

Simultaneous Removal of Heavy Metals from Wastewaters

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Abstract: Heavy metals have become a major concern in last decades. They are frequently detected in the aquatic environments due to anthropogenic activities and industrial and urban wastes discharge into water bodies. Although some of these metals are necessary, at low doses, for growth of biological life, the presence of heavy metals in the environment, in large concentrations, can be detrimental to a variety of living species, including man. The aim of this study was to explore the possibility of simultaneous removing Cr(III), Fe(II) and Fe(III) from wastewaters by precipitation with NaOH. The effects of NaOH dose, mixing time, mixing intensity, settling time and solution temperature were investigated. The optimum conditions of the precipitation process, which resulted from this study, are: NaOH dose: 500 mg/L, mixing time: 5 minutes, mixing intensity: 50 rpm, settling time: 30 minutes, solution temperature: 14 °C.

Keywords: wastewater treatment; chromium; iron; NaOH; precipitation.

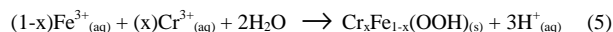
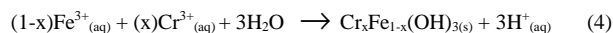
1. Introduction

Toxic heavy metals may cause serious threat to humans, plants, animals and microorganisms. Metals environmental contaminants are particularly problematic because, unlike most organic contaminants, they do not undergo degradation [1]. Since heavy metals have a wide range of industrial use, large quantities are discharged into the environment in places where these industries are located [2]. Chromium can exist in several oxidation states, but only the +3 and +6 are stable under most natural environments [3]. The two environmentally stable oxidation states, Cr(III) and Cr(VI), exhibit very different toxicity, chemical behavior and mobility [4].

Chromium(VI) is known to be toxic to humans, animals, plants and microorganisms [5-11]. Because of its significant mobility in the subsurface environment, the potential risk of natural waters contamination is high [12]. In contrast, Cr(III) toxicity is 500 to 1000 times less to a living cell than Cr(VI) [7], is relatively insoluble in aqueous systems [13], and readily precipitates as simple or mixed Fe(III)-Cr(III) (oxy)hydroxides [14,15] under alkaline or even slightly acidic conditions. In trace amounts, Cr(III) is an essential micronutrient for the human metabolism [16]. However, Cr(III) may also have toxic effects [17,18].

Iron can be found in natural aqueous environments in two main oxidation states: Fe(II) and Fe(III), depending on the pH and the redox potential. Fe(III) predominates in oxygenated surface waters [19,20], while Fe(II) predominates in anoxic groundwaters [20,21]. Iron is a nutrient with limited bioavailability, essential for the growth, development, and long-term survival of most organisms [22]. However, the presence of iron in the environment, in large concentrations, can be detrimental to a variety of living species. High tissue iron concentrations have been associated with the development and progression of several pathological conditions, including certain cancers, liver and heart disease, diabetes, hormonal

abnormalities, and immune system dysfunctions [23]. Although iron does not have carcinogenic properties, when present in excess, iron poses a threat to cells and tissues [24]. Iron is of great biogeochemical significance in natural aquatic systems, especially in pelagic systems where very low iron concentrations can limit ecosystem productivity [25]. In systems fed by iron-rich groundwater, the abundance of some plant species could be limited due to iron toxicity [26]. Thus, removal of chromium and iron is an essential pollution abatement process that should be applied to all industrial effluents that contain these contaminants, prior to discharge them into the natural aquatic environments. At present, the most commonly used technology for the treatment of wastewaters polluted with cationic heavy metals is by chemical precipitation [27]. Cr(III), Fe(II) and Fe(III) may be removed from aqueous solutions, under neutral or alkaline conditions, through the precipitation of simple hydroxides [13,28] or mixed Fe(III)-Cr(III) (oxy)hydroxides [14,15], according to:



where x vary from 0 to 1.

Therefore, the aim of this work was to study the simultaneous removal of Cr(III), Fe(II) and Fe(III) from aqueous solutions by precipitation with NaOH. The effects of NaOH dose, mixing time, mixing intensity, settling time, and solution temperature were investigated.

