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## Separation Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713708471>

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**To cite this Article** Luo, Chien-Shu and Huang, Shang-Da(1993) 'Adsorption of Copper Ion with Metal Hydroxide from Ammonia Solution', *Separation Science and Technology*, 28: 6, 1253 – 1271

**To link to this Article:** DOI: 10.1080/01496399308018035

URL: <http://dx.doi.org/10.1080/01496399308018035>

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## Adsorption of Copper Ion with Metal Hydroxide from Ammonia Solution

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### ABSTRACT

The removal of copper(II) from ammonia solution by adsorption on iron(III), aluminum(III), and tin(IV) hydroxide is studied. The effects of experimental parameters such as solution pH and concentration of total ammonia on adsorption are examined both from the change of solution composition and electrical properties of the solid surface. In a moderately high electrolyte concentration, an optimum solution pH is found for the solution composition when the sum of the species fractions of  $\text{Cu}(\text{NH}_3)_2^{2+}$ ,  $\text{Cu}(\text{NH}_3)_2^{2+}$ , and  $\text{Cu}(\text{NH}_3)_3^{2+}$  reaches its maximum. The ligand number of aminecopper(II) of the solution is near 2.0 under this optimum condition. The decrease in adsorption in the more basic tetraamminecopper(II) solution is attributed to the competing reaction for copper(II) by the free ammonia in the solution. Adsorption isotherms at various concentrations of total ammonia show decreasing adsorption with high electrolyte concentration as a result of a highly positively charged surface and a reduction of available surface sites. The relative extent of adsorption is discussed for various experimental conditions based on the data and the surface complexation concept.

### INTRODUCTION

The neutralization and formation of metal hydroxide precipitates using lime or caustic soda are the conventional technology for the removal of heavy metals from industrial wastewaters or spent liquids (1–3). Some special reagents have occasionally been utilized for the method of chemical precipitations when the solutions contain metal chelating agents and are not readily precipitated as insoluble hydroxides (3, 4). In addition, oxidations of chelating agents may be used in part to make the formation of metal hydroxides possible (3, 5, 6). All the treatments described above

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deal with solutions containing sludge or colloidal particles, and adsorption/coprecipitation of ions on the solid may occur. Some existing technologies for the treatment of low level radioactive wastewater use the method of coprecipitation (7, 8). We feel it is important to study the variables which influence the adsorption of soluble species on solid particles in relation to flocculation, dispersion, and chemical separation.

Numerous experiments have reported the adsorption of metal ions on a variety of solids, such as silica gel, quartz, and hydrous metal oxides (9-21). Among these materials, amorphous iron(III) oxyhydroxide has been intensively studied (21). It can be formed by neutralizing ferric solution with base. This precipitate has a particle diameter of about 30 Å, and the composition of this precipitate is reported to be  $\text{Fe}_2\text{O}_3 \cdot 1.2 \text{ H}_2\text{O}$  (22). The initially formed particles of ferric hydroxide are discrete spheres, and rods composed of 2 or 3 spheres are formed during 3-4 hours aging (23). It is clear that the method of preparation and subsequent treatment of the oxide may change its surface activity. Since amorphous iron(III) oxyhydroxide has a large specific surface area (21) and significant adsorptive properties, it may be considered as a suitable adsorbent for the removal of soluble metal ions. Moreover, the point of zero charge of the oxide is pH 8.0 (21, 24) in dilute simple electrolyte solutions, inferring that it has the capability of being charged positively or negatively in near neutral solutions and consequently allowing the adsorption of anions or cations if coulombic interaction plays an important role.

A survey of the literature on the sorption of simple metal ions from aqueous solution by hydrous particles indicates that the amount of metal adsorbed usually appears drastically increased near the pH of hydrolysis (10, 16). Beyond that pH, precipitation or a solid solution of metal hydroxides can be formed on the particle surface (25). In the presence of a metal ligand, the solubility of the metal ion is much enhanced due to the formation of soluble metal complexes, and the sorption behavior of the hydrous metal oxides may be different. Solutions containing metal complexes, such as mercury(II), halogenide (26, 27) and uranium(VI) carbonate (28), have been studied for sorption with hydrous oxide surfaces. Insoluble hydrous metal oxides or hydroxides in aqueous solutions given an amphoteric property through the hydroxyl functional groups on the surface. The hydroxyl groups also act as the surface adsorbing sites for the adsorption of the metal ion species from the solution. Some concepts have been proposed to deal with the sorption of metal ions on the hydrous oxides. These include ion exchange (12, 19), surface complexation (10, 11), site binding (20, 21, 29, 30), surface precipitation (25), and surface hydrolysis (28, 31).

In this article the solutions of amminecopper(II) complexes are studied. These solutions are the spent etchants from printed circuit board manufacture (4) and are thus of practical interest. The total concentrations of copper and ammonia are well controlled in order to avoid the formation of insoluble copper hydroxide in solution during the tests. The effects of such experimental parameters as pH and concentration of total ammonia on the efficiency of adsorption on metal hydroxide are examined and discussed both from the variations of the composition of solute species in the solution and the surface properties of the adsorbents. Since ammonia is a stronger ligand for copper(II) in comparison with such ligands as hydroxide ions or the hydroxyl groups on the oxide surface, the adsorption of copper ions from the ammonia solution may furnish a suitable approach to resolve the surface reactions based on the surface complexation and site binding models.

## EXPERIMENTAL

### Apparatus

A Varian model AA-20 atomic absorption spectrophotometer was used to determine the copper and iron content in the solution. A computer program dealing with solution equilibria was developed and carried out with a microcomputer.

A microelectrophoresis apparatus (Zeta-Meter Inc.) was used to measure the electrophoretic mobilities of the hydroxide particles. Measurements of mobility were made at a field strength of 4–6 V/cm by the use of a molybdenum anode and platinum-iridium cathode. The zeta potential was calculated from the Helmholtz–Smoluchowski formula.

