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Modification of Rice Straw for Heavy Metal Ion Adsorbents by Microwave Heating

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Summary: Cellulose in rice straw was chemically modified by phosphorylation using conventional heating or microwave heating. Rice straw pretreated by NaOH solution gave the highest phosphorus content when it was phosphorylated using microwave heating at 450 watt (7.07%P, ion exchange capacity 2.60 meq/g). The 3 hour-reaction in oil bath yielded the modified rice straw with lower of phosphorus content (6.32%P) and higher ion exchange capacity (2.99 meq/g) than that of microwave heating. The feasibility of the modified rice straw as cation sorbents for removing heavy metal was investigated. Cd^{2+}, Cr^{3+} and Pb^{2+} were used as sorbates. In sorption test of 40 ppm with 2.0 g/L of the modified rice straw, both modified rice straws could adsorb metal ions faster than the commercial ion exchange resin (dowax) at the time less than 60 min. The modified rice straw prepared by microwave heating (A-MCW2) could remove 90% of Cd^{2+} and Cr^{3+} in 60 minutes and remove 99% of Pb^{2+} after 30 min.

Keywords: biosorbent, cellulose phosphate, heavy metal ion, microwave synthesis, phosphorylation, rice straw, waste water treatment

Introduction

Rice straw is a lignocellulosic agricultural by-product containing cellulose (37.4%), hemi-cellulose (44.9%), lignin (4.9%) and silicon ash (13.1%).[1] In Thailand, about 10 million tons of rice straw are produced annually as a waste of rice production.[2] The disposal of rice straw by open-field burning frequently causes serious air pollution, thus new economical technologies for rice straw disposal and utilization must be developed. Generally, raw biosorbents are modified with chemical treatment to increase their adsorption capacity. Sodium hydroxide treatment has been used in saponification to produce carboxylate site for binding heavy metals.[3] Fourest and Volesky found that the sufonate group in various types of biomass contributes to heavy metal binding.[4] Naoto and Masakazu reported that the sorption capacity of wood was increased by phosphorylation.[5] Phosphoric acid modified rice straw showed high capability for dyes removal from aqueous solution.[6] Rungrodnimitchai and Dokbua succeeded in removing 100% of Cd^{2+} by cellulose phosphate in modified rice straw prepared by conventional heating.[7] However, more effective heating method is still necessary for increasing ion exchange capacity of cellulose phosphate.

In this research, the modified rice straws prepared by microwave heating were compared with the modified rice straw prepared by conventional heating in oil bath. The effect of pretreatment on the raw material was studied. The feasibility of the products as cationic adsorbents for removing Cd^{2+}, Cr^{3+}, Pb^{2+} from aqueous solution was investigated.

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Experimental Part

Materials

Rice straw was collected from a local farm. Rice straw was washed and then dried overnight at 100 °C. Then, it was cut and ground into small pieces. Some of rice straw was pretreated by boiling in 16% NaOH solution for 1 hour. Then it was washed and dried. Some rice straw was immersed in DMF for 1 night, then washed and dried. The size of rice straw material was about 500 micron. All chemicals were reagent grade or analytical grade and used as received.

Chemical Modification of Rice Straws

Three kinds of rice straws; (A) rice straw pretreated by NaOH solution, (B) rice straw pretreated by DMF (dimethylformamide) and (C) rice straw without pretreatment, were used as raw materials. Each kind of rice straw (2.0 g), phosphoric acid (16.8 ml, 0.29 mol) and urea (22.4 g, 0.37 mol) were mixed and preheated at 80 °C for 15 min. Then it was heated by oil bath at 150 °C for 2 or 3 hours, or by microwave irradiation (Electrolux EMM 2005) at 300 W (5 min), 450 W (3 min), 600 W (2 min) or 800 W (1.5 min). The reaction scheme is shown in Figure 1. The mixture was washed by tap water, acetone and dried. The obtained modified rice straws were immersed in 100 ml of 1.0 M HCl solution for 1 night, then washed with de-ionized water and dried before analysis and sorption tests.

