

SYNTHESIS OF SILICA-BOUND COMPLEXING AGENTS CONTAINING DIAMINOANTHRAQUINONES AND THEIR METAL-UPTAKE PROPERTIES

Mohamed E. Mahmoud and Gamal A. Gohar

Chemistry Department, Faculty of Science, Alexandria University,
P.O. Box 426, Ibrahimia, Alexandria 21321, Egypt.

ABSTRACT

A method is described for immobilizing 1,2-diaminoanthraquinone and 1,4-diaminoanthraquinone on the surface of silica gel, manufactured by three different companies, to evaluate their performance. The affinity of the bonded phases for metal ion extraction from aqueous media is studied. The order of increasing the metal capacity is found to be as follows: Mg(II) < Zn(II) ~ Fe(II) < Fe(III) < Mn(II) < Cr(III) ~ Ni(II) < Co(II) < Cu(II). The six studied bonded phases show similar trends to metal ion capacity and extraction. The optimum conditions and parameters controlling the metal capacity, such as time and pH, are evaluated.

Keywords: Silica-Bound Complexing Agents, Diaminoanthraquinones, Metal Ion Extraction.

INTRODUCTION

Silica gel bound complexing agents (SGBCA) are gaining great attention in different application areas. Some of their important applications are the metal ion preconcentration [1,2] and solvent clean up from trace metals [3]. SGBCA were also used as stationary phases for high performance liquid chromatography (HPLC) [4-6]. Several complexing agents were bound to silica gel, such as β -diketones [7], nitrosonaphthol derivatives [8], 2-amino-1-dithiocarboxylic acid (ADCA) [9], 2,3-dihydroxybenzoyl-catechol and 3,4,5-trihydroxybenzoylamide [10]. Macrocyclic compounds, such as crown ether and its derivatives, were found to be highly selective for extraction of alkali metals from aqueous media [11] and organic solvents [12]. The methods of calculating the binding constant of metal cations to silica gel bound macrocycles in organic solvents were also reported [13].

In the present study, we have chosen 1,2-diaminoanthraquinone and 1,4-diaminoanthraquinone to immobilize on the surface of three different silica gel types, manufactured by three different companies, in order to study their behavior towards metal extraction from aqueous media. The objective of selecting diaminoanthraquinone (DAAQ) is three fold. First, the applicability of DAAQ as a good complexing agent for transition metals [14,15], platinum, and palladium ions [16]. The wide

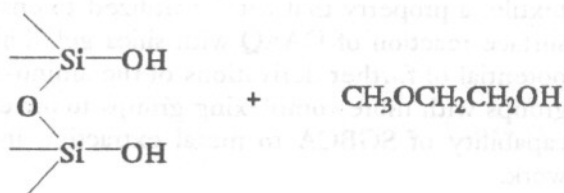
application of DAAQ as dyeing agents through interaction with active surfaces for several types of textile, a property that can be utilized to ensure the surface reaction of DAAQ with silica gel. Third, the potential of further derivations of the amino- or keto groups with more complexing groups to increase the capability of SGBCA to metal extraction in future work.

EXPERIMENTAL

Three types of silica gel, manufactured by Merck-Germany (70-230 mesh), Aldrich-USA (60-240 mesh), and Al-Nasr Chemical Company-Egypt (40-240 mesh) were selected to immobilize DAAQ on their surfaces. Organic solvents were dried according to conventional methods. Reagent grade 1,2-DAAQ and 1,4-DAAQ were purchased from Aldrich Chemical Company and were used as received.

IR spectra were obtained from KBr Pellets by using a Perkin-Elmer 1430 ratio-recording spectrophotometer. Elemental analyses were performed at Cairo University, Egypt. pH measurements were carried out by using a Kent 7020 pH meter which was calibrated against two buffers at pH 4.01 and pH 9.14. Atomic Absorption measurements were performed by using a Perkin-Elmer 2380 atomic absorption spectrophotometer.

