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Copper coprecipitation with hydrous iron oxide in aqueous solutions: spectroscopic, thermal and macroscopic analyses

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ABSTRACT

Copper co-precipitation with hydrous iron oxide was investigated through spectroscopic, thermal and macroscopic analyses at different pH. Solid samples were prepared from aqueous solutions of iron (III) and copper(II) and characterized by scanning electron microscopy/energy-dispersive spectroscopy (SEM-EDS), X-ray diffraction analysis (DRX) and thermal analyses.

The co-precipitation of copper with Fe (III) retards the hydrous iron oxide transformation at pH <8. The X-ray diffraction patterns of the heated samples suggest the formation of hematite and copper ferrite. The results of desorption experiments indicate that copper is bound to the surface and incorporated within the oxide.

Keywords: Copper; Hydrous iron oxide; Coprecipitation; Desorption; Thermal analyses; X-ray diffraction

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1. Introduction

Heavy metals are considered as dangerous pollutants in surface water and ground water. They are discharged by various industries such as electroplating metal, storage batteries and mining. Copper occurs naturally in soil, sediments and water [1]. It is also a commonly generated industrial pollutant and may enter the aquatic environment through wastewater released from metal cleaning, plating, baths tanning, paper, ceramic, fertilizer and mining industries [2].

Among the inorganic colloids known as major sinks for metallic species in aquatic systems, iron oxyhydroxides with their chemical nature and high specific surface area play an important role. Metal coprecipitation with such oxides can remove significant quantities of them from water and can be employed for the treatment of industrial and municipal wastewater.

In a previous study, we have observed a significant removal of copper from aqueous solutions by coprecipitation with hydrous iron oxide under various conditions [3]. The present work focuses on solid samples analyses in the objective to evaluate the mechanism of copper uptake at various pH.

2. Experimental procedures

2.1. Copper coprecipitation

All solutions were prepared from certified reagent grade chemicals (Merck). Coprecipitation experiments involved the formation of hydrous oxide colloid in the

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presence of copper ions. The stock solution of iron was prepared by dissolving ferric chloride into HCl, which was sufficiently acidic to prevent Fe(III) hydrolysis. Copper nitrate was used as the source of divalent copper.

Iron and copper solutions were initially combined in a ratio of 1:1. Solid samples were prepared by raising the pH of an aliquot of 50 mL solution mixer to the desired pH with NaOH solution (1N). The suspension formed was agitated for 60 min.

2.2. Solid samples analyses

Suspensions obtained in the absence and in the presence of copper ions were filtered and the solid samples were air-dried under ambient temperature. Their characterization was achieved by X-ray diffraction (XRD), scanning electron microscopy/energy-dispersive spectroscopy (SEM-EDS), thermogravimetry analyses (TGA) and differential scanning calorimetry (DSC).

2.2.1. Spectroscopic analyses

X-ray powder diffraction analyses were performed on a Siemens D8 diffractometer employing Cu-Kα1 radiation. The spectra were recorded from 5 to 80° 2θ with a scanning speed of 0.02° 2θ step size. The morphology and the composition of the precipitates were examined with LEICA STEREO SCAN 440 Scanning Electron Microscope (SEM) equipped with analyses system EDAX KEVEX SIGMA.

2.2.2. Thermal analyses

Thermogravimetry analyses were performed using a thermobalance conceived in laboratory with an alumina cell (Al_2O_3 crucibles). The DSC thermograms were recorded on a DSC 210 system; samples were weighed into aluminium pans and sealed with a punched aluminium lid, the reference was a pure aluminium cell.

2.3. Desorption experiments

Desorption experiments by $MgCl_2$ (10^{-2} M) and EDTA (10^{-2} M) were carried out by using the solid samples obtained in coprecipitation experiments at various pH. The formed suspensions were agitated for 60 min and centrifuged at 2000 rpm for 15 min. The concentration of the released copper was determined by flame absorption spectroscopy using a Perkin-Elmer 2380 spectrophotometer.

3. Results and discussion

3.1. Solid samples analyses

3.1.1. Hydrous iron oxide

Spectroscopic Analyses The precipitates prepared at pHs of 4, 6 and 8, present the same morphology. Their scanning electron micrographs (SEM) show that they are poorly crystalline iron oxy-hydroxide phases (HFO) (Fig. 1). The XRD patterns (Fig. 2) of the samples obtained at pH 4 and 6 show the presence of the two broad peaks of the 2-line ferrihydrite [4]. However, the spectrum of the sample prepared at pH 8, shows that the precipitate formed is a combination of several iron oxyhydroxide phases.

