

# Preconcentration of Heavy Metals from Aqueous Solution Using Chitosan Flake

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Chitosan flake was used as solid-phase material to separate and preconcentrate Cu(II), Cd(II) and Pb(II) in an aqueous solution by the solid-phase extraction technique. The effect of pH, salt, flow rate and volume of eluent was investigated. The metals were retained by chitosan at pH 5-7 and were easily eluted by 5 ml of 0.1 M EDTA (pH 6) with a flow rate of 0.5 ml min<sup>-1</sup>. The metal concentrations were determined by flame atomic absorption spectrometry. The proposed method was applied to the determination of trace amounts of metals in aqueous solution (20 µg l<sup>-1</sup>). The % recovery and % RSD were within the range of 83-112% and 2-15% respectively. The method detection limit was 20, 3 and 10 µg l<sup>-1</sup> for Pb, Cu and Cd respectively.

**Key Words:** preconcentration, heavy metals and chitosan

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## การเพิ่มความเข้มข้นของโลหะหนักในสารละลายโดยใช้ไคโตซาน

พัชรา เกตุค้ำงพลู ชาญยุทธร พรหมเดชไพบูลย์ และ เฟื่องฟ้า อุ๋นอบ (2548)

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ไคโตซานถูกนำมาใช้เป็นตัวดูดซับในการแยกโลหะตะกั่ว ทองแดงและแคดเมียม ซึ่งอยู่ในสารละลายตัวอย่างโดยวิธีการสกัดด้วยเฟสของแข็งเพื่อเพิ่มความเข้มข้นของโลหะในสารละลายตัวอย่าง มีการศึกษาผลของ pH เกลือ อัตราการไหล และปริมาตรตัวชะ พบว่าโลหะจะถูกจับไว้บนไคโตซานได้ดีที่ pH 5-7 และถูกชะออกมาได้โดยใช้สารละลาย EDTA (pH 6) เข้มข้น 0.1 M ปริมาตร 5 มิลลิลิตร โดยใช้อัตราการไหลของสารละลายตัวอย่างและสารละลายที่ใช้ชะเป็น 0.5 มิลลิลิตรต่อ นาที โดยใช้เทคนิคเฟลม อะตอมมิกแอบซอร์ปชัน สเปกโตรเมตรี ในการวิเคราะห์หาความเข้มข้นของโลหะ เมื่อนำวิธีการนี้ไปใช้เพิ่มความเข้มข้นของโลหะที่มีอยู่ในระดับต่ำในสารละลาย ( $20 \mu\text{g l}^{-1}$ ) พบว่า % recovery เป็น 83-112% และ % RSD เป็น 2-15% โดยวิธีการนี้มี Method Detection Limit อยู่ที่ 20, 3 และ  $10 \mu\text{g l}^{-1}$  สำหรับการวิเคราะห์ตะกั่ว ทองแดง และ แคดเมียม ตามลำดับ

**คำสำคัญ** การเพิ่มความเข้มข้น โลหะหนัก ไคโตซาน



## INTRODUCTION

At the present time, water resources are being polluted by effluent from human activities, especially from industries. Heavy metal is one of the pollutants of most concern due to its high toxicity. It is necessary to monitor the level of heavy metal in both soil and water resources. In general, heavy metals are present in trace levels and are often below the instrument detection limit. To determine correctly the concentration of heavy metals, a preconcentration step prior to the measurement by instruments is often recommended.