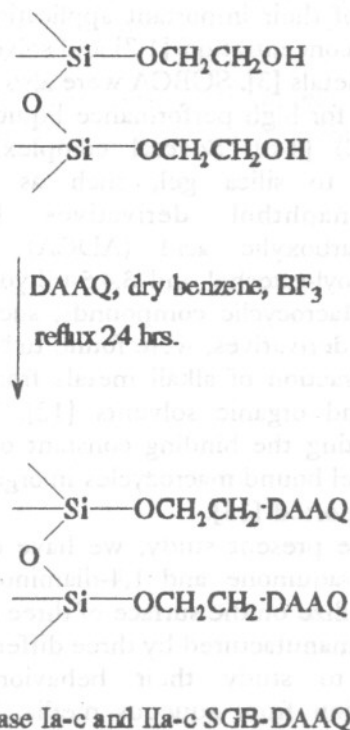
SGB-DAAQ were synthesized according to the following procedure: silica gel was first activated by refluxing in concentrated hydrochloric acid for 4 hours, then filtered and washed several times with double distilled water till acid-free and dried in an oven at 150°C for 6 hours. Fifty grams of dry silica gel were mixed with 200 ml of 2-methoxy ethanol and refluxed at 130°C for 24 hours. The reaction mixture was left to cool, filtered and washed with ethanol and ether and dried at 60°C for 6 hours for the synthesis of ethanol-bonded silica gel (EBSG). Diaminoanthraquinones were bonded to EBSG by reaction of 20 grams of the latter compound in 200 ml dry benzene with 2.0 grams of DAAQ in the presence of 1 ml of boron trifluoride (ethereal solution). The reaction mixture was refluxed for 48 hours and the product was filtered, washed with benzene and ether, and left to dry for 4 hours at 70°C. The product was then washed with double distilled water several times until the filtrate turned colourless, and finally it was washed with acetone and dried overnight at 70°C.



The reaction is shown in Scheme 1, where Phase Ia: Al-Nasr - SGB-1,4-DAAQ; Phase Ib: Merck - SGB-1,4-DAAQ; Phase Ic: Aldrich - SGB-1,4-DAAQ; Phase IIa: Al-Nasr - SGB-1,2-DAAQ; Phase IIb: Merck - SGB-1,2-DAAQ; and Phase IIc: Aldrich - SGB-1,2-DAAQ. Infrared spectral data and the percent carbon and nitrogen of selected phases are compiled in Tables (1) and (2).

Metal capacity of bonded phases (Ia-c and IIa-c):

The capacity of bonded phase to metal ions was determined by batch equilibrium method, in which 100 mg of the SGB-DAAQ phase were added to 9.0 ml of 0.1 M sodium acetate solution and 1 ml of 0.1 M metal ion in a 25 ml measuring flask [10]. This mixture was mechanically shaken for 30 minutes at room temperature. After equilibrium, the mixture was filtered, washed with double distilled water, and the excess metal ion in the filtrate was determined by complexometric titration of Cu(II), Co(II), Ni(II), Zn(II), and Mg(II), and by atomic absorption measurements of Fe(II), Fe(III), Mn(II), and Cr(III). The results of the metal capacity measurements are given in Table 3.



Scheme 1

RESULTS AND DISCUSSION

The method of immobilizing DAAQ on silica gel surface is simple, direct, and needs only reflux for completion of the reaction. The synthesized phases were subjected to stability tests at different pH-values, ranging from pH 2-11, and showed considerable stability over a period of six months. The IR spectra of EBSG, SGB-1,2-DAAQ and SGB-1,4-DAAQ are represented in Table (1). The IR data show the N-H frequency at 3450 cm^{-1} , and the Si-O frequency at 1100 cm^{-1} , which proves that both groups are parts of the structure of SGB-1,2-DAAQ and SGB-1,4-DAAQ. The aromatic peaks are also observed at 1598, 1528 and 1442 cm^{-1} .

