

## Electrolytic recovery of chromium salts from tannery wastewater

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### Abstract

Tannery wastewater collected from a local leather industry in Peshawar, Pakistan was subjected to DC electrolysis in a simple cell having two static sheet electrodes and stirring assembly after proper dilution and adjustment to desired conditions. One percent HNO<sub>3</sub> and 1% NaHCO<sub>3</sub> were used as electrolytes and pH adjusters. The latter salt also worked as sodium source for anodic deposition of Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. Various combinations of electrodes were tested and conditions optimized for best electrode couple with increased recovery and removal of chromium in the form of Cr(OH)<sub>3</sub> and/or Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> at cathode and anode, respectively. The recovery of 99% chromium was achieved after 2 h electrolysis at a cell potential of 1.0 V, pH 5.0 and stirring rate of 500 rpm using Pb sheet as anode and Cu sheet as cathode. The most interesting and novel finding of this work was the recovery of the mentioned salt(s) alone at Cu cathode or Pb anode or collectively at both electrodes by proper control of pH. Such treatment not only minimizes the environmental water pollution, but results in the formation of useful products employed for recycling purpose in tannery or other related industry to make the process economical.

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### 1. Introduction

Chromium (Cr) generally exists in different forms, mostly as trivalent (Cr(III)) and hexavalent (Cr(VI)). Chromium(III) is widely used as tanning agent in the leather industry, and is a significant source of environmental contamination [1].

The trivalent Cr is non-toxic and relatively immobile in nature, whereas the hexavalent Cr is readily soluble in water, highly toxic and mobile and is known to be toxic with potential carcinogenic effects. Cr containing effluents find their way in the environment at disposal sites where Cr undergoes oxidation reactions and forms Cr(VI) [2]. Inter-conversion of these two forms of Cr is greatly dependent upon the nature of environment and one cannot mention the presence of Cr(III) as safer one as it may be converted to Cr(VI) any time. Moreover Cr(III)

has been reported as genotoxic in bacterial cells by causing DNA damage in vitro test systems, however, its vivo toxicity has not been proved till now [3].

A number of articles [4–10] have been reported regarding removal of Cr especially Cr(VI) from various types of samples in the light of its severe hazardous impact upon environment. Donghee et al. [4] and Evans and Yi-tin [5] have employed biomass, protonated brown seaweed *Ecklonia* sp. and *Bacillus* sp. for removal/reduction of Cr(VI), respectively, while Xiaoling et al. [6] have used adsorption and photocatalytic reduction of Cr(VI) to Cr(III) in aqueous solutions by UV/TiO<sub>2</sub> photocatalysis. Dongye et al. [7] have investigated and used a new polymeric ligand exchanger for selective removal of dissolved chromate or CrO<sub>4</sub><sup>2-</sup> at neutral to alkaline pH in the presence of other competing anions. Other workers [8] have employed the chelating resins containing phosphonic or diphosphonic groups for the removal of Cd(II) and Cr(III) from phosphoric acid solutions. According to other report [9], hydrophobic quaternary ammonium compounds dissolved in hydrocarbons are able to effectively extract Cr(III) from alkaline aqueous solutions. According to them, the extraction of Cr(III) goes quickly with its removal exceeding

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99% under optimal conditions. A four-step redox–adsorption system has been developed for removal of Cr(III) from tannery effluents [10].