Determination of Total Phosphorus

Ammonium vanadate-molybdate method was employed for spectrophotometric determination of total phosphorus. Perchloric acid (4.0 mL) was added to each samples (0.02 g) and digested at 165 °C for several hours until the mixtures tuned into colorless clear solution. Solution of vanadate molybdate acid (2.0 mL) was added to the sample (2.0 mL) and diluted to 50 mL and the absorbance was measured at 400 nm against a reagent blank. The total phosphorus content in sample was derived from the calibration curve using standard solution of KH_2PO_4 at the same condition.

Ion Exchange Capacity

0.2 g of H^+-form adsorbents were immersed in 100 mL of 1.0 M NaCl for overnight. By ion exchange reaction, part of H^+ in the samples was substituted by Na^+ and give HCl solution. The mixtures were filtered and rinsed with water. HCl solution was collected and titrated with a standard NaOH solution (5 mM) using phenolphthalein as an indicator.

Sorption Test

Metal ion solutions (40 ppm) for sorption test and standard solutions were prepared from 1000 ppm-standard solutions. The pH values of the solution for sorption experiment were adjusted to 5 ±0.1 by 0.1 M HNO_3 or NaOH solution. Sorption experiments were carried out in a flask and stirred at 150 rpm at ambient temperature (30 °C). Cd^{2+} or Cr^{3+}or Pb^{2+} solution (40 ppm, 100 ml) and 0.2 g of sorbents were added to the flasks. The sample (4 ml) was withdrawn from the flask at 2, 4, 6, 8, 10, 30, 45, 60, 120, 150, 180 minutes. The concentrations of the metal ions were determined using AAnayst 800 (Perkin Elmer Instrument). The experiments were conducted in duplicate.

Results and Discussion

The reaction conditions for preparation of the modified rice straw are shown in Table 1.

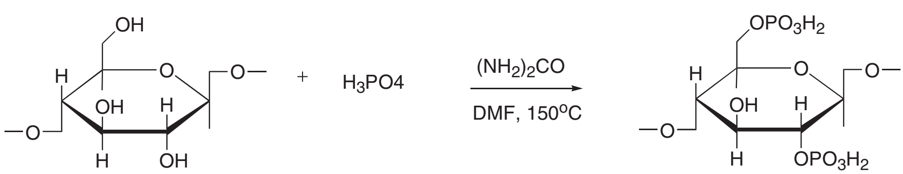

Figure 1.
Phosphorylation of the cellulose unit.

Table 1.
Reaction conditions for preparation of the modified rice straws, ion exchange capacities and phosphorus contents of the modified rice straws

Samples	Heating methods	Pre-treatment	Conditions	Ion exchange capacities (meq/g)	Phosphorus contents (%)
A-O1	Oil bath	NaOH	150 °C, 120 min	2.98	6.23
B-O1		DMF		1.13	2.65
C-O1		-		1.29	2.85
A-O2		NaOH	150 °C, 180 min	**2.99**	**6.32**
B-O2		DMF		2.46	5.74
C-O2		-		0.99	2.11
A-MCW1	Microwave	NaOH	300 W, 5 min	2.21	5.96
B-MCW1		DMF		1.36	3.14
C-MCW1		-		1.30	3.03
A-MCW2		NaOH	450 W, 3 min	**2.61**	**7.07**
B-MCW2		DMF		1.34	3.27
C-MCW2		-		1.73	3.75
A-MCW3		NaOH	600 W, 2 min	2.50	6.99
B-MCW3		DMF		1.48	3.56
C-MCW3		-		1.64	3.66
A-MCW4		NaOH	800 W, 1.5 min	2.58	7.04
B-MCW4		DMF		1.24	3.14
C-MCW4		-		1.51	3.49

IR spectra of unmodified rice straw (C) and modified rice straw (untreated (C-MCW3) and treated with DMF (B-MCW3)) by microwave heating at 600 W are shown in Figure 2.

The unmodified rice straw (C) showed strong broad adsorption at 3350 cm^{-1} from vibration of –OH groups and medium adsorption at 2900 cm^{-1} from $-CH_2-$ group and adsorption at 1160 cm^{-1} and 1110 cm^{-1} from C–O–C bond of glycosidic or β-(1 → 4)-glycosidic bond. These absorption bands indicated the presence of cellulose unit in rice straw. Furthermore, absorption at 1510 cm^{-1} can be attributed to the vibration of aromatic units in lignin of rice straw. In the spectra of the modified rice straw (C-MCW3), a new weak absorption from P-OH bond was found at 2400 cm^{-1} and a shoulder at 2700 cm^{-1}.

