ANALYTICAL SCIENCE & TECHNOLOGY
Vol. 11, No. 3, 1998
Printed in the Republic of Korea

Resorcinol-formaldehyde 수지에 의한 중금속 이온의 흡착과 농축

박찬일 · 차기원
인하대학교 이과대학 화학과
(1997. 11. 14 접수)

Adsorption and Preconcentration of Some Heavy Metals by Resorcinol-Formaldehyde Resin

Chan-il Park and Ki-Won Cha
Department of Chemistry, Inha University, Incheon 402-751, Korea
(Received November 14, 1997)

요 약: Formaldehyde와 resorcinol을 반응시켜 chelating 수지를 제조하였다. 이 수지는 Pb(II)나 Ni(II)와 같은 전이금속에 대해 높은 흡착능을 나타내었다. Pb(II), Ni(II), Co(II), Fe(II)와 Zn(II)의 흡착과 탈착율을 batch법으로 구하였다. 이 수지의 중요한 특성은 금속 이온과 수지의 수소 이온간의 교환과정이다. 금속이온의 흡착과 탈착의 메카니즘은 수지의 작용기인 수소 이온의 탈착과 금속 이온간의 교환반응으로 생각된다. 이 수지를 이용하여 전이금속을 농축시키고, 다른 이온들로부터 Pb(II)를 분리하는데 적용해 보았다.

Abstract: A chelating resin was prepared by the reaction of formaldehyde and resorcinol. It possesses high adsorption selectivity for transition metal ions such as Pb(II) and Ni(II). The adsorption and desorption yields of Pb(II), Ni(II), Co(II), Fe(II) and Zn(II) were determined using batch method. The significant characteristics of the chelating resin is the exchange processes between its hydrogen and metal ions. The mechanism of metal adsorption and desorption seems to be the competing protonation and complexation reaction of the functional group of the resin. This resin was applied to the rapid concentration of trace amounts of these metal ions and to the separation of Pb(II) from other metal ions in bulk solution.

Key words: Chelating resin, Resoricinol-formaldehyde, Metal ion, Adsorption and Desorption

1. INTRODUCTION

Adsorption methods are widely used and are one of the most effective methods for preconcentration and separation of metal ions in aqueous solution. Comprehensive reviews have been written on the synthesis, properties and application of chelating resins.[1~3]

A number of chelating resins containing aminocarboxylic acid,[4~7] hexylthioglycolate[8~10] and bicine[11] groups have been prepared and investigated for their analytical properties. The purpose of the present work is to explore the possibility of separation of some metal ions from matrices by use of a resorcinol-formaldehyde resin. The adsorption behaviour of Ni(II), Co(II), Pb(II), Cr(II), Cd(II) and Zn (II) on the resin was investigated at different pH values. The separations are based on the affinity differences of these metal ions for the chelating resin as a function of pH. The resin has been characterized and adsorption behaviour of different metal ions on the resin studied.

2. EXPERIMENTAL

2.1. Apparatus and reagents

A Shimadzu AA-670 atomic absorption spectrophotometer was used for metal ions determination. A NOVA-310 digital pH-meter was used for pH measurement. IR spectrum was recorded on a Hitachi IR 435 infrared spectrophotometer with KBr pellets.

Resorcinol and formaldehyde were a products of Sigma. The metal ion stock solutions were prepared by dissolving the 1000 ppm AAS standard solutions of Ni(II), Cr(II), Co(II), Zn(II), Cd(II) and Pb(II) obtained from Junsei Chemical Co. The other chemicals were of analytical-reagent grade. The following buffered solutions were prepared: hydrochloric acid-potassium hydrogen phthalate (pH 1~3); acetic acid-sodium acetate (pH 3~6); potassium dihydrogen phosphate-sodium hydroxide (pH 7); and sodium borax-hydrochloric acid (pH 8~9).

