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Hexavalent chromium reduction with scrap iron in continuous-flow system
Part 1: Effect of feed solution pH

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Abstract

The reduction of hexavalent chromium by scrap iron was investigated in continuous system, using long-term column experiments, for aqueous Cr(VI) solutions having low buffering capacities, over the pH range of 2.00–7.30. The results showed that the initial pH of Cr(VI) solution significantly affects the reduction capacity of scrap iron. The highest reduction capacity was determined to be 19.2 mg Cr(VI)/g scrap iron, at pH 2.50, and decreased with increasing the initial pH of Cr(VI) solution. A considerable decrease in scrap iron reduction capacity (25%) was also observed at pH 2.00, as compared to pH 2.50, due to the increased contribution of H^+ ions to the corrosion of scrap iron, which leads to a rapid decrease in time of the scrap iron volume. Over the pH range of 2.50–7.30, hexavalent chromium concentration increases slowly in time after its breakthrough in column effluent, until a steady-state concentration was observed; similarly, over the same pH range, the amount of solubilized Cr(III) in treated column effluent decreases in time, until a steady-state concentration was observed. The steady-state concentration in column effluent decreased for Cr(VI) and increased for Cr(III) with decreasing the initial pH of Cr(VI) solution. No steady-state Cr(VI) or Cr(III) concentrations in column effluent were observed at pH 2.00. Over the entire studied pH range, the amount of Fe(total) in treated solution increases as the initial pH of column influent is decreased; the results show also a continuously decrease in time of Fe(total) concentration, for a constant initial pH, due to a decrease in time of iron corrosion rate. Cr(III) concentration in column effluent also continuously decreased in time, for a constant initial pH, over the pH range of 2.50–7.30. This represents an advantage, because the amount of precipitant agent used to remove Fe(total) and Cr(III) from the column effluent will also decrease in time. The optimum pH for Cr(VI) reduction with scrap iron in continuous-flow system was established at the value of 2.50.

Keywords: Hexavalent chromium; Toxic metals; Scrap iron; Column experiments; Wastewater treatment

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1. Introduction

Chromium is an important metal, which is used in a variety of industrial applications (e.g. textile dying, tanneries, metallurgy, metal electroplating, wood preserving, preparation of chromate compounds); hence, large quantities of chromium have been discharged into the environment due to accidental releases or inadequate precautionary measures [1,2]. Although chromium oxidation states range from (−IV) to (+VI) [3], only the (+III) and (+VI) states are stable in the natural environment [4]. The chemical and toxicological behaviors of chromium depend on its oxidation state. Under environmentally relevant pH values, hexavalent chromium exists as oxyanions of chromate ($pH > 6.5$) and bichromate ($pH < 6.5$) [5]. Because it has a high solubility in water and it is only weakly sorbed onto inorganic surfaces, Cr(VI) has a significant mobility in the environment [6]. Chromium(III), on the other hand, has a lower solubility in water and readily precipitates as $Cr(OH)_3$ [7] or as mixed Fe(III)–Cr(III) (oxy)hydroxides [8,9] under alkaline or even slightly acidic conditions. Hexavalent chromium is toxic to most living organisms [5,10–12] and a known human carcinogen by the inhalation route of exposure [13,14]. Although trivalent chromium is considered an essential nutrient for the human body [15] and the toxicity of trivalent chromium is 500–1000 times

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less to a living cell than hexavalent chromium [16], exposure to excessive doses of Cr(III) for long periods of time may also cause some adverse health effects [17–19]. Thus, removal of chromium, and especially of Cr(VI), is an essential pollution abatement process that should be applied to all industrial effluents that contain this contaminant, prior to discharge them in to the natural water bodies.

Chemical reduction to Cr(III) (followed by precipitation), adsorption, ion exchange and membrane separation processes are the most used techniques for the decontamination of wastewaters polluted with Cr(VI) compounds. However, for developing countries, all these methods can be prohibitively expensive. Waste materials recycling can become a crucial component for those communities in their efforts to prevent the pollution associated with industrial applications. Therefore, in recent years, attention has been focused on the use of low-cost and locally abundant waste materials that can substitute traditional adsorbents or reducing agents, for the abatement of hexavalent chromium pollution. Materials such as soya cake [20], hazelnut shell [21], maple sawdust [22], coal ash [23], blast furnace sludge [24], have been tried as adsorbents. Previous reports have also described the use of different non-conventional reducing agents like magnetite [25–27], siderite [28], mackinawite [29,30], pyrite [31], hematite, biotite [32], copper smelter slag [33].