Thermal analyses The DSC spectra are shown in Figure 3. The removal of adsorbed water is characterized by the endothermic peak. The exothermic peaks can be regarded as thermal decomposition of ferrihydrite to γFe_2O_3 giving off heat and transformation to α-Fe_2O_3 respectively; since the AB_2O_4 structure of γFe_2O_3 is instable [5]. They shift to higher temperature as the pH increases, suggesting an increase in stability.

3.1.2. Solid samples obtained in the presence of copper

Spectroscopic analyses The solid samples prepared in the presence of copper have also an amorphous character. Their diffraction patterns are presented in Figure 4. The diagram of the sample prepared at a pH of 5.8 resembles that of ferrihydrite (Fig. 2); showing that at this pH, the copper uptake is not due to a surface precipitation. As the pH increases, two new bands are observed at approximately $2\theta = 25°$ and $2\theta = 15°$. These can be attributed to the formation of copper hydroxide ($Cu(OH)_2$),

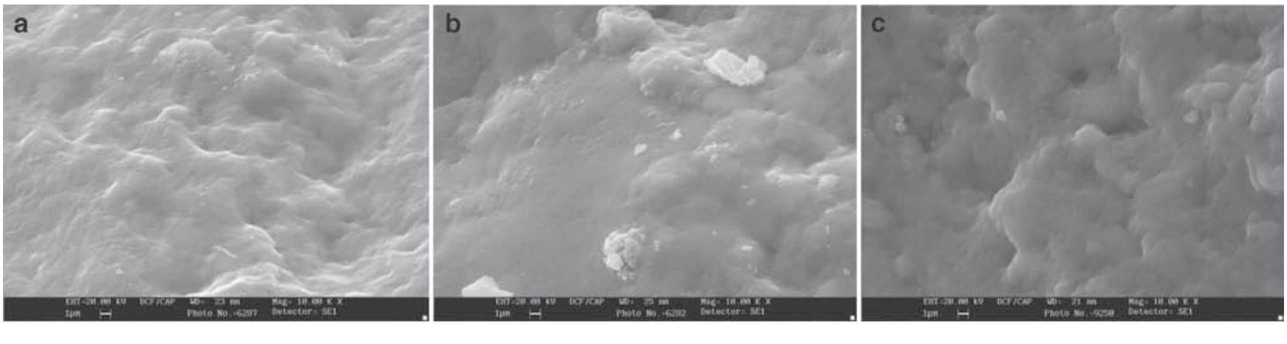

Fig. 1. Scanning electron micrographs of hydrous iron oxide prepared at (a)pH = 4, (b) pH = 6 and (c) pH = 8.