2. Experimental

Synthetic wastewater was prepared by dissolving known amounts of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and FeCl_3 in distilled deionized water, in order to yield the

following concentrations: 50 mg/L Cr(III), 75 mg/L Fe(II), and 50 mg/L Fe(III). Concentrated H_2SO_4 was used for adjusting pH of the synthetic wastewater to 2.50. The composition of the synthetic wastewater was selected because it's within the range of relevant concentrations for real effluents resulted from the continuous reduction of Cr(VI) with zerovalent iron [29]. As precipitant reagent was used NaOH solution 100 g/L. The initial composition of the wastewater and the concentration of precipitant reagent were held constant throughout the study. All chemicals used were of AR grade. The analysis of trivalent chromium in solution was carried out by the diphenylcarbazide colorimetric method, after complete oxidation to hexavalent chromium with potassium permanganate, followed by analysis as hexavalent chromium [30]. The purple color was fully developed after 15 min and the sample solutions were transferred to a Jasco V 530 spectrophotometer; the absorbance of the color was measured at 540 nm in a 1 cm long glass cell [30]. Fe(II) concentrations in the samples were determined by the 1,10-phenanthroline method [30]; the absorbance of the color was measured at 510 nm using the same spectrophotometer. Total Fe was determined by reduction of any Fe(III) to Fe(II) with hydroxylamine hydrochloride and subsequent analysis as Fe(II) [30]. Trivalent iron was determined from the difference between total and bivalent iron. The pH of solutions was measured using an Inolab pH-meter. The removal efficiency of Cr(III), Fe(II), and Fe(III) was calculated and the optimum conditions of the precipitation were established. Jar tests were conducted to investigate the effects of NaOH dose, mixing time, mixing intensity, settling time, and solution temperature on the precipitation process. The required amount of precipitant was added in Berzelius flasks containing 200 mL of the synthetic wastewater and the flask contents were mixed. After the settling time, the supernatant was filtered through filter paper and analyzed for final Cr(III), Fe(II), Fe(III), Fe(total), and pH.

3. Results and Discussion

3.1. Effect of NaOH dose

Jar tests using varying amounts of NaOH were conducted, at 24° C, to determine the optimum dosage. The dosages used were 50, 100, 150, 200, 250, 300, 350, 400, 450, 500, 550, and 600 mg NaOH/L. The evolution of Cr(III), Fe(II), Fe(III) and Fe(total) removal efficiency, and of final solution pH vs. NaOH dose is presented in figs. 1 and 2. By comparing these results with the maximum allowed Cr(total), Fe(total) and pH values in waters discharged into natural aquatic environments (Table 1), it results that the optimum NaOH dose is 500 mg/L.

TABLE 1. Maximum allowed Cr(total), Fe(total) and pH in waters discharged into natural aquatic environments, according to NTPA001/2002 [31]

