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Chromium Removal from Aqueous Solutions by Co-precipitation with Al (III), Fe (III) and Al (III) / Fe (III) Effect of pH and Competitive Ions.

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ABSTRACT

The coprecipitation of Cr(III) with hydrous iron, hydrous aluminium and a mixer of the two was studied in aqueous solution using batch experiments with varying time, pH, iron and aluminium concentrations. The effect of the presence of foreign ions was evaluated as a function of pH. The obtained results show that chromium removal increases with the increase in pH. It is more important and more rapid in the Fe(III) system than in Al(III) or Al(III)/Fe(III) systems. In the presence of sulphate ions, the chromium removal is enhanced in acidic pH range in the three cases.

Keywords: chromium, coprecipitation, hydrous iron oxide, hydrous aluminium oxide, competitive ions

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INTRODUCTION

Heavy metals are considered as dangerous pollutants in aquatic environment. Industrial waste water is a major source of ecosystem contamination by heavy metals. They are discharged by various industries such as electroplating, storage batteries and mining [1]. As common contaminant in industrial wastewaters; chromium and its compounds are widely used in many industrial fields such as plating, dyeing, tanning, wood preserving and refractory technologies [2, 3]. Contamination of aquatic environment caused by toxic elements such as chromium is receiving increasing attention due to its hazardous risk [4]. Many techniques have been proposed for the removal of chromium from aqueous solutions; they include solvent extraction, ion exchange, co-precipitation, membrane processes and sorption. The majority of the studies available in the literature on chromium sorption have been carried out on aged oxides with single-metal solutions [5, 6]. Less consideration has been given to coprecipitation and there is no information available on the use of Fe(III) and/or Al(III) salts for chromium removal as a function of pH and in the presence of other ions. Since ferric chloride and alum are widely used for the treatment of industrial and municipal wastewater, the present work focuses on the uptake of chromium by coprecipitation with amorphous hydrous iron, hydrous aluminum and a mixture of the two in the absence and in the presence of competitive ions

MATERIAL AND METHODS

Iron, aluminium and chromium solutions were prepared by dissolving nitrate salts. In coprecipitation experiments, solutions were initially combined in a ratio 1/1 and adjusted to the desired pH with NaOH (1N) solution. In competition experiments, the metallic cations were used as their nitrates salts and sulfate as sodium salt. The foreign ions were added to chromium solution prior to addition of iron or/and aluminum ions. In all cases, the final pH was measured using pH M210 pH-meter equipped with a combined glass electrode. After centrifugation, chromium analyses was undertaken immediately in the recuperated solutions after conversion to Cr(VI) by oxidation using H₂O₂ in alkaline medium at elevated temperature. The formed Cr(VI) was determined by the colorimetric method using UV-Visible SCHIMADZU 1650 PC spectrophotometer.

RESULTS AND DISCUSSION

Effect of pH

The pH is an important factor in controlling the coprecipitation. It affects the charge of the oxide surface and the speciation of the metal. The results of the chromium removal by Al(III), Fe(III) and Al(III)/Fe(III) are shown in Figures 1, 2 and 3 respectively. For all removal edges, the percentage of chromium removal increases with increasing equilibrium pH, showing typical cationic adsorption behaviour [7]. The much lower amount of Cr(III) removed at low pH reflects on one hand a competition with protons and on the other hand the positive zeta potential of the hydrous oxides surfaces. At high pH, the chromium uptake is attributed to chromium hydroxide precipitation.

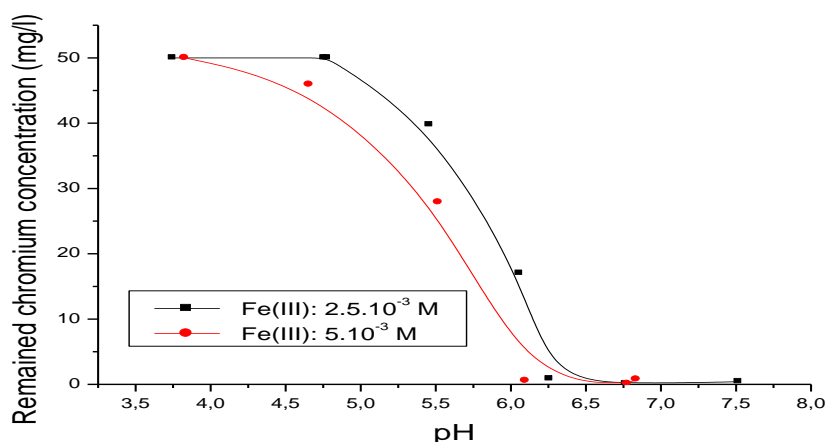


Figure 1: Chromium removal by Fe(III) - Effect of pH (Cr(III): 50 mg/l, t:60min)

