

## Removal of Copper from Aqueous Solutions by Coprecipitation with Hydrated Iron Oxide

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The coprecipitation of Cu(II) ions with hydrated iron oxide in aqueous solution was studied using batch experiments by varying pH, iron and copper concentrations and [Cu(II)]/[Fe(III)] molar ratio and also in the presence of competing ions. Analytical methods for solids analysis were performed to characterize the interaction of copper with the surface of the hydrous oxide. The uptake of Cu(II) showed typical cationic-type behaviour. The effect of the molar ratio was shown to depend on the copper concentration at high concentrations anomalous behaviour was observed. In the presence of Pb(II) and Zn(II), the Cu(II) removal was slightly decreased, whereas, it was enhanced in the presence of  $\text{SO}_4^{2-}$ .

**Key Words:** Copper, Coprecipitation, X-ray diffraction, Hydrated iron oxide.

### INTRODUCTION

Heavy metals are considered as dangerous pollutants in surface water and ground water. Industrially wastewater is a major source of ecosystem contamination by heavy metals. The interactions of metals with surfaces at the solid-water interface are of great importance, they can alter their chemical reactivity, mobility and bioavailability in natural systems.

Among the inorganic colloids known as major sinks for metals species in aquatic systems, iron oxyhydroxides with their chemical nature and high specific surface area play an important role. Coprecipitation of metals with iron oxides could limit their (bio)availability by removing significant quantities of them from water. This process could then be employed for the treatment of industrial and municipal wastewater containing heavy metals.

Copper, occurs naturally in soils, sediments and waters<sup>2</sup>. 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<sup>1</sup>.

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The majority of studies on copper sorption available in the literature, have been carried out on aged iron oxides with single-metal solutions and low concentrations, but less consideration has been given to coprecipitation. However, in aquatic system the presence of multiple competing ions is more frequent than the existence of only one contaminant and high metal concentrations can occur in several industrial wastewater and in mining areas.

In general, the extent of metal uptake by colloidal particles is strongly influenced by several factors *i.e.*, suspension pH, its initial concentration, composition of the solution and the amount of mineral substrate.

This work focuses on the uptake of copper by coprecipitation with amorphous hydrated iron oxide with variation of pH at high and low concentrations and in the presence of competitive ions.

## EXPERIMENTAL

All solutions were prepared from certified reagent grade chemicals and were used without further purification. All experimental vessels and storage containers were Pyrex glass. Iron stock solution as prepared by dissolving ferric chloride into 0.1 M HCl, which was sufficiently acidic to prevent Fe(III) hydrolysis. Copper nitrate was used as the source of divalent copper. A  $10^{-2}$  M copper stock solution was prepared and the other working solutions were prepared by diluting the stock solution with distilled water.

Coprecipitation experiments involved the formation of hydrous oxide colloid in the presence of  $\text{Cu}^{2+}$  ions.  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  solutions were initially combined in a ratio 1/1 adjusted to the desired pH with NaOH (1 N) solution. pH measurements were calibrated to 0.01 pH units using radiometer analytical buffer solutions. In competition experiments, the competing metallic cations were used as their nitrates, for the effect of sulfate ions, two types of salts were used sodium sulfate and copper sulfate. The standard copper solutions for calibration were prepared by diluting commercial standard solution  $1,000 \text{ g L}^{-1}$ .

**Copper coprecipitation:** All experiments were conducted in batch in 100 mL glass beakers. The risk of contamination by silicon was not a problem since the hydrous oxide was formed at low temperature. Hydrous iron oxide colloids were prepared by raising the pH of an aliquot of 50 mL solution mixer to the target pH under atmospheric conditions, to simulate natural conditions. A slow mixing speed using a magnetic stirrer operated at 60 rpm, was employed to facilitate the formation of stable flocks. The suspension formed was then agitated for 1 h; the final pH was measured and the suspension was centrifuged at 2000 rpm for 15 min.

Competing among copper and other ions usually present in some water samples, was studied by introducing copper ions and each competing ion solution simultaneously, by maintaining constant the concentration of copper ( $5 \times 10^{-5}$  M) and varying the concentration of the other ion.

The final pH values were used for the data evaluation. It was necessary to account for changes in volume from addition of standardized NaOH in certain experiments.