Parameter	Cr(total) mg/L	Fe(total) mg/L	pH
Maximum allowed value	1	5	6,5 - 8,5

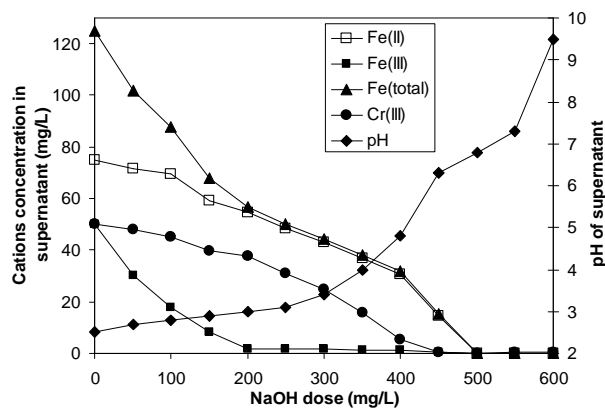


Figure 1. Cations concentration and final pH of supernatant vs. NaOH dose

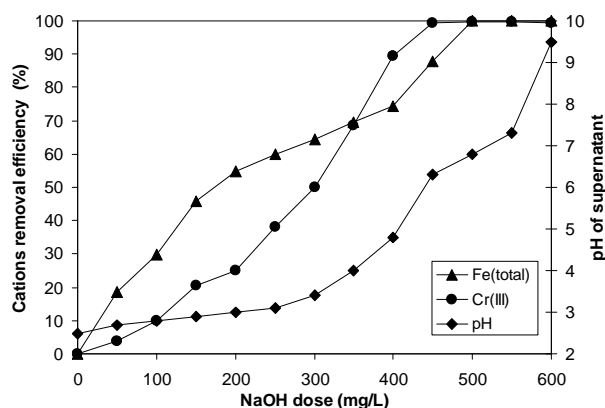


Figure 2. Cations removal efficiency and final pH of supernatant vs. NaOH dose

3.2. Effect of mixing time

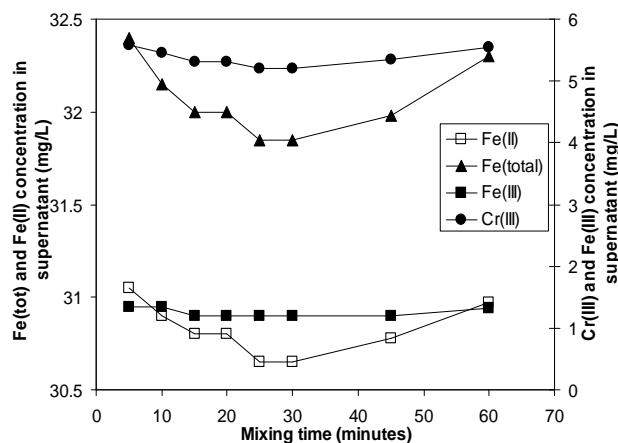


Figure 3. Cations concentration in supernatant vs. mixing time

To determine the optimum mixing time, jar tests were conducted, at 24° C, using mixing times ranging from 5 to 60 minutes. The evolution of Cr(III), Fe(II), Fe(III) and Fe(total) removal efficiency vs. mixing time is presented in figs. 3 and 4. The obtained results show that removal efficiency continuously increased with the increase of

mixing time up to 25 minutes; a further increase of mixing time over 25 minutes leads to a decrease of the removal efficiency. However, even the increase of removal efficiency due to increase of mixing time up to 25 minutes was very low, and, therefore, the optimum mixing time was chosen to be 5 minutes; all further experiments were performed at this mixing time value.

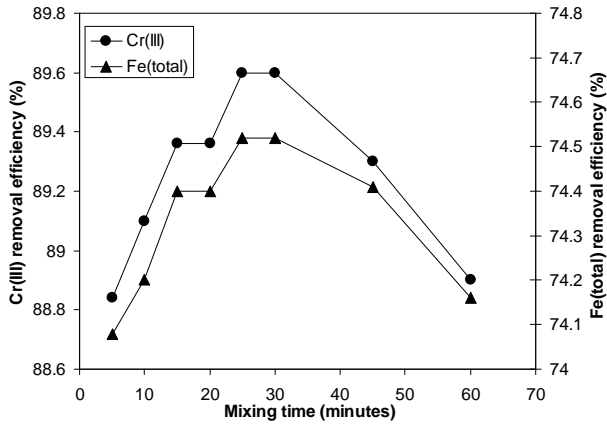


Figure 4. Cations removal efficiency vs. mixing time

3.3. Effect of mixing intensity

To assess the effect of mixing intensity, jar test experiments were conducted, at 24° C, at following mixing speed values: 50, 100, 200, 300, 400, 500, and 600 rpm. The evolution of Cr(III), Fe(II), Fe(III), and Fe(total) removal efficiency vs. mixing intensity is presented figs. 5 and 6. From the analysis of these figures it can be seen that the removal efficiency continuously decreased with the increase of mixing intensity. Therefore, the optimum mixing intensity was considered to be 50 rpm and all further experiments were performed at this mixing intensity value.

