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The Electrochemical Treatment of Toxic Hexavalent Chromium from Industrial Effluents using Rotating Cylinder Electrode Cell

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This paper investigates a method to electro reduce toxic hexavelent chromium to trivalent state using rotating disc electrode (RDE) and rotating cylinder electrode (RCE) cell. Electrolysis of acidic hexavalent chromium solution using a rotating lead cathode reduces the hexavalent chromium Cr^{6+} to trivalent chromium. The effect of chromium, sulphuric acid concentration, current density, time and speed of cathode rotation on current efficiency has been investigated under galvanostatic and linear sweep voltammetric techniques. The effect of these parameters on cell voltage and energy consumption has been also studied. It was found that the efficiency of the reduction method is directly proportional to the hexavalent chromium and sulphuric acid concentration. Trivalent chromium is successfully obtained from acidic industrial wastewater containing 1.5 g l^{-1} Cr^{6+}. High current efficiency is attained at current density 225 mA cm^{-2} for 80 minutes.

Keywords: Chromium; Electroreduction; Current efficiency; Rotating disc electrode cell (RDE); Rotating cylinder electrode cell (RCE)**.**

1. INTRODUCTION

Wastewater loaded with toxic hexavalent chromium is currently purged from various sources such as, metal finishing industries, chromium plating and drug industries [1]. These effluents severely pollute the environment [2-4]. The environmental laws raised strict regulations regarding the maximum permissible levels of chromium in the released effluents. Metal Finishing Regulations for effluent disposals are 0.002 g l^{-1} a day and 0.001 g l^{-1} as a monthly average [1]. Chromium concentration was limited by environmental protection authorities to 0.0001 g l^{-1} in drinking and ground water [5-6].

Based on a previous study [7], it was reported that the removal of chromium metal could be successfully achieved from hexavalent chromium solutions of 1.5 g l^{-1} Cr^{6+}. For more diluted solution, no chromium metal recovery was claimed, and the cathode substrate was covered by an oxide layer with a very low current efficiency. The toxic hexavalent chromium should be firstly reduced, to the nontoxic trivalent form that can be readily precipitated as insoluble Cr $(OH)_3$. The production of hexavalent chromium by electroreduction technique depends on the acidity of the solution [8]. The main problem is that the process becomes inefficient as the insoluble chromium hydroxide masks the surface of the electrode. Reduction of hexavalent chromium from synthetic solutions at a hydrogen evolving rotating cylinder lead cathode was mechanistically studied and it is suggested that the cell can be used in the industrial production of Cr^{+3} chemicals from concentrated chromate solution (obtained by roasting chromite ore with sodium carbonate) [9].

The present paper studied the reduction of hexavalent chromium from dilute acidic solutions (simulated wastewater) at various conditions of different current densities, sulphuric acid concentrations, chromium concentrations and cathode rotation speeds. Moreover, this article is devoted to a study of the effect of chromium and rotation speeds on cathode potential by linear sweep voltammetery and galvanostatic techniques. This study was performed by means of rotating disc electrode cell and rotating cylinder electrode cell. Additionally, the performance of the rotating cylinder electrode cell in simulated industrial wastewater treatment was tested. Sulphuric acid is used to prevent formation of insoluble chromium hydroxide where the delivered industrial wastewater was acidic.

2. EXPERIMENTAL PART

2.1. Materials

Chromic oxide (CrO_3) was used as a source of hexavalent chromium and sulphuric acid as a sulphate electrolyte. All solutions were prepared from distilled water and analytical grade chemicals.

2.2. The electrolysis cell and equipment

2.2.1. Galvanostatic studies

The electrolysis cell used in this study was a double wall glass container with a Perspex cover containing slots to mount the electrodes. A rotating cylinder lead electrode of area 40 cm^2 was used as the cathode and placed in the center of the cell. Five graphite plates of 40 cm^2 area were used as anodes. These graphite plates were surrounded by polypropylene mesh separator to facilitate the generated oxygen to ascend on the diaphragm, minimizing its immigration to the cathodic compartment and decreasing the possibility of reoxidising the reduced species. The lead cylinder cathode was placed at a distance of 2.5 cm from the graphite electrodes. The upper part of the rotating cathode is isolated by a Teflon tape to make sure that the active part of the rotating cylinder locates below the solution vortex caused by the cylinder rotation. The galvanostatic electrolysis system

consists of the cell, the constant d. c. power supply, the digital multimeter and variable resistance. The variable resistance was imposed in the circuit to resist any change in the current of the closed circuit during galvanostatic experiments. A rotation speed from 0.0 to 3000 rpm was applied using a variable speed motor. All measurements were taken against standard calomel electrode (SCE) Hg / Hg_2Cl_2 / Cl connected to the cell by means of a luggin capillary. A d. c. power supply (IMPO type, models FBS 1101) with stabilized current range from 0 to 10 A was used. A digital multimeter (Keithly Model 617 programmable electrometer, U.S.A) was used to follow up the change in cell voltage and potential data.