**X-Ray and SEM analysis:** Solid samples obtained in the absence and in the presence of copper ions were filtered and air-dried. X-ray powder diffraction studies were performed on a Siemens D8 diffractometer using Cu-K $\alpha$ 1 radiation and the spectra were recorded from 5 to 80° 2 $\theta$  with a scanning speed of 0.02° 2 $\theta$  step size. Particles morphology and the composition of the precipitates were examined with LEICA STEREO SCAN 440 Scanning Electron Microscope (SEM) equipped with an analyses system EDAX KEVEX SIGMA.

## RESULTS AND DISCUSSION

### Effect of pH and ions concentrations

Copper coprecipitation with hydrous iron oxide can be controlled through two specific properties; namely the surface chemistry of the hydrous iron oxide and the physicochemical characteristics of copper in solution. The pH is an important factor in controlling this coprecipitation, since it affects the charge of the oxide surface and the speciation of the metal.

As shown in Fig. 1, the importance of the presence of Fe(III) ions at acidic pH is expected, no removal of copper ions for high concentration is observed at pH below 4.5 (probably by precipitation as hydrous copper oxide) in the absence of iron ions. For all removal edges, the percentage of copper removal increases with increasing equilibrium pH, showing typical cationic-type adsorption behaviour<sup>3,4</sup>. As it can be observed, Cu(II) adsorbs over a narrow pH range like most metals, which is called the pH-edge<sup>5</sup>. The much lower amount of Cu(II) removed at low pH, reflects a competition with protons<sup>6</sup> and the positive zeta potential of the hydrous iron oxide. In other studies on the removal of copper by adsorption on several surfaces, various authors have reported different results in relation with copper concentrations and the amount of the adsorbant undertaken in several study; but the majority of them, consider the pH range (5-6) as the interval of maximum adsorption where the copper predominant species<sup>7</sup> are Cu<sup>2+</sup> and CuOH<sup>+</sup>.

For the same molar ratio and with different concentrations of iron and copper (Fig. 2), the copper removal shifts to higher pH when copper and iron concentrations are lowered. The effect of the variation of [Cu<sup>2+</sup>]/[Fe<sup>3+</sup>]

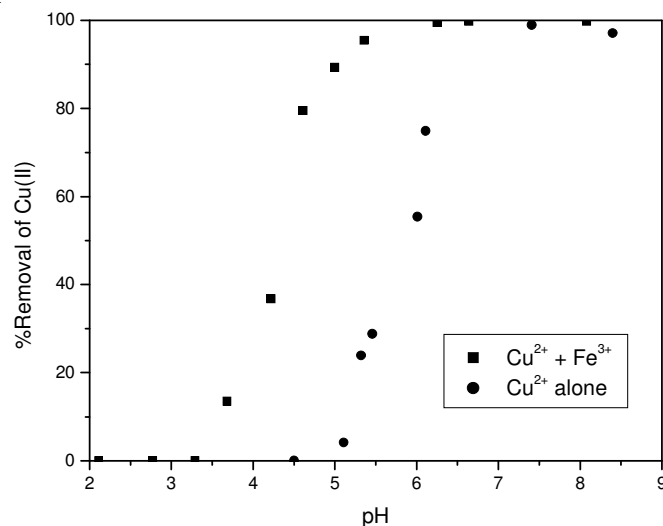


Fig. 1. Coprecipitation of  $5 \times 10^{-3}$  M Cu(II) with amorphous iron(III) oxide compared to precipitation of  $5 \times 10^{-3}$  M Cu(II) alone with variation of pH