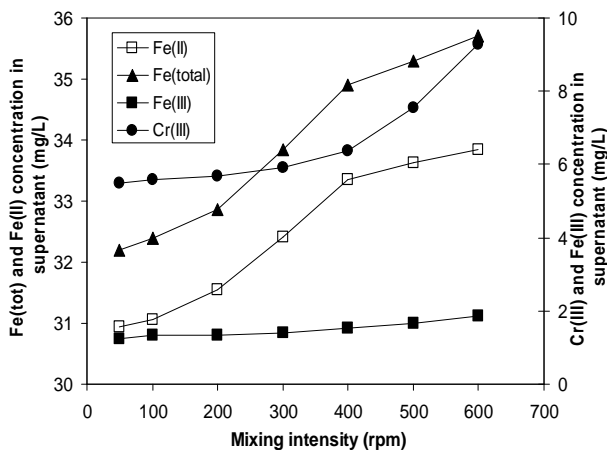


Figure 5. Cations concentration in supernatant vs. mixing intensity

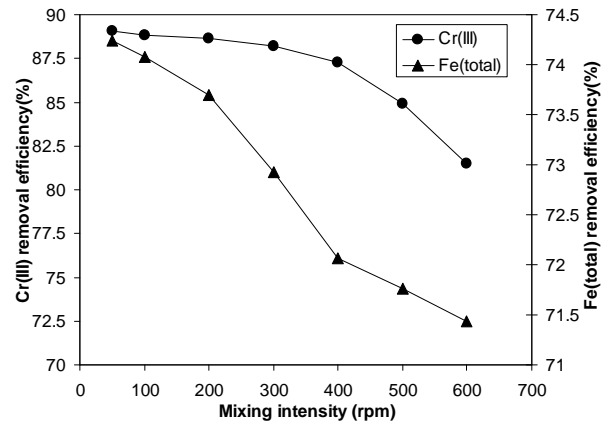


Figure 6. Cations removal efficiency vs. mixing intensity

3.4. Effect of settling time

To assess the effect of settling time, jar test experiments were conducted, at 24° C, at following settling time values: 5, 10, 20, 30, 45, 60, and 90 minutes. The evolution of Cr(III), Fe(II), Fe(III), and Fe(total) removal efficiency vs. settling time is presented figs. 7 and 8.

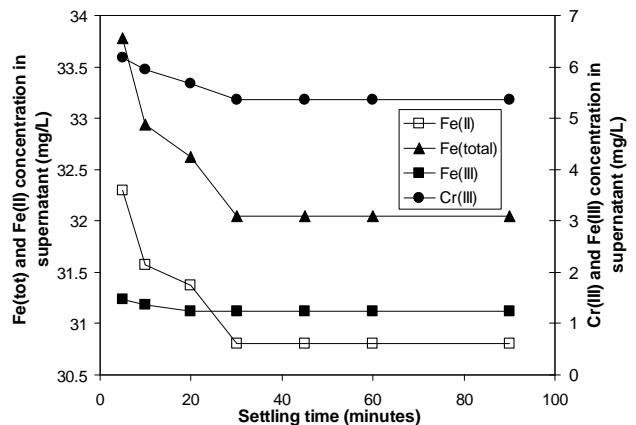


Figure 7. Cations concentration in supernatant vs. settling time

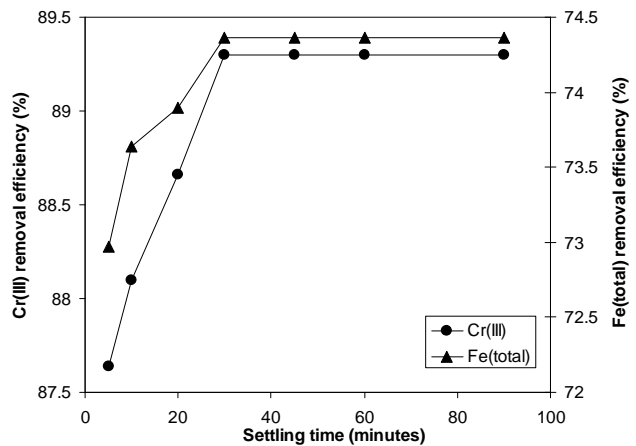


Figure 8. Cations removal efficiency vs. settling time

The obtained results show that removal efficiency continuously increased with the increase of settling time up to 30 minutes; a further increase of settling time over 30 minutes had no effect on the removal efficiency. Therefore, the optimum settling time was considered to be 30 minutes and all further experiments were performed at this settling time value.