The IR data (Table 1) prove that the binding of DAAQ to silica gel surface takes place through chemical bond formation rather than surface adsorption. Such conclusion is further supported by the carbon and nitrogen analysis of two selected phases, namely Ia and IIa, as given in Table (2).

Table 1. Infrared spectral data of the bonded phases.

Bonded Phase	IR band (cm^{-1})	Band Assignment
EBSG	3429 (m)	ν (O-H)
	2894 (w)	ν (C-H)
	1106 (s)	ν (Si-O)
	1017 (m)	ν (C-O)
Ia-c	3450 (m)	ν (N-H) aralkyl
	3416, 3382 (s)	ν (NH_2) aromatic
	3030 (m)	ν (C-H) aromatic
	1665 (s)	ν (C=O)
	1598, 1528, 1442 (s)	ν (C=C) aromatic
	1303 (s)	ν (C-N) aromatic
	1220 (m)	ν (C-N) aliphatic
	1100 (s)	ν (Si-O)
IIa-c	1030 (m)	ν (C-O)
	3455 (m)	ν (N-H) aralkyl
	3407, 3360 (m)	ν (NH_2) aromatic
	3010 (m)	ν (C-H) aromatic
	1660 (s)	ν (C=O)
	1585, 1528, 1466 (s)	ν (C=C) aromatic
	1301 (s)	ν (C-N) aromatic
	1220 (m)	ν (C-N) aliphatic
	1101 (s)	ν (Si-O)
	1035 (m)	ν (C-O)

Table 2. Nitrogen and carbon analysis of selected phases.

Bonded Phase	%C	%N
EBSG	17.50	—
Ia	44.20	8.50
IIa	44.10	8.50

The structure and mode of metal chelation to DAAQ are well established [14,15]. 1,4-DAAQ forms metal complexes through N and O centers at either the 1- and 9- positions or the 4- and 10- positions, which are equivalent in free 1,4-DAAQ but are unequivalent in SGB-1,4-DAAQ. 1,2-DAAQ, on the other hand, possesses two different modes of metal chelation, through either N and N atoms at the 1- and 2- positions or N and O atoms at the 1- and 9- positions. However, the possibility of metal chelation to the SGB-DAAQ is high because of the variety in the centers of chelation.

From the metal capacity data given in Table (3), it can be concluded that the six prepared phases are behaving similarly towards metal uptake, judging by their comparable values of metal capacity. However, the metal capacities of Phases IIa-c are somewhat smaller when compared to Phases Ia-c. This may be due to metal chelation at the N and O centers which is highly assisted in the case of Phases Ia-c, as compared to Phases IIa-c.

Metal ion uptake as a function of time

Figure (1.i, 1.viii) shows the percent extraction of the metal ion as a function of shaking time. Most of the metal ions showed extraction of more than 50 percent after one minute shaking. Between 5 and 10 minutes were needed for about 90 percent extraction of all the metal ions. This indicates rapid extraction of all the metal ions investigated by the six phases. Moreover, for all phases, about 96-98 percent extraction was achieved in only 10 minutes in cases of Cu(II), Zn(II), and Fe(II) extraction, while 20 minutes were needed to reach this level for the other metal ions. Over 95 percent metal extraction was achieved for most metal ions after 20 minutes shaking, except for Mn(II) and Mg(II), which required longer times.

It is evident from Figure (1) that the six studied SGB-DAAQ phases are behaving similarly towards the effect of shaking time on the percentage of metal extraction.

Table 3. Metal capacity (mmol/g) of SGB-DAAQ phases.