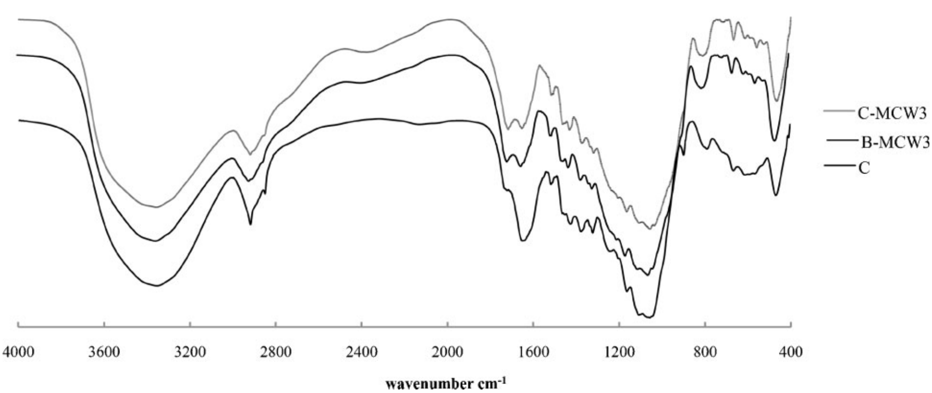

Figure 2.
IR spectra of unmodified rice straw (C) and modified rice straw (untreated (C-MCW3) and treated with DMF (B-MCW3)) by microwave heating at 600 W.

Another absorption at 1710-1720 cm^{-1} was from the vibration of P=O bond, a shoulder at 1200-1300 cm^{-1} was from the vibration of P=O of phosphate ester. At 900–1000 cm^{-1} a shoulder from the vibration of P−OH bond and P−O−C bond was observed.

On the other hand, the spectrum of the modified rice straw treated by DMF (B-MCW3), showed almost the same absorption spectrum as that of C-MCW3. It implied that treatment by DMF led no significant change in the molecular structure of the modified rice straw.

IR spectra of the rice straw treated by NaOH solution (A), the modified rice straw (treated by NaOH solution) by 3-hour reaction in oil bath (A-O2) and the modhified rice straw (treated by NaOH solution) by microwave heating at 600 W (A-MCW3) and are shown in Figure 3.

In Figure 3, the IR spectra of rice straw treated by NaOH before and after modification are similar to spectra of sample C and sample C-MCW3, respectively, except that the absorption at 1510 cm^{-1}, which indicates the presence of lignin, was disappeared. Lignin in rice straw was removed by NaOH treatment. Thus the main component of the rice straw after NaOH treatment was cellulose. The IR spectrum of A-O2 was not different from that of A-MCW3. The result suggests that the reaction by microwave heating gave the same product as from the reaction in oil bath. From IR spectra, it could be concluded that the phosphoric acid group was successfully introduced into the modified rice straws.

Effect of the Pretreatment Methods on Phosphorus Content of Modified Rice Straws

From Table 1, rice straw treated by NaOH solution (C), gave the highest phosphorus content in every condition. Treatment of rice straw by NaOH solution increased cellulose content in rice straw from 37.4% to almost 100%, which means it has more reactive units to react with phosphoric acid. As a result, the phosphorus content of modified rice straws treated by NaOH solution had almost 2 times of phosphorus contents of other kinds of modified rice straw. On the other hand, treatment by DMF had no significant effect on increasing of phosphorus content, except for the case of 3 hours heating by oil bath (B-O2), which gave 5.74% of phosphorus content. DMF treatment might give better thermal stability for a long time reaction.

For the oil bath heating, 3-hour reaction yielded higher phosphorus content than those of 2-hour reactions except for the case of untreated rice straw (C), which the phosphorus content decreased from 2.85% to 2.11%. Long reaction time may cause decomposition of the modified rice straw without pretreatment.

