HEXAVALENT CHROMIUM REMOVAL FROM INDUSTRIAL WATSEWATER BY CHEMICAL PRECIPITATION METHOD

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Abstract
This study was undertaken to investigate the removal of total chromium (Both Hexavalent and Trivalent) from synthetic and industrial effluents by chemical means in order to achieve the 100% removal efficiency. The study was conducted in three phases. In phase 1, the optimum pH, effective dosage and reaction time were optimized using Sodium Metabisulphite as reducing agent for the reduction of hexavalent chromium to trivalent chromium. As a result, pH of 2 and dosage of 80 mg/l was found to be optimized condition for the Cr(VI) reduction. Phase 2 studies were carried out to evaluate the potential of different precipitating agents in removal of Cr(III). In the Phase 2 studies optimum conditions for various precipitating agents were obtained. In phase 3 the experiments were carried out on industrial wastewater for the removal of hexavalent and trivalent chromium with the optimum operating conditions which were obtained from phase 1 and phase 2. The results from phase 3 on industrial wastewater showed the results in par with the synthetic sample except for ferric chloride. The combination of sodium hydroxide and calcium hydroxide is found to be best precipitating agent with dosage of 100 mg/l at pH 7. The volume of sludge produced by the same is very minimal compared to other precipitating agents.

Key words- Chromium removal; Experimental Setup; Chemical sludge; Industrial wastewater

I. INTRODUCTION
As human needs increase and civilization changes, more and more finished products of different types are required. Accordingly, large number of industries born and grown in every country[1] Process waste streams from the mining operations, metal-plating facilities, power generation facilities, electronic device manufacturing units, and

tanneries may contain heavy metals at concentrations exceeding the local discharge limits. These waste streams contain toxic heavy metals such as chromium, cadmium, lead, mercury, nickel, and copper. They are not easily removed without specialized or advanced treatment. Chromium is a common pollutant introduced into natural waters due to the discharge of a variety of industrial wastewaters. On the other hand, chromium based catalysts are also usually employed in various chemical processes, including selective oxidation of hydrocarbons. In India and all over the world, Chromium (Cr) is dominant in most of the effluent streams as compared to other heavy metal ions [2]. Caio F etal found that a reduction of more than 1.0 X 10^5 and 4.0 X 10^5 fold in total chromium and hexavalent chromium concentrations, respectively, was observed by employing steel wool masses as low as 0.4420 g to 30 ml solutions of wastewater [3].The optimum pH for the precipitating chromium from tannery wastewater is 7.7-8.2 with a lime concentration (2g/100ml) and the effective settling rate was 120min. The bioremoval of Cr (VI) using actinomycetes is a suitable mean for reducing the tannery wastewater toxicity. The combination between the chemical precipitation and the biological removal of chromium from tanning wastewater make it meet the environment safely [4].The percent removal of metal ions increases to about 99 % with increasing the MgO dose to some limits. The optimum values of MgO doses were found to be 1.5-3.0 g/l. The pH value ranges are 9.5 to 10 with MgO precipitant and pH of 11.5 to 12 with CaO precipitant [5][6]. Combinations of ferric chloride and polymer at different ratio will also results in better removal efficiencies of the metals in the range 84 – 97% for total chromium, 69-90% for zinc and 69-72% for total iron, also less sludge was produced [7]. There are many factors which affect the efficiency of precipitation (pH, nature and concentration of hazardous substances in water, precipitant dosage, temperature, water balance etc.,). In practice, the optimum precipitant and dosage for a particular application are determined by a “trial and error” approach using Jar test [8]. Moreover Ferrous sulphate requires pH =1for complete reduction as compared to sodium metabisulphite which requires a pH of about 2 [9].

II. MATERIALS AND METHODOLOGY

A. Preparation of Synthetic hexavalent chromium sample
The potassium dichromate ($K_2Cr_2O_7$) is used as source of hexavalent chromium. A stock solution of 1000mg/l of Cr(VI) is prepared by dissolving 2.8287g of potassium dichromate in 1000ml distilled water. The solution is diluted as required to obtain standard solutions containing 10-15mg/l of Cr(VI). pH adjustments were carried out using Sulphuric acid and sodium hydroxide.

B. 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 di phenyl carbazide in acidic condition solution as a complexing agent. The absorbance of the red – violet coloured solution is read at 530 nm- 540 nm after 20 mins [10].