Zero-valence-state metals, such as metallic iron, can also serve as electron donors for reducing redox reactive metals to valence states that are less water soluble [34,35]. Although in last years there has been great interest in using zerovalent iron for in situ reduction of hexavalent chromium from contaminated groundwater [8,9,36–40], from our knowledge, there are only a few references in the literature concerning the use of scrap iron for the reduction of Cr(VI) in above-ground treatment systems. The galvanic reduction of hexavalent chromium with scrap iron using a divided parallel plate cell was investigated by Abdo and Sedahmed [41]; the advantage of this technique is that the reduced chromium salt is free of iron impurities and electrical energy is produced from the galvanic cell as by-product. The kinetics of Cr(VI) reduction in a fixed bed of scrap iron bearings was studied by El-Shazly et al. [42]; the activation energy of the reaction was found to be low (4.51 kcal/mol) which shows that the reaction is diffusion controlled. Ozer et al. [43] studied the reduction of Cr(VI) by steel wool in continuous system; although the results showed that the process depended to a large extent on acid concentration, no optimum pH value was proposed. Our previous batch studies [44,45] have also shown that scrap iron can be a potentially useful reducing material for treating hexavalent chromium contaminated wastewaters, especially at low pH values. However, it was difficult to assess long-term performance of hexavalent chromium reduction by scrap iron using only short-term batch experiments. Therefore, as a continuation of our previous work, the present work examines the use of scrap iron for the continuous reduction of hexavalent chromium in flow-through columns. The main purpose of this paper is to establish the optimum pH for the reduction of hexavalent chromium with scrap iron in continuous-flow system. Additionally, we present data regarding the pH influence on chromium and iron species concentration in column effluent and on scrap iron reduction capacity.

2. Materials and methods

2.1. Materials

In our previous studies [44,45] four different types of scrap iron resulted from the mechanic processing of steel were characterized and tested for Cr(VI) reduction: large spiral fibers, small spiral fibers, iron shavings and fine iron powder; the optimum shape for batch reduction experiments was found to be as iron shavings that pass through 2.5 mm screen; therefore, all column experiments conducted in this study were also performed by using iron shavings.

Hexavalent chromium stock solutions (1 g/l) were prepared by dissolving 2.829 g $K_2Cr_2O_7$ in 1000 ml of distilled deionised water; feed solutions of the desired initial Cr(VI) concentration (10 mg/l) were prepared by diluting the stock solution. H_2SO_4 was used for adjusting pH of the feed solution. All chemicals used were of AR grade.

2.2. Methods

The laboratory apparatus used for the flow-throught experiments is presented in Fig. 1. Reduction experiments were conducted by using a glass column (inner diameter: 2.00 cm; height: 12.00 cm) with a porous plate at the bottom. The column was packed with 30 g scrap iron up to a 6.00 cm height (scrap iron volume: 18.84 cm^3) and 10 mg Cr(VI)/l aqueous solution with low buffering capacity was passed through the column, from the bottom to the top, by using a Unipan peristaltic pump. This concentration was selected because it is within the range of relevant concentrations for electroplating wastewaters [46]. To remove traces of chromium and iron, the column was soaked in HCl 35% and washed with distilled deionised water before each experiment.

The hydraulic contact time in the column was 2.60 min (pumping rate of 0.3 l/h). Column effluent samples were withdrawn at regular time intervals (as a manner of shortened intervals in the beginning of experiments) and pH, Cr(total),

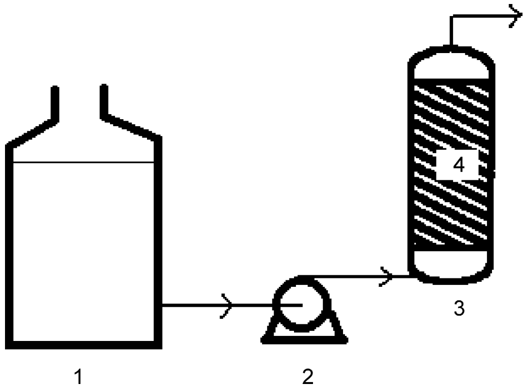

Fig. 1. Experimental setup: (1) storage tank; (2) peristaltic pump; (3) glass column; (4) scrap iron filling.