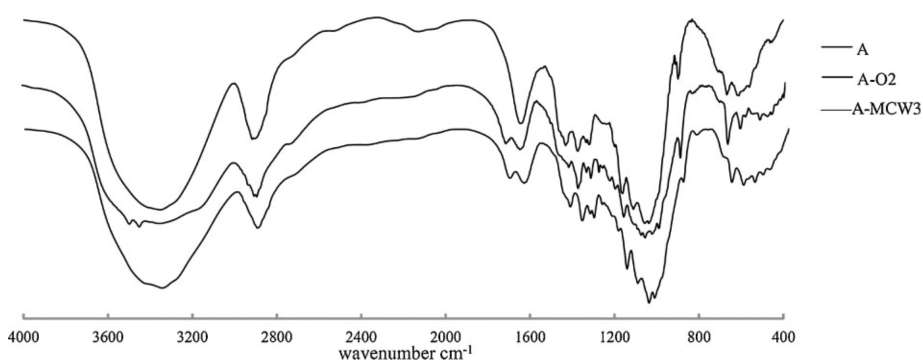

Figure 3.
IR spectra of rice straw treated by NaOH solution (A) and modified rice straw (treated with NaOH; A-MCW3) by microwave heating at 600 W.

Effect of Heating Methods

From Table 1, modified rice straw prepared by oil bath heating (A-O2) gave lower phosphorus content (6.32%) than those of modified rice straws prepared by microwave heating (A-MCW2 (7.07%), A-MCW3 (6.99%), A-MCW4 (7.04%)). However, the ion exchange capacity of modified rice straw prepared by oil bath heating (A-O2) (2.99 meq/g) was higher than any other modified rice straws (A-MCW1 (2.21 meq/g), A-MCW2 (2.61 meq/g), A-MCW3 (2.52 meq/g), A-MCW4 (2.58 meq/g)). The modified rice straws in this work had higher phosphorus contents and ion exchange capacities than the modified rice straw (no pretreatment) reported by Gong and co-worker (2.1%P)[6] and our previous work (2.8%P)[7]. The results suggest that the phosphorylation of cellulose can be achieved by short time reaction by microwave reaction as well as long time reaction in oil bath.

It should be noted that low power of MCW (300 W) with long reaction time could not give better performance of phosphorylation of rice straw.

Adsorption of Heavy Metal Ions

The adsorption ability of 2 kinds of the modified rice straws (A-O2 and A-MCW2) were compared with the unmodified rice straw (C) and a commercial ion exchange resin (Dowax). The ion exchange reaction is shown is Figure 4. The ion exchange capacity of each adsorbent is listed in Table 2. The ion exchange capacities of the modified rice straw from oil bath reaction (A-O2), the modified rice straw from microwave reaction (A-MCW2), the unmodified rice straw (C) and Dowax was 2.99 meq/g, 2.61 meq/g, 0.12 meq/g and 1.20 meq/g, respectively.

Table 2.
Ion exchange capacity of each adsorbent in the sorption test.

Adsorbents	Ion exchange capacities (meq/g)
A-O2	2.60
A-MCW2	2.99
Rice straw	0.12
Dowax	1.20

In the sorption test of 40 ppm Cd^{2+} with 2.0 g/L of the modified rice straw, the modified rice straw prepared by microwave heating (A-MCW2) removed 90% of Cd^{2+} in 60 min, which was faster than dowax in first 60 min (Figure 5). On the other hand, unmodified rice straw (C) adsorbed only 30% of Cd^{2+} in 60 min. It should be noted that the modified rice straw prepared by oil bath reaction (A-O2), with the highest ion exchange capacity could remove only 60% of Cd^{2+} after 180 min adsorption.

On the sorption test of Cr^{3+} ion, A-MCW2 removed Cr^{3+} ion quickly in 10 min, and the concentration remained at 5 ppm throughout the test (Figure 6). A-O2 decreased Cr^{3+} concentration to 10 ppm. On the other hand, Dowax could remove 96% of ions after 180 min.

All of adsorbents could remove Pb^{2+} better than Cd^{2+} and Cr^{3+}. Especially, A-MCW2 removed Pb^{2+} much faster in the first step and reach 99% removal after 30 min, while dowax took 90 min to give the same concentration (Figure 7). Apparently, the modified rice straws reached the adsorption equilibrium faster than the commercial resin.

