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Remmoval Of Hexavalent Chromium From Industrial Waste Water By Chemical Treatment

Sowmya T.P
Department of Chemical Engineering, Dayanandasagar College of Engineering, Bangalore
Prof. G.K. Mahadevraju
Department of Chemical Engineering, Dayanandasagar College of Engineering, Bangalore
A. Ramesh
Senior Environmental Officer , Karnataka Pollution Control Board, Bangalore
V. Sreenivas
Eco Green Solution Systems (P) LTD, KIADB Industrial Area, Veerapura Post, Doddaballapura , Bengaluru

Abstract:

Chromium is one of the heavy metal coming from various industries having high toxicity. The compounds of chromium especially Cr (VI) are known to be detrimental to human beings and animals. Extensive chemical analysis was done to detoxify Cr (VI) by reducing it to Cr (III) by using reducing agents such as ferrous sulphate and sodium metabisulphite, and the precipitation of chromium hydroxide by addition of base. Also experiments were conducted to study the effect of reduction time and pH on the reduction of chromium for various reducing agents. In this work, hexavalent chromium is removed by reduction and precipitation reaction, by using Ferrous sulphate ($FeSO_4$) and Sodium metabisulphite ($Na_2S_2O_5$) as reducing agents to convert Cr(VI) to Cr(III) and Calcium hydroxide ($Ca(OH)_2$), Sodium hydroxide (NaOH) and combination of Calcium hydroxide, Sodium hydroxide are used as precipitating agents to precipitate Cr(III) as hydroxides. The reduction reaction is conducted at low pH (<3) and precipitation reaction is carried out high pH (>8). Because hexavalent chromium is stable under oxidizing conditions, whereas trivalent chromium is stable under reducing conditions. The purpose of this work is to compare the effect of chemicals in the reduction and precipitation reactions of waste water on pH values.

***Key words** : Chromium removal, Reducing agents, Precipitating agents, Hexavalent chromium Cr(VI) ,Trivalent chromium Cr(III), Industrial waste water*

1. Introduction

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 [1]. Hexavalent chromium has been reported to be toxic to animals and humans and it is known to be carcinogenic. Its concentrations in industrial wastewaters range from 0.5 to 270.000 $mg \cdot l^{-1}$ [2,3] . The tolerance limit for Cr(VI) for discharge into inland surface waters is 0.1 $mg \cdot l^{-1}$ and in potable water is 0.05 $mg \cdot l^{-1}$ [4,5]. In order to comply with this limit, it is essential that industries treat their effluents to reduce the Cr(VI) to acceptable levels. A number of treatment methods for the removal of metal ions from aqueous solutions have been reported, mainly reduction, ion exchange, electrodialysis, 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.

2. Experimental Procedure

2.1. Preparation of Synthetic hexavalent chromium sample and analysis of hexavalent chromium concentration

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. 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-diphenylcarbazide to form 1,5-diphenylcarbazone.Test results are measured at 540 nm.

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 pH for hexavalent chromium reduction Cr(VI) from synthetic sample

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

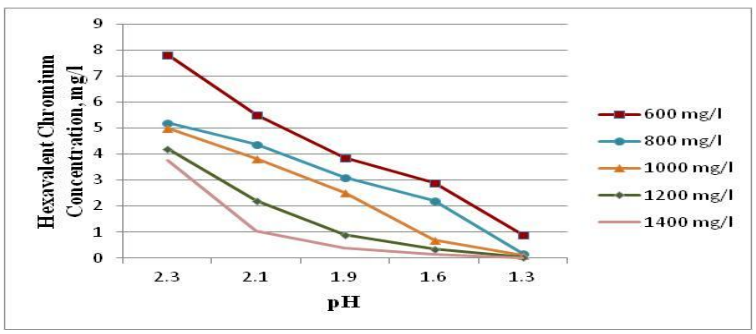

Figure1 : Effect of pH on concentration of Cr(VI) by using Ferrous sulphate.

