Recovery of Chromium From Plating Sludge Using Wet Oxidation with H_2o_2

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ABSTRACT

Chromate plating activities are almost associated with certain amounts of hazardous chromium wastes which might be considered as resource losses that can be detoxified and recovered to usable product. The recycling of chromate from aqueous electroplating sludge by oxidizing Cr (III) species to Cr (VI) form has been studied. Wet chemical oxidation was attempted with hydrogen peroxide to oxidize the Cr (III) contained in a freshly collected aqueous ferri-chromium hydroxide sludge in slightly alkaline media (pH=8-9) at room temperature (25±5). Complete oxidation of Cr (III) with hydrogen peroxide could not be achieved. A maximum Cr (VI) recovery of only 77% was obtained using 30.8 mm/l of Cr (III) as initial concentration initial. The oxidation reaction kinetic was found to be dependent on trivalent chromium concentration and oxidant concentration which is described by the following rate equation:

$$-\frac{d[Cr(III)]}{dt} = 2.596*10^{-3}[Cr\ (III)]^{3/2}[HO_2^-]^{1/3}$$

Keywords: Chromium recovery, electroplating sludge, oxidation, hydrogen peroxide.

استرجاع الكروم من خبث الطلاء بأستخدام الأكسدة الرطبة مع بيروكسيد الهيدروجين

الخلاصة

تصاحب عمليات الطلاء الكهربائي بالكروم غالبا تولد مخلفات حاوية على نسبة عالية من الكروم الذي يجب استخلاصه واسترجاعه من هذه المخلفات تجنبا للمخاطر التي قد تنجم في حالة تسربه وانتشاره في البيئة المحيطة وكذلك لغرض إعادة استخدامه في أحواض الطلاء بصيغته الأيونية السداسية. تم في هذا البحث دراسة كفاءة عملية الأكسدة الكيميائية المتقدمة باستخدام بيرو كسيد الهيدروجين لغرض أكسدة الكروم الثلاثي إلى سداسي في الخبث الكيماوي الذي هو عبارة عن خليط من هيدروكسيد الحد يديك والكروم في محيط قليل القاعدية يتراوح معدل الدالةالحامضية فيه (8-9) وفي درجة حرارة الغرفة (25±5). بلغت نسبة استرجاع الكروم بطريقة الأكسدة باستخدام بيرو كسيد الهيدروجين 77% عند استخدام تركيز ابتدائي لكروم الثلاثي مقداره 30.8 ملي مول/ لتر. تمت دراسة حركية تفاعل الأكسدة والذي أثبتت النتائج العملية اعتمادها على تركيز كل من الكروم الثلاثي والعامل المؤكسد وحسب المعادلة الرياضية التالية والتي تم إيجادها في هذا البحث.

$$-\frac{d[Cr(III)]}{dt} = 2.596*10^{-3}[Cr(III)]^{3/2}[HO_2^-]^{1/3}$$

INTRODUCTION

Among the most important waste treatment problems is that posed by hexavalant chromium. It is known to be a strong oxidant, a mutagen, and carcinogen. Because of its high toxicity, it is imperative to significantly reduce its discharge levels and promote recycling and reuse [1]. Treatment of chromium plating effluents generates metal-rich sludge containing trivalent chromium compounds. In the past these wastes where disposed of without management or regulation as the Cr(III) species are relatively insoluble and nontoxic [2]. Studies suggest that under certain environmental conditions, Cr(III) may be oxidized to Cr(VI) which may potentially leach out of non-stabilized waste sludge and re-enter the biosphere and becoming mobile in the environment causing a threat to it [3]. On the other hand dumping of these chromium bearing wastes may be seen as a loss of a potential resource because economically workable chromium-ore bodies are not widely distributed in the world.

Thus the recovery and recycling of chromium from industrial wastes seems to be a complementary task to environment protection for the followings [4]:

1-Prevents chromate spreading throughout the environment to minimize its harmful effects.   2-Improves the economics of waste treatment and detoxification of the sludge.

3-Prevents exhaustion of non-renewable raw material to conserve existing resources for   future generation.