All these chemical methods for removal of chromium are somewhat complicated, expensive, lengthy and utilizing chemical reagents, while the electrochemical methods are simpler, one-step, economical and rapid. Moreover, the deposited metal(s)/reagent(s) in the latter case may be re-used in the same industry or employed for other purpose(s). An electrically regenerated separation process for removing unwanted ions, such as hexavalent chromium in the form of  $\text{HCrO}_4^-/\text{CrO}_4^{2-}/\text{Cr}_2\text{O}_7^{2-}$  from aqueous waste streams as a minimally polluting, energy-efficient and potentially cost-effective alternative to ion exchange, reverse osmosis, electro-dialysis and evaporation has been described [11]. According to their report Cr(VI) can be lowered from 35 to 2 ppb, well below the acceptable level for the regulatory surface water discharge limit of 11 ppb by using carbon aerogel electrodes. They stated that carbon aerogel is an ideal electrode material because of its low electrical resistivity, high specific surface area and controllable pore size distribution. They also mentioned that the exact speciation of the chromium ions depends upon pH, temperature, concentration and the presence of other ions. A two-stage electrochemical treatment using a platinum anode and a graphite cathode at a current density of  $0.1 \text{ A cm}^{-2}$  has been described elsewhere [12]. In first stage, the acidic process water containing metals passed through the cathode chamber, where the main load of dissolved Cu, Zn, Cr and Pb was eliminated. In second stage, the cathodically pre-treated process water was electrolyzed anodically for removal of residual ions. According to their observation the pH rose from 3.0 to 4–5 during the process. Electrolytic chromium reduction from the chrome tannery wastewater, using a stainless steel plate as cathode and a graphite rod as anode has been reported by other workers [13]. They reported that 100% Cr reduction took place from synthetic water, while 94–99% was true for tannery water after 2 h electrolysis. Other workers [14] have also described the electrolytic removal of hexavalent chromium from a synthetic solution and from an industrial sample, but they used stainless steel plate and titanium mesh cathodes with a two-steps strategy: (1) electro-reduction of Cr(VI) to Cr(III) in highly acidic medium and (2) electrochemical precipitation of Cr(III) in an alkaline medium. According to their observation, electro-reduction is a clean technology as compared to chemical reduction.

The present paper was an attempt to investigate an economical method having a simple cell containing an insoluble anode with a proper cathode combination to remove and recover chromium from tannery wastewater in the form of usable salt(s) which could be recycled in tanning industry as well as utilized in other industries.

## 2. Experimental

### 2.1. Chemicals and solutions

Analytical grade chemicals of Merck, BDH and Fluka Chemicals were used for preparation of solutions. Doubly distilled

water was used for final rinsing of all glassware and preparation of all solutions.

### 2.2. Sample collection and analysis

Sample of tannery wastewater containing chromium was collected from a local leather industry situated at Charsadda Road, Peshawar, in a big plastic bottle of 6 l capacity. The color of collected sample was greenish blue, while it had the pH and temperature value of  $4.3 \pm 0.1$  and  $24.8 \pm 0.1 \text{ }^\circ\text{C}$ , respectively. According to information provided by the authorities, the sample also contained  $\text{NaHCO}_3$  and dilute  $\text{H}_2\text{SO}_4$  which they used for pH adjustment.

Chromium content of the sample and deposits was evaluated by Graphite Furnace Atomic Absorption Spectrophotometer (AAS) model SP9 Pye Unicam Philips Company, England in Mineral Division of FATA DC, Warsak Road, Peshawar. The average contents were  $2550 \text{ mg l}^{-1}$  chromium in a 5-times analyzed sample. This solution was used as stock solution for preparation of dilute solutions required for electrolytic removal/recovery of chromium as its salts. The samples of river water were also collected 1000 m down stream after the mixing point of tanning industry waters and river. The chromium content was ranging from 200 to  $300 \text{ mg l}^{-1}$  for these samples. At this point the residential area just started. The collection of river water was meant to specify the amount of chromium ( $300 \text{ mg l}^{-1}$ ) which is equal to the electrolytically processed dilute tannery waste solution (see Section 2.4). This was to prove that river water could also be electrolyzed in the same way as true for dilute tannery wastewater.

### 2.3. Electrolytic cell assembly

A schematic diagram of the electrolytic set up is given as Fig. 1.