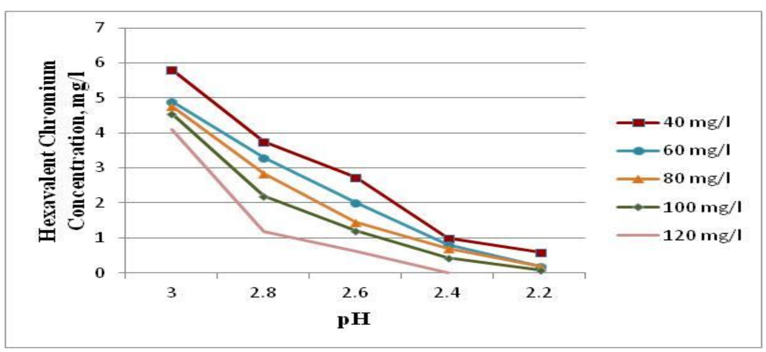

Figure 2 : Effect of pH on concetration of Cr(VI) by using sodium metabisulphite

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 of various dose ranging from 600 mg//l , 800 mg/l, 1000 mg/l, 1200 mg/l and 1400 mg/l was added to each beaker in increments to determine optimum pH and reduction time. After reduction process, the sample was analysed to know hexavalent chromium concentration .Similarly, reduction was carried for sodium metabisulphite for various dose ranging from 40 mg/l, 60 m/l, 80 mg/l, 100 mg/l and 120 mg/l. In case of Ferrous Sulphate 120 min was regarded as the Optimum Reduction period for comparison between various doses of Ferrous sulphate. Similarly for Sodium metabisulphite 80 min should be regarded as the Optimum Reduction period.

As from Fig .1 it can be seen that the concentration of hexavalent chromium decreases as the pH is lowered. For Ferrous sulphate at pH value 1.3 the complete reduction of hexavalent chromium trivalent chromium takes place . From **Fig.2** for Sodium metabisulphite, complete reduction of hexavalent chromium occurs at pH value 2.2

3.2 Precipitation of Cr (III)

After the complete reduction of hexavalent chromium from synthetic sample 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. The addition of precipitationg agents will raise the pH. In order to mix the solution, sample were taken to jar apparatus and samples were mixed for 40 mins with speed of 120 rpm. The precipitate formed was allowed to settle overnight. Supernatant was separated and analyzed for 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.

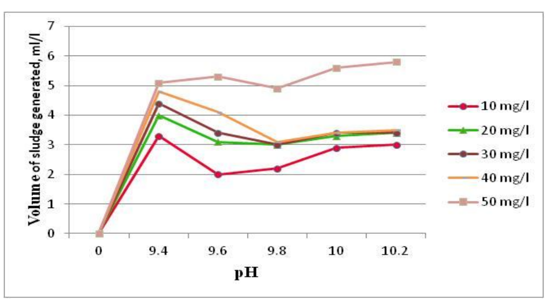

Figure3: Volume of sludge produced per litre under various pH conditions for $Ca(OH)_2$ + NaOH

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

Precipitating agents of optimum dosage	**Optim-ized pH of precip-itation**	**After precip-itation process, Cr(III) mg/l**	**% removal of Cr(III)**
$Ca(OH)_2$, 40 mg/l	11.8	0.823	91.77
NaOH, 40 mg/l	9.0	0.409	95.91
$Ca(OH)_2$+ NaOH, 40 mg/l	10.4	0.001	99.99

Table 1 : Results of various precipitating agents in removal of Cr(III) in synthetic sample, (Cr(III) after reduction = 10 mg/l)

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 40 mg/l shows 99.99 % removal efficiency. The optimum pH for ($Ca(OH)_2$+NaOH) is lesser than that obtained from using $Ca(OH)_2$ and NaOH seperately. Hence the combination of ($Ca(OH)_2$+NaOH) is considered the best precipitating agent in precipitation Cr(III).

The industrial waste water showed hexavalent chromium concentration of 48 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.

Precipitating agents of optimum dosage	**Optim-ized pH of precipitation**	**After precip-itation process, Cr(III) mg/l**	**% removal of Cr(III)**
$Ca(OH)_2$,40 mg/l	12.0	1.1	89.0
NaOH, 40 mg/l	10.2	0.601	93.99
$Ca(OH)_2$ +NaOH, 40 mg/l	10.9	0.22	97.0

Table. 2: Results of various precipitating agents in removal of Cr(III) in effluent sample Cr(III) after reduction = 10 mg/l

From Table. 3 almost 100 % removal of Cr (III) is achieved for combination of $Ca(OH)_2$+NaOH with minimum volume of sludge.

4. Conclusion

As compared to Ferrous Sulphate, Sodium metabisulphite is more efficient in Reducing Cr (VI) to Cr (III). Ferrous Sulphate requires pH =1.3.0 for complete reduction as compared to Sodium metabisulphite which requires a pH of about 2.2. Reduction time required for Sodium metabisulphite is only 80 mins whereas for Ferrous Sulphate at least 120 mins reduction time is required. Combination of $Ca(OH)_2$ and NaOH of optimum dose 40 mg/l is the most efficient for precipitation of Cr(III) to $Cr(OH)_3$ at pH 10.4 with Cr(III) removal efficiency of 99.99% and with minimum . From results it can be concluded that combination of Calcium hydroxide and Sodium hydroxide is the best precipitating agent for chromium removal.

5. Reference

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