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REDUCTION OF OBNOXIOUS Cr(VI) FROM ELECTROPLATING EFFLUENTS BY HYDRAZINE: KINETIC OPTIMIZATION AND MECHANISTIC MODELING FOR WASTEWATER TREATMENT

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Abstract

The simple way to deal with obnoxious hexavalent chromium is to reduce it to its trivalent form, which is comparatively less toxic. In this article, Cr(VI) was reduced to Cr(III) using hydrazine. The effect of various process parameters such as molar ratios of Cr(VI) to N_2H_4, the temperature of the reaction, and the environmental chemistry of solution on the reduction kinetics have been evaluated. Experiments demonstrate an order of three for the reaction. The reaction was first order with respect to N_2H_4 and second order with respect to Cr(VI). A very high percent reduction of 96.8% was obtained at 50°C for the Cr(VI) to N_2H_4 molar ratio of 1:5. The reduction rate constants increased with an increase in temperature, and the activation energy of 35.22 kJ/mol was calculated for the reaction. The sludge generated because of the precipitation of insoluble $Cr(OH)_3$ was characterized using FTIR, XRD, and FESEM.

Keywords: chromium, heavy metals, pollutant, reduction kinetics, wastewater

Received: February, 2020; Revised final: June, 2020; Accepted: July, 2020; Published in final edited form: January, 2021

1. Introduction

The vast application of hexavalent chromium in a wide range of applications has led to the release of toxic Cr(VI) into the wastewater (Yan et al., 2018). The hexavalent form of chromium is highly environment unfriendly. Cr(VI) is carcinogenic to living organisms and may lead to various diseases (Jabłońska-Czapla and Szopa, 2016). The major diseases caused are cancer, kidney and liver damage, and damage to the gastric system (Dubey and Gopal, 2009a). The natural oxidation of Cr(III) to Cr(VI) is a prolonged process and occurs because of pollution (Di Palma et al., 2015). The problem with hexavalent chromium is that it is structurally very analogous to a human metabolite (SO_4^{2-}). As a result, it can penetrate the cell wall and disrupt the mechanism. The maximum discharge limit of Cr(VI) and Cr(III) are 0.05 and 5 mg L^{-1} (Verma and Balomajumder, 2020).

Many chemicals can be used as reducing agents for the conversion of hexavalent to trivalent chromium such as zero-valent iron-based reagents (Zhou et al., 2018), nanoscale zero-valent iron (nZVI), ferrous sulfate (Di Palma et al., 2015), ferrous ammonium sulphate (Di Palma et al., 2015), ferrous sulphide (Patterson et al., 1997), calcium polysulphide (Chrysochoou et al., 2012), hydrogen sulphide, sodium metabisulphite (Ramakrishnaiah and Prathima, 2012), bisulphite, thiosulphite, organic reagents, glucose, and molasses (Mohan and Pittman, 2006). The major disadvantage of using conventional reducing agents such as sodium metabisulphite, ferrous sulphate, and ferrous ammonium sulphate is the large volume of sludge generated and the introduction of other ions, such as SO_4^{2-} and Cl^-, which are difficult to separate. Ferrous pentacarbonyl, which is also reported to reduce Cr(VI), is an acute poison.

This article aims at exploring hydrazine for Cr(VI) reduction, which is very less reported in the

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literature. The effect of various process parameters has been demonstrated, and the reduction kinetics have been developed. The study of reduction kinetics is important since it controls the equilibrium time and influences the reduction mechanism. The kinetic study helps in the design of the reactor.

2. Experimental methodology

2.1. Materials

All the materials used to conduct the experiment were of reagent grade. The glassware was washed with Millipore water before usage. The electroplating wastewater was obtained from Bharat Electronics Limited, India.

2.2. Batch reduction experiment

The reduction experiment was tested as a function of several process parameters such as pH (2-10); Temperature (25°C to 50°C), and the molar ratio of Cr (VI) to N_2H_4 (1:2 to 1:5). The electroplating wastewater was mixed with hydrazine and put on a magnetic stirrer for a definite period. The pH of the solution was varied using 0.1 N NaOH and 0.1 N H_2SO_4.

