

Optimization Of Hexavalent And Trivalent Chromium Present In Waste Water By Chemical Treatment

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ABSTRACT

Chromium is one of the heavy metal coming from various industries having high toxicity. The main objective is to adopt appropriate methods and to develop suitable techniques either to prevent metal pollution or to reduce it to very low levels. Initially, experiments were conducted on Potassium dichromate synthetic sample to find the optimum pH of reduction, optimum dosage of reducing agents and optimum reduction period for Ferrous sulphate and Sodium metabisulphite. The hexavalent chromium reduced synthetic samples were used to find optimum pH of precipitation, optimum dosage of precipitating agents for calcium hydroxide, sodium hydroxide and combination of these two chemicals. Experiments were carried out on industrial waste water for the removal of Hexavalent and Trivalent chromium with optimum operating conditions which were obtained from the experiments on synthetic sample.

Key Words: Reducing agents, Precipitating agents, Hexavalent chromium Cr(VI), Trivalent chromium Cr(III).

1.0 INTRODUCTION

Contamination of the environment by heavy metals has become a major area of concern. The most common heavy metals contaminants are arsenic, barium, mercury, lead, chromium, nickel, copper, cadmium and zinc are of considerable concern because they are highly toxic and carcinogenic [1]. Heavy metals negatively affect the health of humans, vegetation and aquatic life. Chromium is one of the heavy metal coming from various industries having high toxicity. Chromium can occur at several different oxidation states ranging from -2 to 6. Out of which only Cr (III) and Cr (VI) are the stable forms in the natural environments. However Cr (VI) is rarely naturally occurring, relatively soluble in aqueous systems and is readily transformed in groundwater. Exposure to Cr (VI) poses an acute health risk because it is highly toxic and chronic exposure can lead to mutagenesis and carcinogenesis. On the contrary Cr (III) is naturally occurring, is much less toxic and

even essential to human glucidic metabolism, contributing to the glucose tolerance factor necessary for insulin-regulated metabolism [2]. Chromium is used on a large scale in many different industries, including metallurgical, electroplating, production of paints and pigments, paper production tanning and wood preservation. The chromium contents of waste water can be effectively removed to acceptable levels by precipitating the metals to insoluble form. Hexavalent chromium is present in the effluents produced during the electroplating, leather tanning, cement, mining, dyeing and fertilizer and photography industries and causes severe environmental and public health problems [3]. Hexavalent chromium has been reported to be toxic to animals and humans and it is known to be carcinogenic. The tolerance limit for Cr(VI) for discharge into inland surface waters is 0.1 mg/l-1 and in potable water is 0.05 mg/l-1. In order to comply with this limit, it is essential that industries treat their effluents to reduce the Cr(VI) to acceptable levels [4,5].

A number of treatment methods for the removal of metal ions from aqueous solutions have been reported, mainly reduction, ion exchange, electro dialysis, electrochemical precipitation, evaporation, solvent extraction, reverse osmosis, chemical precipitation and adsorption [6,7]. Most of these methods suffer from drawbacks such as high capital and operational costs or the disposal of the residual metal sludge. In this study hexavalent and trivalent chromium is removed by chemical treatment. When we need to remove hexavalent chromium out of solution we first need to reduce it from hexavalent to trivalent form by reducing agents like ferrous sulphate and sodium metabisulphite. The reduced trivalent chromium is then precipitated by addition of precipitating agents like calcium oxide and sodium hydroxide. Moreover Ferrous sulphate requires pH =1 for complete reduction as compared to sodium metabisulphite which requires a pH of about 2 [8,9]

2.0 MATERIALS AND METHODOLOGY

2.1 Preparation of Synthetic hexavalent chromium sample

The potassium dichromate solution ($K_2Cr_2O_7$) is used as source of hexavalent chromium. A stock

solution of potassium dichromate of concentration 100 mg/l is prepared by dissolving 0.283 g of potassium dichromate in 1000 ml demineralised water in a standard volumetric flask. The solution is diluted to obtain standard solutions containing 10 mg/l of Cr (VI). Initial pH of the synthetic sample is determined by using pH meter.

2.2 Analysis of Hexavalent Chromium

The concentration of the hexavalent chromium ions in the sample is determined spectrophotometrically by developing a red-violet colour with 1,5-Diphenylcarbohydrazide in acidic condition solution as a complexing agent. Hexavalent chromium is determined by the 1,5-Diphenylcarbohydrazide method. This 1,5-Diphenylcarbohydrazide, reacts to give a purple colour when hexavalent chromium is present. The hexavalent chromium then reacts with 1,5-diphenylcarbazine to form 1,5-diphenylcarbazone. Test results are measured at 540 nm [10].

