212 *Bull. Korean Chem. Soc., Vol. 13, No. 2, 1992*

Notes

gave 1.65 g(88%) of 1,2,3,4,5,6,7,8-octahydroacridine; mp. 71℃ (lit.[8] mp. 71℃).

References

1. (a) R. P. Thummel in *"Pyridine and its Derivatives,"* G. R. Newkome, Ed; Wiley-Interscience: New York, p. 249 (1984); (b) R. P. Thummel and D. K. Kohli, *J. Org. Chem.,* **42,** 2742 (1977); (c) T. R. Kelly and H. Liu, *J. Am. Chem. Soc.,* **107,** 4998 (1985); (d) R. P. Thummel and Y. Jahng, *J. Org. Chem.,* **52,** 73 (1987).

2. (a) T. W. Bell and A. Firestone, *J. Org. Chem.,* **51,** 764 (1985); (b) T. W. Bell and A. Firestone, *J. Am. Chem. Soc.,* **108,** 8109 (1986).

3. L. Birkofer, S. M. Kim, and H. D. Engels, *Chem. Ber.,* **95,** 1495 (1962).

4. J. Colonge, J. Dreux, and H. Deplace, *Bull. Soc. Chem., Fr.,* **203,** 447 (1957).

5. V. Hedge, Y. Jahng, and R. P. Thummel, *Tetrahedron Letters,* 4203 (1987).

6. G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Am. Chem. Soc.,* **85,** 207 (1963).

7. New compounds are characterized by spectroscopic and elemental analysis to show satisfactory results as follows: **4b** ^{1}H-NMR (CDCl$_3$, 80 MHz) δ 2.95-2.83 (overlapped t, 8H), 2.33 (s, 3H, CH$_3$), 1.92-1.74 (m, 8H); IR (thin film) v 3020, 2930, 2860, 1605, 1570, 1442, 1415, 1305, 1230, 1215 and 730 cm^{-1}; mass spectrum, m/e (rel. intensity) 202 (M+1, 2.2), 201 (M, 10.7), 144 (20.3), 136 (15.4), 91 (100), 76 (45), 56 (35); Anal. Calcd. for N$_{14}$H$_{19}$N: C, 83.52; H, 9.52; N, 6.96. Found: C, 83.44; H, 9.56; N, 7.00; **4d** ^{1}H-NMR (CDCl$_3$, 80 MHz) δ 7.68-7.32 (m, 5H), 2.93 (t, 4H, J=6.7 Hz), 2.81 (t, 4H, J=6.7 Hz), 1.88-1.75 (m, 8H); IR (KBr) v 3020, 2930, 2860, 1605, 1560, 1445, 1410, 1315, 1230, 1215, 750 and 730 cm^{-1}; Anal. Calcd. for N$_{19}$H$_{21}$N: C, 86.65; H, 8.04; N, 5.32. Found: C, 86.76; H, 7.96; N, 5.28; **4e** ^{1}H-NMR (CDCl$_3$, 80 MHz) δ 7.95 (d, 2H, J=8.1 Hz), 7.55 (dm, 2H), 2.91-2.80 (m, 8H), 2.35 (s, 3H), 1.75 (m, 8H); IR (KBr) v 3020, 2950, 2870, 1600, 1570, 1452, 1410, 1305, 1250, 1220, 830 and 730 cm^{-1}; **4f** ^{1}H-NMR (CDCl$_3$, 80 MHz) δ 8.00-7.60 (m, 2H), 7.58-7.43 (m, 2H), 2.95-2.86 (m, 8H), 1.74 (m, 8H); IR (KBr) v 3020, 2930, 2860, 1605, 1570, 1442, 1415, 1305, 1240, 1215, 830 and 750 cm^{-1}; **4g** ^{1}H-NMR (CDCl$_3$, 80 MHz) δ 8.12 (d, 2H, J=8.2 Hz), 7.45 (d, 2H), 2.89-2.78 (m, 8H), 1.76 (m, 8H); IR (KBr) v 3020, 2930, 2860, 1605, 1570, 1450, 1425, 1320, 1230, 1210, 820 and 750 cm^{-1}.

