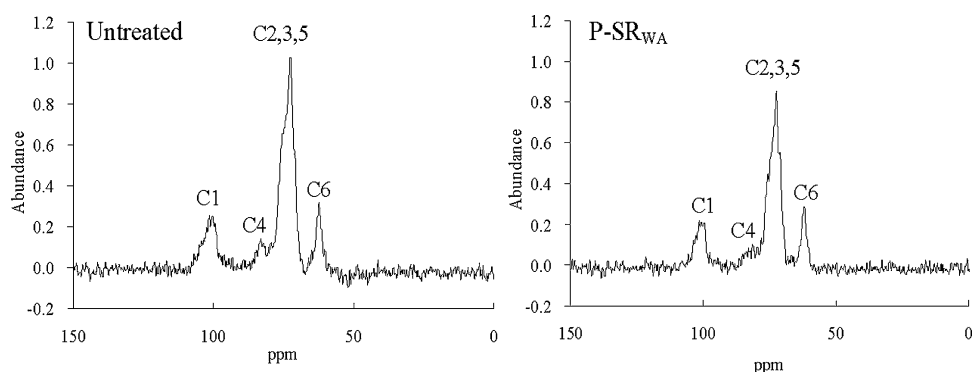


Fig. 3. ^{13}C solid-state NMR spectra for P-SR_{WA}. Untreated: the untreated sago starch-extraction residue. P-SR_{WA}: phosphorylated sago starch-extraction residue produced with amine. Standard material of the carbon: adamantane (C₁₀H₁₆).

untreated extraction residue (Table 3). C1 and C4 are the sites of the glycosidic linkage and thus are not subject to substitution. This is usually attributed to the γ -effect as steric effect [37] which indicates a modification at C2 or C3 (next to C1 and C4, respectively), resulting in the shift of C1 and C4 to a higher resonance. Esterification of a hydroxyl group of a glucopyranosic compound is known to shift the resonances of the adjacent carbons upfield [31,37,38].

3.4. Cadmium sorption characteristics

3.4.1. Effect of pH on cadmium sorption

Fig. 4 shows the amount of sorbed cadmium on P-SR_{WA} at various pH values. At pH 2.0, P-SR_{WA} sorbed 3.72 mg g⁻¹ of cadmium, and the amount of sorbed cadmium increased to about 6.0 mg g⁻¹

at pH 3–6. Because the concentration of hydronium ions in solution increases remarkably at low pH, sorption of cationic metal ions normally decreases drastically at low pH because of the competition with hydronium ions [39]. In addition, P-SR_{WA} is protonated at low pH. Protonation, the reaction whereby an organic functional group (e.g., amine, carbonyl, carboxylate) forms a complex with a surface proton, is expected to be important at low pH [40]. Formation of complexes between the phosphoric ester groups on P-SR_{WA} and hydronium ions at low pH may have limited the sorption of cadmium cations on P-SR_{WA} at low pH.

3.4.2. Effect of contact time on cadmium sorption

Fig. 5 shows the amount of sorbed cadmium on P-SR_{WA} from a 50 mg L⁻¹ cadmium solution at contact times ranging from 10

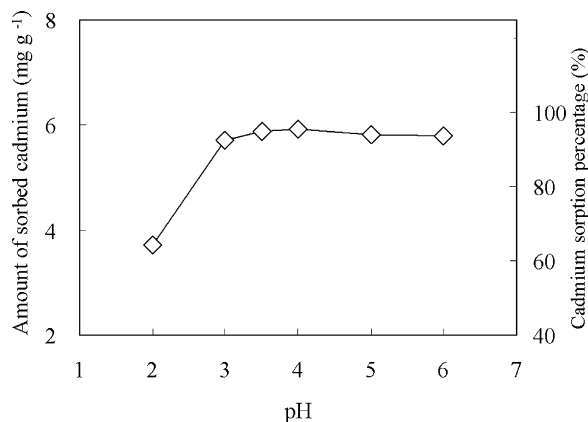


Fig. 4. Effect of pH on the cadmium sorption by P-SR_{WA}. The symbol “◇” shows both of the amount of sorbed cadmium and the cadmium sorption percentage.

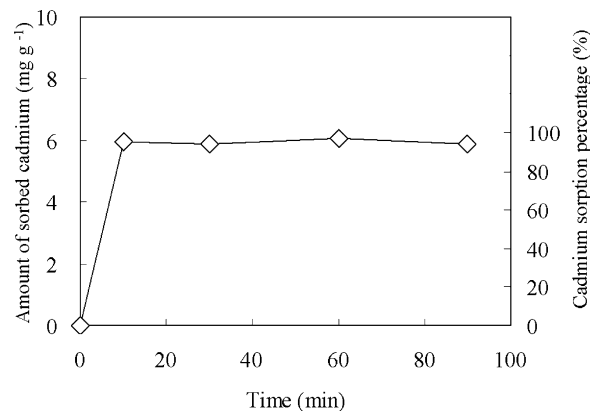


Fig. 5. Effect of contact time on the cadmium sorption by P-SR_{WA}. The symbol “◇” shows both of the amount of sorbed cadmium and the cadmium sorption percentage.