C. Analysis of Total Chromium:

Atomic absorption spectrophotometer A203 Version -04 was used to measure the total chromium concentration. In AAS fuel used was acetylene C_2H_2 and the oxidant used was air or Nitrous oxide for strong flames. Calibration of the 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.

Precipitat-ing Agents	After Precipitat-ion Process Cr(III), mg/l	% Removal of Cr(III)	Sludge Volume generat-ed in ml/l	pH of waste-water after treatme-nt
NaoH	0.34	96.6	12	8.90
$Ca(OH)_2$ +NaoH	0.03	99.7	07	9.42
$FeCl_3$	3.49	65.1	20	3.09

The experiments were carried out under different pH condition and different dosage of Sodium MetabiSulphite and precipitating agents providing different contact time. The experimental set up is as shown in the fig 1.

III. RESULTS AND DISCUSSIONS

A. Optimum condition for chromium (VI) Reduction:

Sodium Metabisulphite is used as reducing agent for hexavalent chromium reduction. Jar test method has been used to determine the effects of each parameter (Six

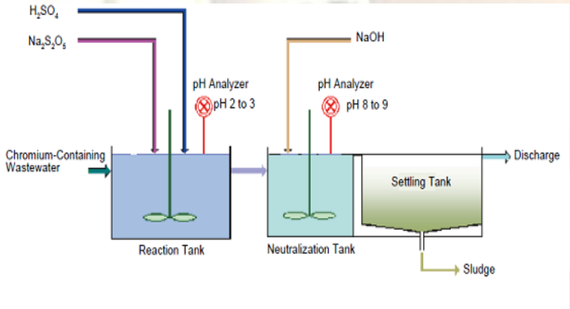

Figure 1: Experimental Setup

beakers have been used for each stage) and 500ml of synthetic sample was added to the each beaker. Sodium metabisulphite is added to each beaker to determine the optimum dosage, pH and contact time. The pH of the sample is maintained using sulphuric acid with mixing speed of 50 rpm. The sample was analyzed to know the hexavalent chromium concentration after reduction process.As a result, pH of 2 and dosage of 80 mg/l was found to be optimized condition for the Cr(VI) reduction at contact time of 5 mins.

D. Optimum condition for chromium (III) Precipitation:

After the complete reduction of hexavalent chromium the precipitating agents viz., Sodium Hydroxide (NaOH), Combination of Sodium Hydroxide and Calcium Hydroxide ($Ca(OH)_2$+NaOH) and ferric Chlorides ($FeCl_3$) were added to each sample separately. In order to mix the solution, sample were taken to jar apparatus and samples were mixed for 5 Mins with the speed of 100 rpm as first step. In the next step samples were mixed for 25 mins with the speed of 20-30 rpm. The precipitate formed was allowed to settle completely. Supernatant was withdrawn from the beaker and analysed for hexavalent chromium and total chromium.

From the results of synthetic samples the optimum operating conditions for different precipitating agents were recorded. The best operating conditions are shown in table 1. The experimental results for chromium removal using combination of NaOH and $Ca(OH)_2$ are shown in Fig 2-4. The effect of pH on the chromium precipitation using combination of NaOH and $Ca(OH)_2$ is as shown in Fig 2. Also the volume of sludge produced and variation in pH after the treatment are shown in the Fig 3 and 4. Fig 5 shows the efficiency of sodium hydroxide,

Table 1.Summary of results of various precipitating reagents in removal Cr(III) in Synthetic Sample. (Concentration of Cr(III) in synthetic sample after reduction process = 10mg/lt)