### Reagents and Chemicals

The iron(III) solution was prepared from iron(III) nitrate for a concentration of 1.11 g Fe/L in which 40 mL of concentrated nitric acid was added for each liter of stock solution. The eventual concentration of iron in the stock solution was further determined by the method of atomic absorption spectrometry after appropriate dilutions. A copper(II) solution with a concentration of 12.9 g Cu/L was obtained by dissolving anhydrous copper(II) sulfate in distilled water to which 20 mL of concentrated nitric acid was added for each liter of copper(II) solution. The copper content of this solution was also measured by AAS. The ammonia solution was made by dissolving 40.12 g ammonium chloride and adding 50 mL of concentrated ammonia water (25%, 0.91 kg/L) for each 500 mL of solution. The concentration of total ammonia in this solution was estimated to be 2.836 M.

Amminecopper(II) solutions were made by mixing the copper(II) solution with an appropriate amount of ammonia solution. The final amminecopper(II) solutions for the test contained total copper and total ammonia in the concentration ranges of 0.050–1.52 g Cu/L and 0.14–1.2 M, respectively. The aluminum(III) solution was prepared from aluminum nitrate at a concentration of 12 g Al/L to which 20 mL of concentrated nitric acid was added for each liter of stock solution, and the tin(IV) solution was obtained by dissolving stannic chloride hydrate to give a concentration of 24 g Sn/L to which 50 mL of concentrated nitric acid was also added for each liter of tin(IV) solution. All chemicals used were of reagent grade.

### Procedure

Iron(III) solution was slowly introduced with magnetic stirring into the amminecopper(II) solution. The pH of the sols was adjusted to the 4.8–9.0 range by adding concentrated nitric acid or 0.5 N NaOH dropwise. After pH adjustment, the beaker was mounted with parafilm to reduce the volatilization of ammonia, and the sols were stirred for 40 more minutes. The sols were left standing for 20 minutes prior to filtration through Whatman GF/F filter paper (0.7  $\mu$ m particle size retention). The pH of the solution was remeasured and recorded. Approximately 20 mL of filtrates were collected for analysis of the copper remaining in the solution. The first 10 mL of filtrate was discarded in order to reduce the possible error in the residual copper measurement due to the adsorption of copper ions on the filter paper. The filtrates collected were acidified with a few drops of concentrated nitric acid and then analyzed for copper. The amount of copper adsorbed was calculated from the concentrations of copper of the initial solution and the filtrate.

In tests of the adsorption of copper from ammonia solution with aluminum(III) hydroxide or tin(IV) hydroxide, the iron(III) solution mentioned above was replaced by aluminum(III) or tin(IV) solution respectively using the same procedure to obtain the adsorption data.

The zeta potential of the hydroxide particles was measured in a proper concentration with their supernatant solution which contained a 0.306 M concentration of total ammonia in the pH 5–9 range. Each measurement was performed by observing at least 20 particles migrating through a known distance, and at least three independent measurements were made to obtain the results.

The concentration or fraction of each copper species present in the ammonia solution was calculated by our homemade computer program (32) after input of the concentrations of total ammonia and total copper. The ligand number of the amminecopper(II) of the solution was also cal-

culated from pH 4 to 10. The equilibrium constants used for the computations were corrected for the variations in different ionic strengths by calculation of the activity coefficients based on the Davies equation (33) or interpolation from the literature (34-37).

Since the concentration of total ammonia exceeds 0.1 M for all tests and the  $\text{NH}_3/\text{NH}_4^+$  electrolyte acts as a buffer, the ionic strength of the solution is regarded as unchanged by the neutralization of the basic amminecopper(II) solution with nitric acid. In this way the ionic strength of these solutions can be approximately related to the concentration of total ammonia.

## RESULTS AND DISCUSSION

The adsorptions of copper(II) species from the ammonia solutions as a function of pH on three different adsorbents, iron(III) hydroxide, aluminum(III) hydroxide, and tin(IV) hydroxide, are given in Figs. 1-3, respectively. Remarkable differences in the efficiency of adsorption are observed at different values of solution pH. It is found that all these curves

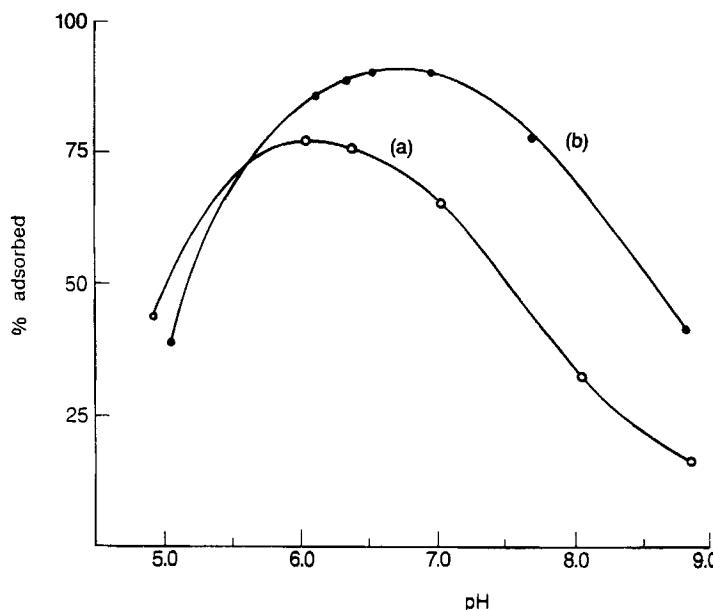


FIG. 1 Effect of pH on the adsorption of copper from ammonia solutions with iron(III) hydroxide. (a) Total ammonia, 1.18 M; iron added, 1850 ppm; total copper, 1270 ppm. (b) Total ammonia, 0.306 M; iron added, 220 ppm; total copper, 57.5 ppm.