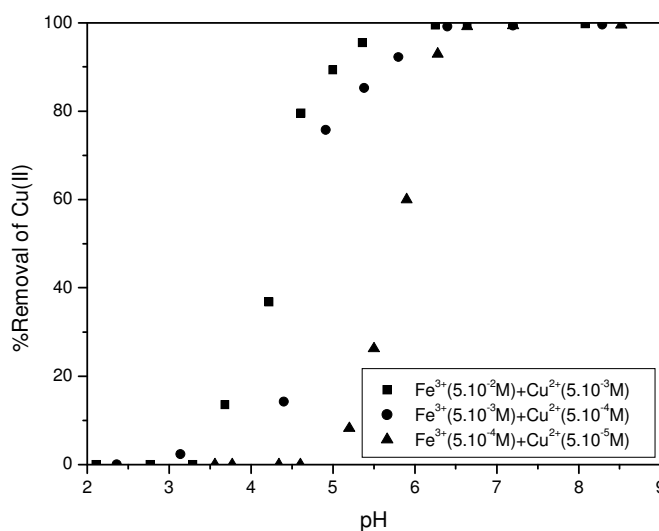


Fig. 2. Coprecipitation of Cu(II) at various concentrations of copper and iron

ratio with the same iron concentration on the uptake of copper by hydrous iron oxide depends on copper concentration. As shown in Fig. 3a, there is no significant changes in the position of the removal edges as  $[\text{Cu}^{2+}]/[\text{Fe}^{3+}]$  molar ratio decreases from 1 to 0.1 for low concentrations. For high concentrations, a variation of the pH edge position is observed, so that, at a given pH, the percent of copper removal decreases as the  $[\text{Cu}^{2+}]/[\text{Fe}^{3+}]$

ratio decreases (Fig. 3b). This anomalous behaviour has already been observed in previous studies<sup>8,9</sup> and has been explained by the competition of  $\text{Cu}(\text{OH})^+$  and  $\text{Cu}_2(\text{OH})_2^{2+}$  species for surface sites. It has been noted that at low Cu(II) concentration the proportion of dimeric species is extremely low but at higher concentrations, its proportion is more important increasing the sorption<sup>9</sup>. In the absence of any complexing species, the speciation of dissolved copper only depends on the pH solution and the dissolved copper concentration, leading therefore to a different distribution of the copper-hydroxyl complexes<sup>10</sup>. The distributions of hydrolyzed copper species as calculated by Chess 2.5 program<sup>11</sup> (Fig. 4), show that for high copper concentration,  $\text{Cu}^{2+}$  is the major species up to pH 5 beyond what the precipitation occurs. For low concentration,  $\text{Cu}(\text{OH})^+$  appears at pH 5, the beginning of precipitation is observed at pH 6.5.

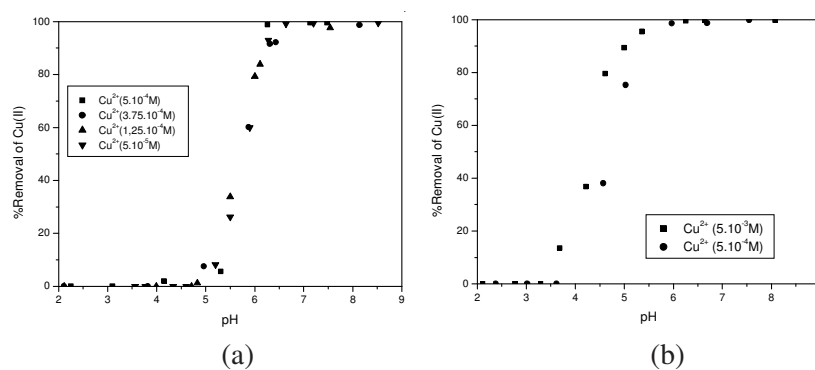


Fig. 3. Coprecipitation of Cu(II) at various molar ratios.  
(a)  $\text{Fe}^{3+}$  ( $5 \times 10^{-4}$  M) (b)  $\text{Fe}^{3+}$  ( $5 \times 10^{-2}$  M)

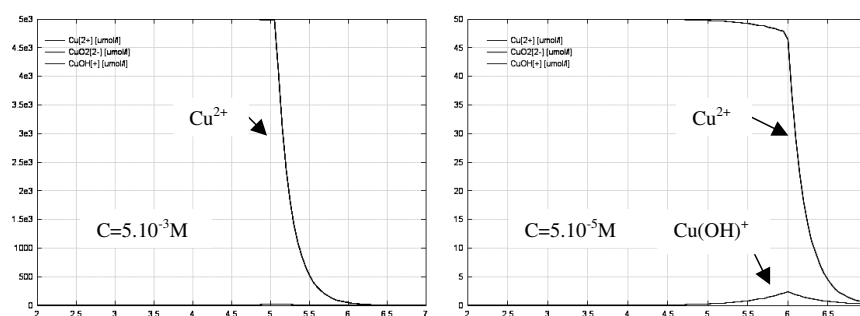


Fig. 4. Distribution of Cu(II) species as a function of pH as calculated by Chess 2.5<sup>11</sup>