Metalion	Phase Ia	Phase Ib	Phase Ic	Phase IIa	Phase IIb	Phase IIc
Mg(II)	0.28	0.28	0.28	0.26	0.25	0.26
Cr(III)	0.38	0.37	0.38	0.35	0.36	0.36
Mn(II)	0.36	0.37	0.37	0.34	0.34	0.34
Fe(III)	0.30	0.31	0.31	0.28	0.29	0.29
Fe(III)	0.34	0.33	0.34	0.31	0.32	0.31
Co(III)	0.39	0.38	0.38	0.37	0.36	0.36
Ni(II)	0.38	0.38	0.38	0.34	0.34	0.34
Cu(II)	0.42	0.43	0.42	0.38	0.39	0.38
Zn (II)	0.30	0.32	0.31	0.26	0.26	0.27

Optimum pH for metal extraction:

The effect of pH variation on the percentage of metal extraction was studied in the pH range of 2.1 - 6.3 in order to determine the optimum pH of extraction, and the results are depicted in Figure 2(i-v). The studied metal ions which show considerable dependence on the pH-value of the aqueous medium, are Mg(II), Co(II), Ni(II), Cu(II) and Zn(II). All of these ions showed low values of percent extraction at low pH-values. At higher pH-values, such percentage increased, with the maximum occurring at pH > 6 except for the case of Zn(II) where the optimum pH of extraction was 5.5. It is also notable that the six studied phases, Ia-c and IIa-c, behaved similarly at the same pH value. This is consistent with the previous results observed for the effect of extraction time on the percentage of extracted metal.

Table (4) shows the optimum pH conditions and shaking times required for 90 percent extraction by SGB-DAAQ of the various metal ions from aqueous medium.

CONCLUSION

The three types of silica gel studied in this work showed great similarities in their binding to metal-complexing agents, such as DAAQ, as well as their applicability to metal ion extraction. The six SGB-DAAQ phases we investigated offer a great potential both for preconcentration of various metal ions in aqueous solutions, and for waste chemical clean up because of the low cost of synthesizing SGB-DAAQ compared to other SGB-complexing agents. The highest metal capacity of any studied phase was

found to be 0.4 mmol/g of Cu(II) ion. This value may be improved by increasing the capability of DAAQ to metal complexation through derivation of the amino- and keto groups by other stronger chelating groups. Studies of this modification are currently in progress. Also, the application of these SGB-DAAQ to extract highly toxic metal ions, such as Hg(II), Pb(II), Sn(II), Sn(IV), Sb(III), As(II), As(IV), V(III), Mo(III) and Ti(III) from aqueous solution are under investigation.

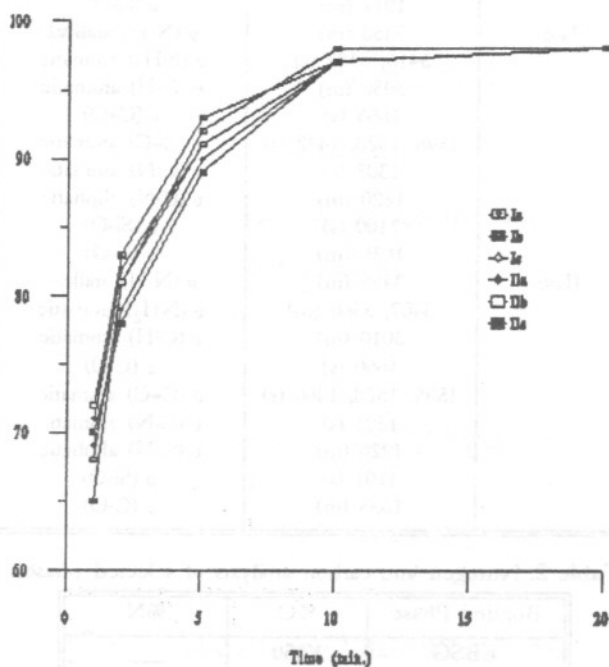


Figure 1. Percent metal ion extraction by different phases as a function of shaking time for (i) Cu(II)