2.2. Synthesis of resorcinol-formaldehyde resin

Dissolve 110 g of resorcinol (1 M) in 1 L of water. Add 16.8 g of lithium hydroxide monohydrate, and warm, with stirring, in a 2 L beaker. As the temperature reaches to 70°C, add 120 mL of 38% formaldehyde solution cautiously. The temperature will rise to 85°C. Reduce the temperature with continueous stirring until gelling occurs, at about 95°C. As gelling occurs, stop heating and cool the solution, to prevent further reaction in hot water, thereby remove the gel from the beaker. Allow the gel to cool at room temperature. A pale red resin was obtained. A total of 100 g resin was prepared and the 100~150 mesh fraction of the resin was used for metal adsorption studies.

2.3. Batch equilibrium experiment

2.3.1. Optimum pH for metal ion adsorption

The adsorption behaviors of various metal ions were examined under batch equilibration technique. Excess amount of metal ion (50 mL, 20 μg/mL) was shaken with 0.5 g of resin for 24 hr. The pH of the metal ion solution was adjusted prior to equilibration over a range of 1~8 with buffer solutions. After the equilibrium, the solution was filtered through a Whatman #2 filter paper. The filtrate was diluted with deionized water and the concentration of metal ions remained was determined by an AAS.

2.3.2. Resin capacity

A batch equilibrium technique was used to determine the metal exchange capacities. Typically, 100 mg resin was mechanically equilibrated with excess metal ion (50 mL, 100 μg/mL) solution for 24 hrs at the optimum adsorption pH. After the equilibrium, the resin was filtered off and the concentration of the remaining metal ion in the solution was determined by an AAS.

2.3.3. Adsorption equilibration rate

The equilibrium time of the metal ions were determined at pH 6.0 by the batch equilibrium technique. A portion of 0.5 g dry resin was pored into each metal ion solution (50 mL, 10 μg/mL) and equilibrate for 5~18 min with mechanical stirring. After equilibrium, the solution was filtered through Whatman #2 filter paper. The concentration of metal ion remained was determined by an AAS.

2.4. Separations of metal ion

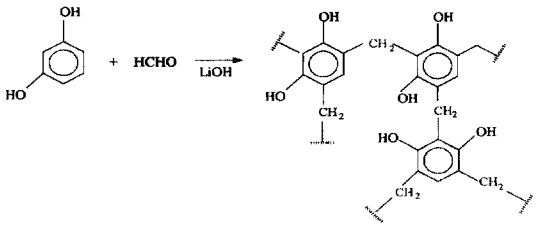
Separations of metal ion were carried out by a column method. A fixed volume of aqueous solution of the metal ions was adjusted to a suitable pH and percolated through the column at the flow rate of 1.0 ± 0.2 mL min^{-1}. The adsorbed metal ion was desorbed from the resin with a suitable eluent.

3. RESULT AND DISCUSSION

3.1. Characteristics of resorcinol-formaldehyde resin

The resin used was synthesized according to *Scheme* 1. In the IR spectrum of resorcinol-formaldehyde resin (*Fig.* 1), the major absorption band appears at 3422 cm^{-1} ($\nu_{C\text{-}OH}$).

The chemical stability of the resin was evaluated by measuring the change of adsorption capacity for Pb(II) after a successive contact of resorcinol-formaldehyde resin with an acidic solutions in various concentration range. When this resorcinol-formaldehyde resin was contacted with an acidic solu-



Scheme 1.

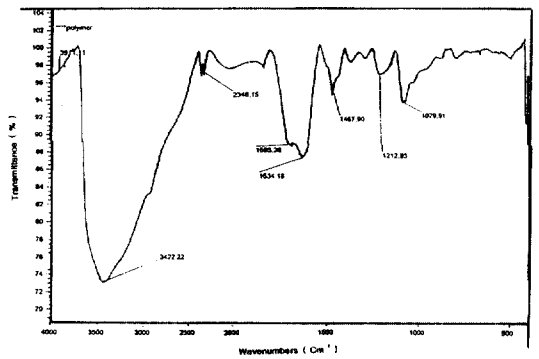


Fig. 1. Infrared spectra of the resorcinol-formaldehyde resin (KBr disk).

tion weaker than 2.5 M HNO_3 or 3 M HCl, the decomposition was negligibly small and no significant decrease in the adsorption capacity for Pb(II) was observed. From these result, it is beleived that this chelating resin has sufficient stability.