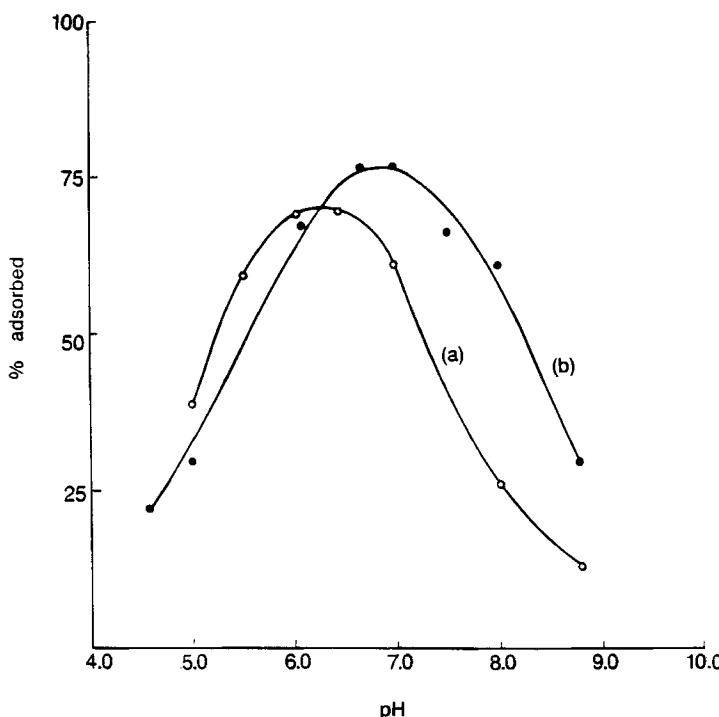


FIG. 2 Effect of pH on the adsorption of copper from ammonia solutions with aluminum(III) hydroxide. (a) Total ammonia, 1.18 M; aluminum added, 800 ppm. (b) Total ammonia, 0.306 M; aluminum added, 240 ppm. Copper added, 51.6 ppm for both tests.

show a maximum in the neutral pH region. The pH at this maximum efficiency is an optimum pH for the removal of copper from the solution. It depends on the concentration of total ammonia but is independent on what kinds of adsorbents are used. For instance, with a 0.306 M concentration of total ammonia, the maximum efficiency occurs at approximately pH 6.7 for all three adsorbents, iron(III) hydroxide, aluminum(III) hydroxide, and tin(IV) hydroxide. (Figs. 1b, 2b, and 3). In addition, the maximum efficiency can be found at pH 6.1 for a 1.18 M concentration of total ammonia although the different adsorbents of iron(III) hydroxide and aluminum(III) hydroxide may be used independently (Figs. 1a and 2a).

The characteristic distribution of copper species in the solution is affected by the concentration of total ammonia and solution pH. The adsorption results shown in Figs. 1-3 reveal that the solution factors may play an important role under the experimental conditions, whereas the change of

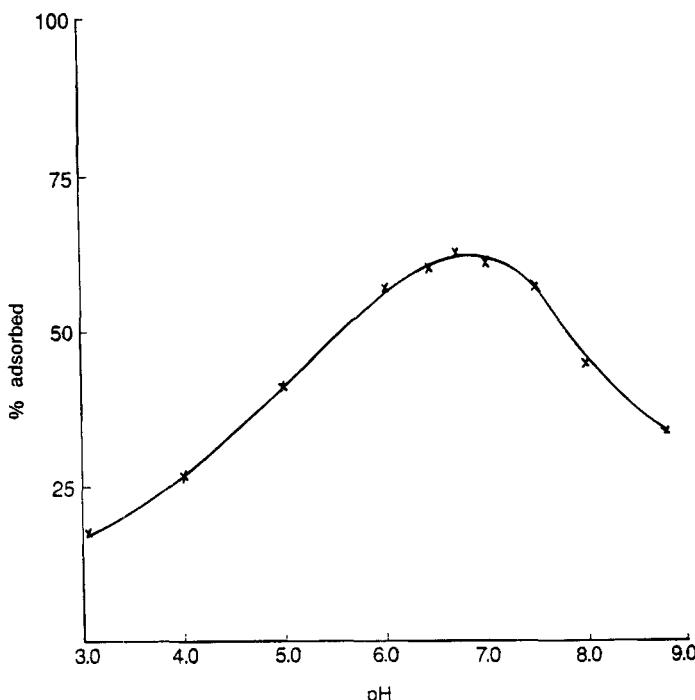


FIG. 3 Effect of pH on the adsorption of copper from ammonia solutions with tin(IV) hydroxide. Total ammonia, 0.306 M; tin added, 96 ppm; copper added, 51.6 ppm.

surface activities of the metal hydroxides as a function of solution pH may give a smaller contributions to the adsorption variations.

The distributions of copper species in ammonia solutions are calculated and given in Figs. 4 and 5 for total ammonia concentrations of 1.18 and 0.306 M, respectively. The dashed lines in the Figs. 4 and 5 show the sum of the species fractions of  $\text{Cu}(\text{NH}_3)^{2+}$ ,  $\text{Cu}(\text{NH}_3)_2^{2+}$ , and  $\text{Cu}(\text{NH}_3)_3^{2+}$ . The ligand number of amminecopper(II) of the solution is given in Fig. 6. On comparison of the copper species distribution plots in Figs. 4 and 5 and the optimum pH at which the maximum efficiency is observed in Figs. 1-3, it can be seen that optimum adsorption will occur at the solution pH which gives the maximum value of the sum of the fractions of the species  $\text{Cu}(\text{NH}_3)^{2+}$ ,  $\text{Cu}(\text{NH}_3)_2^{2+}$ , and  $\text{Cu}(\text{NH}_3)_3^{2+}$ . The ligand numbers of amminecopper(II) are approximately 2.0 under these optimum adsorptions. Table 1 gives the solution characteristics where the adsorption on iron(III) hydroxide exhibits the best efficiency compared with the adsorption results