### Effect of competitive ions

As is shown in Fig. 5, for equal concentrations of metallic cations, lead seems to reduce the removal of copper ions in the pH range (5-6). At higher pH values, it is difficult to distinguish this effect since the macroscopic removal data for single metal and competitive metals sorption experiments merge, due to precipitation of copper hydroxide phase. An increase of lead influence is observed when its concentration increases, showing competition between the two metals for surfaces sites. Different results are cited in previous studies for competitive effect of lead on copper sorption. No significant competitive effects in adsorption experiments between Cu and Pb were observed using amorphous iron oxide<sup>4</sup>. Elsewhere, the competitive effects between Cu and Pb were only observed in a narrow pH range between pH 4.5 and 6.3 in a sorption study on hematite<sup>12</sup>.

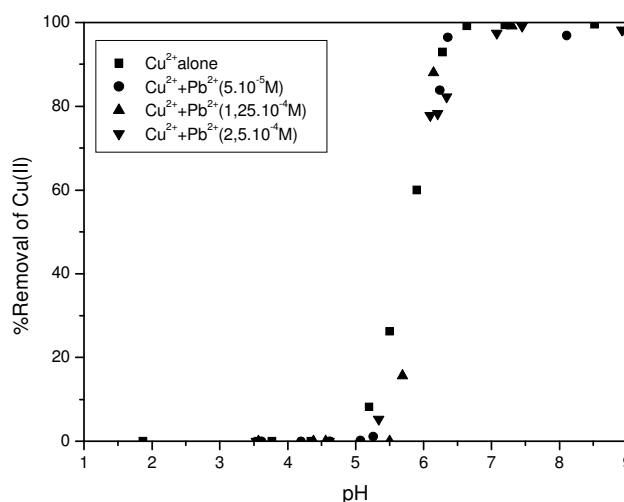


Fig. 5. Coprecipitation of  $5 \times 10^{-5}$  M Cu(II) with hydrous iron(III) oxide in the presence of Pb(II)

The effect of the presence of zinc ions is more important in reducing the uptake of copper ions. A shift of pH edge to higher pH is observed at  $\text{pH} < 6$ . At pH above 6 and in the opposition to lead, the presence of zinc decreases copper removal; this effect is more pronounced with the increase in zinc concentration (Fig. 6). As it is known that zinc uptake occurs at higher pH, this effect can be in relation to copper speciation in such system. The influence of the presence of a competing metal on the uptake of another one can be occur at the sorbant surface or in the solution; in a way that the distribution of the species in multiple metal systems can may be different from that when the metal is alone<sup>5</sup>.

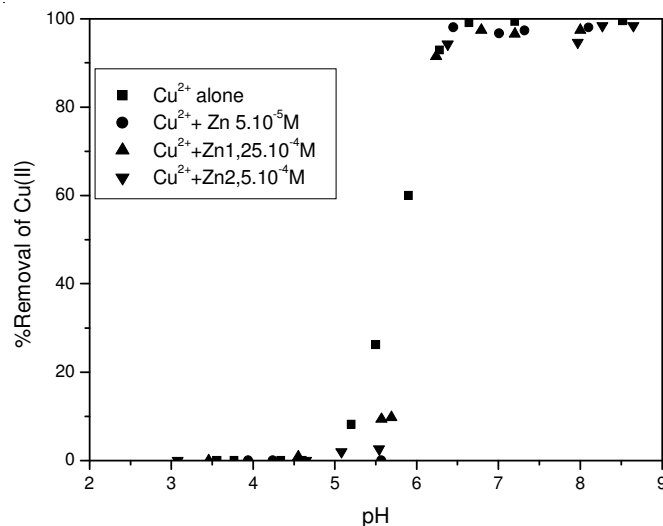


Fig. 6. Coprecipitation of  $5 \times 10^{-5}$  M Cu(II) with hydrous iron(III) oxide in the presence of Zn(II)

The results obtained for the competition of sulphates ions on the removal of copper are summarized in Fig. 7. They show that the interaction of copper with the anion enhances the uptake of the metal at the pH range 4.5-6 whether the anion is used as an associated anion or as sodium sulphate. The removal of copper ions begins at more acidic pH and its maximum is reached at lower pH; so that, the removal edge shifts to lower