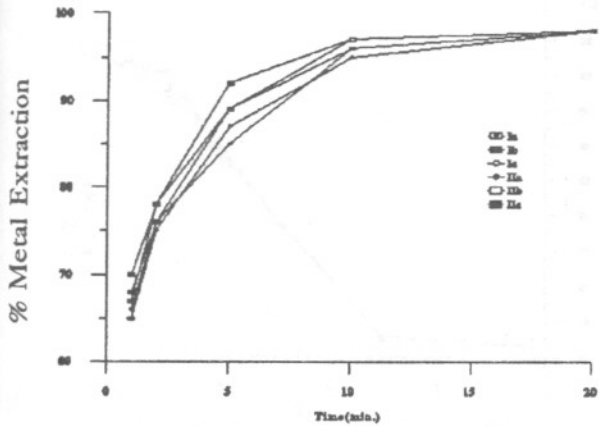


Figure 1. (cont'd) (ii) Zn (II)

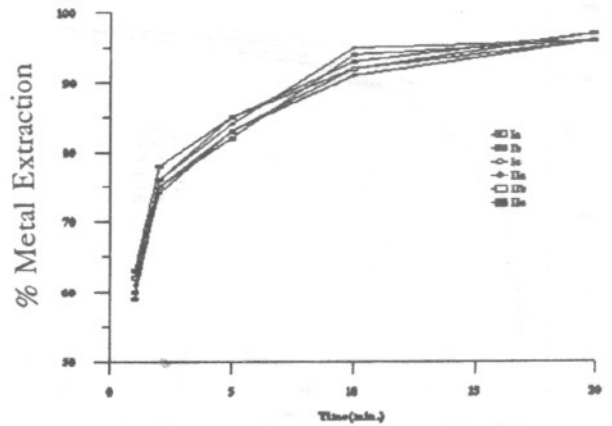


Figure 1. (cont'd) (v) Ni (II)

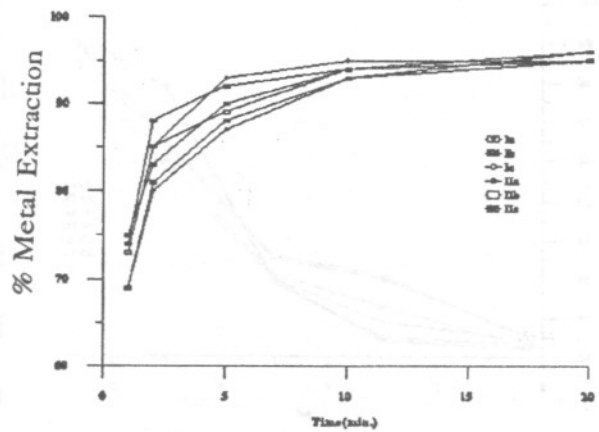


Figure 1. (cont'd) (iii) Mg (II)

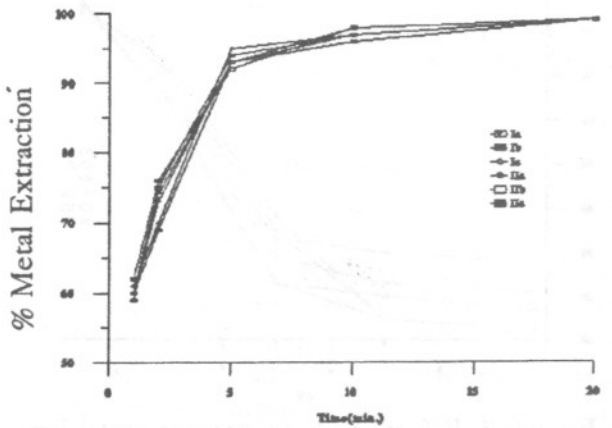


Figure 1. (cont'd) (vi) Fe (II)

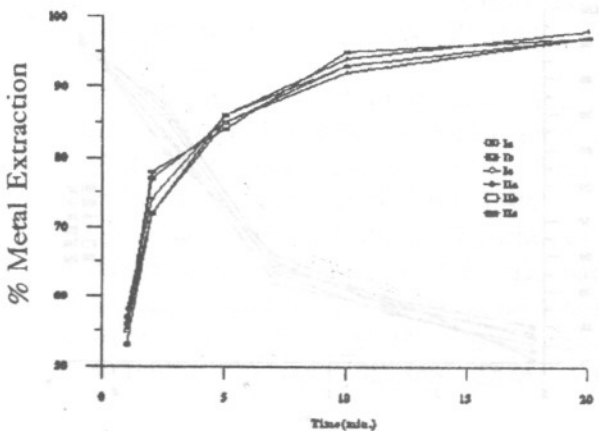


Figure 1. (cont'd) (iv) Co (II)