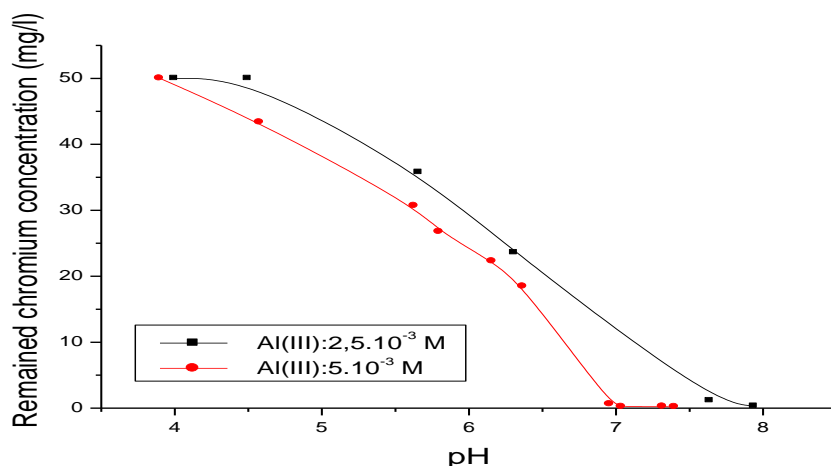


Figure 2: Chromium removal by Al(III)- Effect of pH (Cr(III): 50 mg/l, t:60min)

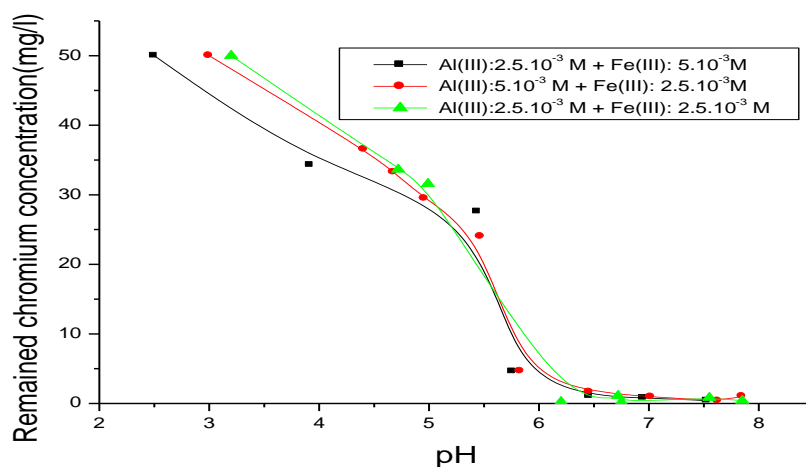


Figure 3. Chromium Removal by Fe(III)/Al(III) - Effect of pH (Fe(III)/Al(III):1; Cr(III): 50mg/L; t:60min)

The results show that Fe(III) is more effective in chromium removal than Al(III) and Al(III)/Fe(III). The PZC values of Fe hydroxides and Fe-Al hydroxides (Al(III)/Fe(III):1) varied between 7.0-8.5 and 8.7-9.1 respectively [8] implying that the solid formed in the combined system is more positively charged. In the present work, the chromium removal shifts to higher pH when the concentration of iron or aluminium is lowered in single systems (Figure 1, 2). In combined systems, it shifts to lower pH when iron concentration is increased; no effect is observed when aluminium concentration is increased (Figure 3). Consequently, the observation that Fe(III) system yields better rate removal implies the intervention of electrostatic interaction. In the pH range greater than 5.5, all the used systems have the same chromium removal capacity.