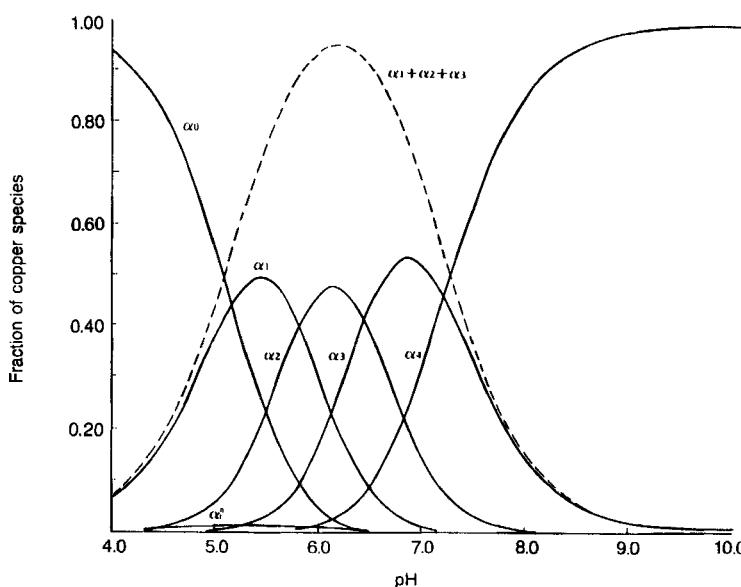


FIG. 4 Distribution of copper species in ammonia solution. Total ammonia, 1.18 M; total copper,  $C_M = 1270$  ppm.  $\alpha_0 = [Cu^{2+}]/C_M$ ;  $\alpha_1 = [Cu(NH_3)^{2+}]/C_M$ ;  $\alpha_2 = [Cu(NH_3)_2^{2+}]/C_M$ ;  $\alpha_3 = [Cu(NH_3)_3^{2+}]/C_M$ ;  $\alpha_4 = [Cu(NH_3)_4^{2+}]/C_M$ ;  $\alpha_5 = [Cu(OH)^{+}]/C_M$ .

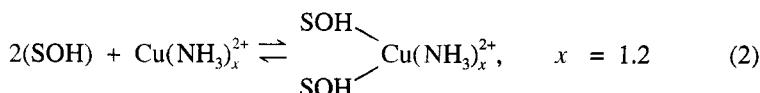
at nearby solution pHs. At the optimum pHs of adsorptions, the solutions give the maximum value of the sum of the species fractions of  $Cu(NH_3)^{2+}$ ,  $Cu(NH_3)_2^{2+}$ , and  $Cu(NH_3)_3^{2+}$ , and this maximum value reaches approximately 0.92–0.94. Figure 7 shows the optimum pH as a function of the concentration of total ammonia for the adsorption of copper deduced from the correspondences stated above. It can be seen that the higher the concentration of total ammonia, the lower will be the optimum solution pH.

The dependence of zeta potentials of the metal hydroxides on pH in the solution containing 0.306 M total ammonia are shown in Figs. 8–10. The surfaces of the metal hydroxides are negatively charged in basic ammonia solution.

In the neutral pH region, the adsorption reactions can be considered as



(where S denotes the surface of hydrous metal oxide or hydroxide), or a bidentate complex reaction (31).



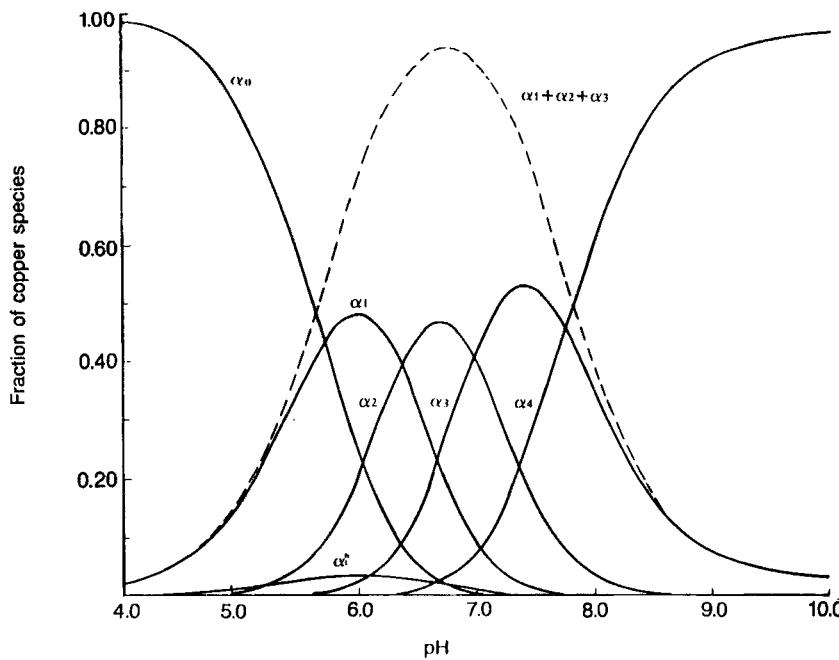


FIG. 5 Distribution of copper species in ammonia solution. Total ammonia, 0.306 M; total copper,  $C_M = 57.5$  ppm.  $\alpha_0 = [Cu^{2+}]/C_M$ ;  $\alpha_1 = [Cu(NH_3)^{2+}]/C_M$ ;  $\alpha_2 = [Cu(NH_3)_2^{2+}]/C_M$ ;  $\alpha_3 = [Cu(NH_3)_3^{2+}]/C_M$ ;  $\alpha_4 = [Cu(NH_3)_4^{2+}]/C_M$ ;  $\alpha_5 = [Cu(OH)^{+}]/C_M$ .