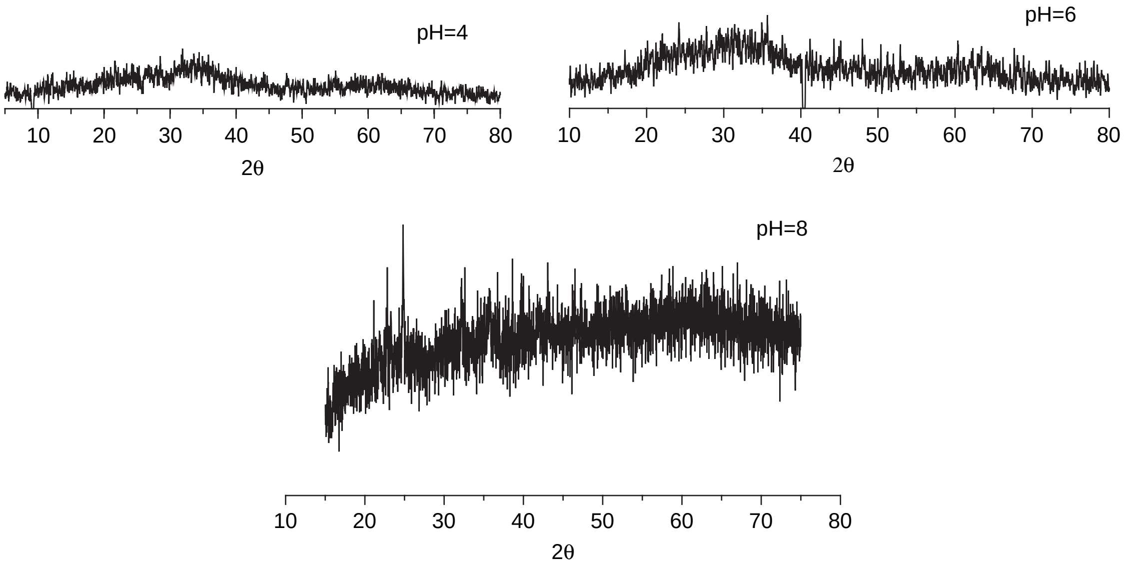

Fig. 2. X-ray diffraction patterns of hydrous iron oxide prepared at various pH.

considered as the solubility-limiting solid phase in the pH 3–12 range [6]. The presence of the heterogeneous phase of copper ferrite ($CuFe_2O_4$) cannot be verified, because its most intense peaks (35.54, 62.74 and 30.17°2θ) can be masked by the broad bands of the hydrous iron oxide.

Thermal analyses The TGA results (Table 1 and Fig. 5) show several processes leading to gradual weight loss. The weight losses observed in the temperature ranges (100°C–200°C) and (350–400°C) are associated to desorbed water and ferrihydrite transformation respectively. The weight loss occurring at temperatures around 800–900°C which has not been observed in the absence of copper ions, can be in a relation with the reduction of Cu(II) to Cu(I). It has been noted that this reduction begins at about 900°C [7].

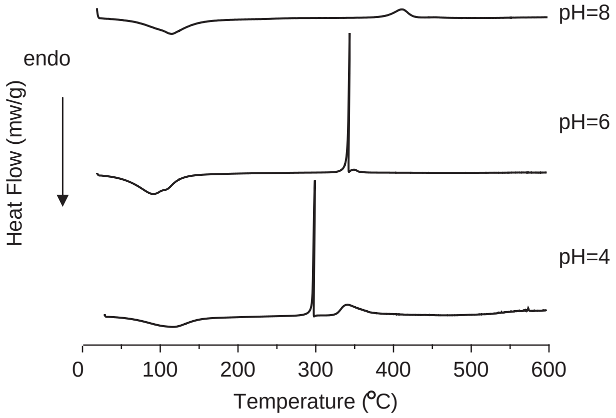

Fig. 3. DSC curves of hydrous iron oxide samples prepared at various pH.

The removal of surface adsorbed water is accompanied by the endothermic peak at about 100°C. The exothermic peak ascribed to solid transformation is more sharp for samples prepared at pH <8. It shifts to a higher temperature as the pH increases (Fig. 6). The second weak exothermic peak observed in the case of hydrous iron oxide prepared in the absence of copper (Fig. 3) disappears, showing the direct transformation of ferrihydrite to hematite. Copper coprecipitation with Fe(III) retards the rate of ferrihydrite transformation, indicating that the copper can be distributed within the oxide structure. Cornell and Gionvanoli [8], observed that coprecipitated copper stabilized the ferrihydrite about the dissolution and the reprecipitation in the form of goethite.

DRX analyses of heated samples The X-ray diffraction patterns of heated samples (Fig. 7), show more crystalline structures. The peaks observed at about 33 and 35°2θ are attributed to the presence of hematite (αFe_2O_3) and copper ferrite ($CuFe_2O_4$). The additional peaks observed in the spectrum of the sample prepared at a pH of 9.2 can be due to the formation of Cu_2O.

The formation of a mixture of hematite, copper ferrite and copper oxide, indicate the existence of more than one mechanism of copper fixation on the hydroxide.

These results are not in agreement with those of other studies. Slim and coworkers [9], have observed the formation of only Cu_2O and $CuFe_2O_4$ in a study carried out to evaluate the interaction of CuO and Fe_2O_3. An old study cited in the literature [10,11], noted the formation