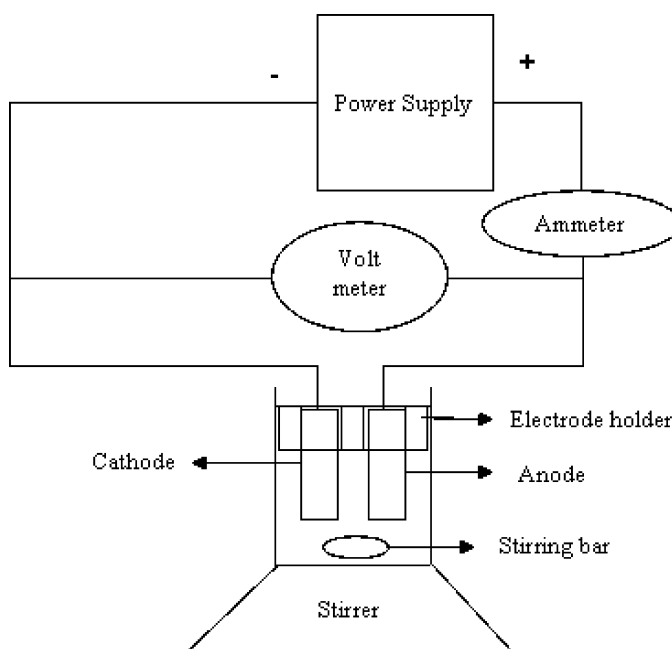


Fig. 1. Schematic diagram of electrolytic set up.

A DC power supply model PS-6000N, Nakamura Sci. Co. Ltd., Japan, was used for electrolytic recovery of chromium salts from mentioned solution of tannery wastewater at respective electrodes.

#### 2.4. Electrolytic recovery/removal of chromium salt(s)

Dilute 100 ml solution of  $300 \text{ mg l}^{-1}$  Cr ions containing tannery wastewater was chosen for electrolysis, because concentrated solution was creating problems after formation of loose electro-deposits at electrodes which were easily detached and floated due to stirring during electrolysis. The pH of this solution was  $4.5 \pm 0.1$ . The electrolysis of the mentioned dilute solution was performed according to procedure described earlier [15] under all optimized conditions. Anodic dissolution was worked out as weight loss in a pre-weighed anode after electrolysis. The electrode having the deposited salt of chromium was dipped in a beaker containing concentrated 25 ml  $\text{HNO}_3$  to wash out the salt and digestion of washing was carried out by heating it on a hot plate until the formation of a transparent solution. This solution was cooled to room temperature and diluted to 100 ml. Cr content in the deposit(s) was then determined as average of triplicate analyses of this solution by AAS. Contaminations of iron and copper were also determined with AAS.

### 3. Results and discussion

#### 3.1. Potential study at various electrode couples

##### 3.1.1. Steel electrodes

Fig. 2 shows the electrolytic recovery of chromium from  $300 \text{ mg l}^{-1}$  chromium ions containing solution (dilute tannery water) at steel cathode and dissolution of steel anode at various cell potential values in the range of 1.0–3.0 V with constant parameters, such as pH 4.5, stirring rate 300 rpm and room temperature  $30 \pm 1^\circ \text{C}$ . The electrolysis time was 20 min.

It is seen from figure that the deposition of chromium as  $\text{Cr}(\text{OH})_3$  increases first slowly and then rapidly with increasing potential up to a maximum value of 21.2% chromium at 2.7 V and then decreases. Contamination of  $\text{Cr}(\text{OH})_3$  deposit with iron impurities was also noticed during this study. The amount of

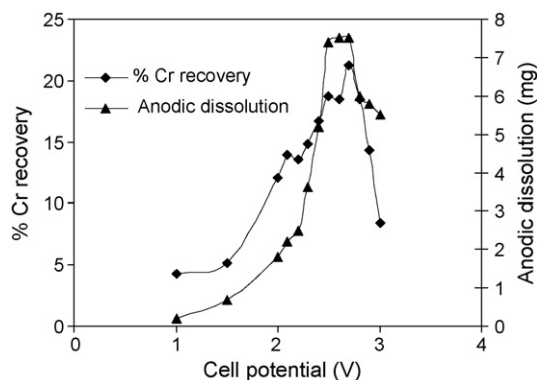
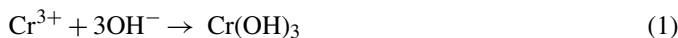


Fig. 2. Electro-deposition of chromium as  $\text{Cr}(\text{OH})_3$  on steel cathode and dissolution of steel anode at different cell potential values.

iron deposited along with  $\text{Cr}(\text{OH})_3$  was 2.4% of chromium at optimum potential. Anodic dissolution of steel anode was also noted and observed to follow the same plot trend as true for deposition of  $\text{Cr}(\text{OH})_3$ . The deposition of  $\text{Cr}(\text{OH})_3$  at cathode is due to the presence of  $\text{Cr}(\text{III})$  which is converted to  $\text{Cr}(\text{OH})_3$  at cathode, according to following mechanism:



According to a report [11], the  $\text{Cr}(\text{III})$  is in the form of  $\text{Cr}(\text{OH})^{2+}$ ,  $\text{Cr}(\text{OH})_2^+$ ,  $\text{Cr}(\text{OH})_4^-$  or  $\text{CrO}_2^-$ . The supply of  $\text{OH}^-$  ions is possible by three sources [16]: (i) electrolysis of water at cathode, (ii) oxidation of anodic iron to  $\text{Fe}(\text{II})$  ions and (iii) further oxidation of  $\text{Fe}(\text{II})$  to  $\text{Fe}(\text{III})$  ions. The formation of  $\text{Fe}(\text{II})$  ions is proved by dissolution of steel anode with nearly the same trend as true for chromium recovery. The formation of  $\text{Cr}(\text{OH})_3$  from  $\text{Cr}(\text{OH})^{2+}$  and  $\text{Cr}(\text{OH})_2^+$  occurs at cathode as these species are cationic in nature [11,17]. The electro-deposition of  $\text{Cr}(\text{OH})_3$  at cathode along with other heavy metal ions, such as Ni, Cu, Cd, Pb and Zn has been described in literature [18]. However, these authors have described a potential value of 6.0 V which is essential for removing other heavy metals mentioned above. The higher value of potential in the latter case is due the application of their process for removal of bulk metals along with Cr, which requires greater energy (higher potential) in that particular case.

Some authors [13] have used stainless steel plate as cathode and graphite rod as anode for electrolytic separation of Cr from tannery wastewater showing a potential range of 4–6 V. According to another study [19], 0.7 V has been used as optimum potential for electro-coagulation of chromium from tannery effluents using iron anode as a sacrificial electrode. These citations Refs. [11,13,19] prove that cell potential is greatly dependent upon the type of electrodes and optimized conditions.

The dissolution of anode is due to the use of same type of cathode in combination which makes it a concentration cell. The dissolution of various types of alloy anodes has been studied by some workers [20] for the purpose of preparing anodes for chromium plating in chloride containing 'chromispel-C' electrolytes.

##### 3.1.2. Copper electrodes

In order to investigate another electrode couple for efficient removal and recovery of chromium as chromium salt(s), Cu–Cu couple electrode was used at the above-mentioned constant parameters. Fig. 3 describes the recovery of chromium after 20 min electrolysis as  $\text{Cr}(\text{OH})_3$  in a potential range of 0.1–1.5 V.

It is seen that chromium recovery increases with increase of cell potential from 0.1 V to an optimum potential of 0.9 V with Cr recovery of 35.2% and then decreases with further increase in potential. In this case, copper contamination was noticed with most of deposits of  $\text{Cr}(\text{OH})_3$ . The copper was deposited at cathode as a result of dissolution of anode and was 3.4% of deposited chromium at optimum potential. The  $\text{Cr}(\text{OH})_3$  formation in this case is also supported by the same mechanisms as described earlier [11,16], however, in this case,  $\text{Cu}(\text{I})$  and  $\text{Cu}(\text{II})$  ions results from anodic dissolution instead of  $\text{Fe}(\text{II})$  and  $\text{Fe}(\text{III})$  in case of steel anode (see Section 3.1.1).

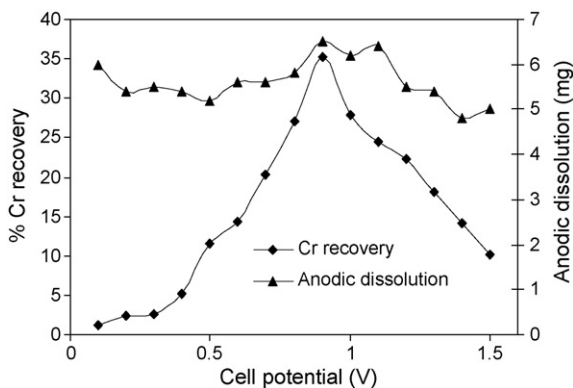


Fig. 3. Deposition of chromium as  $\text{Cr}(\text{OH})_3$  on Cu cathode and dissolution of Cu anode at different cell potentials.