Chitosan is a biopolymer obtained from the deacetylation of chitin. It has many useful features such as hydrophilicity, biocompatibility and biodegradability. Due to its chelating properties, the uptake of heavy metals by chitosan has been investigated by many authors.<sup>(1-4)</sup> It has been used in metal removal from wastewater. The functionalization of chitosan with different complexing agents such as 8-hydroxyquinoline,<sup>(5)</sup> mercaptan<sup>(6)</sup> was carried out in order to obtain a chelating resin more selective for individual heavy metal. The complexation of chitosan and its derivatives with heavy metals were reviewed by Varma.<sup>(7)</sup> Furthermore, chitosan has also been used in a preconcentration procedure.<sup>(8-10)</sup> To reduce solid phase preparation time, chitosan flake without any modification was often used. Muzzarelli<sup>(11)</sup> reported the preconcentration of Zn, Cd, Pb and Cu using a chitosan flake column. The metals were eluted separately in order to facilitate the determination by polarography. In 1996, Chui *et al.*<sup>(12)</sup> proposed a preconcentration procedure of Cu, Cr and Ni using chitosan. The studied concentrations of metals were high (20-100 mg/l) and the recoveries of metal were in the range of 80-100%. Many works presented the preconcentration procedure of metals by dissolving metal-adsorbed chitosan with acid and determining the metal concentration by electrothermal atomic absorption spectrometry. These studies examined the preconcentration of single elements such as Pb, Cu and In.<sup>(13-15)</sup> In this work, we are interested in using chitosan flake in simultaneous preconcentration and recovery of Cu, Pb and Cd. The effect of pH, flow rate and salt on the process were investigated. The procedure was applied to preconcentrate trace metals in aqueous solutions.

## MATERIALS AND METHODS

### Materials

Chitosan flakes (85% deacetylation) were obtained from Seafresh Chitosan (Lab) Co. (Bangkok, Thailand). Cadmium sulfate ( $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ ), lead nitrate ( $\text{Pb}(\text{NO}_3)_2$ ) and copper nitrate ( $\text{Cu}(\text{NO}_3)_2$ ) were purchased from Fisher Scientific. All reagents were standard analytical grade and used without further purification. The metal solutions used for the preconcentration experiments were prepared by dissolving the metal salt in de-ionized water. The analytical standards for metal determination by atomic absorption spectrometer were prepared by stepwise dilution of  $1000 \text{ mg l}^{-1}$  stock standard solution (BDH). The pH of solutions was adjusted to the desired value by using either NaOH or HCl. De-ionized water was used for the preparation and dilution of solutions.

### Methods

The model solutions were passed through a column containing 0.2 g of chitosan flake. 10 ml of de-ionized water were percolated through the column, followed by the metal solution. The filtrate was collected and analyzed for unsorbed metals. The effects of pH of the metal solution, the flow rate and the amount of salt on the retention of metals were studied. To elute the retained metals, 0.1 M EDTA solution was passed through the column at the same flow rate as that used in the adsorption step. The eluate was collected and analyzed by flame atomic absorption spectrometer. The effect of volume of eluent was also studied. To investigate the effect of the parameters mentioned earlier, solutions containing metals in the range of 1 -  $100 \text{ mg l}^{-1}$  were used. Then, the selected parameters were applied to the preconcentration of trace metals in aqueous solutions.

A flame atomic absorption spectrometer (AAAnalyst100, Perkin-Elmer) was used to determine metal concentrations. The analytical wavelength of Cd, Cu and Pb are 228.8, 324.8 and 283.3 nm, respectively. The limit of detection of Cd, Cu and Pb are 0.1, 0.03 and  $0.2 \text{ mg l}^{-1}$  respectively. The SPE was performed using a Visiprep<sup>TM</sup> Vacuum Manifold and 6 ml polyethylene tubes with polyethylene frits (pore size of  $20 \mu\text{m}$  and thickness of 2.4 mm) provided by Supelco. A digital pH meter (pH211, Hanna instruments) was used for all pH measurements.

**RESULTS AND DISCUSSION**

The results of our preliminary study show that a chitosan column can retain Pb, Cd and Cu in the range of 0.3 – 3.2 mg metal/g chitosan.