8. N. S. Gill, K. B. James, F. Lions, and K. T. Potts, *J. Am. Chem. Soc.,* **74,** 4293 (1952).

9. T. W. Bell and S. D. Rothenberger, *Tetrahedron Letters,* 4817 (1987).

10. The effect of the concentration of Lewis acids was also examined, which showed the best results with 0.9 molar equivalents.

11. R. Stardi, D. Pocar, and C. Cassio, *J. Chem. Soc., Perkin Trans.,* **1,** 2671 (1974). Unpublished spectral data of 5 are as follows: ^{1}H-NMR (80 MHz, CDCl$_3$) δ 8.77 (dd, H$_6$, J=4.8 Hz, J=1.2 Hz), 8.00-7.25 (overlapped m, H$_3$,

H$_4$, and H$_5$), 4.87 (s, vinylic H), 4.519 (s, vinylic H), 3.97 (m, O-CH$_2$-), and 3.00 (m, N-CH$_2$-); IR (thin film) v 2940, 2840, 2810, 1600, 1578, 1552, 1645, 1445, 1370, 1350, 1300, 1260, 1140, 1090, 982, 922, 982, 860, 790 cm^{-1}; mass spectrum, m/e (rel. intensity) 192 (M+2, 0.10), 191 (M+1, 0.93), 190 (M, 6.79), 132 (14.43), 105 (100), 104 (60.09), 78 (27.00), 52 (10.17) and 51 (20.13).

12. (a) B. Tabyaouri, T. Aubert, M. Farnier, and R. Guilard, *Synth. Commun.,* **18,** 1475 (1988); (b) K. T. Potts, D. A. Usifer, A. Guadelupe, and H. D. Abruna, *J. Am. Chem. Soc.,* **109,** 3961 (1987); (c) K. T. Potts, M. J. Cipullo, P. Ralli, G. Theodolis, and P. Winslow, *P. Org. Syn.,* **66,** 189 (1985); (d) Although reference 12(b) describes the shortest sequence to 2,2′;6′,2″-terpyridine to show an about 45% overall yield of, the more efficient metho[13] appeared during the preparation of this paper.

13. D. L. James and L. E. Guise, *Tetrahedron Letters,* 1999 (1991).

The Adsorption Behaviors of Heavy Metal Ions on the Sawdusts

Yong Soon Chung*, Kang Woo Lee, Yeo Seong Yoon, Soo Han Kwon, and Kwang Soo Lim

Department of Chemistry, Chungbuk National University, Cheongju 360-763, Korea

Ion-exchange resins have been used to separate and preconcentrate metal ions[1-4] and organic compounds[5-6]. Activated charcoal has been used to remove metal ions and organic compounds in the water supply facilites[7]. However, ion-exchange resins and activated charcoal couldn't be used to remove heavy metal ions from waste water because of their cost.

The aim of this work was to furnish the basic data to remove heavy metal ions in the industrial and laboratory waste water with the low-priced adsorbent. We thought that sawdusts would be a proper one for that purpose if they adsorb heavy metal ions favorably. Therefore, we examined in this experiment the pH effect on the distribution coefficients (Kd values) of the heavy metal ions on the sawdusts to inspect the optimum adsorption condition and whether the break through points at the frontal chromatography of the heavy metal ions in the solution of the condition by a column packed with a sawdust would be large enough or not.

Experimental

Instrumental. The pH of the sample solution was measured with Chemcadet Model 5984 pH meter and the metal ion concentrations were determined with Hitachi Model Z-8,000 atomic absorption spectrophotometer. The horizontal shaking of the sample vials to determine the Kd values of

Notes

Bull. Korean Chem. Soc., Vol. 13, No. 2, 1992 213

Table 1. The Nitrogen Content(%) of Various Kinds of Sawdusts and Log Kd Values of the Heavy Metal Ions on the Sawdusts at pH 9.0[a]