2.2.2. Linear sweep voltammetric studies

The rotating disc electrode experiments were executed by computerized Volta lab 21 potentiostate / galvanostate (PGP 201 model) controlled by a P C running the electrochemical software (Volta master 070). A high-speed rotator (EG&G Instruments, INC. model 616) was used to rotate the disc electrode at the desired speeds during experiments. The working disc electrode was a rotating lead electrode of area 0.5 cm^2, which placed at a distance 0.5 cm from the counter electrode. Graphite rode of 5 cm^2 area was used as the counter electrode. A setting period of 5 min was allowed to ensure steady state hydrodynamic conditions at the electrode surface before starting the experiment.

The rotating cylinder electrode cell is sketched in Figure 1a and the electrolysis system is sketched in Figure 1 b.

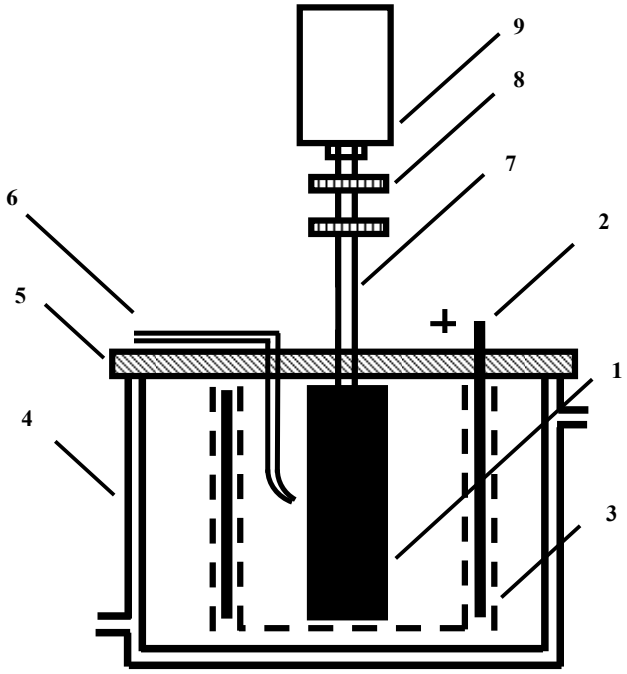

Figure 1a. Schematic diagram of the rotating cylinder electrode cell for electro reduction of hexavalent chromium. Key: (**1**) lead rotating cylinder cathode, (**2**) graphite plates anode, (**3**) polypropylene cloth separator, **(4)** double wall Pyrex cell, (**5**) Teflon cover, (**6**) salt Bridge, **(7)** current feeder, **(8)** shaft, and **(9)** motor.

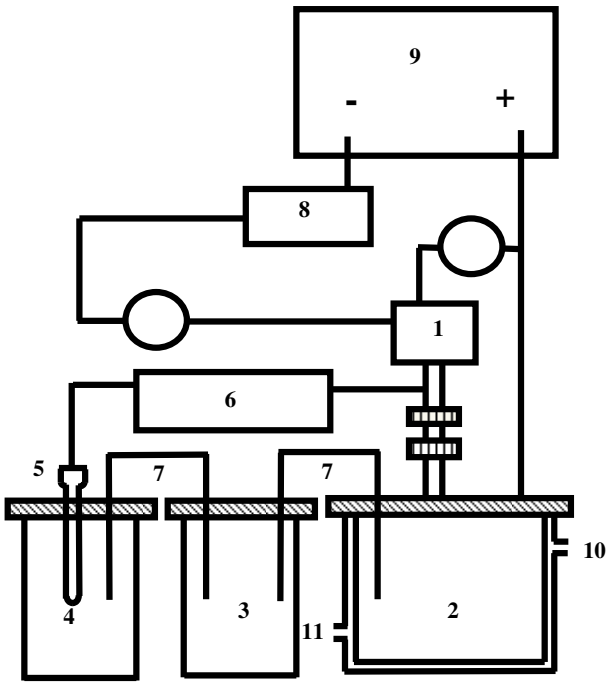

Figure 1b. Schematic diagram of the electrolysis system. Key: (**1**) motor, **(2)** double wall Pyrex cell, **(3)** Cr^{6+} electrolytic solution, **(4)** KCl solution, (**5**) reference electrode, **(6)** multimeter, **(7)** salt bridge, (**8**) variable resistance, **(9)** power Supply, (**10**) inlet of water, and **(11)** outlet of water.