**Effect of pH on the adsorption**

In aqueous solutions, metals exist in different species depending on the pH of the solution.<sup>(16)</sup> In order to obtain a good recovery of metals from a chitosan column, it is necessary to investigate the effect of pH on metal retention. In this experiment, the solutions of metal with an

initial pH in the range of 5 – 8 were used. A pH out of this range led to the agglomeration of chitosan (pH < 4) and the precipitation of metals (pH > 8). Table 1 shows the % sorption of Cu, Pb and Cd at different pH levels. The percentage sorption of the metals retained on the chitosan column was calculated from the difference between the starting amount of each metal (N<sub>s</sub>) and the amount of metal left in the filtrate (N<sub>f</sub>) as in equation 1.

$$\% \text{ Sorption} = \frac{N_s - N_f}{N_s} \times 100 \quad \dots (1)$$

**Table 1. Effect of pH on the sorption of metals.**

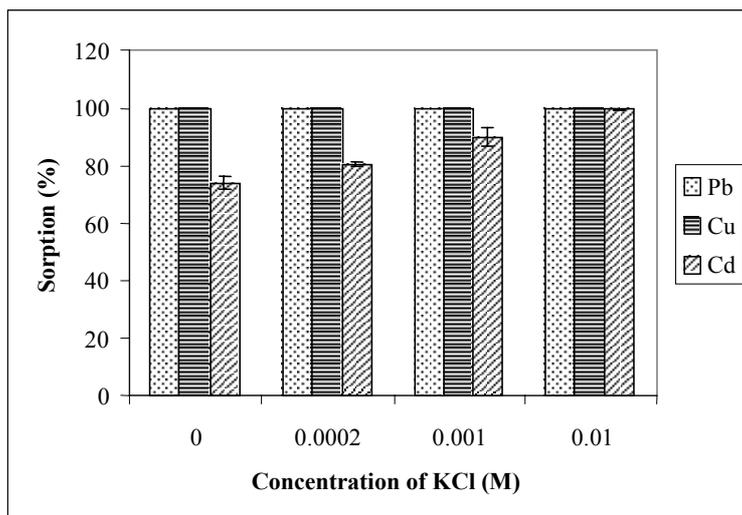
pH	Sorption <sup>a</sup> , %		
	Cu	Pb	Cd
5	62 ± 1	41 ± 4	59 ± 2
6	66 ± 4	45 ± 4	62 ± 1
7	62 ± 2	39 ± 2	57 ± 3
8	53 ± 2	44 ± 2	51 ± 2

<sup>a</sup> mean value ± SD, n = 3  
metal concentration : 40 mg l<sup>-1</sup>, volume 25 ml

The results in Table 1 show that pH of the solution in the studied range does not effect the adsorption of Pb. On the other hand, the retention of Cu and Cd by the chitosan column was decreased when the pH of the solution was 8. In general, the pH of natural water is in the range of 5-7. Therefore, the chitosan column is suitable for the adsorption of these metals in natural water. When 0.1 M EDTA (pH 8) was used as eluent, the recovery of metals from the column was in the range of 92-108%. The recovery of metals higher than 100% might be due to the contamination of metals in the reagents used in the elution step.

**Effect of salt on the adsorption of metals**

In natural water, some elements such as Na, K, Cl are always present in the form of salt (e.g. NaCl). In this study, the effect of salt on the retention of metals was investigated. KCl was chosen as a representative of salts found in natural water. In natural water, the concentration of K varies from 3.4 x 10<sup>-5</sup> mol/kg in river water to 0.01 mol/kg in sea water.<sup>(17)</sup> In this study, the concentration of KCl present in the solutions was varied from 0.0002 to 0.01 M. In order to investigate the effect of salt on adsorption of metal at low levels, the metal concentrations used were 0.8 mg l<sup>-1</sup> for Pb and Cu and 3 mg l<sup>-1</sup> for Cd. The sorption of metals on the column in the absence and in the presence of KCl is shown in Figure 1.



