

A Comparative Study of the Removal Efficiency of Calcium Hydroxide and Sodium Hydroxide as Precipitating Agents for Chromium (III)

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Abstract: The extensive industrial application of chromium results in heavy pollution to the environment and dangerous effects to flora and fauna. Precipitation is rapid and most efficient method for the removal of metal ions from industrial effluents. We herein present a comparative analysis of two well known precipitating agents for the removal of Chromium (III) ion. Waste lime and sodium hydroxide are commercially available low cost chemicals, so these can be easily utilized as precipitating agents for industrial effluents treatment. The comparative studies are carried out for chromium removal under different experimental conditions viz. doses of precipitating agents, pH and settling time. The trivalent chromium removal efficiency using Calcium Hydroxide was found to be approx 76% and that using Sodium Hydroxide was found to be approx 90%. Hence, it can be concluded that the Sodium Hydroxide is better precipitating agent than Calcium Hydroxide for chromium ion removal from aqueous solution.

Keywords: Removal Efficiency; Calcium Hydroxide; Sodium Hydroxide; Trivalent Chromium.

1. INTRODUCTION

Water pollution is any chemical, physical or biological change in the quality of water that has harmful effects on any living thing that drinks or uses or lives in it. Water pollution occurs when pollutants are directly or indirectly discharged into water bodies without adequate treatment to remove harmful compounds. Heavy metals like chromium, nickel, copper, cobalt, manganese, mercury, lead, zinc, cadmium, silver, arsenic, and barium are most abundantly found in wastewater. Hexavalent chromium is a main pollutant because of its strong toxic, mutagenic and carcinogenic properties. Hexavalent chromium discharged into the water from industries such as leather tanning, metallurgy, refractory, and chemical manufacturing involving numerous commercial processes like paint and paper milling, mining, wood preservation, electroplating, and manufacturing of dye [1, 2].

Chromium has high toxicity and induces many harmful diseases to human beings and animals. So there is a need for developing an efficient method for its removal from effluent

water. The maximum levels permitted in drinking water are 5 mg/L for trivalent chromium and 0.05 mg/L for hexavalent chromium. Currently there are many methods applied for the removal of Cr(VI) from industrial effluents, which include chemical reduction–precipitation [3, 4], adsorption [5, 6], ion exchange [7, 8], membrane separation [9, 10] and biological reduction [11–12]. The chemical reduction–precipitation method is mostly adopted for treatment of Cr(VI); because hexavalent chromium usually exists in wastewater as an oxidizing anion and does not precipitate easily using conventional precipitation methods, hexavalent chromium is reduced to trivalent chromium using a reducing agent such as Ferrous Sulphate (FeSO₄), and subsequent precipitation of the trivalent chromium as chromium hydroxide by addition of base. In the present work we have carried out the comparative studies on chromium (III) removal by using two different precipitating agents: Calcium Hydroxide and Sodium Hydroxide.

2. MATERIALS AND METHODS

2.1 Materials

- Potassium Dichromate (Fisher Scientific), Sulphuric Acid (Qualikems Fine Chem. Pvt. Ltd.), Ferrous Sulphate (Qualikems Fine Chem. Pvt. Ltd.), Diphenyl carbazide (Fisher Scientific), Calcium Hydroxide (Fisher Scientific) and Sodium Hydroxide (Fisher Scientific) were used as received. Precipitating agents and all other chemical solutions used in the present study are certified AR grade chemical. All glasswares were soaked in tap water and then, rinsed with deionised water. Before being used, they were dried in an oven and cooled for further use.

2.2 Solutions

A stock solution of 1000 ppm Hexavalent Chromium ion was prepared by dissolving potassium dichromate (K₂Cr₂O₇) in distilled water. This stock solution was used for making

solutions containing different chromium ion concentration by dilution.

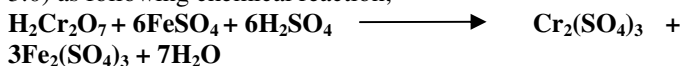
3. EXPERIMENTAL PART

3.1 Reduction of hexavalent chromium to trivalent chromium using reducing agent Ferrous Sulphate

The pH of the sample and dosage of reducing agent has a strong effect on the reduction rate of hexavalent chromium. Hexavalent chromium is reduced to trivalent chromium by using reducing agent. After reduction of Cr (VI) to Cr (III), Cr (III) was removed by precipitation by raising the pH of the sample on alkaline side using precipitating agents. For this purpose batch test apparatus was used.

Procedure: Many batches of 10 ml of 10 mg/l Hexavalent Chromium solution were taken in separate 100 ml volumetric flask. pH of solution was adjusted (pH<3.0) by adding 1-2 ml sulphuric acid. Varying doses of reducing agent were added in chromium solution for reduction of Cr(VI) to Cr(III). Diphenyl carbazide solution was used to analyze the remaining Cr concentration in the aqueous solution (about 250 mg of 1, 5-diphenylcarbazine was dissolved in 50 ml of acetone). After reduction of hexavalent chromium to trivalent chromium, the absorbance was measured and the % reduction of chromium was calculated. During reduction of Cr(VI) to Cr(III), pH of solution increased and pH of solution was adjusted by adding sulphuric acid (H₂SO₄).