2.3. Analysis of Cr(VI) and characterization of sludge generated

The filtrates were analyzed for their hexavalent chromium concentration using the standard Diphenyl-Carbazide method at a wavelength of 540 nm with a UV Spectrophotometer (Model: HACH DR-5000, HACH Co., USA). The surface micromorphology of the sludge was investigated using a high-resolution Field Emission Scanning Electron Microscope (FESEM). The FTIR spectra of the sludge were obtained using a Perkin- Elmer BX series FT-IR-5000 spectrophotometer (Perkin Elmer, Nicolet, USA). Also, XRD analysis was carried out in a Bruker D8 advance present at the Institute instrumentation center at an angle range of $5° – 90°$. All the characterizations were performed at the Institute Instrumentation center, IIT Roorkee, Roorkee, India.

2.4. Analysis of electroplating effluent

The electroplating effluent was characterized using a UV spectrophotometer by using the DPC method at 540 nm. The cations, as well as anions, were analyzed using Ion Chromatography at the Department of Chemical Engineering, IIT Roorkee. All other heavy metals were analyzed using Inductively Coupled Plasma Mass Spectroscopy at the Institute Instrumentation Center, IIT Roorkee.

3. Results and discussions

3.1. Analysis of electroplating effluent

Due to the use of chromium trioxide in chrome plating performed at the electroplating facility, the effluent contains a considerable amount of Cr(VI). The Cr(VI) concentration found in electroplating effluent was around 120 mg/L. The pH of the effluent was 2, and the concentration of nickel, aluminum, iron, and copper in the effluent were 11.25 mg/L, 10.42 mg/L, 3 mg/L and 2 mg/L, respectively.

3.2. The molar ratio of Cr(VI) to N_2H_4

To study the change caused by varying amounts of N_2H_4 added into the solution, the molar ratio has been varied from 1:2 to 1:5, and the trend is shown in Fig. 1. It is easily deduced that more than 65 percent of hexavalent chromium has been reduced in the first 20 minutes. As expected, the percent reduction is increased by increasing the amount of N_2H_4 in the reaction. The removal efficiency of Cr(VI) has been calculated as 72.2%, 86.4%, 89%, and 91.6% for molar ratios of 1:2, 1:3, 1:4, and 1:5 respectively. Also, it has been noticed that when the molar ratio was increased beyond 1:12, almost all Cr (VI) was removed in about 40 minutes, even at room temperature. The reaction between Cr(VI) and N_2H_4 is as follows (Eq. 1):

$$4CrO_4{}^{2-} + 3N_2H_4 + 4H_2O \rightarrow 3N_2 + 20OH^- + 4Cr^{3+}$$
(1)
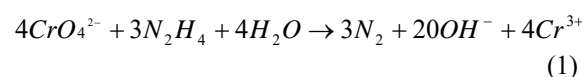
Theoretically, the amount of N_2H_4 required to reduce 1 mole of Cr(VI) completely is 0.75 mol. However, amounts much more than this are needed to reduce Cr(VI) completely. This is because the dissolved oxygen present in the solution might consume a part of hydrazine.

3.3. Effect of temperature on the reduction of Cr(VI)

Temperature also affects the reduction kinetics of hexavalent chromium, as can be seen from Fig. 1. The percent reduction has been increased from 72.2% to 78%; 86.4% to 88.2%; 89% to 92%; and 91.6% to 96.8% for molar ratios of 1:2, 1:3, 1:4 and 1:5 at 25°C, 35°C and 50°C. At higher temperatures, the kinetic energy of Cr(VI) ions in the solution is high, and consequently, there is a higher chance of collisions between the Cr(VI) ions and hydrazine molecules.