**Figure 1. Effect of salt on metal adsorption by chitosan column: Pb 0.8 mg l<sup>-1</sup>, Cu 0.8 mg l<sup>-1</sup> and Cd 3 mg l<sup>-1</sup>, 25 ml**

The results show that the adsorption of Pb and Cu in the chitosan column was not affected by the presence of KCl. On the other hand, the retention of Cd increases with an increasing amount of KCl. These results indicate that chitosan can be used as an adsorbent for trace metal preconcentration from natural water where salts are often present. These results are in accordance with the results obtained by Muzzarelli and Tubertini.<sup>(18)</sup> They reported that chitosan could adsorb trace amounts of Cu found in sea water. However, our preliminary results show that KCl has an undesired effect on metal adsorption when the metals are present in high concentration (40 mg l<sup>-1</sup>). In this case, it was found that the adsorption of metal was significantly reduced in the presence of 0.01 M KCl.

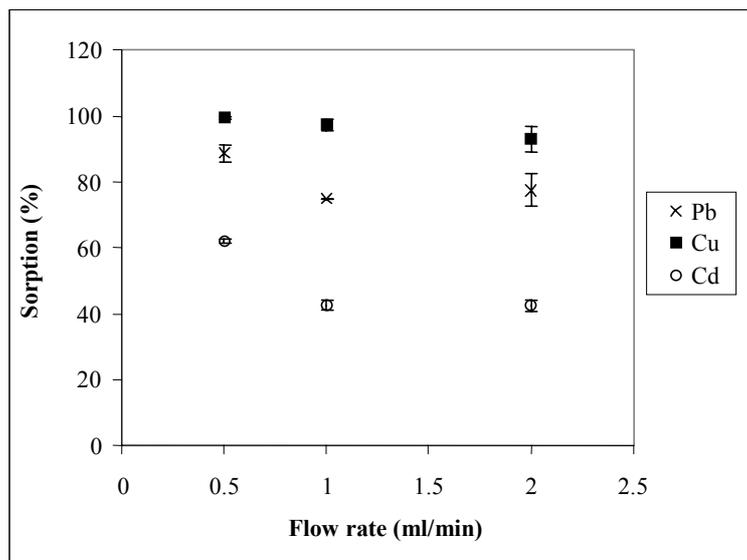
It is known that the amine groups in chitosan have the ability to chelate heavy metals. Rhazi *et al.*<sup>(2)</sup> demonstrated that chitosan has a selectivity of complexation with metals. It shows a better selectivity for the Cu(II) ion and to a lesser extent for the Cd(II) ion. This is in accordance with what is observed in this experiment. In the presence of salt, cation and anion from salt probably interact with binding sites of chitosan via electrostatic interaction. The

presence of salt in a high concentration will result in the reduction of the available binding sites for metals. When solutions contain high concentrations of metals and salts together, the capability of chitosan to retain the metals are decreased.

In Figure 1, the retention of Cd by the chitosan column increases with an increasing amount of KCl. The salt seems to have a beneficial effect on cadmium complexation and the binding sites of chitosan.

#### Effect of flow rate

The effect of flow rate on metal retention by the chitosan column was studied. The flow rates used were 0.5, 1.0 and 2.0 ml min<sup>-1</sup>. Solutions containing Pb (19 mg l<sup>-1</sup>), Cu (40 mg l<sup>-1</sup>) and Cd (107 mg l<sup>-1</sup>) were used in these experiments. The results are shown in Figure 2. At the high flow rate, the retention of the metals on the chitosan column decreased significantly. The same flow rate was also applied in the elution step. The recovery of the metals from the column by 0.1 M EDTA was not affected by the flow rate used in this study. To obtain a good retention of metals, a flow rate of 0.5 ml min<sup>-1</sup> was used in further experiments.



**Figure 2. Effect of flow rate on metal retention on chitosan column.**

**Selection of the eluent volume**

To increase the enhancement factor, the volume of eluent was optimized. The less volume used to elute metals, the more the eluate is concentrated. In this study, 50 ml of metal

solution was passed through the column. The adsorbed metals were eluted with 5 and 10 ml of 0.1 M EDTA (pH 6). The enhancement factor was 10 and 5 respectively. The results are summarized in Table 2.