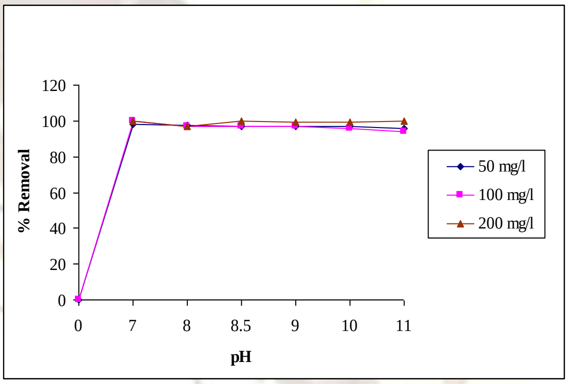

Figure 2: Effect of pH on Cr (III) precipitation using $Ca(OH)_2$ + NaoH

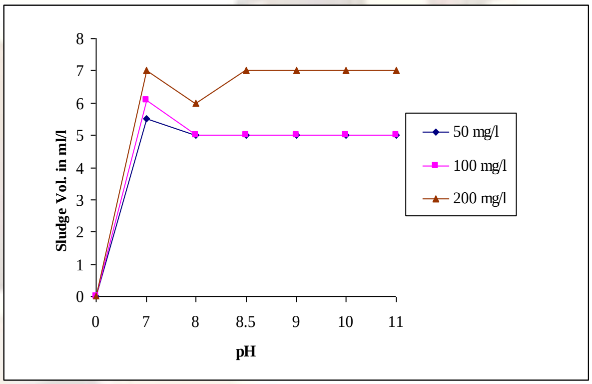

Figure 3: Volume of sludge produced per litre under various pH conditions for $Ca(OH)_2$ +NaOH

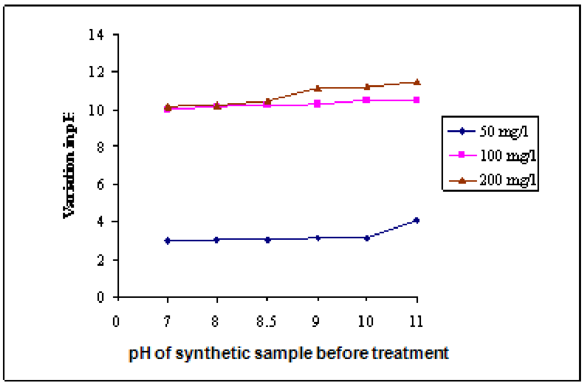

Figure 4: Variation in pH of synthetic sample after the treatment with Ca $(OH)_2$ + NaOH

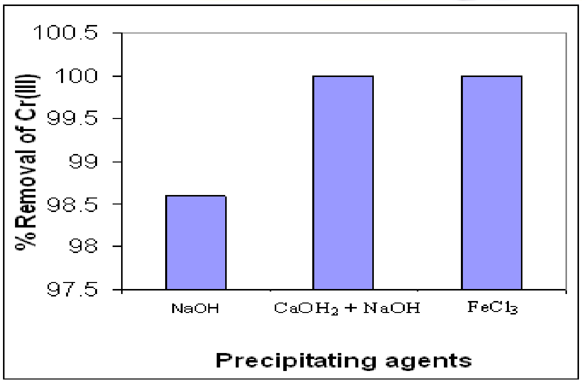

Figure 5: Variation in % Removal of Cr(III) in Synthetic Sample for various precipitating

combination of NaOH and $Ca(OH)_2$ and Ferric chloride in removing chromium. Both combination of NaOH and $Ca(OH)_2$ and Ferric chloride shows the 100 % chromium removal efficiency. The variation in pH and Volume of sludge produced has also been recorded (Fig 6 and 7). Compare to all NaOH produced large volume of sludge since because sludge produced by NaOH is gelatinous and light in nature but whereas sludge produced by Ferric chloride in voluminous with dense in nature. The combination of NaOH and $Ca(OH)_2$ has produced minimum volume of sludge compared to other two. Hence the combination of NaOH and $Ca(OH)_2$ is considers as best precipitating agent among three in precipitation of chromium.

A number of comparative experiments were conducted in third phase on industrial wastewater. The typical industrial wastewater characteristics showed higher concentration of hexavalent chromium concentration as 3222.6 mg/lt. Firstly industrial wastewater was diluted to obtain concentration of Cr(VI) in the range 10 mg/lt.

Precipi-tating Agents	After Precipita-tion Process Cr(III), mg/l	% Removal Cr(III)	Sludge Volume Genera-ted in ml/l	pH of synthetic sample after treatment
NaOH	0.14	98.6	28	8.90
$Ca(OH)_2$+ NaOH	00	100	6.1	10
$FeCl_3$	00	100	22	6.85