3.4. Effect of pH on the reduction of Cr(VI)

The most pivotal part is played by the pH of the solution on the reduction, as can be seen in Fig. 2. Adding N_2H_4 to chromium solution raises the pH from 5.5 (pH of 100 PPM Cr(VI) solution) to around 10. The pH was varied by adding a requisite amount of 0.1N H_2SO_4. It was discovered that the maximum percent reduction of Cr(VI) was attained at a lower pH. The maximum percent reduction was found to be 99.52% and was obtained at a pH of around 2. It was verified from the literature that the maximum Cr(VI) reduction is obtained at a lower pH (Parlayici et al., 2015). Researchers have reported that optimum pH for the reduction of Cr(VI) using scrap iron was 2.5 (Gheju et al., 2008).
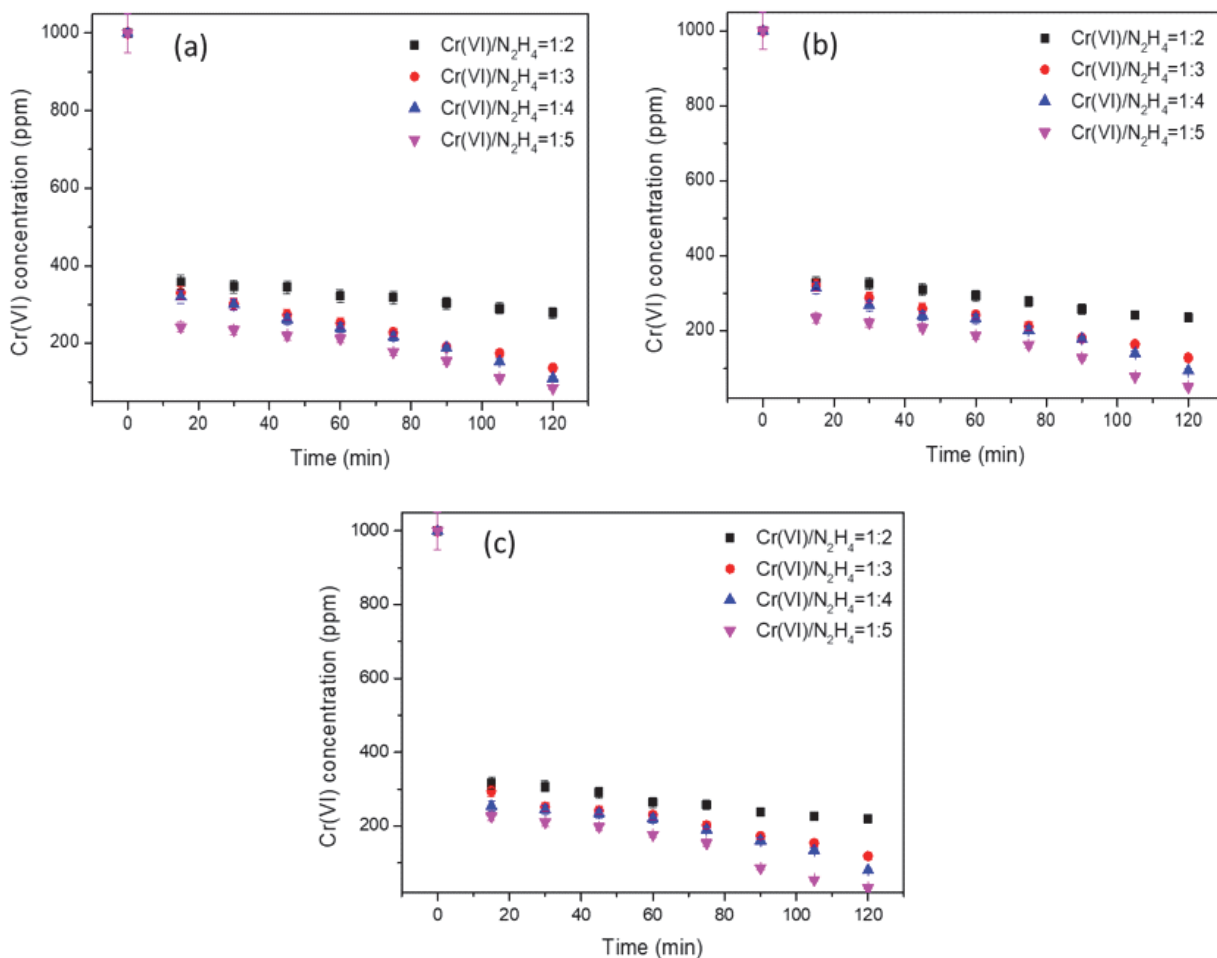
Fig. 1. Effect of molar ratio with initial Cr(VI) concentration=1000ppm at (a) 25°C, (b) 35°C, (c) 50°C
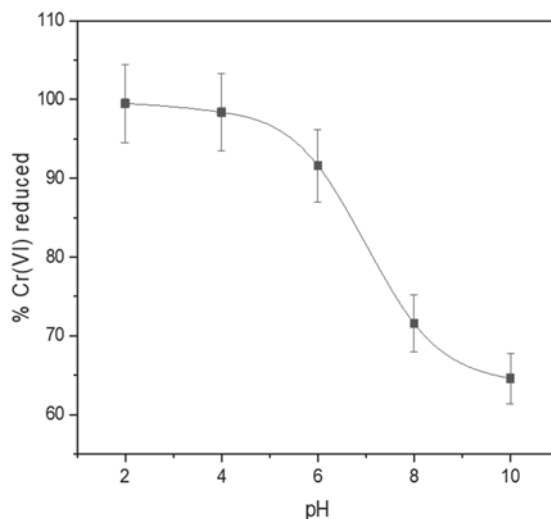