4-Reduce the waste volume for less cost and space of landfilling.

Chromium reclamation can be carried out either from wastewater by direct recycling or from sludge by transforming the insoluble forms into reusable compounds through oxidation of the Cr(III) species to Cr(VI). The technique which is more likely to be used for chromium recovery from plating sludge, results in the conversion of Cr(III) into Cr(VI), being soluble in water for easier separation in a purer form from the residual sludge. Wet oxidation of chromium bearing sludge can be carried out with the persulfate, permanganate salts, chlorine, ozone, peroxide or fluorine [4]. Duffy [5] described a technique for the recovery of chromium from sludge using gaseous chlorine for the oxidation of Cr(III) to Cr(VI). This method is feasible when a solution of the recovered chromates is reused directly in plating. Ismail & Abdul-Majeed [6] found that excellent chromate recovery up to 100% can be achieved by roasting the sludge at 875 to 900° C for three hours followed by leaching with water. This technique seems to be more practical, ecologically sound and a superior method for chromate recovery. The main objectives of this research are as follows:

1-Determine the efficiency of the chromate recovery by wet chemical oxidation of Cr(III) contained in an electroplating sludge at its actual pH and room temperature using H$_2$O$_2$ as a strong oxidant.

2- Study the oxidation rate and determine global kinetic parameters of use in modeling the process.

Experimental

The experimental work was intended to treat freshly precipitated ferri-chromium hydroxide suspension by wet chemical oxidation method. This process was performed by utilizing hydrogen peroxide to selectively oxidize trivalent chrome in the mixed ferri-chromium hydroxide sludge at room temperature in a slightly alkaline media at pH ranged 8-9. The hydroxide precipitates performed in this work resulted

from the normal operation of an electrochemical treatment pilot plant for treating the chromate laden wastewater discharged from chromate electroplating workshop in the state company for electrical industries in Baghdad.

Apparatus

All runs were conducted in two liters beakers using initial one liter reaction volume. Mixing was provided by three paddle stainless steel stirrer (100rpm). The pH of solutions was measured by a PYE Unicom model 290 MK pH meter.

Experimental procedure

The experimental procedure of the oxidation process was accomplished by the direct addition of the oxidant to the hydroxide suspension. Oxidation of the aqueous hydroxide suspension samples was attempted with commercially available 20% hydrogen peroxide. The stoichiometry of the reaction is as follows:

$$2CrO_2^- + 3OOH^- \longrightarrow 2CrO_4^{-2} + OH^- + H_2O \qquad \text{.... (1)}$$

The brownish-red colored suspension was stirred after the addition of H_2O_2 until the solution had turned bright yellow. During each experiment, samples were taken at time intervals of 10 minutes for the quantitative analysis of hexavalant chromium concentration. Tests have indicated that the reaction proceeds to completion in about half an hour. In addition to performing stochiometric amount of H_2O_2, excess amounts were used to achieve maximum chromate recovery. Upon the completion of the oxidation reaction, the products were drained through a filter cloth. The filtrate was rich with the recovered chromate ready for reuse in the plating bath. The filter cake consisted mainly of ferric hydroxide with small amounts of chromic hydroxide.

Analytical Method

A Shimadzu Model UV-160 spectrophotometer was used to determine the recovered Cr(VI) at 370 nm. Cross check analysis for Cr(VI) bearing samples were carried out using the diphenylcarbazide method. This technique was in accordance with that given in the *Standard Methods* [7]. Atomic absorption spectrometry of type PERKIN-EIMER Model 5000 was used to determine total chromium using ammonium perchlorate to prevent interference from other ions. The treated sludge samples were dried at 105° C for 24 h and ground to fine powder ready for metal analysis which was accomplished with SRS 200 sequential x-ray spectrometer.