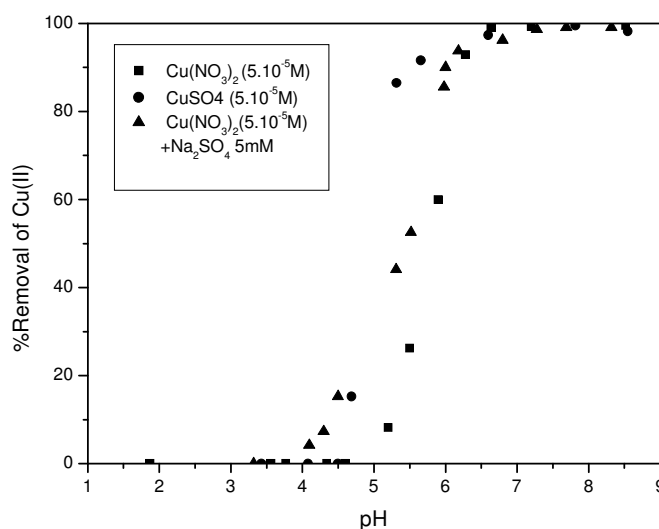


Fig. 7. Coprecipitation of  $5 \times 10^{-5}$  M Cu(II) with hydrous iron(III) oxide with  $\text{SO}_4^{2-}$

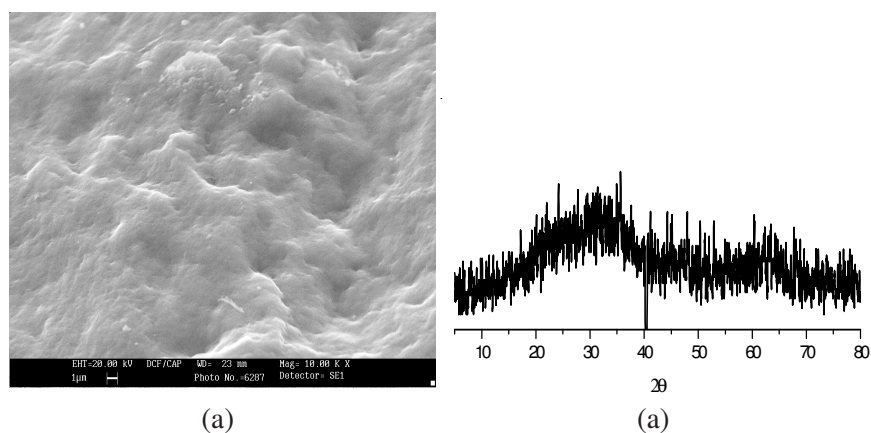
pH. Since the sulphate ions strongly adsorb at low pH on the surface of the hydrous iron oxide freshly prepared<sup>13</sup>, the ligand may bind to the surface at low pH, consequently, the positive charge of the hydrous iron surface decreases, supporting the uptake of positively charged copper species. Such enhancement has been observed in many cases of metallic ions sorption and has been the subject of different discussions<sup>14,15</sup>. The formation of a ternary complex has been proposed for the sorption on goethite in the presence of sulphate ions for copper<sup>16</sup>, lead<sup>17</sup> and cadmium ions<sup>18</sup>. On the other hand, spectroscopic studies have suggested that both electrostatic effects and ternary complex formation, may cause  $\text{SO}_4^{2-}$  ions to enhance trace metal adsorption<sup>19,20</sup>.

The effect of the presence of sulphate ions will tend to limit the mobility of copper(II) ions in polluted areas, which can be then retarded over a wide pH range, especially in mine drainage system where  $\text{Fe}^{3+}$  and  $\text{SO}_4^{2-}$  concentrations are typically high.

### Solid analyses

The amorphous character of the solids prepared in the absence and in the presence of copper, is observed from the surface morphology expressed through SEM micrographs of vacuum-dried solids (Fig. 8). The presence of copper in precipitates obtained is confirmed by EDAX spectrums presented in Fig. 9, where it can be seen that the amount of copper is lower at pH 4.4. The presence of chloride ions at this pH, shows the positive charge of the surface encouraging electrostatic bounds of anions.

