

The reduction of hexavalent chromium by sulphite in wastewater

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Abstract

The reduction of hexavalent chromium, Cr(VI), in unbuffered aqueous solution by sulphite was investigated as a function of pH, possible dosage and contact time required to reach equilibrium. Dissolved $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ served as the aqueous source of Cr(VI). The rate of the reaction between Cr(VI) and sulphite exhibited a very strong dependence on the pH of the reaction mixture, with a decrease in reaction rate with an increase in pH from 2.0 to 5.0. For a $5.0 \times 10^{-4} \text{ mol-dm}^{-3}$ Cr(VI) solution ($\sim 26 \text{ mg/l}$) a sulphite concentration of at least 5 times the initial Cr(VI) concentration was needed for complete reduction in this pH range. Above pH 6 very large concentrations of sulphite were needed to reduce Cr(VI) effectively. To check the industrial relevance of the results, baghouse dust from a ferrochromium plant was leached to serve as a model source of industrial wastewater containing aqueous Cr(VI), for conducting various comparative experiments. The results clearly indicated that sulphite would be a suitable reductant for Cr(VI) in wastewater under specific conditions ($2.0 \leq \text{pH}_{\text{initial}} \leq 5.0$ and $[\text{sulphite}] = 5 \times [\text{Cr(VI)}]_{\text{initial}}$).

Introduction

It is estimated that South Africa holds approximately 72% of the world's chromium reserves. Currently South Africa is the largest chromite and ferrochromium, as well as the sixth largest stainless steel producing country in the world (Mintek, 1994). It is suggested that by the year 2000 this industry will export products to the value of \$6.2 billion, which is approaching that of gold exports, which is estimated at \$7.1 billion (Robinson, 1996).

Although chromium has found many useful applications, the impact of the chromium industry on the local environment is extensive, complicated and not fully quantified. Landfill disposal of waste containing chromium compounds is common practice arising from industrial chromium production as well as chromium utilising industries (Gericke, 1995). Contaminated landfill sites and industrial effluents are likely to contain only trivalent chromium, Cr(III), and hexavalent chromium, Cr(VI). Divalent chromium, Cr(II), is fairly unstable and is rapidly oxidised to Cr(III). Elemental chromium, Cr(O), is also oxidised to Cr(III) unless it is made passive by superficial oxidation.

Trivalent chromium is considered a trace nutrient for human and animals alike (Wong and Trevors, 1988). The low solubility of Cr(III) solid phases (mostly Cr_2O_3 and Cr(OH)_3) is likely to be the major reason why Cr(III) generally makes up a small percentage of the total chromium concentration in polluted groundwater (Calder, 1988). Mobilisation of the Cr(OH)_3 precipitate is slow, unless enhanced by dissolution in strong acidic environments or complexation with organics (Rai et al., 1987). Oxidation of Cr(III) is mostly achieved through MnO_2 , which acts as a catalyst in the oxidation of chromium(III) (Rai et al., 1989).

In contrast, hexavalent chromium is considered toxic and carcinogenic (Yassi and Nieboer, 1988). There are no significant solubility constraints in groundwater for Cr(VI) (Rai et al., 1989). When Cr(VI) is transported by groundwater, it may be transformed to and precipitated as Cr(III). However, the reducing capability of

a soil is limited to the amounts of reductant (organics, Fe(II), sulfides, etc.) present. Hence excessive chromium loading on soil might not only upset, but destroy, the natural balance, giving way to Cr(VI) formation, even if the original load was exclusively Cr(III). Due to the toxicity and carcinogenicity of Cr(VI), the U.S. E.P.A. has set a drinking water limit for chromium of 0.05 mg/l (Calder, 1988). As a result, removing chromium(VI) from industrial wastewater has become necessary in order to avoid contamination of natural water and raw water used for public supply.

According to Lin and Vesilind (1995), removing Cr(VI) by chemical reduction from industrial wastewater involves a two-step process: reduction of hexavalent chromium under acidic conditions (usually pH 2 to 3) and the precipitation of trivalent chromium as hydroxyl species. The most commonly used reducing agents are gaseous sulphur dioxide, sodium sulphite, sodium metabisulphite and ferrous sulphate (Lin and Vesilind, 1995; Conner, 1990). Sodium dithionite has also been identified as a useful reducing agent for Cr(VI) (Pal and Yost, 1995).

The capacity of the ferrous ion to reduce Cr(VI) has been investigated in relative detail (Sedlak and Chan, 1997; Buerge and Hug, 1997; Fendorf and Li, 1996; Lin and Vesilind, 1995; Eary and Rai, 1988; 1989). Some investigations have also been conducted on the reduction of Cr(VI) by sulphite (Wawrzenczyk and Cyfert, 1994; Haight et al., 1965; Brandt and Elding, 1998). However, the use of buffers and the relatively small pH range in which these studies were carried out, make their results less applicable for industrial applications. In this paper the suitability of sulphite as a reductant for Cr(VI) in an unbuffered systems, over a wide pH range ($2.0 \leq \text{pH} \leq 8.0$), is reported. The results therefore give a good indication of the industrial applicability of sulphite for this purpose.

Materials and methods

Materials

Analytical grade reagents with the highest purity level were bought from the different suppliers and used without any further purification. Sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$) (UniLab) was used as

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