Fig. 2. Effect of pH; Cr(VI) =1000 ppm; 25°C; Molar ratio 1:2

Another study concluded that the maximum reduction of Cr(VI) using zero-valent iron occurred at a pH of 3 (Gheju, 2011). Cr (VI) in acidic solution tends to have a very high positive redox potential (E_o within 1.33 and 1.38V) (Kotaś and Stasicka, 2000), which signifies that it is strongly oxidizing and also quite unstable in the presence of electron donors.

Besides, when HCrO$_4$ gets reduced, it is accompanied by the reduction in formal potential following the reaction (Eq. 2):

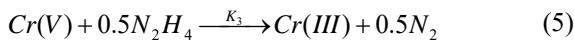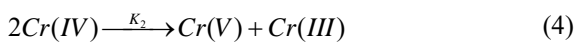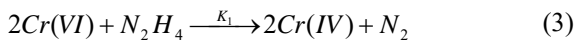$$HCrO_4^- + 7H^+ + 3e^- \leftrightarrow Cr^{3+} + 4H_2O \qquad (2)$$
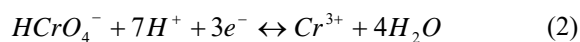
Therefore, it is verified that higher percent reductions

of Cr(VI) are observed at a lower pH. Under acidic conditions, the reducing ability of hydrazine is reduced and it exists in the form of hydrazinium ion. However, the highly oxidizing nature of chromium and high stability of Cr(III) under low pH still favors the reduction of Cr(VI) under acidic conditions. Similar results for hexavalent chromium removal from water has been reported by other authors (Dubey and Gopal, 2009b).

3.5. Reduction kinetics

The reduction mechanism of Cr(VI) can be demonstrated by the following Eqs. (3-5) (Wang and Xu, 2005):

$$2Cr(VI) + N_2H_4 \xrightarrow{K_1} 2Cr(IV) + N_2 \quad (3)$$

$$2Cr(IV) \xrightarrow{K_2} Cr(V) + Cr(III) \quad (4)$$

$$Cr(V) + 0.5N_2H_4 \xrightarrow{K_3} Cr(III) + 0.5N_2 \quad (5)$$

The rate-determining step is the first step, and the rate equation (Eq. 6) can be written as:

$$r = -\frac{dC_A}{dt} = k_1 C_A{}^2 C_B \quad (6)$$

where C_A is the Cr (VI) concentration, and C_B is the concentration of N_2H_4. Also, from the theoretical relationship of Cr (VI) to N_2H_4 from (Eq. 1), it can be written as:

$$C_B = C_{B0} - \frac{3}{4}(C_{A0} - C_A) \quad (7)$$

In the (Eq. 7), C_{A0} and C_{BO} represent the initial concentrations of Cr(VI) and N_2H_4, respectively. By replacing the value of C_B in the rate equation integrating we get, a straight equation of the following format (Eq. 8):

