Treatment of Cr(VI) Polluted Wastewater with Scrap Iron. Part 2: Removal of Species Resulted from Cr(VI) Reduction

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Abstract: - Hexavalent chromium, a widespread industrial waste, is a strong toxic, mutagenic and carcinogenic agent. It is highly soluble and easily spreads in the environment. Therefore, it should be removed from wastewaters before their disposal to natural aquatic environments. One way of detoxifying waters polluted with Cr(VI) is by reduction of Cr(VI) to the less dangerous Cr(III), using chemical reducing agents. Scrap iron is a non-conventional Cr(VI) reducing agent that can replace commonly used reducing agents such as ferrous sulphate, sulphur dioxide and sodium sulphites. The effluent that results from the total reduction of Cr(VI) with scrap iron still contains Cr(III), Fe(II), and Fe(III) species, which must be removed from the aqueous solution in a final treatment step. The aim of this study was to explore the simultaneous removal of Cr(III), Fe(II) and Fe(III) from aqueous solutions by precipitation with Na₂CO₃. The effects of Na₂CO₃ 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: Na₂CO₃ dose: 1000 mg/L, mixing time: 5 minutes, mixing intensity: 50 rpm, settling time: 45 minutes, solution temperature: 33°C.

Key-Words: - wastewater treatment; scrap iron; heavy metals; Na₂CO₃; 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. Redox reactive metals, however, often do different degrees of toxicity, depending on the specific metal oxidation state [1]. Chromium is a heavy metal that has a wide range of industrial use (e.g. textile dyeing, tanneries, metallurgy, metal electroplating, and wood preserving); hence, large quantities of chromium 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 exhibit very different toxicity, chemical behavior and mobility. Hexavalent chromium is known to be toxic to humans, animals, plants and microorganisms [4-10]. Because of its significant mobility in the subsurface environment, the potential risk of natural waters contamination is high [11]. In contrast, trivalent chromium toxicity is 500 to 1000 times less to a living cell than Cr(VI) [6], is relatively insoluble in aqueous systems [12], and readily precipitates as Cr(OH)₃ or as mixed Fe(III)-Cr(III) (oxy)hydroxides [12,13,14] under alkaline, neutral, or even slightly acidic conditions. In trace amounts, Cr(III) is an essential micronutrient for the human metabolism [15]. However, Cr(III) may also have toxic effects [16,17], but its concentration is usually very low (below water quality standards) due to the low solubility of chromium hydroxide in the pH range of natural waters. Several methods are available for the decontamination of waters polluted with Cr(VI) compounds; these include: reduction followed by chemical precipitation, ion exchange, adsorption, membrane separation, electrokinetic remediation, reverse osmosis, biosorption [18]. The conventional process currently used to remove hexavalent chromium is its reduction to trivalent chromium by chemical means and subsequent adjustment of
solution pH to neutral or alkaline values, to precipitate Cr(III) as hydroxides. The reducing agents commonly used are ferrous sulfate, sulfur dioxide, sodium sulfite, sodium bisulfite. In recent years, there has been great interest in using zerovalent iron for the in situ treatment of Cr(VI) polluted groundwater [13,14,19-22]. It also has been reported the use of scrap iron for the reduction of Cr(VI) in above-ground wastewater treatment systems [23-26]. When scrap iron is used for the reduction of Cr(VI), the effluent that results contains Cr(III), Fe(II) and Fe(III) (assuming a total reduction of Cr(VI)) [26], species that must be further removed from the aqueous solution. At present, the most commonly used technology for removal of heavy metals from wastewaters is by chemical precipitation [27]. Within this context, the removal of heavy metals from wastewaters is by present, the most commonly used technology for reduction of Cr(VI)) [26], species that must be further removed from the aqueous solution. At present, the most commonly used technology for removal of heavy metals from wastewaters is by chemical precipitation [27]. Within this context, the removal of heavy metals from wastewaters is by present, the most commonly used technology for reduction of Cr(VI)) [26], species that must be further removed from the aqueous solution. At present, the most commonly used technology for removal of heavy metals from wastewaters is by chemical precipitation [27]. Within this context, the removal of heavy metals from wastewaters is by present, the most commonly used technology for reduction of Cr(VI)) [26], species that must be further removed from the aqueous solution. At present, the most commonly used technology for removal of heavy metals from wastewaters is by chemical precipitation [27]. Within this context, the removal of heavy metals from wastewaters is by present, the most commonly used technology for reduction of Cr(VI)) [26], species that must be further removed from the aqueous solution. At present, the most commonly used technology for removal of heavy metals from wastewaters is by chemical precipitation [27]. Within this context, the removal of heavy metals from wastewaters is by present, the most commonly used technology for reduction of Cr(VI)) [26], species that must be further removed from the aqueous solution. At present, the most commonly used technology for removal of heavy metals from wastewaters is by chemical precipitation [27]. Within this context, the removal of heavy metals from wastewaters is by present, the most commonly used technology for reduction of Cr(VI)) [26], species that must be further removed from the aqueous solution. At present, the most commonly used technology for removal of heavy metals from wastewaters is by chemical precipitation [27].