Results and Discussion
General features of Cr(VI) recovery

It was found from the experimental work of this research that will selectively oxidize the chromium species and the reaction proceeds to completion within half an hour producing a bright yellow colored solution as the hexavalant chromium species are formed. Complete oxidation of trivalent chromium hydroxide sludge with H_2O_2 could not be achieved even with the addition of excess H_2O_2 as shown in table 1. These results which are almost expected as they were confirmed by many investigators [3] & [8] may be due to the formation of Cr(VI) peroxy complexes when peroxide levels are sufficiently high. Therefore further addition of this oxidant will not increase the formation of Cr(VI) species since these chromium hydrolytic

polymers with Cr-O-Cr and Cr-OH-Cr bridges are present in the hydroxide sludge [9].

Table (1). Chromate recovery from oxidation of Cr (III) with H_2O_2 at initial pH (8-9)

H_2O_2 [mole/mole Cr(III)]	Percentage recovery %
0	0
1.5*	63
3	66.8
4.5	71.7
6	76.7
7.5	77.1
10	77

*stochiometric

Effect of Temperature and pH

At the outset of this study certain assumption was made regarding the Cr(III) oxidation reaction kinetics. This assumption was that the temperature effect was neglected since all the runs were conducted at room temperature. Although one of the main aims of this research is to determine the efficiency of the chromate recovery by oxidation of chromate bearing sludge at its actual pH and which is normally ranged (8-9), a series of bench scale experiments was run with the object of evaluating the influence of pH. The experimental results indicate that the Cr(III) oxidation reaction with hydrogen peroxide can not be achieved in acidic and neutral media.

This result is not unexpected because alkaline solutions of Cr(III) are easily oxidized to Cr(III) [10], whereby neither acidic nor neutral solutions of Cr(III) can be oxidized to Cr(III) without pH adjustment.

Kinetic study

In order to describe quantitatively the rate of Cr(III) removal and disappearance by oxidation, a simple rate equation is written as follows:

$$-\frac{d[Cr(III)]}{dt} = K\,[Cr(III)]^x\,[Oxidant]^y \qquad ...(2)$$

Where:

$$-\frac{d[Cr(III)]}{dt} = \text{Rate of trivalent chromium removal}$$

K= Rate constant of oxidation reaction (mole$^{-5/6}$.min$^{5/6}$.m$^{5/2}$)
(x), (y) =Reaction orders with respect to [Cr(III)] and [oxidant] respectively
[Cr(III)]=Trivalent chromium concentration in mole/m^3.
[Oxidant]= hydroperoxide anions (HO$_2^-$) in mole/m^3.
t= time in minutes.

Figure 1 presents the plots of residual concentrations of trivalent chromium as a function of time at various initial concentrations of H_2O_2.It is clear on examination of these plots that, as soon as H_2O_2 is admitted, oxidation will begin and the concentrations of Cr(III) will decreased gradually as converted to Cr(VI) and the reaction proceeds to completion within 30 minutes.

 By fitting the results from figure 1 to linear equations, the oxidation reaction order with respect to [Cr(III)] was found to be (3/2) and the corresponding correlation coefficient is consistently in excess of 0.95. Accordingly by plotting of $(C_a^{-0.5} - C_0^{-0.5})$ versus time at various initial H_2O_2 concentrations as shown in figure 2, straight lines are obtained from those (3/2) order plots with slopes as indicated in this figure. In accordance with the graphically obtained slopes, the rate constant of oxidation reaction (K) and the reaction order with respect to [HOO⁻] are calculated from the given amounts of H_2O_2 and they found to be $(2.596*10^{-3})$ and (1/3) respectively giving an overall rate oxidation equation for Cr(III) oxidation with H_2O_2 as follows:

$$-\frac{d[Cr(III)]}{dt} = 2.596*10^{-3}[Cr(III)]^{3/2}[HO_2^-]^{1/3} \qquad \dots (3)$$