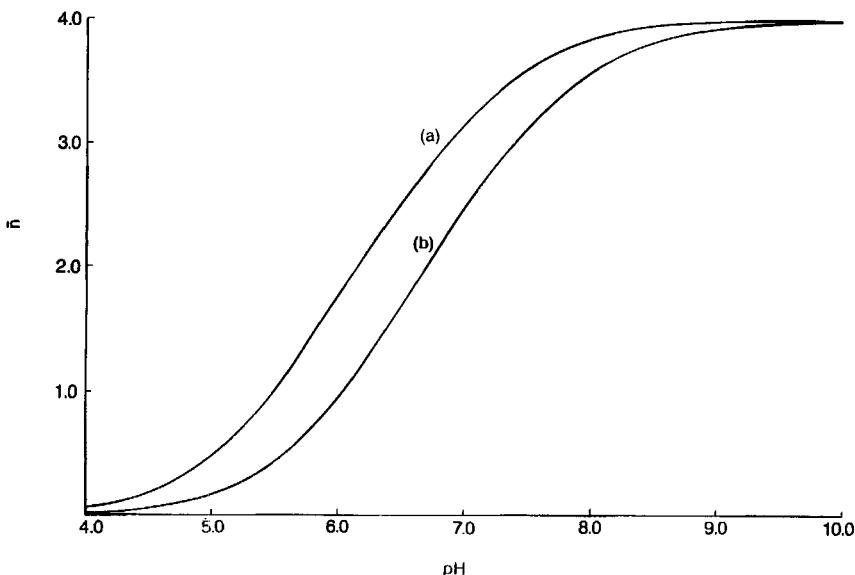


FIG. 6 Ligand number for the amminecopper(II) system at (a) total ammonia, 1.18 M; total copper concentration,  $C_M$  1270 ppm; (b) total ammonia, 0.306 M; total copper concentration,  $C_M$  57.5 ppm.

TABLE 1

Correlation between the Efficiency of Adsorption of Copper and Solution Characteristics

Solution conditions					
Total ammonia (M)	pH	Copper species		Residual copper in solution (µg/mL)	Copper adsorbed (mmol Cu/g Fe)
		$\alpha_1 + \alpha_2 + \alpha_3$	Ligand number, $\bar{n}$		
0.140 <sup>a</sup>	6.7	0.84	1.4	18.2	10.9
	7.1	0.92	2.0	17.5	11.2
	7.4	0.89	2.5	19.2	10.6
0.306 <sup>b</sup>	6.4	0.89	1.5	6.2	3.72
	6.7	0.94	2.0	5.0	3.80
	7.0	0.91	2.4	5.1	3.80
0.536 <sup>c</sup>	6.1	0.88	1.4	22.0	3.57
	6.4	0.94	1.9	19.3	3.76
	6.7	0.93	2.4	20.3	3.69

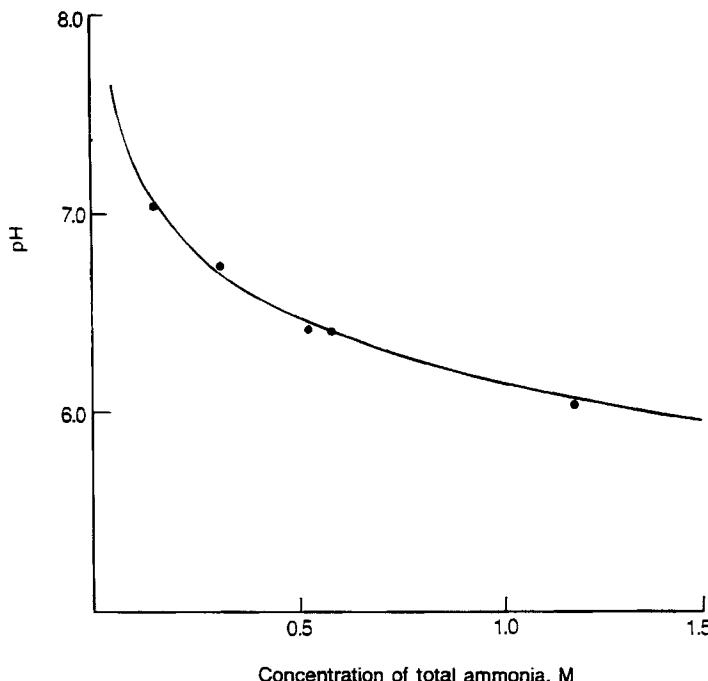
<sup>a</sup>Total copper 50.0 ppm, iron(III) 46.7 ppm.<sup>b</sup>Total copper 57.6 ppm, iron(III) 218 ppm.<sup>c</sup>Total copper 73.0 ppm, iron(III) 224 ppm.

FIG. 7 The optimum pH for the adsorption of copper from different concentrations of total ammonia media. The point data are experimental results.

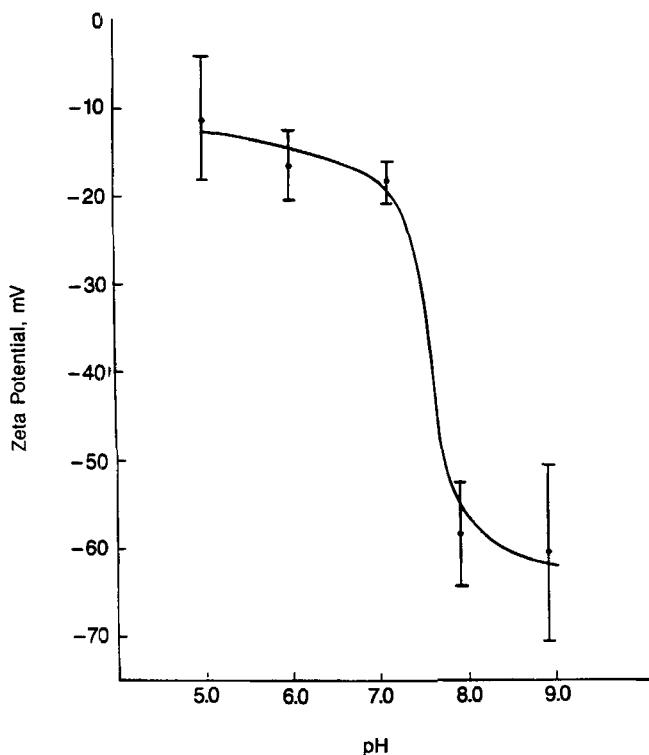
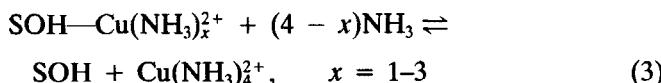
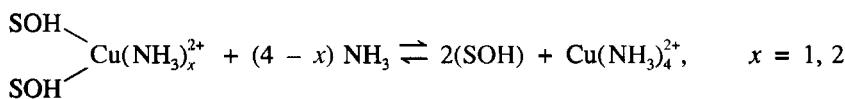


FIG. 8 Zeta potential of iron(III) hydroxide as a function of pH of solution with 0.306 M total ammonia.