2.3. Physical and chemical method of measurements

Hexavalent chromium and trivalent chromium were analyzed before and after the electrolysis run volumetrically and using Atomic Absorption Spectrophotometery. Sample was taken for hexavalent chromium analysis by adding a known excess of a standard ferrous ammonium sulphate solution and titrating it against standard $K_2Cr_2O_7$ using diphenylamine as indicator. We oxidized trivalent chromium and analyzed it as hexavalent chromium [10]. From the volumetric and atomic absorption analysis we followed up the change in hexavalent chromium concentration. In all experiments the current efficiency was precisely calculated by dividing the experimentally hexavalent chromium concentration actually reduced by passing a definite quantity of electricity per the expected theoretical chromium concentration that should be reduced according to Faraday's law. The current efficiency (c. e.) of hexavalent chromium reduction to trivalent chromium was calculated under different conditions from the equation (c. e. = actual amount reduced / theoretical amount reduced) [11].

3. RESULTS AND DISCUSSION

The electrochemical reactions governing the reduction of Cr^{6+} to Cr^{3+} are summarized as follows:

At the cathode, the following reactions take place [9, 12-14]:

$$Cr_2O_7^{2-} + 14\ H^+ + 6\ e^- = 2\ Cr^{3+} + 7\ H_2O \qquad [E^0_{250C}\ (SCE) = 1.09\ V]\ [1]$$

$$2\ H_3O^+ + 2\ e^- = 2\ H_2O + H_2 \qquad [E^0_{250C}\ (SCE) = 0.24\ V]\ [2]$$

At the anode the reaction involved is [15]:

$$2\ H_2O = 4\ H^+ + O_2 + 4\ e^- \qquad [E^0_{250C}\ (SCE) = 0.99\ V]\ [3]$$

3.1. Linear sweep voltammetric studies using rotating disc electrode cell

3.1.1. Effect of hexavalent chromium concentration

Linear sweep voltammetric curves generate by sweeping catholically from 0 to -1600 mV vs. SCE at scan rate of 10 mV s^{-1} and rotation rate 600 rpm. Electrolysis performs using different hexavalent chromium concentrations, namely, 1.54, 0.8 and 0.5 g l^{-1}. These concentrations are the same as that produced from the wastewater of chromium industries [16]. Sulphuric acid is the supporting electrolyte and the pH value of the industrial samples is ranged from 0.5 to 1.6.

Lead cathode was selected due to its high hydrogen over potential, which favors high rate of hexavalent chromium reduction [9, 17]. A graphite anode was chosen because trivalent chromium is not oxidized at its surface [18-21]. The results obtained are shown in Figure 2.

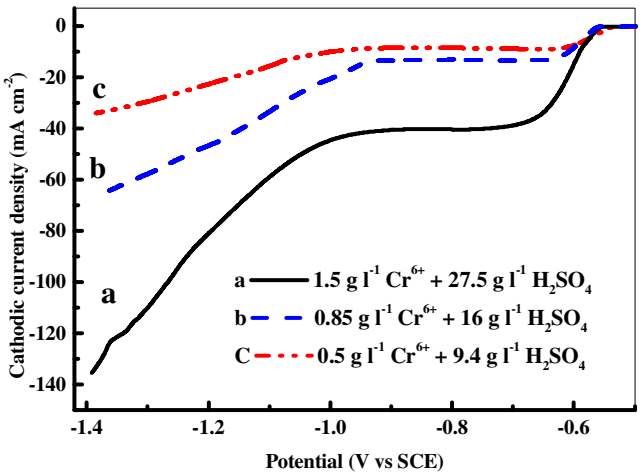

Figure 2. Linear sweep voltammtric curves of chromium electroreduction on lead RDE from different concentrations.