3.2. Adsorption behaviours for metal ion

The effect of pH on adsorption of Fe(II), Co(II), Zn(II), Ni(II) and Pb(II) in pH 0.9~7.5 was examined by a batch process and the result is presented in *Fig.* 2. A similar trend was observed for metal ions examined. *Fig.* 2 shows that adsorption of metal ions depends apparently on the pH of the solution due to the competing protonation and complexation reactions of the functional group of resin. However, alkali metal and alkaline earth metal ions such as Na(I) and Mg(II) which have a lower tendency to form chelates with resorcinol-formaldehyde resin were not sorbed at all even at pH 6.0 as expected.

The capacity of the resin is an important factor to determine the amount of the resin necessary for quantitatively remove of a metal ion from a solution.

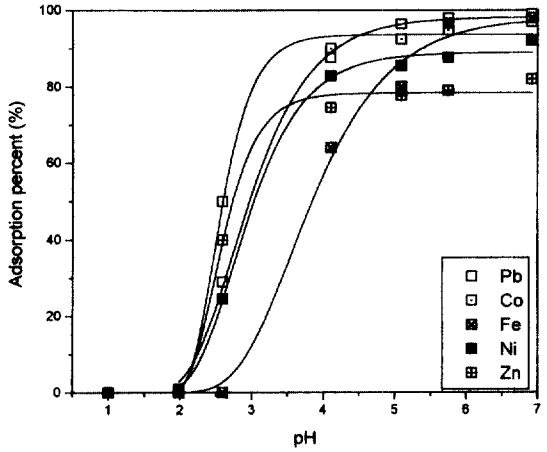


Fig. 2. Effect of pH on the adsorption of metal ions with resorcinol-formaldehyde resin. Resin weight: 500 mg; Conc. of each metal ion: 1.0 mg/50 mL; Shaking time: 24 hr.

The capacity of each metal ion is reported in the *Table* 1. The data indicate that this resorcinol-formaldehyde resin has a great affinity for metal ions studied.

The effect of shaking time on the adsorption of metal ions in the batch process is shown in *Fig.* 3. Over 92% Pb(II) is adsorbed on the resin after shaking within 20 min. However Co(II) and Ni(II) require longer time for complete adsorption. These properties of the adsorbent enable the Pb(II) ion in aqueous solution to readily approach the functional group.

3.3. Effects of ligand and mineral acid

The metal ion adsorption is not inffluenced by sulfosalicylic acid as a ligand over the concentration range of 0.001~0.01 M (*Fig.* 4A). The distribution coefficient of the resin toward metal ions were found to depend on the NH_4NO_3 concentration (*Fig.*

Table 1. Adsorption capacity of the resin for different metal ions

Metal ion	Capacity (mmol g^{-1})
Ni (II)	0.46
Co (II)	0.55
Pb (II)	0.74
Zn (II)	0.49

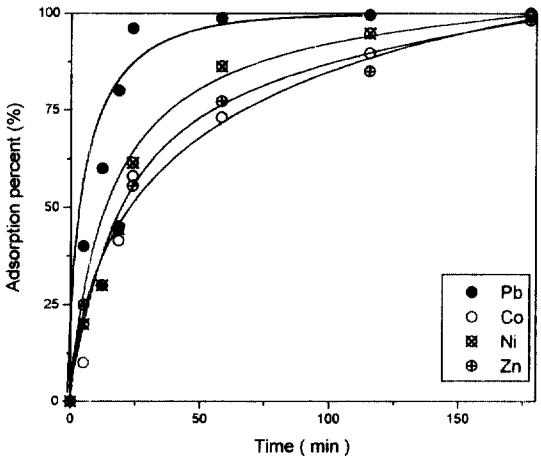


Fig. 3. Effect of shaking time on the loading capacities of the resorcinol-formaldehyde resin. Resin weight: 500 mg; Conc. of each metal ion: 0.5 mg/50 mL, pH: 6.0, Shaking time: 24 hr.