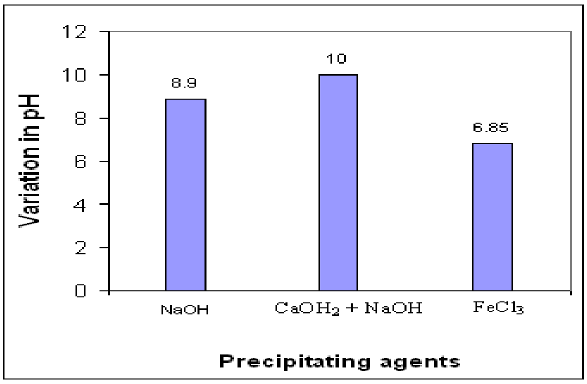

Figure 6: Variation in pH of synthetic sample for various Precipitating agents

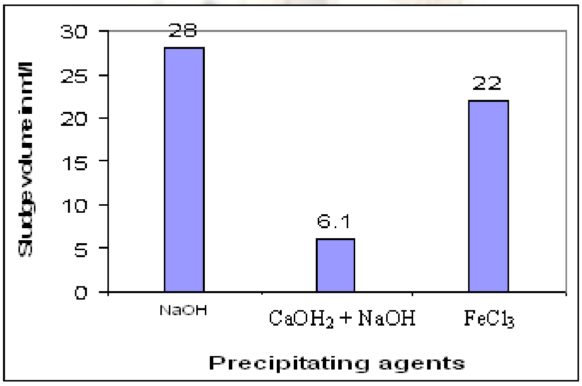

Figure 7: Variation in Volume of Sludge produced in ml/l for Various Precipitating agents

The diluted industrial wastewater is treated with the minimum required concentration of sodium metabisulphite to convert Cr(VI) to Cr(III) and resulted partially treated wastewater is subjected to precipitation process using previously used chemicals.

Almost 100% removal efficiency has been achieved for the precipitating agents NaOH + $Ca(OH)_2$ combination. The results obtained are in par with the results recorded for the experiments which were conducted on the synthetic sample. But in case of Ferric Chloride only 65% removal has been achieved and the resulted concentration has not met the effluent disposal standards. For the same dose and operating condition the removal efficiency in synthetic sample was 100%. The variations in pH values after the treatment are also follows the same trend as in case of synthetic wastewater except for Ferric Chloride. A pH of 3.49 has been recorded for industrial wastewater and is quite acidic condition compared to that of value 6.85 which was recorded for the synthetic sample. The figures 8 show the comparative results for chromium removal for industrial wastewater and synthetic sample.

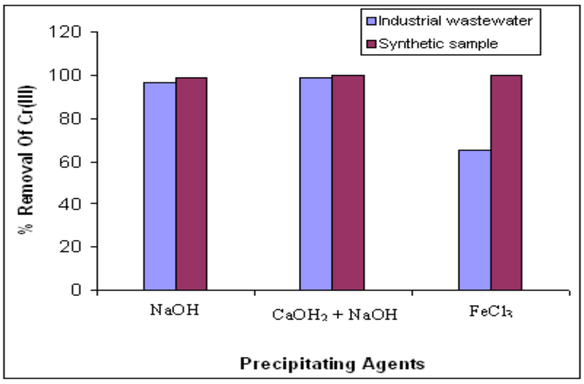

Figure 8: Comparison of % Removal Of Cr(III) in Industrial wastewater and synthetic sample after treatment

Table 2: Results of Precipitation of Trivalent Chromium in Industrial wastewater (Concentration of Cr(III) in Industrial wastewater after reduction process = 10mg/lt)

The variation in pH in industrial wastewater for various precipitating agents has shown in the Fig 9. The volume of sludge produced has been recorded and tabulated in the Table 2 and also shown in the Fig 10 .The volume of sludge collected for all precipitating agents are inline with the results which were recorded for synthetic sample except in the case of NaOH. Synthetic sample treated with NaOH shows the volume of sludge produced as 28 ml where as for actual industrial wastewater it is only 12 ml. The variation in chromium removal efficiency was found to be very minimum except for ferric chloride. The Cr(III) removal efficiency achieved using Ferric chloride was only 65%.

The variation in pH for industrial wastewater and synthetic sample was observed more in case of ferric chloride. The combination of NaOH and $Ca(OH)_2$ pH value obtained for industrial wastewater after the treatment is inline with pH value which is obtained for synthetic sample. The volume sludge produced for synthetic sample was found to be 28 ml/l and for industrial waste water it is 12 ml/l. Fig 10 shows the variation in volume of sludge produced for industrial wastewater and synthetic sample.