As the solution pH rises to the basic region, the activity of free ammonia in the solution increases. Thus, competing reactions between the free ammonia and the surface sites for the copper species which are already adsorbed may occur:



or:



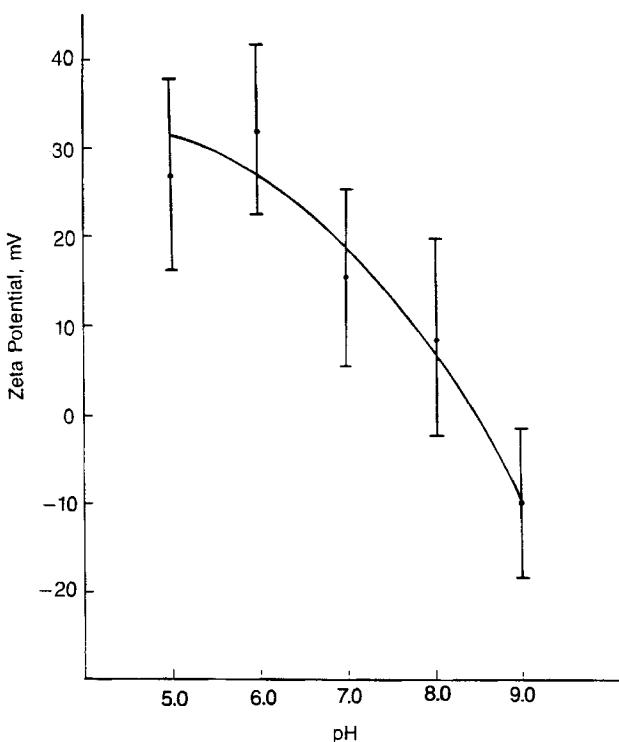


FIG. 9 Zeta potential of aluminum(III) hydroxide as a function of pH of solution with 0.306 M total ammonia.

This effectively leads to a desorption reaction, and hence the efficiency of the adsorbent is low in basic ammonia-copper(II) solution. Moreover, the fact that the adsorption efficiency decreases in more basic ammonia solution also indicates that the ion-exchange reaction for the tetraammine-copper(II) species provided by the negatively charged surface sites gives a smaller contribution to copper adsorption in comparison with surface complexation by the hydroxyl group on the solid surface as stated in Eqs. (1) and (2).

In addition to the activity of the adsorbing species and the surface sites, adsorption can be governed by other factors such as the properties of the electrical double layer at the solid surface and the binding strength between the surface hydroxyl groups and the solute species adsorbed. On the other hand, the surface may be highly positively charged if the acidity of the solution is too high. This leads to an unfavorable adsorption condition

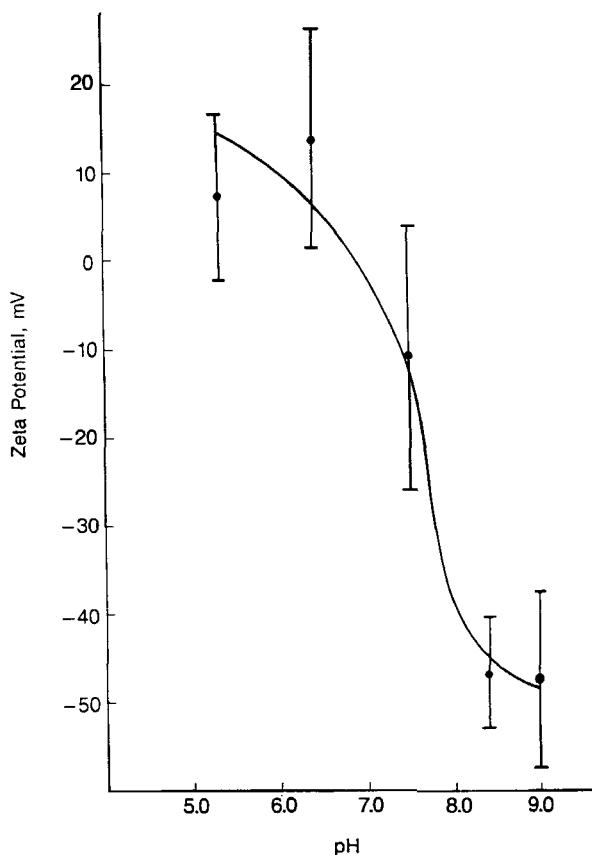


FIG. 10 Zeta potential of tin(IV) hydroxide as a function of pH of solution with 0.306 M total ammonia.

because of electrostatic repulsion between the adsorbing cation and the solid surface. For these reasons the adsorption is decreased in highly acidic solution.

The adsorption isotherm for various concentrations of total ammonia is shown in Fig. 11. Except for Curve (e), the isotherms shown in Fig. 11 were obtained under the optimum pH for each concentration of total ammonia. The solutions at such conditions are consequently of the same composition of copper species. It can be seen from Fig. 11 that the concentration of total ammonia has a large effect on adsorption. Increasing the concentration of total ammonia will lead to a lower adsorption density even though the solutions have the same composition of copper species.