4B). The adsorption capacity of Co(II) and Ni(II) ions decreased gradually with increasing the NH_4NO_3 concentration from 0.1 to 1.0 M. However, adsorption capacity of Pb(II) ion did not vary over the range of 0.25~1.0 M NH_4NO_3. Also, the adsorption percentage for metal ions decreased with increasing mineral acids concentration (*Fig.* 5).

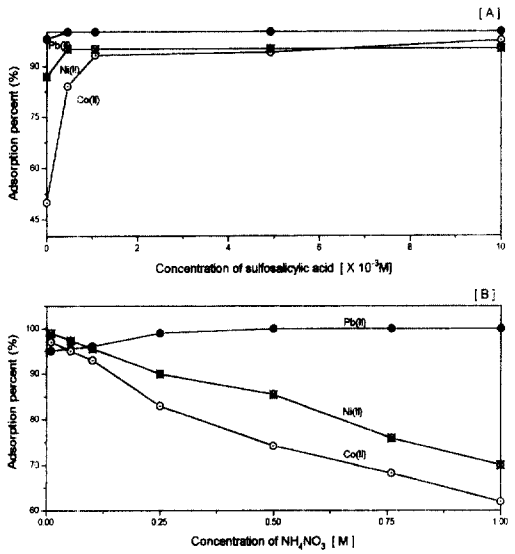


Fig. 4. Effect of [A] sulfosalicylic acid and [B] ammonium nitrate on the adsorption of metal ions with resorcinol-formaldehyde resin. Resin weight: 500 mg; Conc. of each metal ion: 0.5 mg/50 mL, pH: 6.0, Shaking time: 24 hr.

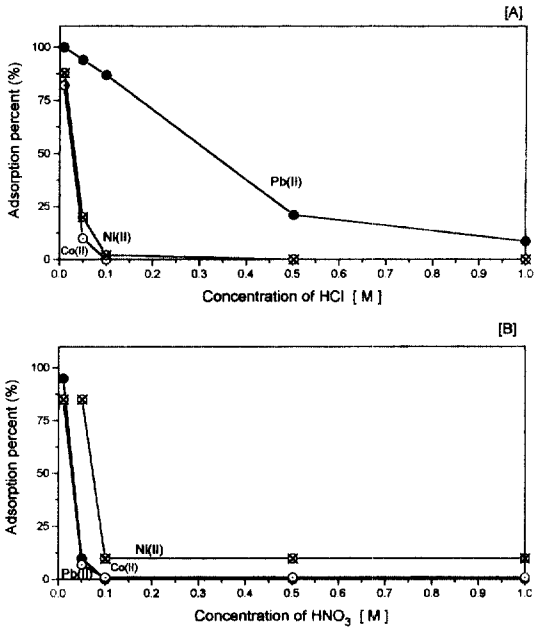


Fig. 5. Effect of [A] HCl and [B] HNO_3 concentration on the desorption of metal ions with resorcinol-formaldehyde resin. Resin weight: 500 mg; Conc. of each metal ion: 0.5 mg/50 mL, Shaking time: 24 hr.

3.4. Effect of flow rate

The effect of flow rate of the sample loading and the elution through the column was studied over the range of 0.5~3.0 mL min^{-1}. The elution curve of metal ions remains almost unchanged regardless of any change in the flow rate. In subsequent experiments a flow rate of 1.0 ± 0.2 mL min^{-1} was maintained for both adsorption and elution.

3.5. Preconcentration and separation of metal ions

Preconcentration of the metal ions on the resin was carried out and the results are shown in *Table* 2. Metal ions could be enriched up to 50 times with resorcinol-formaldehyde resin. The results have been shown that the present resin can act as an effective adsorbent for preconcentration of the metal ions studied.