2.2 Analysis Total Chromium

Atomic absorption spectrophotometer of version A-400 was used to measure the total chromium concentration. In AAS fuel used was acetylene C_2H_2 and the oxidant used was Nitrous oxide. Calibration of AAS was done according to the equipment manual using certified standards and the analysis of calibrated standards was attained to ensure the accuracy of results.

3. RESULT AND DISCUSSION

3.1 Optimum time, Optimum pH and Optimum dosage for hexavalent chromium reduction Cr(VI) from synthetic sample

Experiments were conducted to study the effect of Reduction time on the reduction of Chromium against various doses of reducing agents like Ferrous Sulphate and Sodium metabisulphite.

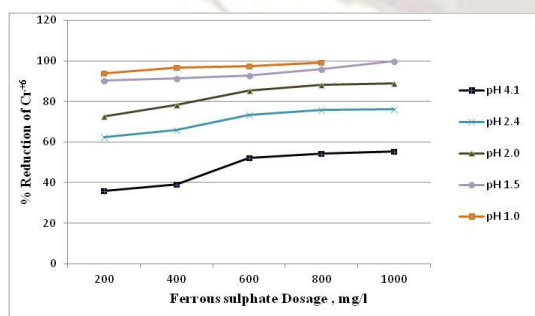


Fig. 1 : Effect of ferrous sulphate dose and pH on Reduction of Cr(VI).

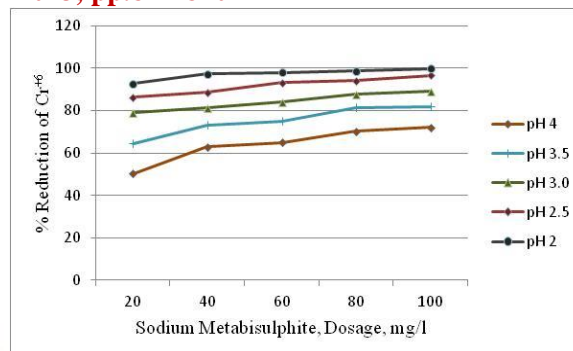


Fig. 2 : Effect of sodium metabisulphite dose and pH on Reduction of Cr(VI).

Jar test method has been used to determine the effect of each parameter. 500 ml of synthetic sample is taken in four different beakers. First ferrous sulphate was added to each beaker in increments to determine optimum dosage, optimum pH and reduction time. After reduction process, the sample was analysed to know hexavalent chromium concentration. Similarly, reduction was carried for sodium metabisulphite. Ferrous Sulphate it was seen that for a dose varying from 200 to 400 mg/l, the change in % reduction Cr (VI) was rapid in first 30 min and then it tapers towards the end. Same was observed for Sodium metabisulphite corresponding to the dose of 20 to 100 mg/l. In case of Ferrous Sulphate the reduction process is slow between 60 to 75 min. Therefore 75 min was regarded as the Optimum Reduction period for comparison between various doses of Ferrous sulphate. Similarly for Sodium metabisulphite 50 min should be regarded as the Optimum Reduction period.

As from Fig. 1, it can be seen that the reduction of 52.33 % can be obtained corresponding to a dose of 600 mg/l. When the dose was increased to 800 and 1000 mg/l, % reduction of only 54.30 and 55.50 % respectively were obtained. This shows that % reduction depends upon the concentration of hexavalent chromium Cr (VI) remaining in the solution.

Secondly Sodium metabisulphite dose was varied from 20 mg/l. From Fig. 2 we can make out that as compared to Ferrous Sulphate, % reduction obtained by using sodium metabisulphite was more. It increased from 65.0 %, 70.36 % to 72.0 % as the dose increased from 40, 60 to 80 mg/l resp.

Moreover the reduction process of Sodium metabisulphite completes within 50 mins while that of Ferrous sulphate takes 75 mins for completion. Merely increasing the dose beyond a certain limit is of no use. Hence it is better to go for pH adjustment. So the pH was adjusted and its effect on % reduction was observed. In the case of Ferrous sulphate % reduction increased from 55.5 % to 100 % for the dose 1000 mg/l corresponding to pH value from 2.4 to 1.0 respectively. From Fig. 2 we can see that using Sodium metabisulphite 100% reduction can be obtained at a dose of 100 mg/l for pH value 2.0 after only 50 mins of reduction time.

This % reduction was faster than that obtained using Ferrous sulphate. One more point to be noted is that the reduction process is over after 50 mins compared to 75 mins for Ferrous sulphate. Thus 50 min as the Optimum Reduction time for Sodium metabisulphite.