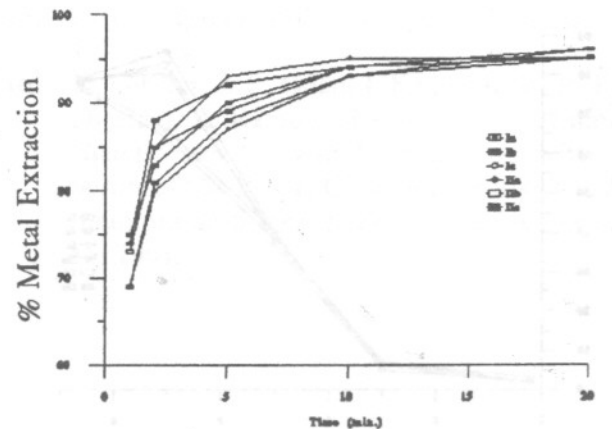


Figure 1. (cont'd) (vii) Fe (III)

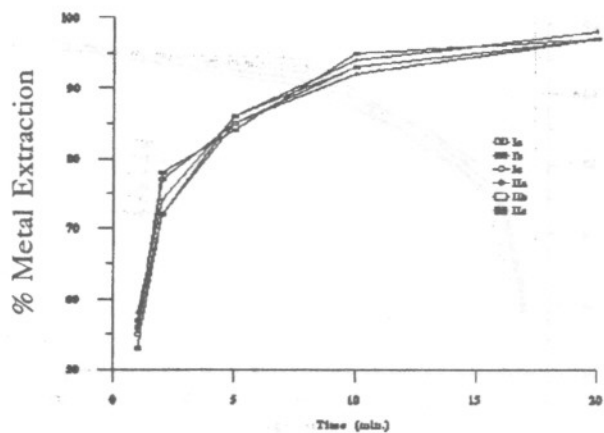


Figure 1. (cont'd) (viii) Mn (II)

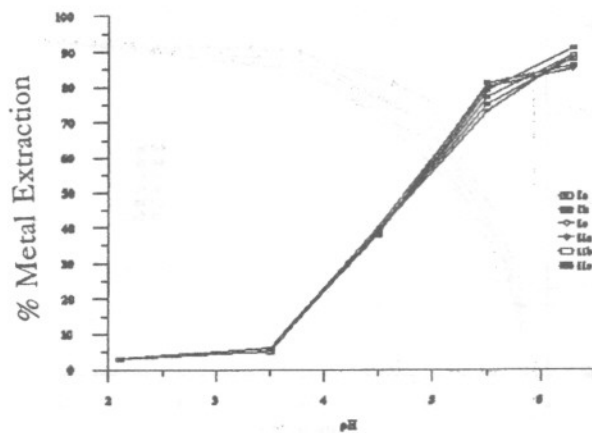


Figure 2. (cont'd) (iii) Mg (II)

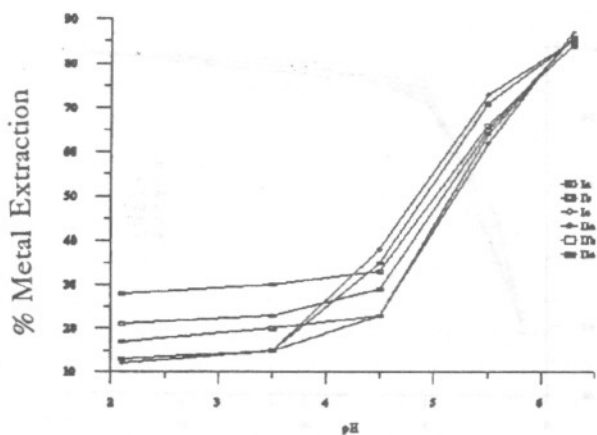


Figure 2. Effect of ph on percent metal ion extraction by different phases for (i) Cu (II).

