Reduction of Chromate by Sponge Iron

H.R. Zafarani1+, M.E. Bahrololoom1, M. Javidi1, M.H. Shariat1 and J. Tashkhourian2

1Department of Materials Engineering, Shiraz University, Shiraz, Iran
2Department of Chemistry, Shiraz University, Shiraz, Iran

Abstract. Hexavalent chromium ion, present in hard chromium plating effluent, is the most toxic form of chromium ions and it is considered as a hazardous pollutant because it is a human carcinogen. So removing this ion from effluents is very important. Reduction of Cr(VI) to Cr(III) is environmentally favorable as the latter species is not toxic to most living organisms and also has a low mobility and bioavailability. In recent years reducing chromate ion by metallic iron is highly regarded. The sponge iron was used in this study, and the influence of parameters such as the effect of acid washing of sponge iron, initial pH and temperature of the reaction on the efficiency of the reduction of chromate ion were studied. XRD analysis and SEM images were employed to investigate the chemical composition and surface morphology of the sponge iron before and after the treatment.

Keywords: Chromate ion, Hazardous pollutant, Sponge iron

1. Introduction

Rapid industrialization has led to tremendous increase in the use of heavy metals over the past few decades and inevitably resulted in an increased flux of metallic substances in the aquatic environment. Growing attention is being given to health hazards caused by the existence of heavy metals in the aqueous environment since their accumulation in living tissues poses a serious health problem[1, 2]. Unlike most organic pollutants, metals contaminants are particularly problematic because they are non-biodegradable and can accumulate in living tissues [3]. Chromium is a heavy metal which is found in the industrial effluents (such as chromium plating) and is considered as a priority pollutant by the US Environmental Protection Agency [4]. Cr(VI) is a well-established human carcinogen [5]. In addition, Cr(VI) compounds exhibit a high mobility in the environment and have been shown to exert toxic effects in most living organisms [6]. On the contrary, Cr(III) is up to 1000 times less toxic to a living cell than Cr(VI) [7], has lower mobility in the environment and lower solubility in water and readily precipitates as Cr(OH)3 [8, 9] or as mixed Fe(III)–Cr(III) (oxy)hydroxides [10]. Thus, Reduction of Cr(VI) to Cr(III) in natural and engineered environmental systems can be beneficial because a more toxic and more mobile chromium species is converted to a less toxic and less mobile form. Removal of hexavalent chromium has been investigated by using methods such as adsorption [11], reduction to Cr(III) followed by precipitation [12], biological [13] and membrane [14] separation processes. Chemical reduction to Cr(III) followed by precipitation is the most used technique for the removal of Cr(VI) ions from polluted wastewaters. The major drawback of this method is the high cost of chemicals used for the reduction and precipitation purposes. Therefore, in the last few years, there has been great interest in using low-cost materials that can substitute traditional reducing agents. Use of zerovalent iron (Fe0) for reduction of redox active metals is a promising alternative method for in situ reduction of hexavalent chromium from contaminated groundwater. Hexavalent chromium reduction by Fe-based particles is a surface-mediated process; the increased surface area relative to the mass of iron increases the reduction rate. One reason that sponge iron particles might exhibit greater rates of reaction with

+ Corresponding author. Tel.: +98-711-6322137; fax: +98-711-6322575
E-mail address: hrzafarani@gmail.com
contaminants is simply that their large specific surface area provides more sites for reaction to occur and also it is a low-cost reductant. It has been shown that many factors affect the process of chemical precipitation. This work will present data regarding the influence of sponge iron on chromium, acid cleaning of sponge iron, solution initial pH, and the effect of temperature on the process.

2. Materials and Methods

Direct-reduced iron (DRI), also called sponge iron, is produced from direct reduction of iron ore (in the form of lumps, pellets or fines) by a reducing gas produced from natural gas or coal. The final product, when observed under a microscope, resembles a honey comb structure and is spongy in texture; hence, the name “Sponge Iron”. Because of its nature and structure, DRI reacts differently in many ways when compared to solid compact iron. Several inherent characteristics of DRI are high porosity, low density and high surface area. The sponge iron which used in this study is provided from Mobarakhe Steel Company (Esfahan, Iran). Synthetic wastewater solutions were prepared by dissolving CrO$_3$ in 0.1 M NaNO$_3$ (Merck) background electrolyte solutions. All experiments were performed in 250 ml Cr(VI) solution with initial Cr(VI) concentrations of 10 mg/l. This concentration was selected because it is within the range of environmentally relevant concentrations [15]. The pH was adjusted by concentrated H$_2$SO$_4$ and 1.0 M NaOH (Merck). To remove traces of chromium and iron, the glassware were soaked in 0.1N HCl before each experiment. The pH of the solutions was measured using a Metrohm pH-meter. The Cr(VI) concentration was measured throughout treatments using the 1,5-Diphenylcarbazide method (AWWA 3500-Cr D colorimetric method) [16]. A Cintra 5 spectrophotometer with the absorption readings obtained at 540 nm. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were employed to investigate the chemical composition and surface morphology of the sponge iron before and after the experiments. The SEM analysis was performed by Cambridge S360 scanning electron microscope and the XRD measurements were performed by Bruker D8 Diffractometer.