Concerning the difference in the range of potential range of 1.0–3.0 V (see Section 3.1.1) and current range of 0.1–1.5 V, it seems that the deposition of Cr is greatly dependant upon the electrode material used. So, the Cu electrodes are more efficient (with greater deposition and lesser energy (potential)) consumption as compared to steel electrodes (with lesser deposition and greater energy) consumption.

Also, comparing the anodic dissolution value in Figs. 2 and 3, it is seen that the anodic dissolution in the former case (steel electrode) increases with increase in potential, but in latter case, it is high even at lower potential value. This may be due to greater affiliation of Cu with  $\text{SO}_4^{2-}$  ions present in tannery waters (see Section 2.2) to form Cu(I) or Cu(II) ions as compared to steel (iron) electrode which only follows the potential.

### 3.1.3. Lead anode and copper cathode

The anode material plays a very important role in the electro-deposition of metal or compounds. Lidia et al. [21] studied the effect of anodic material based on noble metals and metal oxides (Ti/Pt–Ir, Ti/PbO<sub>2</sub>, Ti/PdO–Co<sub>3</sub>O<sub>4</sub> and Ti/RhO<sub>x</sub>–TiO<sub>2</sub>) on the treatment of tannery waste water and showed that the rate of pollutant removal was significantly influenced by the type of anode material and electrochemical parameters. As it was also aimed to find out an insoluble anode which could result in provision of smooth current and enhanced recovery of chromium, so lead sheet was used as anode in combination with copper cathode. Fig. 4 reflects the data obtained for a Pb–Cu couple at all optimized condition as true for Fig. 2.

It is evident from the results that maximum amount of 30.4% chromium is deposited as  $\text{Cr}(\text{OH})_3$  at an optimum potential value of 1.0 V on Cu cathode, but the maximum recovery of 11.4% chromium as  $\text{Na}_2\text{Cr}_2\text{O}_7$  occurs at 1.2 V on Pb anode. However, the total optimum recovery of chromium of 39.8% was true at the former cell potential. The mechanism of deposition of  $\text{Na}_2\text{Cr}_2\text{O}_7$  on anode is described on the basis of oxidation of Cr(III) to Cr(VI) and its conversion to  $\text{Cr}_2\text{O}_7^{2-}$  ions at Pb anode which then form  $\text{Na}_2\text{Cr}_2\text{O}_7$  due to the presence of  $\text{Na}^+$  ions. The same type of mechanism has been cited earlier [16] for formation of  $\text{K}_2\text{Cr}_2\text{O}_7$  at anode. According to another citation Ref. [11], trivalent anionic species, such as  $\text{Cr}(\text{OH})_4^-$  and  $\text{CrO}_2^-$  would be forced to the anode, where anodic oxidation

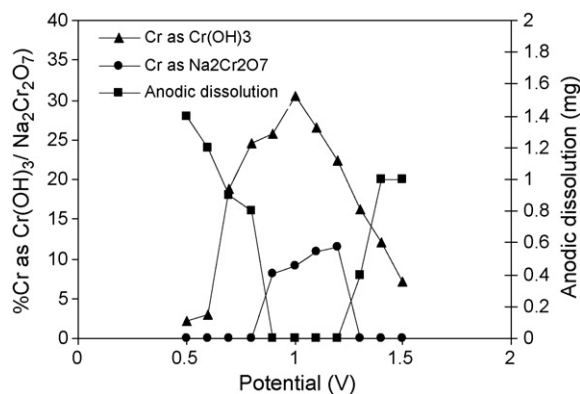


Fig. 4. Deposition of chromium as  $\text{Cr}(\text{OH})_3$  on Cu cathode and deposition of  $\text{Na}_2\text{Cr}_2\text{O}_7$ /dissolution of Pb anode at different potentials.

to  $\text{HCrO}_4^-$ ,  $\text{CrO}_4^{2-}$  or  $\text{Cr}_2\text{O}_7^{2-}$  would be possible. They have described starting potential of 0.9 V and final potential of 1.2 V for separation of Cr(III) and Cr(VI) at cathode and anode, respectively, using carbon aerogel electrodes. However, in our case, the  $\text{Na}^+$  ions facilitate the formation of  $\text{Na}_2\text{Cr}_2\text{O}_7$  anodically, which is more favorable because of dominance of  $\text{Cr}_2\text{O}_7^{2-}$  in the presence of oxidizing species, such as  $\text{HNO}_3$  and  $\text{NaHCO}_3$ , according to the following mechanism:



An example of formation of  $\text{Cr}_2\text{O}_7^{2-}$  in the presence of oxidizing species, such as  $\text{MnO}_2$  is given elsewhere [22]:



Concerning the dissolution of Pb at lower and higher potential values, one can say that an intermediate range of potential exists there, where its dissolution is zero and fortunately, this range is responsible for maximum recovery of Cr as chromium salts. However, no data is available in literature to verify this effect.

It is a fact that Pb is among the highly toxic heavy metals and its dissolution can create serious environmental threat to living things, but in our study, the best Cr deposition took place at those potentials, where the dissolution of Pb was zero.

### 3.2. pH study

Fig. 5 shows the effect of pH on electro-deposition of chromium as  $\text{Cr}(\text{OH})_3$  on Cu cathode and on  $\text{Na}_2\text{Cr}_2\text{O}_7$  or dissolution of Pb anode at previously optimized parameters at a potential of 1.0 V. One percent of each  $\text{NaHCO}_3$  and  $\text{HNO}_3$  was used during pH studies.

It is evident from results that the maximum recovery of 40% chromium as  $\text{Cr}(\text{OH})_3$  takes place at an optimum pH value of 5.0, while 22.2% as  $\text{Na}_2\text{Cr}_2\text{O}_7$  occurs at pH 3.0. So, one can choose specific pH for obtaining the salt(s) of choice at enhanced rate. It is also seen that very little dissolution of only 0.3 and 0.2 mg Pb anode occurs at pH value of 3.5 and 4.0, respectively, while there is no dissolution of anode at other pH values.  $\text{HNO}_3$  seems to act as oxidizing agent by conversion of Cr(III) to Cr(VI) thus, favors the formation of more  $\text{Cr}_2\text{O}_7^{2-}$  ions and hence, increased deposition of  $\text{Na}_2\text{Cr}_2\text{O}_7$  as evident from its elevated



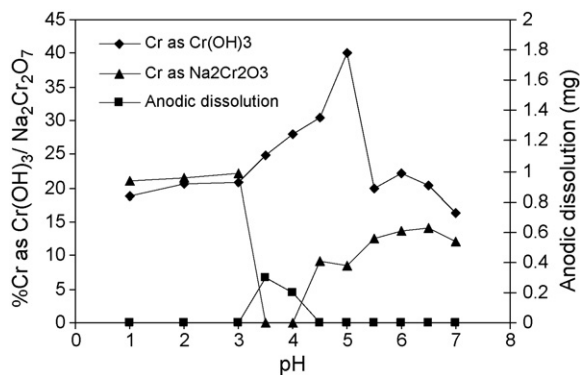


Fig. 5. Effect of pH on % recovery of chromium as chromium salt(s) and dissolution of Pb anode.

value at lower pH. However, its non-deposition at pH 3.5 and 4.0 is not explainable. The effect of pH for removal of Cr(III) by electro-coagulation has been observed by some workers [23]. According to them, removal of Cr(III) improved at higher pH due to combined effect of precipitation, co-precipitation as solid solution like species, adsorption, cathodic reduction and sweep coagulation. According to another citation Ref. [24], the total chromium concentration could be reduced from 60 to 2 mg l<sup>-1</sup> at an optimum pH of 4.0.

### 3.3. Stirring effect

Stirring speeds up the flow of ions toward electrodes which results in formation of greater amount of products. Fig. 6 shows the dependence of stirring rate upon the electro-deposition of Cr(OH)<sub>3</sub> and Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> at copper cathode and lead anode, respectively, at a cell potential of 1.0 V, pH 5.0, time of electrolysis 5 min and room temperature 30 ± 1 °C in a simple cell containing 300 mg l<sup>-1</sup> chromium ions solution.