$$Y = k_1 t \quad (8)$$

The expressions for Y and b are provided in Eqs. (9-10):

$$Y = \frac{4}{3b^2}\left[b\left(\frac{1}{C_A} - \frac{1}{C_{A0}}\right) + \ln\frac{C_A(b + C_{A0})}{C_{A0}(b + C_A)}\right] \quad (9)$$

$$b = \frac{4}{3}C_{B0} - C_{A0} \quad (10)$$

To calculate the values of K_1, the reduction kinetics data were plotted in Fig. 3. The rate constants of 0.42 L² mmol⁻²min⁻¹, 0.64 L² mmol⁻²min⁻¹, and 1.26 L² mmol⁻²min⁻¹ were obtained at 25°C, 35°C and 50°C respectively. The activation energy of the reduction reaction was calculated from Fig. 4 and found to be 35.28 kJ mol⁻¹.
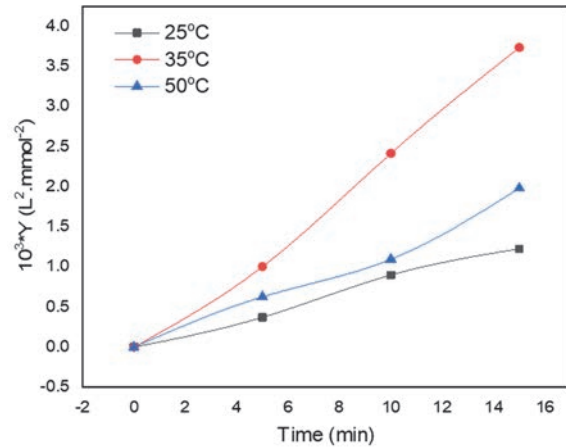

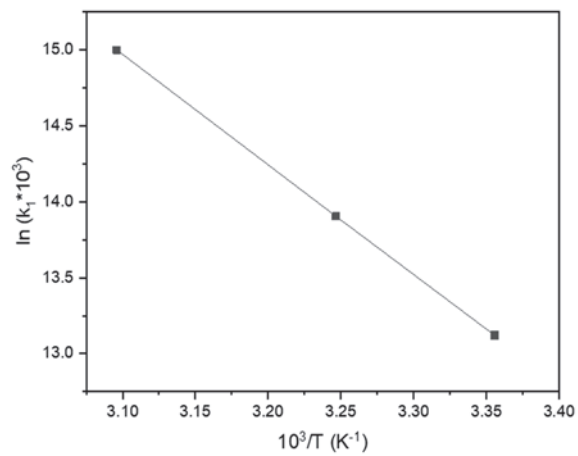**Fig. 3.** Fitting reduction kinetics data

Fig. 4. Empirical activation energy plot

3.6. Characterization of sludge

The FTIR spectra in Fig. 5 were obtained for the sludge produced by the reduction of Cr(VI) using a Perkin- Elmer BX series FT-IR-5000 spectrophotometer (Perkin Elmer, Nicolet, USA). The peak appearing at 3423 cm⁻¹ is indicative of O-H stretching, demonstrating the presence of a water molecule. The peak appearing at 1622 cm⁻¹ is attributed to the C=C stretching. The peak at 608 cm⁻¹ indicates the Cr-O bond demonstrating the presence of Cr(VI) in sludge (Deng and Bai, 2004).