**Table 2. Recovery of metals from chitosan column with various eluent volumes.**

Metal	Adsorbed metal (µg)	Recovered metal (µg)	
		Eluent 5 ml	Eluent 10 ml
Pb	64	58	60
Cu	93	96	104
Cd	186	71	83

Metal solution 50 ml: Pb 65 µg, Cu 93 µg and Cd 280 µg. The experiments were duplicated.

In our preliminary study, EDTA of various concentrations (0.05, 0.10, 0.25 M) was used as eluent. When 0.05 M EDTA was used, the metal recoveries were less than that obtained by 0.10 M EDTA. No difference in recoveries was observed when EDTA of 0.10 and 0.25 M were used. The effect of pH of EDTA solution was also investigated. There was little difference in metal recoveries using eluent of pH 4, 6 and 8. Therefore, 0.10 M EDTA with pH 6 was chosen as the eluent.

From Table 2, metals could be eluted in the same extent when the eluent volume of 5 and 10 ml were used. In the case of Cu and Cd, the found amounts are higher than the amount that

was adsorbed by the columns. This might be due to the contamination of these metals in the reagents used. It was found that only 39 and 45 % of Cd, or approximately 70 µg of Cd, could be recovered from the column. It is likely that when the amount of Cd adsorbed by the column is less than 70 µg, the higher % recovery could be obtained. In general, the metals in natural water are found in trace levels. This procedure can probably be used to preconcentrate and recover Pb, Cu and Cd from natural water. The optimized volume of eluent in this study was 5 ml and the enhancement factor obtained was 10. To obtain higher enhancement factors, larger sample volume is recommended.

**Preconcentration of metal at low level in solution**

The preconcentration of solution containing metals in low levels was investigated. The solution (50 ml) was percolated through the chitosan column (0.2 g) with a flow rate of 0.5 ml min<sup>-1</sup>. Then 5 ml of 0.10 M EDTA (pH 6) was used as eluent. The eluates were analyzed

by flame atomic absorption spectrometer. The results are shown in Table 3. The % recovery was calculated from the amount of metals in starting solution (N<sub>s</sub>) and the amount of metals eluted from the column (N<sub>f</sub>) as in equation 2. The results are summarized in Table 3.

$$\% \text{ Recovery} = \frac{N_f}{N_s} \times 100 \quad \dots (2)$$

**Table 3. Recovery of metals with column preconcentration procedure.**

Metal	Metal amount <sup>a</sup> (µg)	Recovered amount <sup>b</sup> (µg)	Recovery, %	% RSD (n=5)
Pb	65	58 ± 2	92 ± 3	3.26
Cu	1	1.01 ± 0.16	101 ± 16	15.84
Cd	1	1.12 ± 0.12	112 ± 12	10.71

<sup>a</sup> solution: Pb 1.3 mg l<sup>-1</sup>, Cu 0.02 mg l<sup>-1</sup> and Cd 0.02 mg l<sup>-1</sup>, 50 ml

<sup>b</sup> mean value ± SD, n = 5

From Table 3, the recovery of metals and % RSD is in the range of 92 – 112% and 3.26 – 15.84% respectively. The acceptable range of % recovery and % RSD (concentration level of 0.1 mg l<sup>-1</sup>) are 80-110% and 15% respectively.<sup>(19)</sup> The results obtained show a satisfactory accuracy and precision of the preconcentration procedure.

**Method Detection Limit**

The method detection limits were calculated by three times the standard deviation (n=5) of the blank. The values are 20, 3 and 10 µg l<sup>-1</sup> for the determination of Pb, Cu and Cd respectively. These limits were based on 50 ml of blank solution undergoing the preconcentration procedure. It can be improved by increasing the sample volume.

**CONCLUSIONS**

A simultaneous preconcentration of Cd, Cu and Pb from aqueous solution by chitosan column was developed. The optimization of conditions was carried out using model solutions. The accuracy and precision of the proposed method was reported in terms of % recovery ranging from 92 to 112, and % RSD ranging from 3.26 to 15.84. These values are within the acceptable limits. The method shows potential as an application for the

preconcentration of metals in natural water by chitosan flake.

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