It is seen from Fig. 6 that the maximum deposition of 45.4 and 11.2% chromium as Cr(OH)<sub>3</sub> and Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> occurs at optimum stirring of 500 and 600 rpm, respectively. The decrease in chromium recovery at higher rate is due to formation and detachment of loose deposits of these salts which disturb the recovery process by enhanced floating around the electrodes. So, to get a comparatively sticky but easily scratchable deposit,

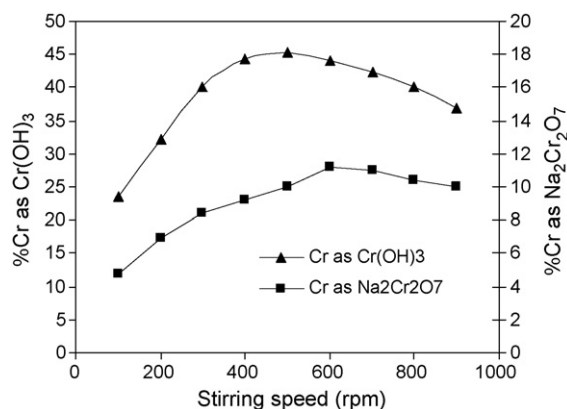


Fig. 6. Effect of stirring rate on % chromium recovery of chromium salts.

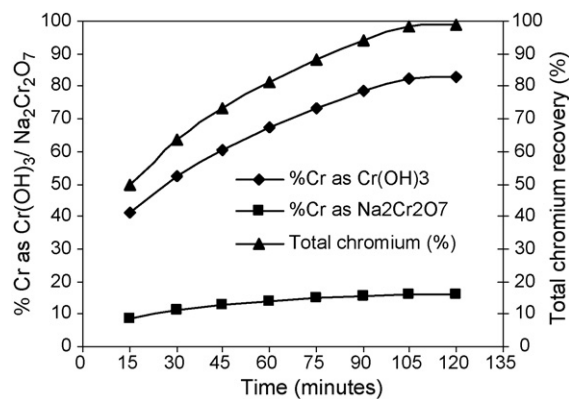


Fig. 7. Time vs. % chromium recovery as chromium salt(s) at Cu cathode and Pb anode.

500 rpm was selected as optimum stirring rate for both of the deposited salts. Stirring rate has also been reported [25] during deposition of nickel–cobalt alloys by controlled potential electrolysis. Some workers [26] have used rotating electrodes with optimization of rotating velocity for electro-co-deposition of metals between 0 and 60 rpm with increase and decrease in co-deposition of species.

### 3.4. Time study

Fig. 7 shows the variation of % chromium with time of electrolysis at all optimized conditions as mentioned before. It is evident from figure that the recovery of chromium in the form of Cr(OH)<sub>3</sub> is taking place at an enhanced rate due to its greater deposition capacity under optimized conditions reaching to 82.8% in 2 h. However, the deposition of chromium as Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is not increasing as rapidly as in case of former salt with an amount of 16.2%, but the trend is nearly the same. It is due to limited capability of formation of the latter salt at given conditions.

The plot also shows the increase in the amount of chromium in the form of chromium salts with increase in time of electrolysis up to 99% chromium in 2 h. It is seen that the deposition rate is decreasing as the time passes due to the possibility of concentration polarization [16], where the ions are continuously going to decrease due to concentration difference of Cr(III) and Cr(VI) ions in the bulk and around electrodes.

## 4. Conclusions

The electrode combination of Pb anode and Cu cathode for the electrolytic recovery of chromium from tannery waste water in the form of Cr(OH)<sub>3</sub> and Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is a new finding, but the most important parameters, such as pH, potential and stirring rate handle the choice of formation of respective salt(s) at these electrodes. The 99% recovery of chromium in 2 h at a very low cost (lower potential) using sheet electrode makes the process quite economical and simpler. Moreover, the recovered salts at electrodes, especially former one may be re-used in tanning industry, where usually Cr(III) salts are utilized [1]. These recovered salts can also be used in other industries of

interest and chemical laboratories for several purposes. Electrolytic recovery of chromium salts by the present method can thus, provide a useful strategy for minimizing environmental pollution by chromium ions from tanning industry as well as help to save some foreign exchange being used for purchase of these chemicals for mentioned purposes. The technology could also be useful in other industries discharging chromium ions, such as electro-plating and steel producing industry.

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