The X-ray diffraction analysis of the sludge generated after the reduction of hexavalent chromium was carried out using a Bruker D8 Advance. After analyzing the same data in X'pert High Score, the peaks had been identified at the angle (2θ) of 44.6° and 64.678°, which corresponds to elemental chromium, so it could be validated that the sludge generated after the chromium reduction process contained vast amounts of chromium. Also, the d- spacing values of individual species found in the XRD of sludge generated is provided in Table 1, which shows the presence of most of the compounds of chromium in which the oxidation state of chromium is +3 (in the sludge), hence confirming the reduction of hexavalent chromium.
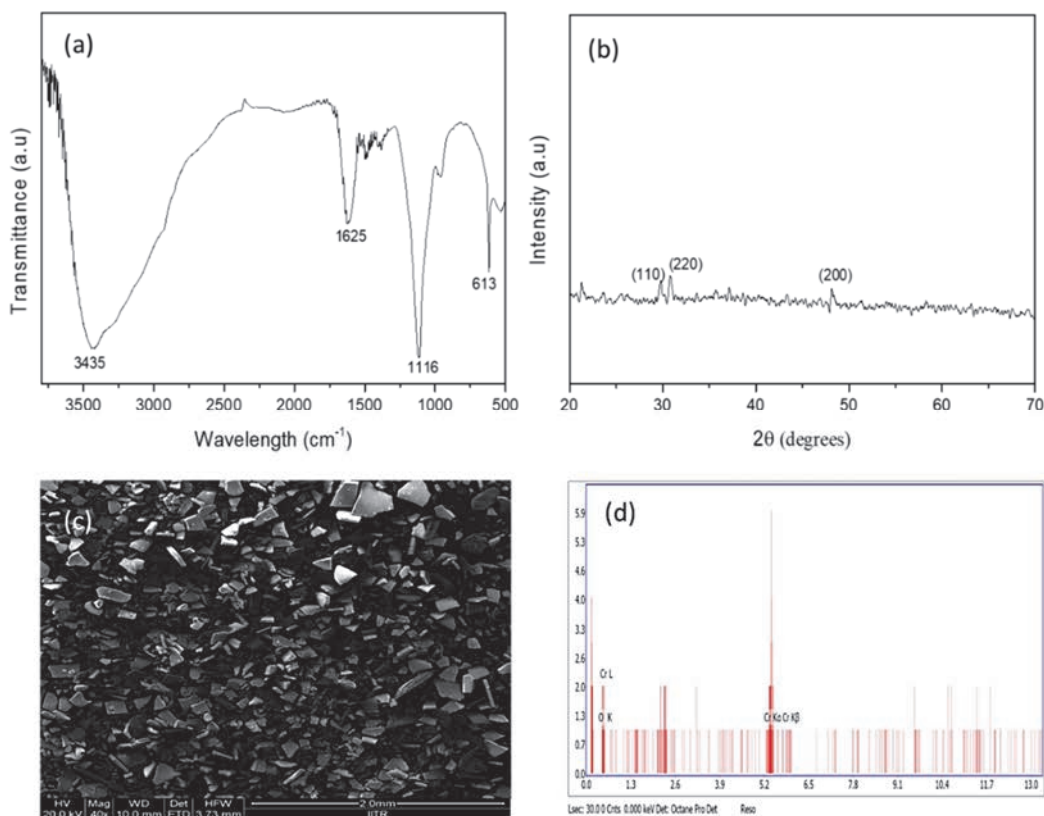
Fig. 5. (a) FTIR, (b) XRD, (c) SEM image, (d) EDAX plot of the sludge generated after Cr(VI) reduction

The morphology study of the sludge was achieved with FESEM (FE-SEM Quanta 200 FEG). The EDAX plot confirms the presence of chromium in the sludge, which is attributed to the reduction of hexavalent chromium using N_2H_4.

Table 1. d-spacing values of probable species from XRD of sludge

d (Å)	Probable species
3.63	Chromium Oxide (Cr_2O_3)
2.22	Chromium Hydride (CrH_2)
2.3	Chromium (Cr)
3.21	Chromium Oxide Hydroxide (CrOOH)
4.93	Bracewellite (CrO (OH))
8.45	Chromium Oxide (Cr_2O_5)
11.8	Chromium Oxide (Cr_3O_8)

4. Conclusions

The use of hydrazine can efficiently reduce hexavalent chromium. The pH of the solution and the molar ratio of Cr(VI)/N_2H_4 plays a significant role in the reduction efficiency of Cr(VI).

The reduction efficiency increases on increasing the molar ratio of Cr(VI)/N_2H_4 as well as the temperature of the solution. Also, if the pH of the solution is lowered, the reduction efficiency can be significantly enhanced. The apparent activation energy was found to be 35.28 kJmol^{-1}.

The electroplating effluent containing vast amounts of Cr(VI) can be substantially reduced by using little amounts of hydrazine.

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