Sawdust		Log Kd values of metal ion			
Name	Nitrogen content[b]	Cu(II)	Cd(II)	Ni(II)	Pb(II)
Alder	0.15	2.97	2.32	2.19	2.99
Pine	–	2.08	2.93	1.68	2.62
Oak	0.22	3.00	2.83	2.57	2.70
Larch	–	2.46	2.16	2.10	2.72
Popular	–	2.15	1.94	1.72	2.74
Acacia	0.26	1.84	1.81	1.62	1.88
Bean stem	0.79	1.81	1.98	1.71	1.64
Larch(c)	–	4.31	4.28	2.26	4.00
Acacia(c)	0.57	2.07	2.07	1.70	2.52
Larch(d)	–	2.71	2.22	2.35	3.19
Bean stem(e)	0.49	2.15	2.35	2.04	2.49
Charcoal(f)	–	3.20	2.77	2.53	3.29
Zeolite(g)	–	1.26	1.75	1.03	2.16

[a]The condition of Kd measurement; metal ion solution: 20 m*l* of 10 ppm solution, sawdust taken: 250 mg, shaking time: 30 min. [b]Obtained from the elemental analysis data. [c]Extracted with acetone. [d]Extracted with acetone and 1%-NaOH successively. [e]Extracted with 1%-NaOH. [f]Activated and reagent grade. [g]Natural one produced at Sanchong, Korea.

the heavy metal ions on the sawdusts was performed with Korean Manhattan Co. Model 12055W1 shaking water bath and a peristaltic pump from the company was used to elute metal ion solution for frontal chromatography. Carlo Elba Model E. A. 1,108 elemental analyzer was used to determine the content of nitrogen in the sawdusts.

Reagents. The sawdusts used in this experiment were prepared from the timber mills located at outskirts of Cheongju City, Korea. The sawdusts removed water soluble components by repeated extraction with distilled-deionzed water were dried in an electric oven at 50℃ for 2-3 days and sieved with U.S. standard sieves. The 50-100 meshes particles collected by sieving were used to determine Kd values and to prepare a column of frontal chromatography. The larch and acacia sawdust and bean stem particles extracted with acetone, those extracted with 1%-NaOH, or those extracted with successive extraction with acetone and 1%-NaOH (Table 1 and Figure 1(B)) were prepared and compared with the water-extracted ones for the pH effect on the Kd values. All other chemicals were used of reagent grade purchased from Aldrich or Tokyo Kasei Chemical Co., and without further purification. Distilled-deionized' water was used for all experiments.

Determination of Kd Values. The method of determination of Kd values is given elsewhere[14-6]. 250 mg of sawdust as an adsorbent and 20 m*l* of 10 ppm heavy metal ion solution as a study solution were used in this work.

$$Kd = \frac{mg \text{ of adsorbed metal ion on adsorbent}/0.250}{mg \text{ of remained metal ion in solution}/20.00}$$

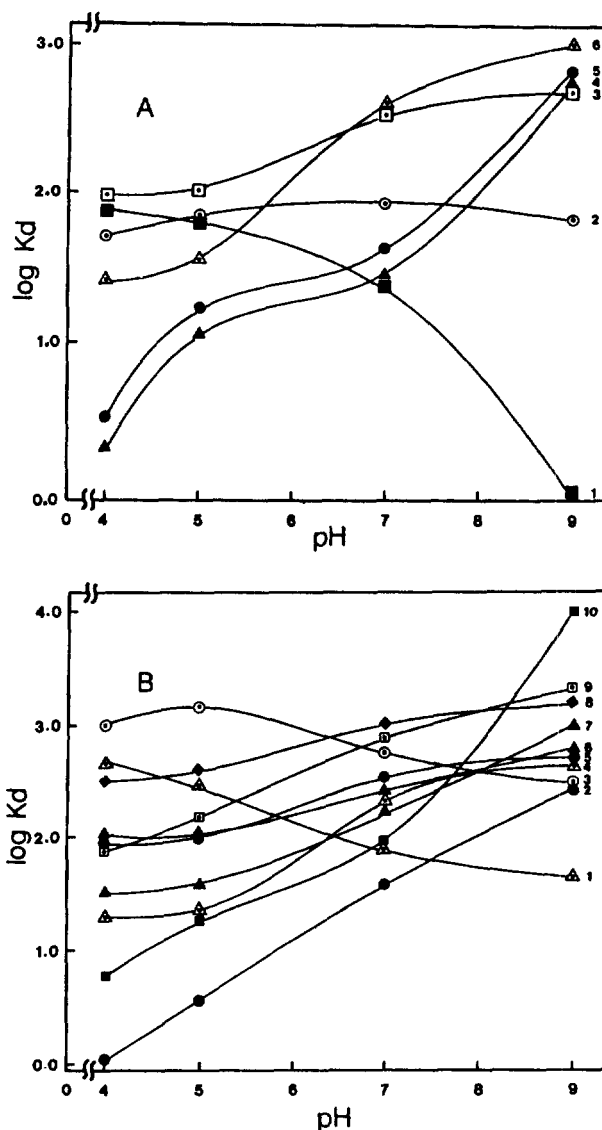**Frontal Chromatography.** Mixed metal ion solution

