On the precipitation of dissolved chromium from raw sewage following a chromate spillage

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Abstract

Following a spillage of 100 kg Cr(VI), the activated sewage treatment process at a local municipality was poisoned. The dissolved chromium was successfully reduced and precipitated at around neutral pH with iron(II) sulphate heptahydrate. More than 97% of the dissolved chromium was removed from solution. Acetate ions or other organic ligands in sewage facilitate the Cr(VI) – Fe(II) reaction at neutral pH.

Introduction

In March 1982, the Hydrological Research Institute was approached following a spillage of 100 kg Cr(VI) into the sewers of a local municipality. The Cr(VI) reached the sewage works where it poisoned the bacteria in the activated sludge process. The municipality was faced with the problem of how to dispose of 5 Mℓ of sewage containing 20 mg/ℓ Cr(VI) in solution. A practical method had to be found within 24 h for removing the dissolved chromate from solution. A laboratory investigation showed that iron(II) sulphate heptahydrate was an effective and economical reagent for the removal of both Cr(III) and Cr(VI) from a contaminated sewage sample.

The purpose of this paper is to describe the observations made during both the laboratory investigation and field application of the use of Fe(II) sulphate as a reagent for removing dissolved chromium. It was felt that the experience could benefit other municipalities faced with a similar problem in the future.

Laboratory Investigation

A sample of the contaminated sewage was filtered through a Whatman No. 43 filter paper. The filtrate had the typical orange-yellow colour of the chromate ion, and was found to contain 20 mg/ℓ Cr on analysis by Inductively Coupled Plasma (ICP) Emission Spectrometry. The pH of the sewage sample was 7,2.

As a first trial run, sodium metabisulphite was added to an aliquot of the raw, Cr(VI) contaminated sewage. This reagent is used by electroplating industries to reduce Cr(VI) to Cr(III), which is then precipitated as the hydroxide in alkaline medium. While sodium metabisulphite did reduce Cr(VI) to the green Cr(III) form, the Cr(III) remained in colloidal solution even when the pH was increased to 10 and greater with sodium hydroxide.

As a second trial run, iron(II) sulphate heptahydrate was added as a solid to an aliquot of the Cr(VI) containing sewage at its original pH of 7,2. The $Fe(II)SO_4.7H_2O$ salt dissolved readily and rapidly reduced the Cr(VI) to the Cr(III) form. Subsequent addition of limewater to increase the pH to 8,4 resulted in a heavy floc which settled rapidly leaving a clear colourless supernatant.

The amount of $Fe(II)SO_4.7H_2O$ used to effect the reduction and precipitation of the Cr(VI) from the sewage sample was 400 mg/ℓ. For a 3:1 stoichiometric ratio of Fe(II):Cr(VI) a 20 mg/ℓ Cr(VI) solution requires 320 mg/ℓ $Fe(II)SO_4.7H_20$ for complete reduction of Cr(VI) to Cr(III). The supernatant from this second laboratory trial was decanted off and found to contain 1,0 mg/ℓ Fe and less than 0,005 mg/ℓ Cr by ICP Emission Spectrometry.

As a third trial, the use of $Fe(II)SO_4 . 7H_2O$ was investigated for precipitating Cr(III) from sewage treated with sodium metabisulphite. The Fe(II) salt was added at the same dosage used in the second trial to the Cr(III) metabisulphite containing sewage after the pH had been adjusted to 7,2. A gelatinous greenish-brown floc formed which settled slowly after the pH was increased to 8 with limewater. The supernatant was found to contain 0,8 mg/ℓ Fe and 0,034 mg/ℓ Cr on analysis.

Field Application

As the municipality had already added sodium metabisulphite to a portion of the contaminated sewage, the chromium was present both as Cr(III) and Cr(VI) when the use of $Fe(II)SO_4.7H_2O$ was tried on a field scale. The laboratory experiments had, however, shown that the same dosage of iron(II) sulphate heptahydrate effectively removed both Cr(VI) and Cr(III) from solution in the sewage.

In the field trial 2000 kg commercial grade $Fe(II)SO_4.7H_2O$ was added to the 5 Mℓ aeration tank at the sewage works. The aerators were left on for about 10 min to ensure mixing. A bulky floc formed rapidly, and the pH decreased from 7,4 to 6,8. After allowing a sample aliquot to settle, the supernatant was decanted off and found on analysis to contain 8,3 mg/ℓ Fe and 0,50 mg/ℓ Cr. The following day 250 kg calcium hydroxide was added, with mixing, to increase the pH to 8,4. The floc settled rapidly and the supernatant was found to contain 7,7 mg/ℓ Fe and 0,47 mg/ℓ Cr before filtration. After filtration the iron and chromium concentrations were found to be 0,18 mg/ℓ and 0,05 mg/ℓ respectively.

A sample of the sludge was taken for analysis and found to contain 11 000 mg Cr/kg sludge (dried at 100°C for 1 h). More than 97% of the chromium originally present in solution was accounted for in the sludge.

The unfiltered supernatant in the aeration tank now contained less than the 0,5 mg/ℓ Cr effluent standard (Act 54 of 1956) and could be discharged to the river.

Discussion

The stoichiometric reduction of Cr(VI) by Fe(II) is normally only carried out in strongly acid medium. In pure solution iron(II) sulphate will not reduce Cr(VI) at pH 7. The reaction occurs, however, very rapidly in sewage. Laboratory experimentation on the reaction of Fe(II) with Cr(VI) in pure solutions showed that in the presence of acetate ion the reduction of Cr(VI) to Cr(III) occurs readily at neutral pH. Organic ligands in sewage probably play a role analogous to acetate in pure solution in making possible the redox reaction between Cr(VI) and Fe(II) at neutral pH. It is, however, beyond the scope of this paper to speculate on the chemical reactions occurring.

Ginnocchio (1982) briefly mentions that iron(II) sulphate may be used for removing Cr(VI) from drinking water. Our investigation has shown that iron(II) sulphate is also effective in removing Cr(VI) from sewage.

Conclusion

Iron(II) sulphate heptahydrate was found to be an economical (20c/kg) and effective reagent for treating chromium contaminated sewage. The addition of iron(II) sulphate heptahydrate, as a solid, at a dosage of 400 mg/ℓ to the Cr(VI) containing sewage at pH 7, followed by addition of calcium hydroxide to increase the pH to 8, resulted in the removal of more than 97% of the dissolved chromium from solution. Acetate ions or other organic ligands in the sewage are possibly involved in the reduction of Cr(VI) to Cr(III) by Fe(II) at pH 7.

Acknowledgements

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