3.1.1 Precipitation of Cr (III)

After the complete reduction of hexavalent chromium the precipitating agents viz., calcium hydroxide Ca(OH)_2 , Sodium hydroxide (NaOH) and combination of Calcium hydroxide and Sodium hydroxide were added to each sample separately of varying dosage. In order to mix the solution, sample were taken to jar apparatus and samples were mixed for 20 mins with speed of 60 rpm. The precipitate formed was allowed to settle completely. Supernatant was withdrawn from the beaker and analysed for hexavalent chromium and total chromium. The mathematical subtraction of total chromium and hexavalent chromium gives trivalent chromium value. The experimental results for trivalent chromium removal using combination of Ca(OH)_2 and NaOH are shown in Fig 3 and Fig 4

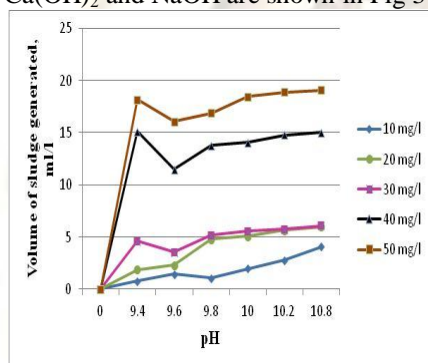


Fig. 3: Volume of sludge produced per litre under various pH conditions for Ca(OH)_2 + NaOH (Synthetic sample reduced by FeSO_4)

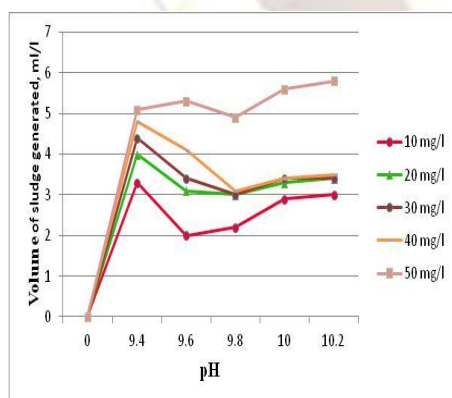


Fig. 4 : Volume of sludge produced per litre under various pH conditions for Ca(OH)_2 +NaOH (Synthetic sample reduced by $\text{Na}_2\text{S}_2\text{O}_5$)

From the results of synthetic sample, the best optimum operating conditions for different precipitating agents are shown in Table 1 and Table 2

Table. 1 : Results of various precipitating agents in removal of Cr(III) in synthetic sample, (FeSO_4 is used as a reducing agent , Cr(III) after reduction = 10 mg/l)

Precipitating agents of optimum dosage	Optimized pH of precipitation	Volume of sludge generated, ml/l	After precipitation process, Cr(III) mg/l	% removal of Cr(III)
Ca(OH)_2 , 30 mg/l	11.5	16.6	0.515	94.8
NaOH, 40 mg/l	9.6	25.6	0.254	97.5
Ca(OH)_2 + NaOH, 30 mg/l	10.2	5.8	0.016	99.8

Table. 2 : Results of various precipitating agents in removal of Cr(III) in synthetic sample, ($\text{Na}_2\text{S}_2\text{O}_5$ is used as a reducing agent , Cr(III) after reduction = 10 mg/l)

Precipitating agents of optimum dosage	Optimized pH of precipitation	Volume of sludge generated, ml/l	After precipitation process, Cr(III) mg/l	% removal of Cr(III)
Ca(OH)_2 , 40 mg/l	11.2	10.1	0.64	93.6
NaOH, 30 mg/l	9.2	18.4	0.05	95
Ca(OH)_2 + NaOH, 30 mg/l	9.8	3.0	0.00	100

From Table 1, NaOH produces large volume of sludge because sludge produced by NaOH is gelatinous in nature whereas sludge produced by Ca(OH)_2 is dense in nature. Combination of Ca(OH)_2 +NaOH of dosage 30 mg/l shows 99.8 % removal efficiency. From Table 2 , combination of Ca(OH)_2 +NaOH produced less volume of sludge with higher 100 % removal of Cr(III) . The optimum pH for (Ca(OH)_2 +NaOH) is lesser than that obtained from using Ca(OH)_2 and NaOH . Hence the combination (Ca(OH)_2 +NaOH) is considered the best precipitating agent in precipitation Cr(III).

The industrial waste water showed hexavalent chromium concentration of 26 mg/l, it was diluted to obtain concentration of Cr(VI) in the range of 10 mg/l. The diluted industrial waste water is treated with optimum dosage Ferrous sulphate and Sodium metabisulphite individually to convert Cr(VI) to Cr(III) and resulted partially treated waste water is subjected to precipitation process using previously used chemicals.