Kinetics study

The evolution of chromium removal by coprecipitation with iron or/and aluminum with time at pH around 5 and 6 is illustrated in Figures 5 and 6. As it has been expected previously, the chromium removal is more important in the presence of Fe(III), showing the significant affinity for hydrous iron oxide in comparison with the aluminum one. The chromium coprecipitation is more rapid at pH 6 than at pH 5 for the three systems. According to the chromium speciation diagram [2], in the pH range 4-6, the dominant chromium species are CrOH^{2+} , $\text{Cr}_3\text{OH}_4^{5+}$ and $\text{Cr}(\text{OH})_2^+$. The increase in chromium removal rate at pH 6 in regard at pH 5 can be in a relation to the decrease of CrOH^{2+} implying more affinity of the formed hydrous oxides for the two other chromium species.

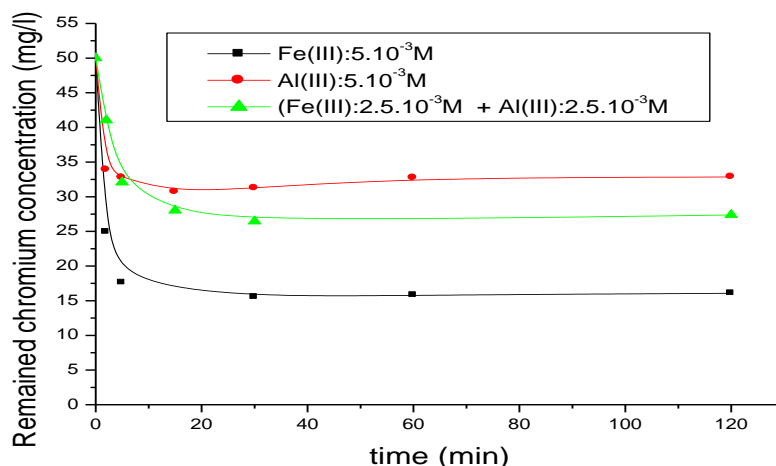


Figure 4: Chromium removal – Effect of time (Cr(III): 50 mg/l, t:60min, pH:5)

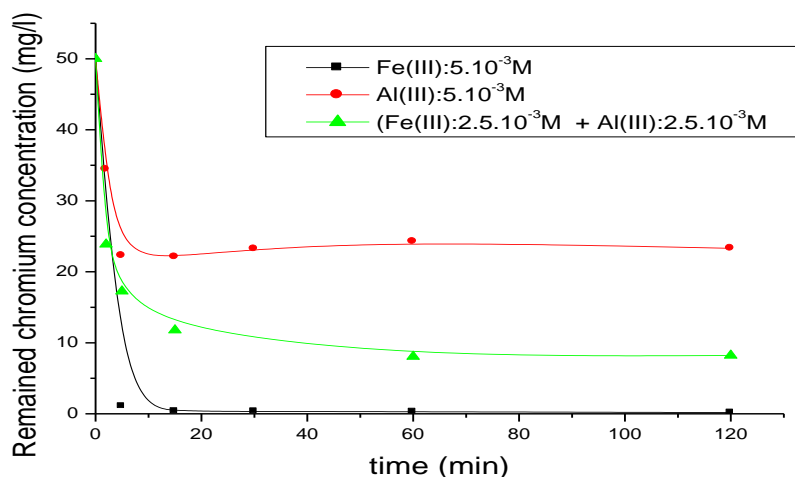


Figure 5: Chromium removal – Effect of time (Cr(III): 50 mg/l, t:60min, pH:6)

In order to characterize the chromium removal kinetics, the linear equation of the first order model ($\ln C_0/C = f(t)$) is applied to the experimental data obtained at pH 5. The calculated kinetics constants in each case are presented in Table 1. They reveal that Fe(III) ions are more rapid in removing chromium ions. The coprecipitation rate follows the order $\text{Al(III)} < \text{Al(III)/Fe(III)} < \text{Fe(III)}$. In the presence of Fe(III), the removal is eight times and four times more rapid than in the presence of Al(III) and Al(III)Fe(III) respectively.