3. Results and Discussion

Previous investigators have shown that Cr(VI) may be removed from solution via reduction to Cr(III) according to[17]:

$$2\text{Cr}_2\text{O}_7^{2-}(aq) + 6\text{Fe}(s) + 28\text{H}^+(aq) \rightarrow 4\text{Cr}^{3+}(aq) + 6\text{Fe}^{2+}(aq) + 14\text{H}_2\text{O}$$

$$\text{Cr}_2\text{O}_7^{2-}(aq) + 6\text{Fe}^{2+}(aq) + 14\text{H}^+(aq) \rightarrow 2\text{Cr}^{3+}(aq) + 6\text{Fe}^{3+}(aq) + 7\text{H}_2\text{O}$$

The two equations can be added together to yield Eq. (3), which is the net reaction for the reduction process.

$$\text{Cr}_2\text{O}_7^{2-}(aq) + 2\text{Fe}(s) + 14\text{H}^+(aq) \rightarrow 2\text{Cr}^{3+}(aq) + 2\text{Fe}^{3+}(aq) + 7\text{H}_2\text{O}$$

All experiments were performed by agitation of 2g sponge iron in 250 ml Cr(VI) solution with the concentration of 10mg/l.

3.1. Effect of Acid Cleaning of Sponge Iron

Generally, nonpretreated commercial iron is covered with a discontinuously passive layer of Fe$_2$O$_3$, formed during the high-temperature manufacturing process. Additionally, a mixture of nonstoichiometric iron oxide and oxyhydroxide species may form in storage [18]. Thus, a pretreatment method is needed to remove the passive oxide layers to activate the iron surface. Pieces of iron were washed with water and several different common acids. The results obtained after washing with water were not significantly different from the reduction obtained using iron without any treatment. The performance of the iron with acid washing was much better and was found to be dependent on the acid concentration. It is generally accepted that acid-washing can increase the initial iron reactivity significantly by removing nearly all the indigenous iron oxides on the iron surface. The 0.1M HCl solution was selected for acid washing and the effect of acid cleaning time is shown in Fig. 1. Increasing acid washing time to 20 minutes had a significant effect on Cr(VI) removing.
3.2. **Effect of Initial pH of the Cr(VI) Solution**
Experiments indicated that Cr(VI) reduction was very fast in acidic conditions, but proceeded slowly when pH increased (Fig. 2). This is in accord with the stoichiometry of this reaction (Eq. (2)) which requires 7 moles of hydrogen ions for each mole of Cr(VI) and is highly dependent on H⁺ concentration. The effect of pH on the Cr(VI) reduction was studied at room temperature (24±2 °C), over the pH range of 2.3–4.7. Because the solutions were poorly buffered, pH values increased over the course of the reaction in all batch tests. The final pH was in accordance with the previous studies [19] and increased from the initial value with 0.5–1.0 pH units. This also may cause decreases in the reduction rates with time. Iron corrosion and the reduction of Cr(VI) by sponge iron (Eq. (2)) were probably responsible for the observed pH increase.

3.3. **Temperature Dependence**
The effect of temperature on the reduction of Cr(VI) by sponge iron was examined in Cr(VI) solution with the concentration of 10mg/l at pH 3.7, for temperature values ranging from 27 to 45 °C. The results, presented in Fig. 3, show an important dependence of the reaction rate on temperature. The yellow color of the Cr₂O₃ solution changed to green when Cr(III) was produced.

3.4. **Sponge Iron Surface Studies before and after the Reaction**
The near plateau segment of the plots was probably due to the passivation of the surface with the consequent loss of reactivity. The SEM results (Figs. 4-5) confirmed that, at the end of the experiment, the
sponge iron surface was partially covered with a newly formed layer. As presented in Figs. 6-7, the reacted sponge iron was covered by Fe-Cr oxides (such as Cr$_{0.26}$Fe$_{1.74}$ and Cr$_2$FeO$_4$ oxides). This was accord with other studies which have reported the presence of different iron oxides on the surface of metallic iron[18, 20].

Fig. 4: SEM image of sponge iron surface before the reaction (Mag.500).

Fig. 5: SEM image of sponge iron surface after the reaction (Mag.500)

Fig. 6: XRD pattern of un-reacted sponge iron.

Fig. 7: XRD pattern of exhausted sponge iron

4. Conclusions

Sponge iron is one of the cheapest and the most effective of Cr(VI) reductants. Acid washing of the sponge irons, decreasing pH of the solution and increasing temperature of the reaction improve the reduction rate.
5. References