As it can be seen from diffraction patterns of the solid samples obtained at pH 6 (Fig. 8b), a certain change is detected by comparison of original and treated sample with copper ions spectra. The band observed at around  $15^\circ 2\theta$  can be attributed to the formation of hydrous copper oxide ( $\text{Cu}(\text{OH})_2(\text{s})$ ), considered as the solubility-limiting solid phase in the pH 3-12 range<sup>21</sup>.





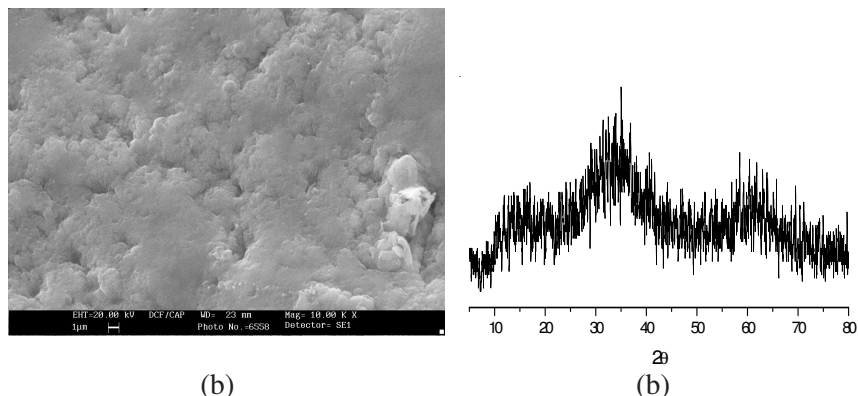


Fig. 8. SEM and XRD pattern of the hydrous iron(III) oxide (a) in the absence of copper ions (b) in the presence of copper ions

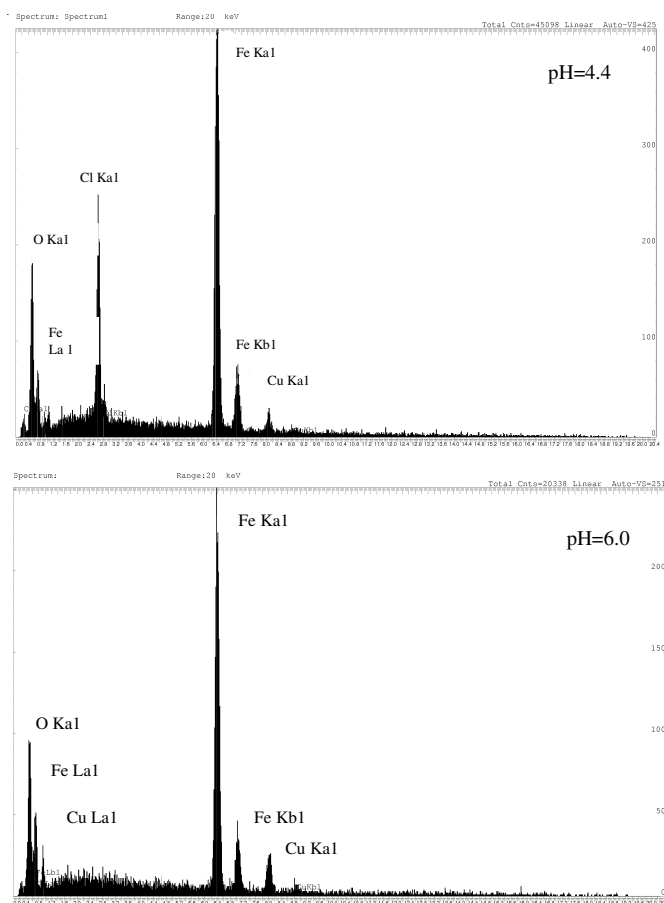


Fig. 9. Energy dispersive X-ray spectra of solids obtained in the presence of copper

## Conclusion

Copper removal by coprecipitation with hydrous iron oxide is pH dependent. It increases with the increase in pH in a narrow range. The significant percentages of removal observed under various conditions shows the effectiveness of the process in waste water treatment. The interaction of copper with sulphate ions induces a significant increase of its uptake from aqueous solution at acidic pH. Consequently, the mobility of Cu(II) ions is reduced in polluted sites where the concentrations of Fe(III) and  $\text{SO}_4^{2-}$  are significant

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