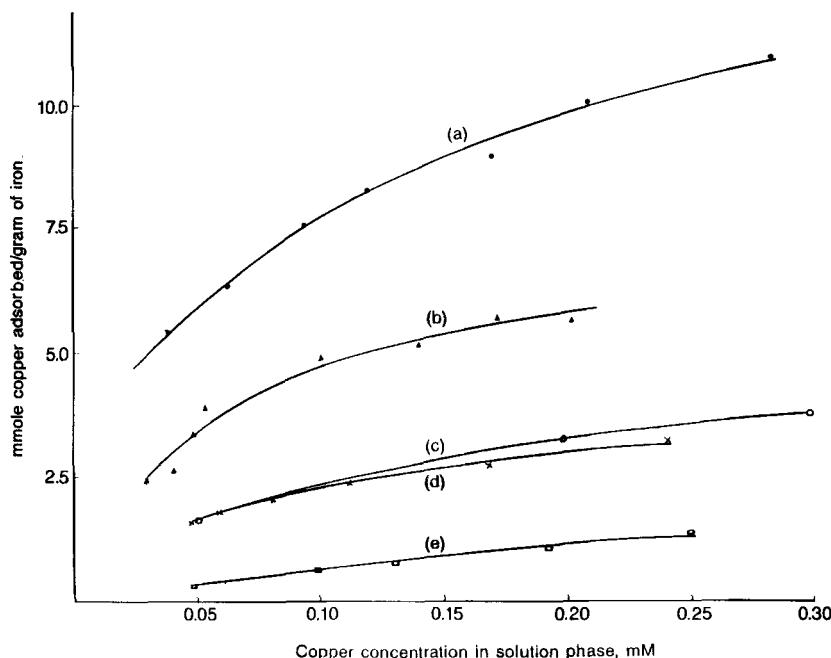
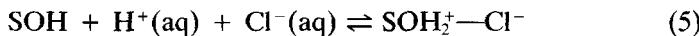


FIG. 11 Isotherm for the adsorption of copper on iron(III) hydroxide from ammonia solution. Total ammonia (M): (a) 0.140, (b) 0.306, (c) 0.536, (d) 0.568, (e) 1.18. pH: (a) 7.0, (b) 6.7, (c) 6.4, (d) 6.4, (e) 7.0.

A solution at a high concentration of indifferent electrolyte may increase the surface charge of the hydrous oxide (38-41). This is attributed to the specific adsorption of the electrolyte cations or anions on the solid surface. The surface charge may be caused in large part by the specific adsorption of the electrolyte ions if the electrolyte is at a moderately high concentration (20). The ammonia solutions in this study contain the major electrolytes  $\text{NH}_4^+$ ,  $\text{Cl}^-$ , and  $\text{NO}_3^-$ . In the acidic surface region ( $\text{pH} < \text{pH}_{\text{pzc}}$ ), the electrolyte anions may have the following reaction:



The specific adsorption of chloride increases the anion-exchange capacity (42); in other words, the apparent capacity for cation adsorption is reduced at a high electrolyte concentration.

The adsorption density can be expressed in the convenient Langmuir form:

$$Q = Q_{\text{max}} C K_{\text{app}} / (1 + C K_{\text{app}}) \quad (6)$$

where  $K_{app}$  is the apparent adsorption constant

$Q_{max}$  is the apparent maximum amounts of metal ions that can be adsorbed per unit weight of adsorbent

The values of  $Q_{max}$  and  $K_{app}$  can be calculated from the slope and intercept on the plot of  $C/Q$  vs  $C$ . The term  $Q_{max}K_{app}$  in Eq. (6) is Henry's constant, which is the initial slope on the plot of  $Q$  vs  $C$ . Figure 12 shows the values of Henry's constant as a function of the concentrations of total ammonia for the adsorption of copper at the optimum pH. Extrapolation to zero concentration of total ammonia yields a value of  $257 \text{ (g Fe/L)}^{-1}$  for iron(III) hydroxide adsorbent. Henry's constant is reduced to half value as the concentration of total ammonia increases from zero concentration to 0.33 M.

A plot of  $K_{app}$  against the concentration of total ammonia (given in Fig. 13) shows a limiting value of  $16.8 \text{ mM}^{-1}$  in a very dilute concentration of total ammonia. It is also noted that  $Q_{max}$  in Eq. (6) is the apparent adsorption capacity of the hydrous oxide surface and is subject to a remarkable change as the concentration of electrolyte is changed, especially in

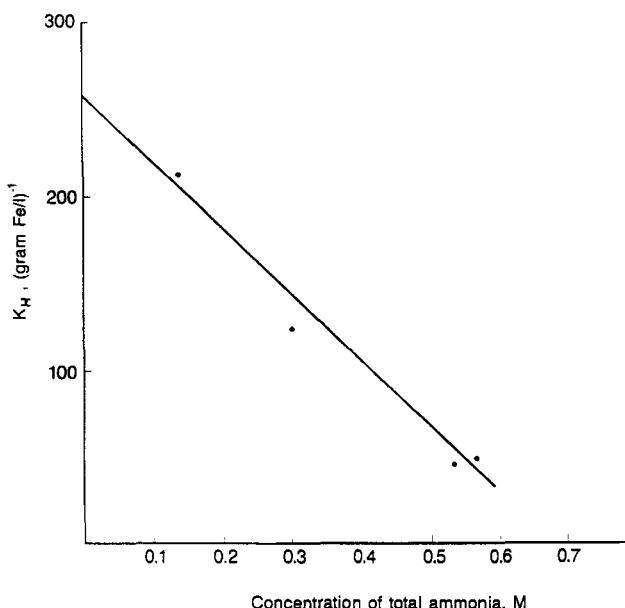


FIG. 12 Plot of Henry's constant against the concentration of total ammonia for the adsorption of copper at optimum pH.