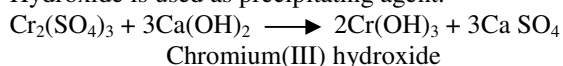
Hexavalent chromium reduced to trivalent chromium (at pH < 3.0) as following chemical reaction;



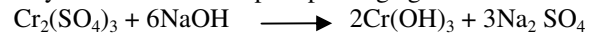
3.2 Chemical precipitation of trivalent chromium from wastewater as hydroxide using precipitating agents: Calcium Hydroxide [Ca(OH)₂] and Sodium hydroxide (NaOH):

Procedure: After reduction of hexavalent chromium to trivalent chromium, 10 ml portions of samples containing Cr (III) were taken in five 100 ml volumetric flask. Cr (III) was removed by precipitation by raising the pH of the sample on alkaline side using precipitating agents. Varying doses of precipitating agents were added in trivalent chromium solution. Precipitation of Cr(III) was observed at different pH values. The precipitation affinity of Chromium(III) is high on alkaline side. Maximum precipitation can be obtained in the pH range of 8.0 to 11.0. It is to be noted that the supernatant was analyzed after subsequent 0, 15, 30, 45 and 60 mins. of settling time and the optimum dose and optimum pH of precipitation are determined. The reactions involved in chromium precipitation are following:

1. Precipitation reaction [Cr⁺³ to Cr(OH)₃] when Calcium Hydroxide is used as precipitating agent.



1. Precipitation reaction [Cr⁺³ to Cr(OH)₃] when Sodium Hydroxide is used as precipitating agent.



4. RESULTS AND DISCUSSION

Comparative analysis of Calcium Hydroxide [Ca(OH)₂] and Sodium Hydroxide (NaOH) for precipitation of Trivalent Chromium:

Effect of Different Parameters

4.1 Effect of dose of precipitating agents

The removal efficiency of Cr(III) varies with the dose of precipitating agents. So it is very necessary to optimize the dose of precipitating agent. Therefore, a study determining the optimum dose for each precipitating agent was conducted to achieve maximum chromium precipitation at equilibrium condition. To find the effect of optimum dose on the removal efficiency of Cr(III), the amount of dose was varied from 100 to 1400 mg/l. Equilibrium condition was achieved by varying the dose at specified conditions. After certain time interval, the supernatant was collected for chromium analysis using a spectrophotometer. The amount of total Cr(III) removed was taken as the concentration difference between the originally added and the finally remaining or difference between initial absorbance and final absorbance. The removal efficiency of precipitating agent on Cr(III) (% Removal) was defined as follows as:

$$\% \text{Removal} = \frac{(C_o - C_1)}{C_o} \times 100$$

where: C_o and C₁ are the initial and final concentration of chromium (mg/l), respectively.

Or

$$\% \text{Removal} = \frac{(A_o - A_1)}{A_o} \times 100$$

where: A₀= Initial Absorbance and A₁=Final Absorbance

Cr removal efficiency was observed by adding varying doses of precipitating agents (100 to 1400 mg/l) in 10 mg/l of Cr solution. The removal performances of both precipitating agents were evaluated after one hour settling time. It has been inferred from the experiment that less amount of sodium hydroxide is required than Calcium Hydroxide for the precipitation from same initial concentration of chromium solution.

The results, presented in Fig.1, shows that the removal efficiency of Calcium Hydroxide progressively increases from 19 to 76% with an increase in the amount of dose from 100 to

1400 mg/l; beyond this dose, the removal efficiency of Sodium Hydroxide was 58 to 90%. Here we can see that sodium hydroxide is better precipitating agent.

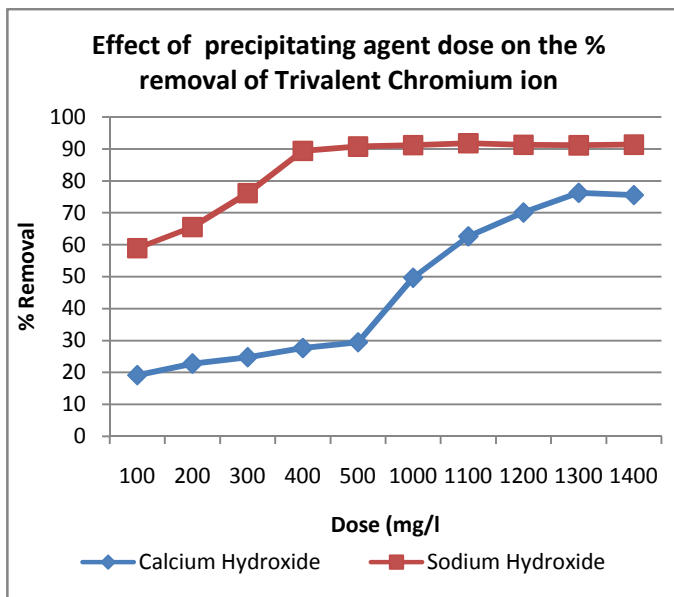


Figure 1: Effect of precipitating agent dose on % removal of trivalent chromium ion

4.2 Effect of pH

Prior studies have indicated that awareness of the optimum pH is very important as pH is considered as the most influencing factors in the chemical precipitation. pH of waste water was increased due to addition of reducing agent. Cr(VI) converted to Cr(III) and Cr(III) precipitated when the pH of solution reached above 7. The pH of solution was measured prior to the addition of precipitating agent and again measured at the end of reaction.