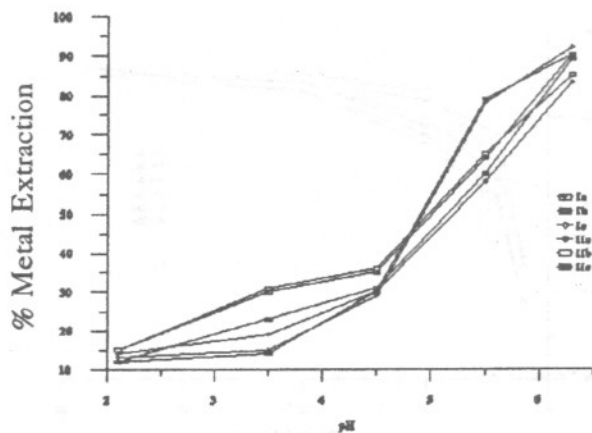


Figure 2. (cont'd) (iv) Co (II)

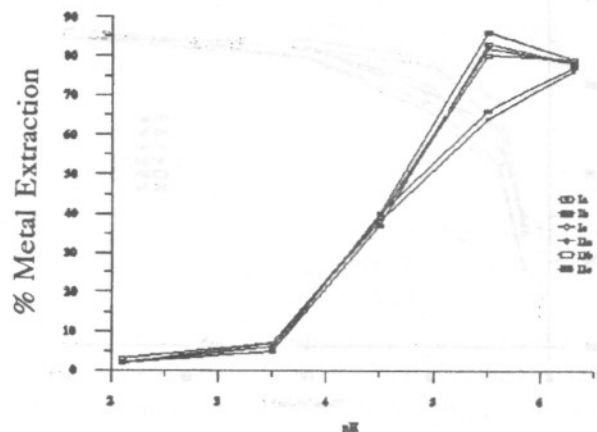


Figure 2. (cont'd) (ii) Zn (II)

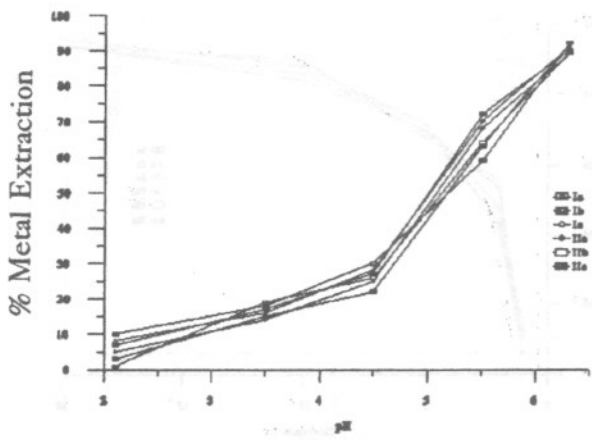


Figure 2. (cont'd) (v) Ni (II)

Table 4. Optimum pH and shaking time (min) required for 90% metalion extraction.

Metalion	Ia		IIa		Ib		IIb		Ic		IIc	
	Time	pH	Time	pH	Time	pH	Time	pH	Time	pH	Time	pH
Mg(II)	<10	6.3	<10	6.3	5	6.3	5	6.3	5	6.3	5	6.3
Mn(II)	<20	-	10	-	<20	-	<20	-	<20	-	<20	-
Fe(II)	5	-	5	-	5	-	5	-	5	-	5	-
Fe(III)	5	-	5	-	10	-	10	-	5	-	<10	-
Co(II)	<10	6.3	<10	6.3	<10	6.3	<10	6.3	<10	6.3	<10	6.3
Cu(II)	<5	6.3	5	6.3	<5	6.3	5	6.3	5	6.3	5	6.3
Zn(II)	5	5.5	<10	6.3	5	5.5	5	5.5	<10	6.3	5	6.3

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