Table. 3: Results of various precipitating agents in removal of Cr(III) in effluent sample, (FeSO₄ is used as a reducing agent , Cr(III) after reduction = 10 mg/l

Precipitating agents of optimum dosage	Optimized pH of precipitation	Volume of sludge generated, ml/l	After precipitation process, Cr(III) mg/l	% removal of Cr(III)
Ca(OH) ₂ , 40 mg/l	11.8	85.9	0.99	90.1
NaOH, 30 mg/l	9.8	15.4	0.28	97.2
Ca(OH) ₂ + NaOH, 30 mg/l	10.5	36.0	0.03	99.0

Table. 4: Results of various precipitating agents in removal of Cr(III) in effluent sample, (Na₂S₂O₅ is used as a reducing agent , Cr(III) after reduction = 10 mg/l)

Precipitating agents of optimum dosage	Optimized pH of precipitation	Volume of sludge generated, ml/l	After precipitation process, Cr(III) mg/l	% removal of Cr(III)
Ca(OH) ₂ , 40 mg/l	11.6	14.7	0.98	90.2
NaOH, 30 mg/l	9.5	22.6	0.59	94.1
Ca(OH) ₂ + NaOH, 30 mg/l	10.2	10.5	0.04	99.6

From Table. 3 and Table. 4, almost 100 % removal of Cr (III) is achieved for combination of Ca(OH)₂+NaOH with minimum volume of sludge

4.0 CONCLUSION

As compared to Ferrous Sulphate, Sodium metabisulphite is more efficient in Reducing Cr (VI) to Cr (III). Optimum Dose requirement of Ferrous Sulphate is more 1000 mg/l ,while that of Sodium metabisulphite is only 100 mg/l. Ferrous Sulphate requires pH =1.0 for complete reduction as compared to Sodium metabisulphite which requires a pH of about 2.0. Reduction time required for Sodium metabisulphite is only 50 mins whereas for Ferrous Sulphate at least 75 mins reduction time is required. Combination of Ca(OH)₂ and NaOH of optimum dose 30 mg/l is the most efficient for precipitation of Cr(III) to Cr(OH)₃ at pH 10.5 and 10.2 with Cr(III) removal efficiency of and with minimum volume of sludge produced 36.0 ml/l and 10.5 ml/l. From results it can be concluded that combination of Calcium hydroxide and Sodium hydroxide is the best precipitating agent for chromium removal.

REFERENCES

- [1]. Hossain M.A, Alam M. and Yonge D.R., Estimating the dual-enzyme kinetic parameters for Cr (VI) reduction by *Shewanella oneidensis* MR-1 from soil column experiments., *Water Research*, 39, 3342–3348, (2005).
- [2]. Viamajala S., Peyton B.M., Apel W.A. and Petersen J.N., Chromate reduction in *Shewanella oneidensis* MR-1, Is an inducible process associated with anaerobic growth., *Biotechnology. Prog.*, 18, 290–295, (2002)
- [3]. Arumugam V., Recovery of chromium from spent chrome tan liquor by chemical precipitation, *Indian J. of Environmental Health*, 39(2), 192-198, (1976).
- [4]. MINAS, Pollution control acts, rules, and notification there under Central Pollution Control Board, Ministry of Environment and Forests, Government of India, New Delhi, 2011.
- [5]. Water discharge standard of Central Pollution Control Board . ISI, 1991. Methods of sampling and test (Physical and chemical) for water and waste water: 3025: IS 105005. Indian Standard, Drinking water-specification (first revision). 1991. IS 10500.
- [6]. B.H. Hintermeyer, N.A. Lacour, A.Perezpadilla, and E.L.Tavani,, 2008, "Separation of the chromium(III) present in a tanning waste water by means of precipitation, reverse osmosis and adsorption" *Latin American Applied Research*, vol.38, pp.63- 71, 2008
- [7]. J. Kotai. Z. Stasicka. Chromium Occurrence in the Environment and Methods of its Speciation. ELSEVIER. Amsterdam.107, 2000 (263- 283)
- [8]. Tiwari D.P. et.all., Removal of toxic metals from electroplating industries, *Indian J. of Environmental Health*, 31(2), 122-126, (1989).
- [9]. R.S. Karale, D.V.Wadkar and P.B.Nangare, Removal and Recovery of Hexavalent Chromium from Industrial Wastewater by precipitation with due consideration to cost optimization, *Journal of Environmental Research and Development*, Volume 2(2), pp 209-216, 2007.
- [10]. Standard Methods for the Examination of Water and Wastewater, American Public Health Association (APHA), the American Water Works Association (AWWA), and the Water Environment Federation (WEF) Publication, 2006