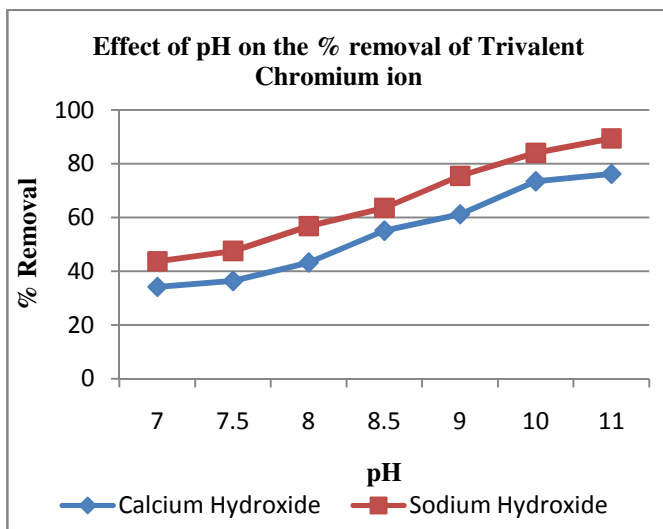


Figure 2: Effect of pH on % removal of trivalent chromium ion

Cr(III) can be precipitated in alkaline state. So it is necessary to maintain the pH of solution 7 or above 7 for better precipitation. Cr removal efficiency of both precipitating agents was strongly dependent on pH. At optimum dose and at different time intervals, pH of chromium solution was increased when precipitating agent was added in Cr solution. At optimum dose, % removal increases with increasing pH. Maximum precipitation can be obtained in the pH range of 8.0 to 11.0.

At optimum dose of precipitating agent and at different time intervals Fig. 2 shows that the removal efficiency of Calcium Hydroxide increased from 34 to 76% as pH increases from 7.0 to 11.0 and removal efficiency of Sodium Hydroxide was increased from 43 to 89% as pH increases from 7.0 to 11.0. Hence it is observed that Sodium Hydroxide is better precipitating agent than Calcium Hydroxide for precipitation of trivalent chromium ion.

4.3 Effect of settling time

As the reaction proceeds, the amount of precipitate increases as small size precipitate gets adhered together and lead to maximum precipitation, sometimes other chemical entities (ions and molecules) also get adhered with precipitate and mass of precipitate increases. When the reaction mixture is kept for settling, the removal of chromium ion increases with increase of settling time. The effect of settling time on the Cr removal efficiency of precipitating agents (Calcium Hydroxide and Sodium Hydroxide) was observed by performing the experiments with an initial Cr concentration of 10 mg/l. This study was conducted at optimum conditions of dose and pH.

Fig. 3 shows that at optimum dose of precipitating agent the removal efficiency of Calcium Hydroxide increased from 55 to 76% as settling time varies from 15 to 60 min and removal efficiency of Sodium Hydroxide was also increased from 64 to 89% as settling time varies from 15 to 60 min. It is observed that Sodium Hydroxide removed more chromium from chromium solution in comparison with Calcium Hydroxide. Hence Sodium Hydroxide is better precipitating agent for removal of trivalent chromium ion.

5. CONCLUSION

Both precipitating agents Sodium Hydroxide (NaOH) and Calcium Hydroxide {Ca(OH)₂} are inorganic bases. The solution of Calcium Hydroxide in water is a medium strength base that reacts with acids and attacks many metals whereas sodium hydroxide is well known strong base and reacts with metals and metal ions aggressively. The solubility of Sodium Hydroxide in water is 111 g/100 mL (at 20°C) and the solubility of Calcium Hydroxide in water is 0.173 g/100mL (at 20°C). The dosage of reducing agent Ferrous Sulphate (FeSO₄) and pH of the sample has strong effect on the

reduction rate of Hexavalent Chromium ion. If pH is low (around $2.0 < 3$) then solution is highly acidic. The dosage of Ferrous Sulphate as 1500 mg/l at pH value of 2.0 and contact time 60 mins were found to be optimum operational parameters for the reduction of Hexavalent Chromium to Trivalent Chromium. The precipitating agents Calcium Hydroxide and Sodium Hydroxide were used for precipitating the Trivalent Chromium as hydroxides on alkaline side. The optimum dosage of Calcium Hydroxide and Sodium Hydroxide are recorded as 1300 mg/l and 400 mg/l respectively. The removal efficiency using Calcium Hydroxide was found to be approx 76% and the removal efficiency using Sodium Hydroxide was found to be approx 90% for trivalent chromium removal from wastewater. Hence it can be concluded that the Sodium Hydroxide is better precipitating agent than Calcium Hydroxide for chromium ion removal from aqueous solution.

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