Figure. 1. The pH effect on the log Kd of the heavy metal ions by the oak sawdust (A) and that of Pb(II) ion by various kinds of sawdusts (B). Metal ion identification in (A); 1: Cr(VI), 2: Fe(III), 3: Pb(II), 4: Ni(II), 5: Cd(II), 6: Cu(II), Sawdust identification in (B); 1: bean stem, 2: natural zeolite, 3: bean stem extracted with 1%-NaOH, 4: pine, 5: oak, 6: popular, 7: alder, 8: larch extracted with 1%-NaOH and acetone successively, 9: activated charcoal, 10: acacia extracted with acetone.

was passed through a column packed with 50-100 mesh oak sawdust particles by the peristaltic pump, the effluents were collected by 10-100 m*l* of graduated cylinders, volumetric flasks, and the metal ion concentrations in each fraction were determined by atomic absorption spectrometry with acethylene-air flame.

Results and Discussion

The pH effect on the Kd values of the heavy metal ions by the oak sawdust and that on the log Kd of Pb(II) ion by various kinds of sawdusts are appeared in Figure 1. As can be seen in the figure, the most of the heavy metal ions
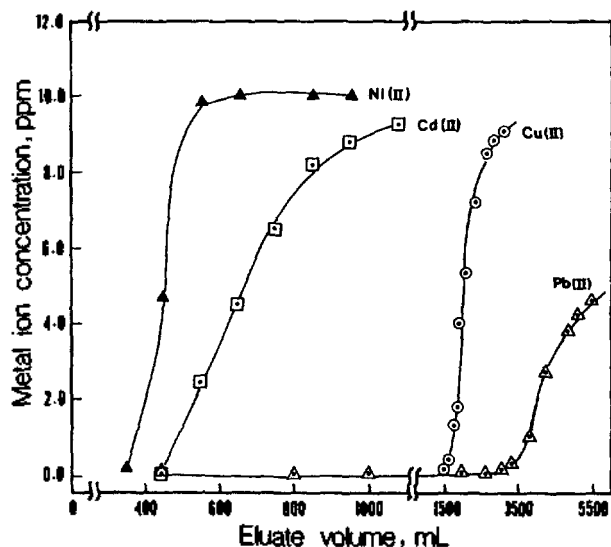
214 *Bull. Korean Chem. Soc., Vol. 13, No. 2, 1992*

Notes

Figure. 2. Frontal chromatogram obtained with oak sawdust column (1.5 cm(i.d.)×23 cm(L)). Sample solution: 10 ppm heavy metal ions in 0.05F ammonium acetate and 0.05F potassium sodium tartrate (pH 5.0).