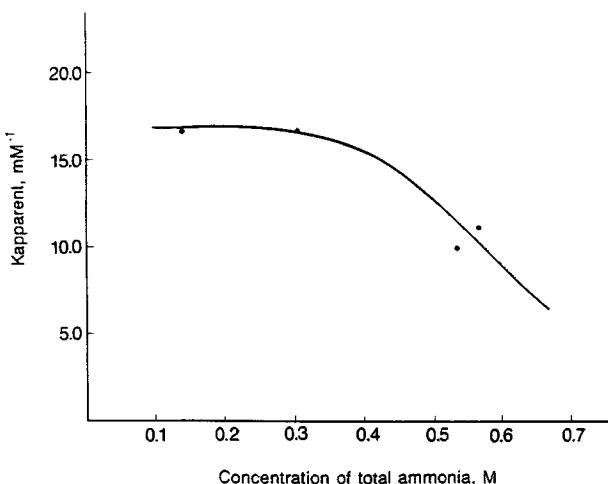


FIG. 13 Effect of the concentration of total ammonia on Langmuir's constant at optimum solution pH.

the 0.1–0.3 M range. As zero electrolyte concentration is approached,  $Q_{\max}$  is obtained as 15.3 mmol sites/g Fe from the extrapolation value of Henry's constant and that of  $K_{app}$ . This is the value of available sites for the metal ion adsorption on the iron(III) hydroxide surface in the absence of competing electrolyte. Davis (21) reported a similar value of 15.7 mmol sites/g Fe for the amorphous iron(III) oxyhydroxide.

Table 2 gives a comparison of Henry's constants in various conditions when using iron(III) hydroxide as the adsorbent. It can be seen that the value of Henry's constant at pH 7.0 is reduced to 3% as the concentration

TABLE 2  
Variation of Henry's Constants for Copper in Various Solutions Using  
Iron(III) Hydroxide as Adsorbent<sup>a</sup>

pH	Total ammonia (M)				
	0.14	0.306	0.536	0.568	1.18
6.1			45		
6.4			46	50	
6.7	134	123	47		
7.0	214				6.6
7.4	202				

<sup>a</sup>Henry's constant in (g Fe/L)<sup>-1</sup>.

of total ammonia increases from 0.14 to 1.18 M. The results are largely due to the effect of electrolyte ions on the reduction of available surface sites as well as to an increase of surface charge. A solution of 0.536 M concentration of total ammonia shows almost the same value of Henry's constant within the pH range of 6.1 to 6.7. In a solution of 0.14 M concentration of total ammonia, a greater change in Henry's constant is observed as the solution pH decreases from 7.4 to 6.7. The value of Henry's constant is  $202 \text{ L}\cdot\text{g Fe}^{-1}$  at pH 7.4 while a lower value of  $134 \text{ L}\cdot\text{g Fe}^{-1}$  at pH 6.7 is attained in a 0.14 M concentration of total ammonia. At a high electrolyte concentration, the surface charge is less affected by a change of the solution pH. As a consequence, the variation of adsorption by a change of solution pH in such a condition is attributed mainly to the change of solution composition of the related species. Since the change of solution composition at a 0.536 M concentration of total ammonia is not large within the pH 6.1 to 6.7 range as shown in Table 1, the variation of adsorption due to any change of solution pH is small within this pH range. The solid surface in a solution of 0.14 M concentration of total ammonia may lead to a less charged surface in comparison with that in 0.536 M concentration of total ammonia and thus gives a higher variation of adsorption by a decrease of solution pH due to a stronger effect on the surface charge by the change of solution pH.

Table 3 shows the differences on adsorption efficiency caused by using the adsorbents of iron(III) and aluminum(III) hydroxides. Aluminum(III) hydroxide gives a smaller adsorption density than iron(III) hydroxide. Alu-

TABLE 3  
Comparison on the Adsorption Efficiency between Iron(III) and Aluminum(III)  
Hydroxide as Adsorbents

Solution conditions				Copper adsorbed [mol Cu/mol Fe (or Al)]	
pH	Total ammonia (M)	Chloride (M)	Residual copper in solution ( $\mu\text{g/mL}$ )	Fe(OH) <sub>3</sub>	Al(OH) <sub>3</sub>
6.7	0.306	0.15	11.9	$3.2 \times 10^{-1}$	$7.0 \times 10^{-2}$
			10.9		$9.0 \times 10^{-2}$
6.4	0.568	0.28	16.3	$1.8 \times 10^{-1}$	$4.4 \times 10^{-2}$
			15.4		$2.9 \times 10^{-2}$
			6.4	$1.1 \times 10^{-1}$	
			5.2		
			3.2		
			3.1		

minum(III) hydroxide in a solution with a pH range of 6.4–6.7 leads to a higher surface potential as indicated by the zeta potential measurement. Furthermore, the lower specific surface area value for aluminum(III) hydroxide (20, 43) may be another reason for its lower adsorption density.

## CONCLUSIONS

The adsorption of copper from amminecopper(II) solution by metal hydroxides shows that an optimum solution pH can be found and that it depends on the total ammonia concentration in the solution. The optimum pH of adsorptions corresponds to the solution composition as the sum of the species fractions of  $\text{Cu}(\text{NH}_3)_3^{2+}$ ,  $\text{Cu}(\text{NH}_3)_2^{2+}$ , and  $\text{Cu}(\text{NH}_3)_1^{2+}$  reaches its maximum.

A solution which contains tetraamminecopper(II) as the major copper species gives a low adsorption density on the metal hydroxide surface due to the competing reaction for copper(II) between the free ammonia in the solution and the hydroxyl group on the solid surface.

The solution composition becomes the determining factor for adsorption as a function of solution pH at a moderately high concentration of total ammonia, and thus the same optimum pH on adsorption is obtained regardless of the different adsorbents of metal hydroxides being used.

Adsorption isotherms at the same solution composition show that increasing the concentration of total ammonia in the solution can result in a pronounced decrease of adsorption density. This is due to the reduction of adsorptive sites on the solid surface as well as to an increase of surface charge by the increase of electrolyte concentration.

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Received by editor March 30, 1992

Revised August 4, 1992