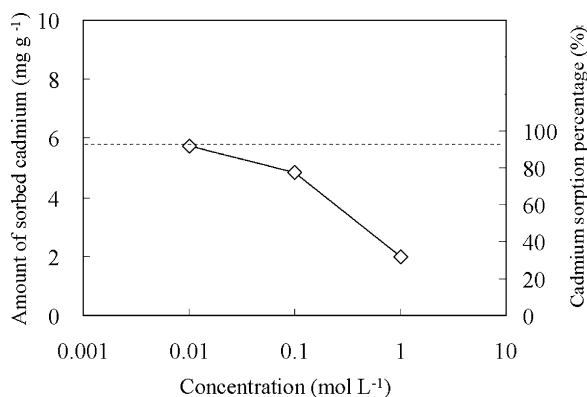


Fig. 6. Effect of electrolyte concentration on the cadmium sorption by P-SR_{WA}. The symbol “◇” shows both of the amount of sorbed cadmium and the cadmium sorption percentage. Electrolyte: NaNO₃ (0.01, 0.1 and 1.0 mol L⁻¹). Dotted line: the amount of sorbed cadmium on P-SR_{WA} without NaNO₃ (5.87 mg g⁻¹).

to 90 min. The amount of sorbed cadmium reached its maximum value within 10 min. For comparison the amount of cadmium sorbed on phosphorylated cellulose reaches a maximum within 30 min [41], and the sorption of heavy metal ions (Ni, Cu, As, and Sr) reaches a maximum after about 45 min [29]. In addition, rice husk treated with sodium hydroxide, sodium bicarbonate, or epichlorohydrin has been used as cadmium sorbent, and these treated materials require more than 1 h to reach maximum cadmium sorption [14]. Therefore, by comparison P-SR_{WA} showed relatively rapid sorption behavior.

3.4.3. Effect of the electrolyte concentration on cadmium sorption

When the electrolyte concentration in the cadmium solution increased, the amount of sorbed cadmium on P-SR_{WA} tended to decrease, owing to competition with Na⁺ (Fig. 6). The amount of sorbed cadmium at 0.01 mol L⁻¹ NaNO₃ (5.76 mg g⁻¹) was almost the same as the amount sorbed in the absence of NaNO₃ (5.87 mg g⁻¹). In 0.1 and 1.0 mol L⁻¹ NaNO₃, the amounts of sorbed cadmium decreased to 4.83 and 2.00 mg g⁻¹, respectively.

3.4.4. Maximum sorption capacity of cadmium

Fig. 7 shows the cadmium sorption behavior on the different doses of P-SR_{WA} and P-SR_{OW}. P-SR_{WA} could be fitted to Langmuir isotherm and it can be seen that the plot exhibits a good linear

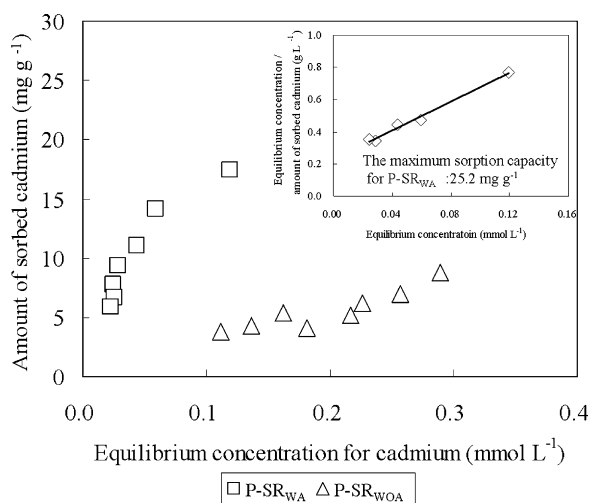


Fig. 7. Cadmium sorption behavior on P-SR_{WA} and P-SR_{WOA} Langmuir isotherm for the cadmium sorption on P-SR_{WA} was shown in this figure. P-SR_{WA}: phosphorylated sago starch-extraction residue produced with amine. P-SR_{WOA}: phosphorylated sago starch-extraction residue produced without amine.

Table 4

Cadmium sorption and desorption behaviors for P-SR_{WA}.

Sample	The repetition of sorption and desorption (times)		
	1	2	3
Cd sorption (%)	98.5	79.5	54.1
Cd desorption (%)	98.0	93.4	93.9

portion. On the other hand, P-SR_{WOA} did not fit to it. Cadmium sorption behavior on P-SR_{WOA} was clearly lower than that of P-SR_{WA}. The maximum sorption capacity (Q_{max}) of P-SR_{WA} for cadmium was 25.2 mg g⁻¹ (Fig. 7). Several researchers have reported that the maximum cadmium-sorption capacities of wood, an agricultural by-product, and biomass are clearly improved by phosphorylation [16,18,42]. Saito and Aoyama [18] and Holan and Volesky [43] reported that the maximum cadmium-sorption capacities of phosphorylated wood and sawdust are 24.2 and 56.0 mg g⁻¹, respectively, and our value for the maximum sorption capacity of P-SR_{WA} was similar to the former value. The maximum cadmium-sorption capacities of various commercially available strongly and weakly acidic cation exchange resins range from 46.7 to 270 mg g⁻¹ [7,44,45], and the maximum sorption capacity of P-SR_{WA} was nearly half the lower value.