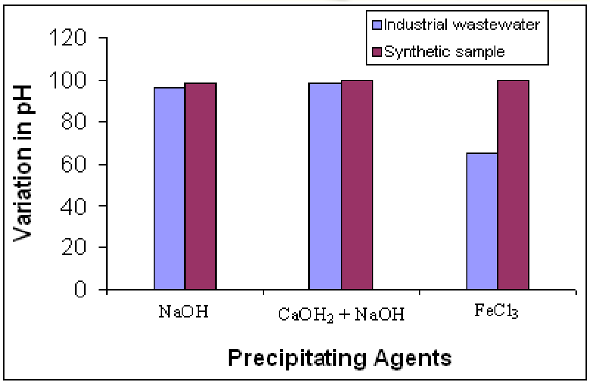

Figure 9: Comparison of Variation in pH in Industrial wastewater and synthetic sample after treatment

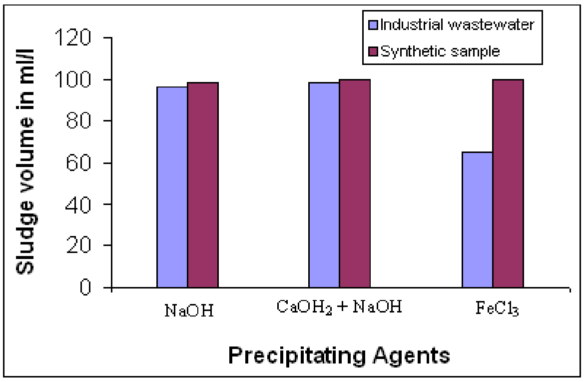

Figure 10: Comparison of volume of sludge generated in Industrial wastewater and synthetic sample after treatment

The results obtained for industrial wastewater after the treatment using sodium hydroxide and calcium hydroxide combination are in par with the synthetic sample results. The sodium hydroxide and calcium hydroxide combination shows the better removal efficiency with less volume of sludge compared to other precipitating agents.

IV. CONCLUSIONS

The pH of the sample and dosage of sodium metabisulphite has a strong effect on the reduction rate of hexavalent chromium. The pH value of 2 and contact time of 5 Mins with the dosage of sodium metabisulphite as 80 mg/l were found to be optimum operational parameters for the reduction of hexavalent chromium. The optimum dosage recorded are 100mg/l and 400mg/l of $Ca(OH)_2$ + NaOH and $FeCl_3$ respectively. Experiments on industrial wastewater show that, removal efficiency is in par with the efficiency obtained for synthetic sample experiments, except for Ferric Chloride. The Cr(III) removal efficiency using Calcium hydroxide and sodium hydroxide combination was found to be 99.7% and with volume of sludge produced as 7 ml/l. From results it can be concluded that the combination of Calcium hydroxide and sodium hydroxide is the best precipitating agent for chromium removal.

REFERENCES:

[1] N.Manivasakam, Industrial Effluents-Origin, Characteristics, effects and analysis and Treatment, Sakti Publication, 1997.

[2] Mojdeh Owlad, Mohamed Kheireddine Aroua , Wan Ashri Wan Daud and Saeid Baroutian, Removal of exavalent Chromium-Contaminated Water and Wastewater: A Review, Water Air Soil Pollution-Springer

[3] Caio F.Gromboni,George L.Donati,Wladiana O.Matos, Eduardo F.A.Neves,Ana Rita A.Nogueira and Joaquim A.Nobrega, Evaluation of metabisulphite and a commercial steel wool for removing chromium(VI) from wastewater,Environmental Chemistry Lett, Springer, 2010.

[4] Hesham M. Abdulla , Engy M. Kamal , Amr H. Mohamed and Ahmed D. El- Bassuony , Chromium Removal From Tannery Wastewater Using Chemical And Biological Techniques Aiming Zero Discharge

Of Pollution, Proceeding Of Fifth Scientific Environmental Conference, pp 171 – 183, 2010.

[5] Dr.Mahmood M. BrbootI, Dr. Balasim A. AbiD and Dr. Najah M. Al-ShuwaikI, Removal of Heavy Metals Using Chemicals Precipitation, Eng.& Tech. Journal,Vol.29 , No. 3 , pp 595 -612, 2011.

[6] Suresh Gupta, B. V. Babu, Economic feasibility analysis of low cost adsorbents for the removal of Cr(VI) from wastewater, pp 1-7

[7] Amuda.OS, Amoo.IA, Ipinmoroti.KO and Ajayi.OO, Coagulation/Flooculation process in the removal of trace metals present in industrial wastewater, Journal of Appl.Sci>Environ.Mgt.,Volume 10(3), pp 159-162, 2006.

[8] Robert Noyes, “Unit operations in environmental Engineering”, Noyes, Publications, 1994.

[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.