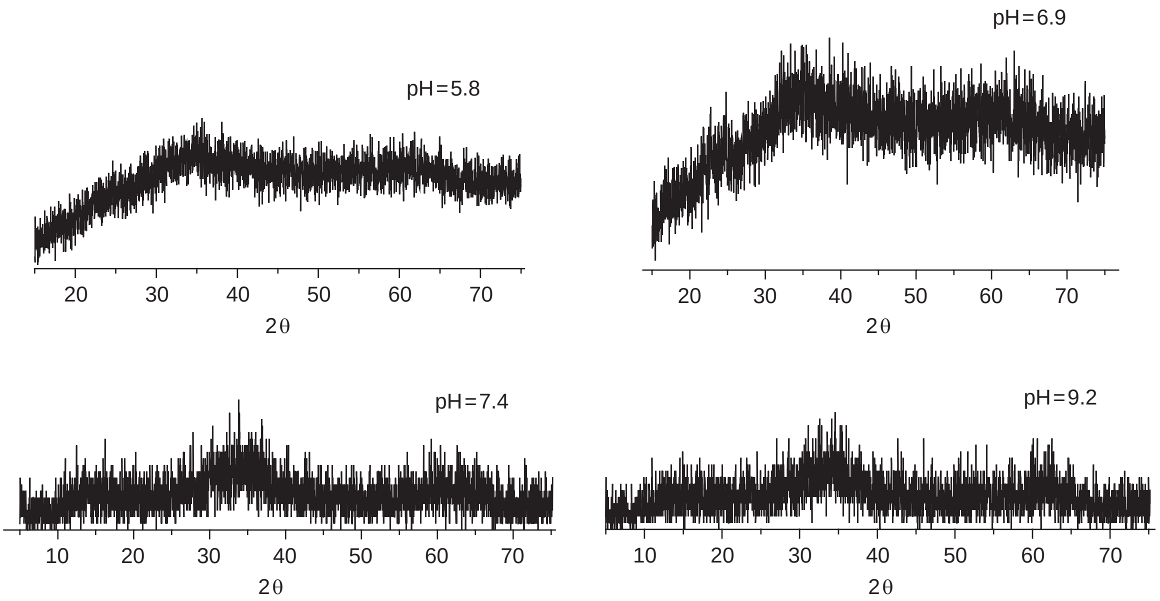

Fig. 4. X-ray diffraction patterns of samples prepared in the presence of copper at various pH.

Table 1
Weight losses determined by TGA analyses (%).

pH	200°C	300°C	400°C	500°C	600°C	700°C	800°C	900°C	1000°C
5.8	20.65	22.39	24.01	24.38	24.63	24.87	26.49	28.36	28.61
6.9	27.55	28.89	29.98	30.49	30.65	30.90	32.33	34.17	34.42
7.4	27.09	28.34	28.72	29.40	29.68	29.97	31.41	34.10	34.39
9.2	22.92	24.19	24.55	24.73	24.82	24.91	26.08	29.69	30.05

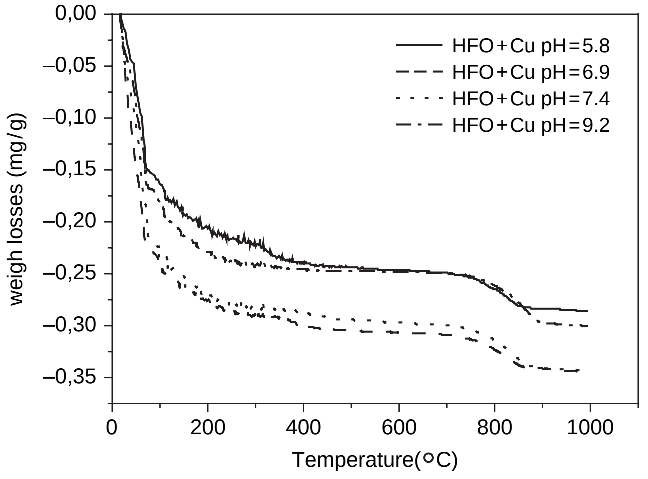

Fig. 5. TGA curves of solid samples obtained in the presence of copper at various pH.

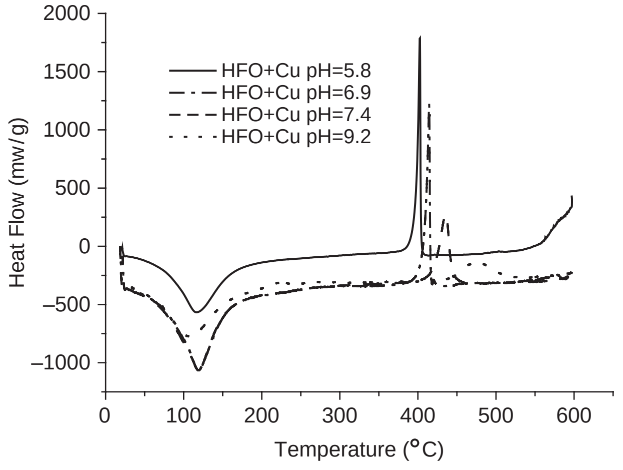

Fig. 6. DSC curves of solid samples obtained in the presence of copper at various pH.