Where
$2.596*10^{-3}$ represents the rate constant of chromium oxidation with H_2O_2 in $(mole^{-5/6}.min^{5/6}.m^{5/2})$.
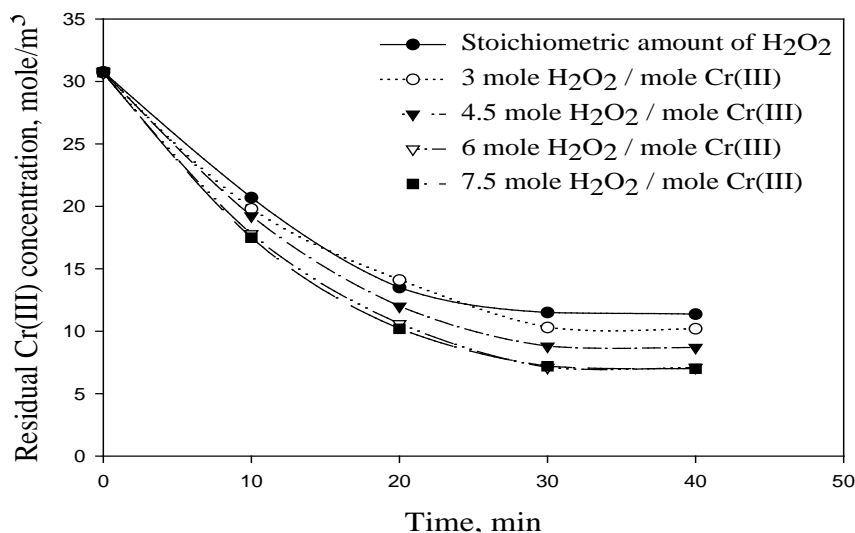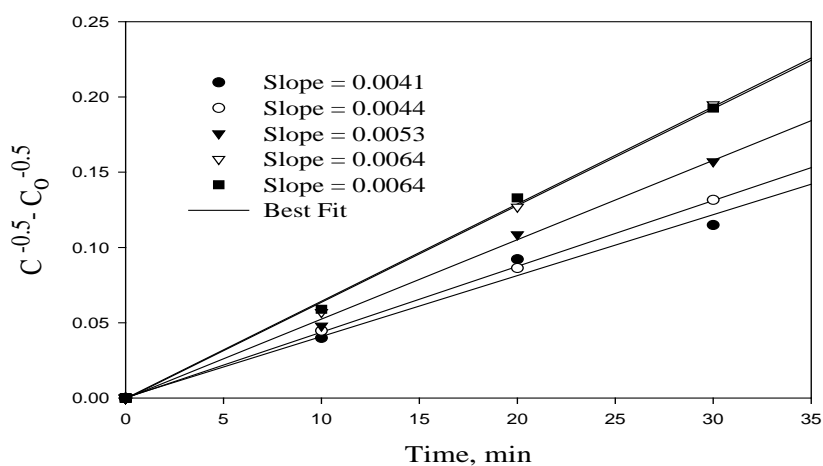

Figure (1). Kinetics of Cr(III) oxidation with various amounts of H_2O_2

Figure(2). One and a half order plot of Cr(III) oxidation with various amounts of H_2O_2

From the above obtained results, although wet chemical oxidation method worked quite well but suffered from chemicals handling and storage problems in addition it is evident that application of hydrogen peroxide for oxidation of Cr(III) bearing sludge studied is not significantly recommended due to the relatively limited Cr(III) oxidation achieved.

CONCLUSION

In the present work the main point under investigation was chemical oxidation rate which in turn gives the extent of Cr(VI) recovery. The following conclusions can be drawn from the direct wet chemical oxidation of electroplating chromium sludge using H_2O_2:

1-   Kinetic results show good Cr(VI) yields from direct oxidation with H_2O_2 of electroplating Cr(III) bearing sludge.

2-   The oxidation of Cr(III) hydroxide suspension at room temperature results in the formation of chromate species ready for reuse in the plating bath.

3-   Not more than 77% chromate recovery was obtained by using H_2O_2 for chromium oxidation even by performing excess amounts.

4-   Modeling of this type of oxidation can be developed mainly through the use of apparent Cr(III) removal or Cr(VI) yields as a kinetic parameters.

5-   In future work it may be able to apply the kinetic information obtained in this study to model the oxidation process to predict/simulate its behavior.

6-   From a practical point of view it seems that the cost of chemicals used is much higher than the value of chromate recovery. However an economic study which lies outside the scope of this research is recommended in a future work to decide the feasibility of this technique.

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