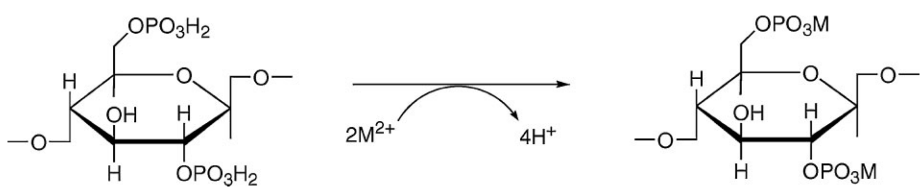

Figure 4.
Ion exchange mechanism of cellulose phosphate.

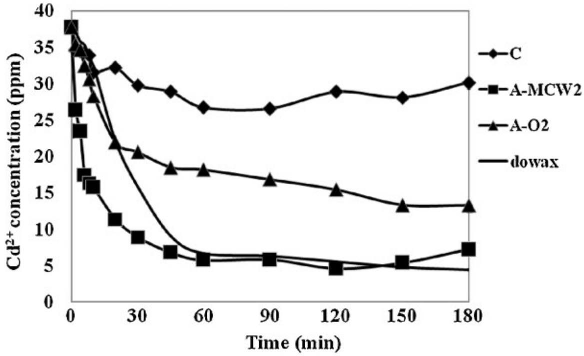

Figure 5.
Change of Cd^{2+} concentrations in the sorption experiments.

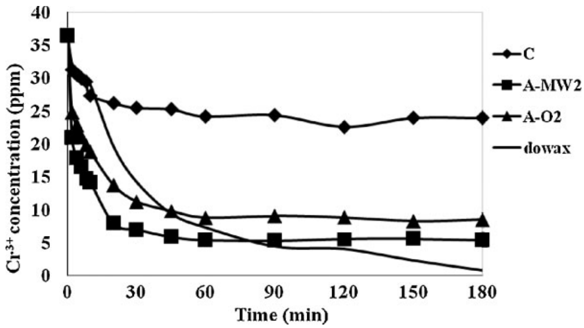

Figure 6.
Change of Cr^{3+} concentrations in the sorption experiments.

Even the ion exchange capacity of MCW2 was lower than that of A-O2, MCW2 could remove more ions with faster speed. It is considered that the microwave reaction takes place at the whole particle of cellulose. But the oil bath reaction takes place only on the surface of the particle of cellulose. It seems that the modified rice straw from the microwave reaction might be more porous than the modified rice

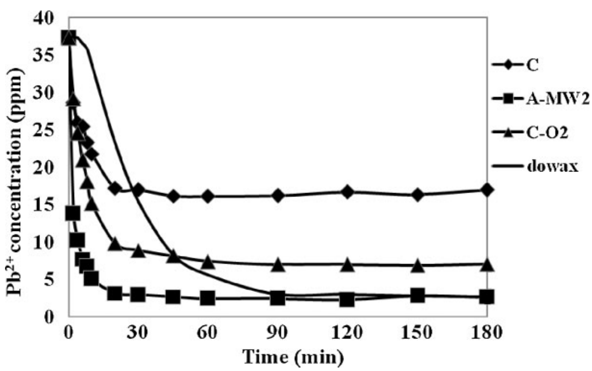

Figure 7.
Change of Pb^{2+} concentrations in the sorption experiments.

straw from the oil bath reaction. So that the adsorption ability of the modified rice straw from the microwave reaction may be contributed not only from the ion exchange capacity but also from the porosity of the material.

Conclusion

The rice straw pretreated by NaOH solutions gave the highest phosphorus content when it was phosphorylated by microwave heating at 450 W (7.07%P, 2.60 meq/g). The 3-hours reaction in oil bath gave the modified rice straw with 6.32% phosphorus content (2.99 meq/g). On the sorption test, the modified rice straws reached adsorption equilibrium faster than the commercial resin (dowax). In spite of lower ion exchange capacity, the modified rice straw prepared by microwave heating (A-MCW2) showed greater adsorption ability than the modified rice straw prepared by oil bath heating (A-O2). It can be concluded that microwave heating give modified rice straw with greater adsorption ability than the conventional heating. The result suggests that the modified rice straw, with biodegradiblity can be one of ion exchange resin alternatives.

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