3.5. Effect of solution temperature

The effect of temperature on the removal of Cr(III), Fe(II), and Fe(III) was examined by performing jar test experiments at following temperatures: 6, 15, 24, 33, and 44 °C. The evolution of Cr(III), Fe(II), Fe(III) and Fe(total) removal efficiency vs. the solution temperature is presented figs. 9 and 10. From these figures it can be seen that Fe(total) removal efficiency increased with the increase of temperature up to 24 °C and decreased afterwards when temperature was further increased over 24 °C; on the contrary, Cr(III) removal efficiency decreased with the increase of temperature up to 24 °C and increased afterwards when temperature was further increased over 24 °C. Therefore, optimum solution temperature was considered to be 14 °C, when Cr(III) and Fe(total) have similar removal efficiencies.

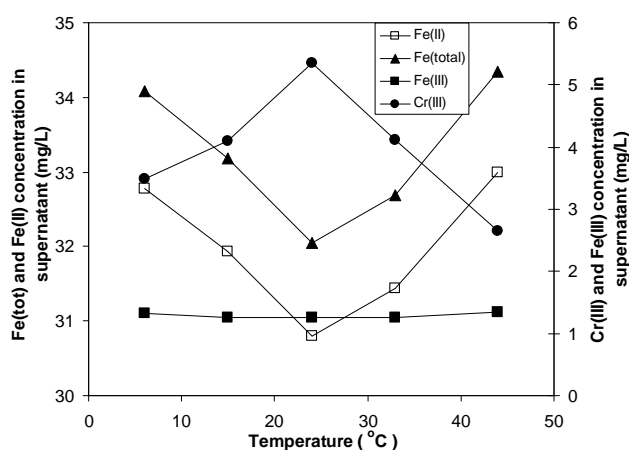


Figure 9. Cations concentration in supernatant vs. solution temperature

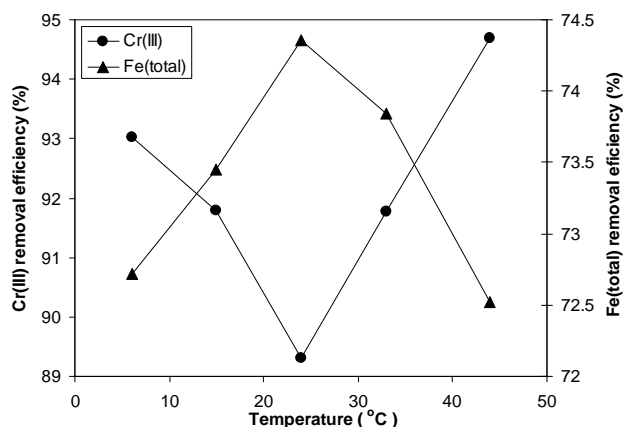


Figure 10. Cations removal efficiency vs. solution temperature

4. Conclusions

Trace quantities of heavy metals are nowadays constituents of most wastewaters. Although some of these metals, at low doses, are necessary for growth of biological life, their presence in the environment, in high concentrations, can be detrimental to a variety of living species, including man. The most commonly used technology for treatment of cationic heavy metals in wastewaters is chemical precipitation. The aim of this work was to study the simultaneous removal of Cr(III), Fe(II) and Fe(III) from aqueous solutions by precipitation with NaOH. The optimum conditions of the precipitation process, established with this study, are: NaOH dose: 500 mg/L, mixing time: 5 minutes, mixing intensity: 50 rpm, settling time: 30 minutes, solution temperature: 14 °C.

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