were adsorbed more at the high pH range. However, the adsorption of Cr(VI) ion on the oak sawdust(Figure 1(A)) and that of Pb(II) ion on the bean stem particles (Figure 1(B)) were increased at the low pH range. It was thought that most of sawdusts were anionic in the high pH and neutral to cationic in the low pH, we couldn't explain the increase in adsorption of Pb(II) ion on the bean stem particles in the low pH. Nitrogen contents of various sawdusts and the Kd values of copper, cadmium, nickel, and lead ions on oak sawdust at pH 9.0 are given in Table 1. From the results of these experiments, it could be illustrated that the uptake of these heavy metal ions on the sawdusts is quantitative, the nitrogen content in the sawdust has no influence on the adsorption, and the removal of orgnic compounds in the sawdusts, such as alcohols and fats, by extraction with acetone or 1%-NaOH solution gave increased adsorption. Selectivities were a little different; oak has a selectivity on Cu(II) and Ni(II), pine on Cd(II), and alder on Pb(II). Therefore, among the sawdusts, the oak sawdust was a good adsorbent. The increasing order of Kd values on oak sawdust at pH 5.0 was Ni(II)<Cd(II)<Cu(II)<Cr(VI)<Fe(III)<Pb(II) and at pH 9.0 was Cr(VI)<Fe(III)<Pb(II)<Ni(II)<Cd(II)<Cu(II) (Figure 1(A)).

The Kd values for activated charcoal and natural zeolite were also measured to compare with those of sawdusts. In Table 1, the values on the activated charcoal were similar to those on oak sawdust, but those on the natural zeolite were smaller than those on the most of sawdusts.

To confirm the increasing order of Kd values of the heavy metal ions on the sawdusts and removal possibility on them in the industrial and laboratory waste water by the sawdust, it was examined whether the break through points of the heavy metal ions on a column packed with oak sawdust would be larger enough than the column's void volume (14 mⅼ in this case) (Figure 2). Although the pH of the sample solution was the one (pH 5.0) in which the Kd values of

the metal ions were comparatively smaller than those at the higher pH, the break through points of them were large enough(Ni(II) : 350 mⅼ, Cd(II) : 430 mⅼ, Cu(II) : 1,490 mⅼ, and Pb(II) : 3,300 mⅼ) and the increasing order of the break through points was same as that of the Kd values. Therefore, it was thought to be possible that heavy metal ions in the industrial and laboratory waste water could be removed favorably by the sawdust column.

References

1. K. S. Lee, D. W. Lee, and S. W. Kang, *Anal. Chem.*, **43**, 876 (1971).
2. Zs. Horvath and R. M. Barnes, *Anal. Chem.*, **58**, 1532 (1986).
3. Y. S. Chung and R. M. Barnes, *J. Anal. Atomic Spectrometry*, **3**, 1079 (1989).
4. Y. S. Chung, T. H. Lee, S. H. Oh, and K. W. Lee, *Anal. Sci.*, **7**, (ICAS '91 Proceeding), 1525 (1991).
5. K. S. Lee, D. W. Lee, and W. Lee, *Anal. Chem.*, **47**, 2270 (1975).
6. K. S. Lee, D. W. Lee, and Y. S. Chung, *Anal. Chem.*, **45**, 396 (1973).
7. B. D. Beaudet, L. J. Bilello, E. M. Keller, J. M. Allan, and R. J. Turner, *Proceedings of the 36th Industrial Waste Water Conference in Purdue Univ.*, pp. 381-391, *Ann. Abor. Sci.*, (1980).

The Cathodic Reduction of N'-Phenyl-N-Alkyl-N-Nitrosoureas

Mi-Sook Won, Jack C. Kim, and Yoon-Bo Shim*

Department of Chemistry, Pusan National University, Pusan 609-735

There are many reports for the chemical syntheses and the biological applications[1] for N-nitrosourea analogues since Montgomery and coworkers[2] published papers, some of which can be used as the antitumor agents. However, there are no any reports for the electrochemical behaviors and the electrochemical reduction of N-alkyl-N-nitrosourea to N-alkyl aminourea or urea. On the other hand, as not like this coimpound the electrochemical synthesis and the investigation of electrochemical properties for the N-nitrosoamine analogues have been taken so much[3], which is a carcinogen and a similar compound to N-nitrosourea.

Two electrode system have sometimes applicated for the electrochemical synthesis of N-nitrosoamine analogues. However, in a certain case authors miss that the anodic products formed on counter electrode react often with the starting materials or the resultant products formed on cathode. This disturbs a specific reduction of reactants on cathode and ofhen lead to the formation of unexpected if a two electrode system or a cell without liquid junction is used.