2 Problem Formulation

Synthetic effluent resulted from the continuous reduction of Cr(VI) with scrap iron was prepared by dissolving known amounts of Cr(NO3)3·9H2O, FeSO4·7H2O, and FeCl3 in distilled deionized water, in order to yield the following concentrations: 50 g/L Cr(III), 75 mg/L Fe(II), and 50 mg/L Fe(III). Concentrated H2SO4 was used for adjusting pH of the synthetic wastewater to 2.50. The composition of the synthetic effluent was selected because it’s within the range of relevant concentrations for real effluents resulted from the continuous reduction of Cr(VI) with scrap iron [26]. As precipitant reagent was used Na2CO3 solution 100 g/L. The initial composition of the synthetic effluent 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, by oxidizing all trivalent chromium with potassium permanganate, followed by analysis as hexavalent chromium [28]. 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 [28]. Fe(II) concentrations in the samples were determined by the 1,10-phenanthroline method [28]; 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) [28]. Fe(III) was calculated 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.

3 Problem Solution

3.1. Effect of Na2CO3 dose

Jar tests using doses of Na2CO3 ranging from 100-1400 mg/L were conducted, at 24°C, to determine the optimum dosage. The required amount of precipitant was added in Berzelius flasks containing 200 mL of the synthetic effluent and the flask contents were mixed 15 minutes at 100 rpm. After 30 minutes settling time, the supernatant was filtered through filter paper and analyzed for final Cr(III), Fe(II), Fe(total), and pH. The evolution of Cr(total), Fe(total) and pH in waters discharged into natural aquatic environments (Table 1), it results that the optimum Na2CO3 dose is 1000 mg/L.

Table 1. Maximum allowed Cr(total), Fe(total) and pH in waters discharged into natural aquatic environments, according to NTPA001/2002 [29]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Cr(total) mg/L</th>
<th>Fe(total) mg/L</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum allowed value</td>
<td>1</td>
<td>5</td>
<td>6,5 - 8,5</td>
</tr>
</tbody>
</table>

![Fig.1. Cations concentration and final pH of supernatant vs. Na2CO3 dose](image-url)
3.2. Effect of mixing time

To determine the optimum mixing time, jar tests were conducted, at 24° C, using mixing times ranging from 5 to 60 minutes. A 400 mg/L Na₂CO₃ dose was added in Berzelius flasks containing 200 mL of the synthetic effluent and the flask contents were mixed for the required time at 100 rpm. After 30 minutes settling time, the supernatant was filtered through filter paper and analyzed for final Cr(III), Fe(II), Fe(III), and Fe(total). 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 30 minutes; a further increase of mixing time over 30 minutes leads to a decrease of the removal efficiency. However, even the increase of removal efficiency due to increase of mixing time up to 30 minutes was insignificant, and, therefore, the optimum mixing time was chosen to be 5 minutes; all further experiments were performed at this mixing time.

3.3. Effect of mixing intensity

To assess the effect of mixing intensity, jar test experiments were conducted at 24° C and following mixing speed intensities: 50, 100, 200, 300, 400, 500, and 600 rpm.
A 400 mg/L Na$_2$CO$_3$ dose was added in Berzelius flasks containing 200 mL of the synthetic effluent and the flask contents were mixed 5 minutes at the required mixing intensity. After 30 minutes settling time, the supernatant was filtered through filter paper and analyzed for final Cr(III), Fe(II), Fe(III) and Fe(total). 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 two 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 using this mixing intensity.

### 3.4. Effect of settling time
To investigate the effect of settling time on cations removal, jar test experiments were conducted at 24°C and following settling times: 5, 10, 20, 30, 45, 60, and 90 minutes.

![Fig.7. Cations concentration in supernatant vs. settling time](image7)

![Fig.8. Cations removal efficiency vs. settling time](image8)

### 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.

![Fig.9. Cations concentration in supernatant vs. solution temperature](image9)

![Fig.10. Cations removal efficiency vs. solution temperature](image10)
An ice bath was used to work at 6 °C; cold tap water was used to work at 15 °C; 24 °C was the room temperature; a Julabo OB02 temperature controlled water bath was used for experiments conducted at 33 °C and 44 °C. A 400 mg/L Na₂CO₃ dose was added in Berzelius flasks containing 200 mL of the synthetic effluent and the flask contents were mixed 5 minutes at a 50 rpm mixing intensity. After 45 minutes settling time, the supernatant was filtered through filter paper and analyzed for final Cr(III), Fe(II), Fe(III), and Fe(total). 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 Cr(III) and Fe(total) removal efficiency continuously increased with the increase of temperature. However, since the increase of temperature over 33 °C resulted in a lower increase of the reduction efficiency, the optimum temperature was considered to be 33 °C.

4 Conclusion
Hexavalent chromium is toxic and wastewaters contaminated with this pollutant needs to be detoxified before there are disposed to natural water environments. Cr(VI) reduction to Cr(III) can be beneficial because a mobile and toxic chromium species is converted to a less mobile and less toxic form. When scrap iron is used as Cr(VI) reducing agent, the effluent that results from this process is not totally purified, since it still contains Cr(III), Fe(II) and Fe(III). These species can be removed from the aqueous solution by precipitation with Na₂CO₃. The optimum conditions of the precipitation process, established with this study, are: Na₂CO₃ dose: 1000 mg/L, mixing time: 5 minutes, mixing intensity: 50 rpm, settling time: 45 minutes, solution temperature: 33 °C.

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References:


[29] Regulation regarding the maximum allowed loads of pollutants from industrial and urban wastewater discharged into natural aquatic environments, NTPA – 001/2002.