Table 1: Rate constants of chromium removal (pH 5)

System	Rate constant (k) (min^{-1})
Fe(III)	0.0816
Al(III)	0.0096
Fe(III) + Al(III)	0.0181

Effect of foreign ions

As is shown in Figure 6, chromium removal by coprecipitation with iron or aluminium ions in acidic pH is enhanced in the presence of copper and zinc. The influence of the presence of a competing metal on the uptake of another one can occur at the sorbent surface or in the solution in a way that the distribution of the species in multiple metal systems may be different from that when the metal is alone [9]. At higher pH

values, it is difficult to distinguish this effect since the macroscopic removal data for single metal and combined with the competitive metals merge, due to precipitation of the hydroxide phase.

In the presence of sulphate ions (Figure 7), the chromium removal edge shifts to lower pH. The chromium uptake is significantly enhanced in the pH range 4 – 6 especially in the presence of Fe (III). Sulphate ions strongly adsorb at low pH on the surface of the hydrous iron oxide [10]. This induces the decrease of the positive charge of the hydrous iron surface supporting the uptake of positively charged chromium species. In addition, spectroscopic studies have suggested that both electrostatic effects and ternary complex formation, may cause SO_4^{2-} ions to enhance metal adsorption [11].

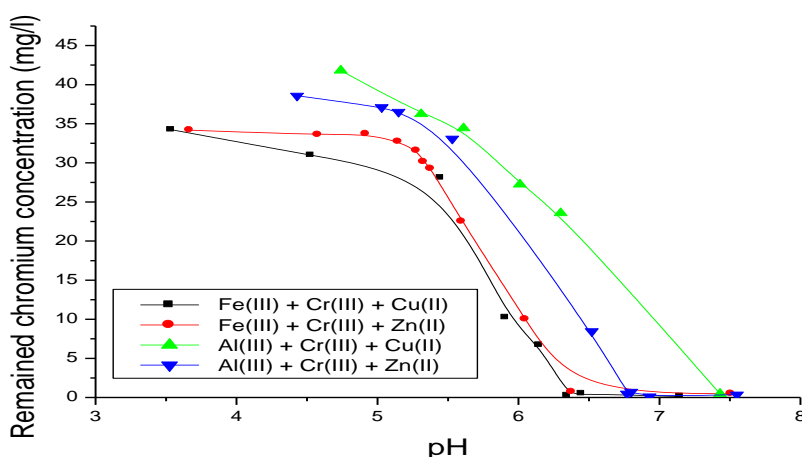


Figure 6: Chromium removal in the presence of competitive cations (Fe(III): $2.5 \cdot 10^{-3}$ M, Al(III): $2.5 \cdot 10^{-3}$ M, Cr(III): 50 mg/l, Cu(II): 25mg/l, Zn(II): 25mg/l, t:60min)

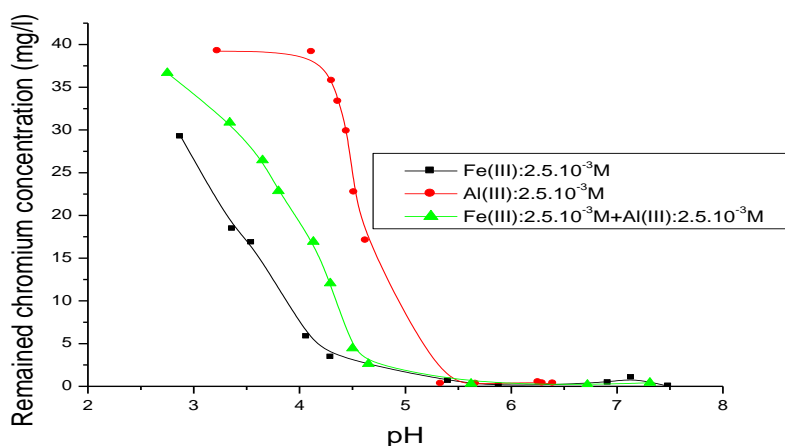


Figure 7: Chromium removal in the presence of sulphate (Cr(III):50mg/l, SO_4^{2-} mg/l:96; t:60min)

CONCLUSION

The results of the present study show that the chromium removal by coprecipitation with Fe(III) or/and Al(III) is pH dependent. It increases with the increase in pH in a narrow range. Hydrous iron oxide gives more efficiency in chromium uptake than hydrous aluminium oxide or a combined of the two. at all systems, chromium coprecipitation shifts to lower pH in the presence of sulphate ions.

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