There have been some reports of low-cost sorbents, such as sodium hydroxide-treated agricultural residue, for the removal of heavy metals [46–50], and the maximum cadmium-sorption capacities of those materials range from 3 to 20 mg g⁻¹ [6]. The maximum sorption capacity of P-SR_{WA} was relatively high compared to the capacities of these other materials.

3.4.5. Cadmium sorption–desorption cycling with P-SR_{WA}

The cadmium-sorption percentages for three sorption–desorption cycles with P-SR_{WA} were 98.5, 79.5, and 54.1% (Table 4). Gong et al. [51] also reported that the amount of sorbed copper decreases as the number of cycles increases. Although the cadmium-sorption percentage of P-SR_{WA} decreased gradually as the number of cycles was increased, our results indicate the P-SR_{WA} can be reused. Reuse of the sorbent will reduce the cost of removing cationic heavy metal ions from wastewater. It is noted that the cadmium-desorption percentage exceeded 90% for all three cycles (Table 4).

To investigate the reason for the decrease in cadmium sorption with the number of cycles, we collected most of the sorbed cadmium on P-SR_{WA} using nitric acid solution, and obtained FT-IR spectra of P-SR_{WA} before and after the cadmium sorption–desorption cycling (Fig. 8). The relative absorbance of the

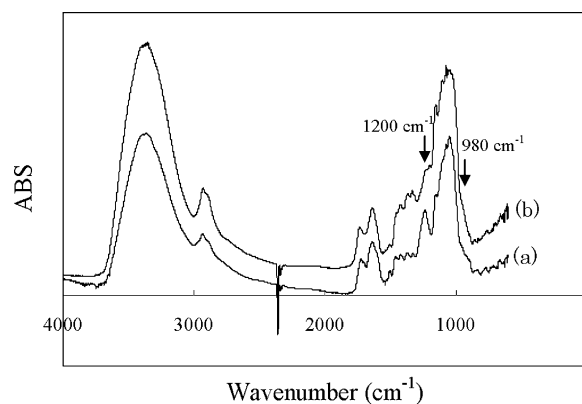


Fig. 8. The change of FT-IR spectra for P-SR_{WA} by desorption. (a) P-SR_{WA} (before the cadmium sorption–desorption cycle). (b) P-SR_{WA} (after the cadmium sorption–desorption cycle). P-SR_{WA}: phosphorylated sago starch-extraction residue produced with amine.

Table 5The change of relative absorbance of C–O–P bonds for P-SR_{WA} by desorption.

Sample	Relative absorbance ^a	
	1200 cm ⁻¹ /1325 cm ⁻¹	980 cm ⁻¹ /1325 cm ⁻¹
P-SR _{WA} (before desorption) ^b	2.09	0.88
P-SR _{WA} (after desorption)	1.23	0.61

^a Band intensity of C–O–P group/band intensity at 1325 cm⁻¹.^b Phosphorylated sago starch-extraction residue produced with amine.

bands at 1200 and 980 cm⁻¹ (which are ascribed to C–O–P bonds on P-SR_{WA}) was 2.09 and 0.88 before cycling and 1.23 and 0.61 after the third cycle (Table 5). That is, the relative absorbance of the bands for the C–O–P bonds was reduced by the cycling. This result seems to indicate that the reduction in cadmium sorption was due to a change in the surface condition of P-SR_{WA} that occurred during the cycling process.

4. Conclusion

The residue from the extraction of sago starch can be phosphorylated and used as a heavy metal sorbent. The phosphorus content of P-SR_{WA} was higher than that of P-SR_{WOA}. The presence of the phosphoric ester in P-SR_{WA} was confirmed by infrared microspectrometric analysis and solid-state NMR analysis. The cadmium sorption of P-SR_{WA} varied with pH and electrolyte concentration in the cadmium solution. P-SR_{WA} rapidly sorbed cadmium. The maximum sorption capacity of P-SR_{WA} for cadmium was 25.2 mg g⁻¹, which is almost half the capacity of commercially available weakly acidic cation exchange resins. The amount of sorbed cadmium gradually decreased with the number of sorption–desorption cycles. FT-IR analysis indicated that the cycling process affected the surface conditions of the phosphoric ester of P-SR_{WA}.

The rapid sorption behavior of P-SR_{WA} can be expected to be favorable for continuous operation in a column because the required contact time between the metal ion solution and the sorbent was generally short. In addition, P-SR_{WA} could be reused several times, and most of the sorbed cadmium on P-SR_{WA} could be collected.

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