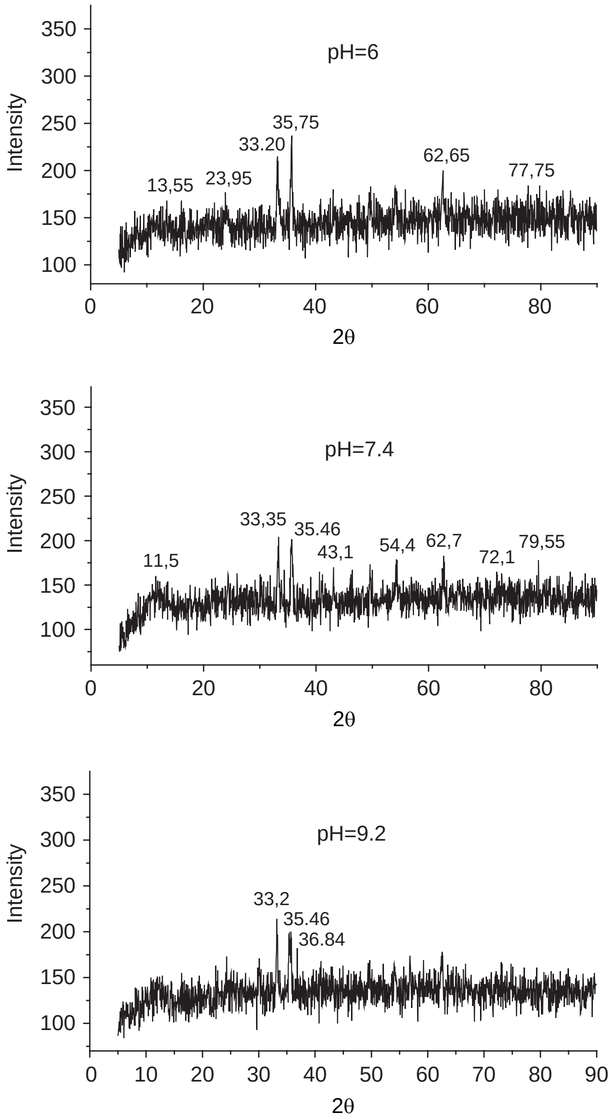

Fig. 7. X-ray diffraction patterns of samples prepared in the presence of copper and heated.

of only one solid heterogeneous phase by examining the solid formed from copper coprecipitation with iron hydroxide by diffraction X and thermogravimetry. Adamovich et al. suggested the formation of copper ferrite after heating [12]. However, the effect of pH has not been considered in these studies.

3.2. Desorption experiments

The copper desorbed by $MgCl_2$ does not exceed 6% (data not shown), suggesting a strong attraction with the surface of the hydroxide and the formation of inner sphere complex. In the presence of EDTA, the evolution of copper desorbed and iron dissolved at various pH (Fig. 8), suggests that copper is bound to the surface and incorporated within the oxide.

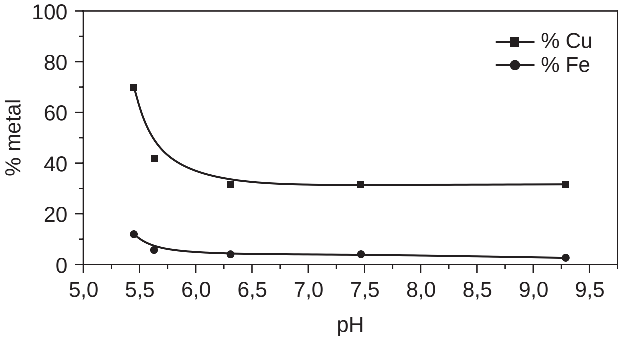

Fig. 8. Evolution of copper and iron released by EDTA.

4. Conclusion

The coprecipitation of copper ions with hydrous iron oxide is related to pH. It occurs by different mechanisms. X-ray diffraction and thermal analyses suggest both adsorption on the surface, incorporation inside the hydroxide and surface precipitation. Macroscopic analyses show the formation of inner-sphere complex at the surface of the hydrous oxide.

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