The separation of trace amounts of Pb(II) in the presence of diverse metal ions was examined by a column method (*Fig.* 6). From the results presented in *Fig.* 4 and 5, NH_4NO_3 and HNO_3 solution have

Table 2. Preconcentration and recovery of metal ion

Metal ion	Taken	Eluent	Found* (mg)	Preconcentration effect**
Pb(II)	0.1 mg/L	0.1 M HCl	0.103	50
	1.0 mg/L	0.1 M HCl	0.973	50
Ni(II)	0.5 mg/L	0.1 M HNO_3	0.492	40
	1.0 mg/L	0.1 M HNO_3	0.983	35
Co(II)	0.5 mg/L	0.1 M HNO_3	0.492	45
	1.0 mg/L	0.1 M HNO_3	1.014	40

*Values agreed with a precision of ±1.5%, Column: 3.14 $cm^2 \times 5$ cm. **One liter sample solutions containing 0.1~1.0 mg metal ion were loaded on the column and eluted with 20 mL of 0.1 M HCl.

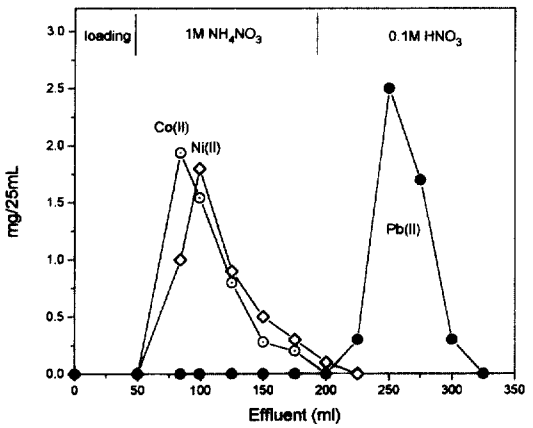


Fig. 6. Elution curve of Co(II), Ni(II) and Pb(II). Resin: resorcinol-formaldehyde, Column: 3.14 $cm^2 \times 5$ cm, Loading: 5 mg of Co(II), Ni(II) and Pb(II) in 50 mL, pH 4.0, Elution: 1 M NH_4NO_3 and 0.1 M HNO_3, Flow rate: 1.0± 0.2 mL min^{-1}.

been considered as an eluent for the separation of the synthetic metal ion solution. Lead(II) is able to separate from Ni(II), Co(II) and Zn(II) because they are not retained on the resin with 1.0 M NH_4NO_3 eluent. Lead(II) retained on the resin is eluted with 0.1 M HNO_3.

4. CONCLUSION

The resorcinol-formaldehyde resin offers the possibility of preconcentration and separation of Pb(II). Pb(II) can be separated from Ni(II), Co(II) and Zn(II) with NH_4NO_3 and acidic media as an eluent. The sorbent is easy to prepare, stable, maintains reproducibility and exhibits fast adsorbability. Metal ions in a large volume of water sample can be treated with a relatively small column and preconcentrated metal ions can be eluted in a small volume of eluent, resulting in a high preconcentration factor.

Alkali and alkaline earth metals are not retained on the sorbent over a wide acidic range, which is of advantage from the viewpoint of posible applications of the sorbent to the analysis of natural waters and biological materials.

REFERENCES

1. R. Hering, "Chelatbildende Ionenaustauscher", Akademie, Berlin (1967).
2. S. K. Sahni and J. Reedijk, *Coord. Chem. Rev.*, **59**, 1 (1984).
3. G. V. Myasoedova and S. B. Savvin, *CRC Crit. Rev. Analyt. Chem.*, **17**, 1 (1986).
4. M. Marhol and K. L. Cheng, *Talanta.*, **21**, 751 (1974).
5. S. Tomoshige, M. Hirai and H. Ueshima, *Anal. Chim. Acta.*, **115**, 285 (1980).
6. E. M. Moyers and J. S. Fritz, *Anal. Chem.*, **49**, 418 (1977).
7. P. Figura and B. McDuffie, *Anal. Chem.*, **49**, 1950 (1977).
8. M. D. Arguello and J. S. Fritz, *Anal. Chem.*, **49**, 1595 (1977).
9. G. M. Orf and J. S. Fritz, *Anal. Chem.*, **50**, 1328 (1978).
10. E. M. Moyers and J. S. Fritz, *Anal. Chem.*, **48**, 1117 (1976).
11. K. Dev and G. N. Rao, *Talanta.*, **42**, 591 (1995).