The current density increases negatively with scanning the electrode potential in the negative direction. The curves display two major sections: The first starts from -550 to -1000 mV. This represents the reduction of hexavalent chromium ions to the trivalent ions. The solution in the cathodic vicinity turns to violet confirming the formation of the trivalent chromium. The second starts from –1000 mV to –1400 mV. This region is associated with a high current density where hydrogen ion reduction reaction is accompanied with the reduction of Cr^{6+} to Cr^{3+}. The plateau represents the limiting current density of chromium reduction. The observed limiting current densities for solutions containing 1.5, 0.85 and 0.5 g l^{-1} Cr^{6+} are - 44, - 20 and - 18 mA cm^{-2} respectively. The plateau increases with the increase in hexavalent chromium content in solution.

3.1.2. Effect of rotation of cathode

Figure 3 shows the LSV curves of hexavalent chromium reduction from solutions containing 1.5 g l^{-1} Cr^{6+} + 27.5 g l^{-1} H_2SO_4, at different cathode rotations. The limiting current density of the hexavalent chromium reduction to trivalent state increases with the increase in the cathode rotation. This may postulate an irreversible electrochemical reaction limits the diffusion nature of the reduction step. Mechanistic study of the reaction has shown that reduction of Cr^{6+} to Cr^{3+} is partially diffusion controlled process whereas, at higher cathode rotation, the reaction becomes chemically controlled [9, 22].

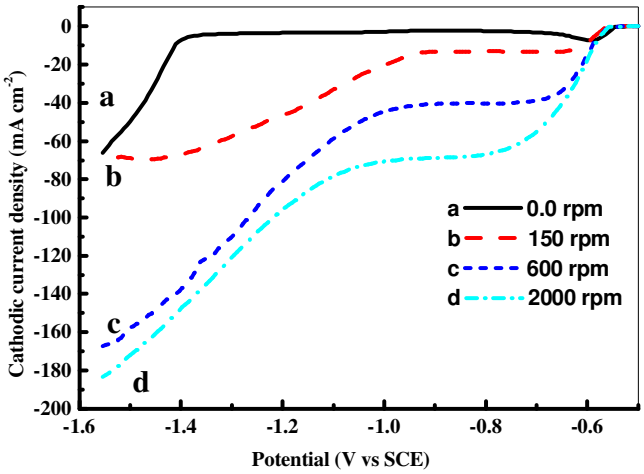

Figure 3. Linear sweep voltammtric curves of electroreduction on lead RDE from solutions containing 1.5 g l^{-1} Cr^{6+} + 27.5 g l^{-1} H_2SO_4 at various rotation speeds.

3.2. Cell voltage studies using rotating cylinder electrode cell

3.2.1. Effect of current density

Figure 4 represents the effect of current density on the cell voltage and cathode potential from acidic solutions containing 1.5 g l^{-1} Cr^{6+} at 600 rpm. The increase of the applied current density causes

an increase in cathode potential (curve a) and cell voltage (curve b). Hydrogen ion reduction to hydrogen gas starts during the experiments. The increase in current density causes cathode passivation due to the increase in hydrogen ion reduction and in electrolyte resistance.

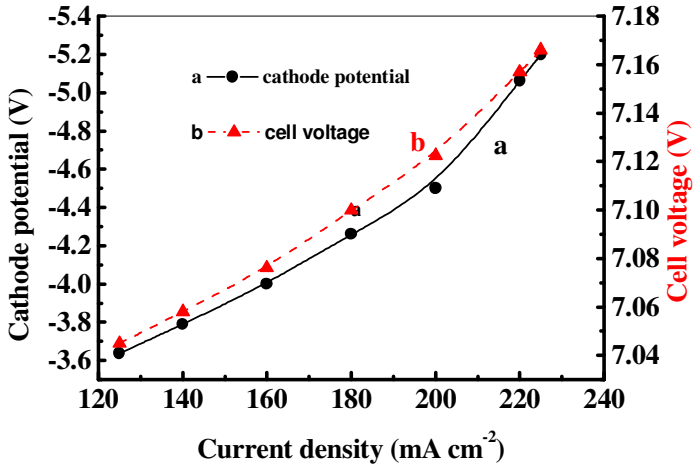

Figure 4. Effect of current density on cathode potential and cell voltage during chromium electroreduction in 1.5 g l^{-1} Cr^{6+} + 27.5 g l^{-1} H_2SO_4.

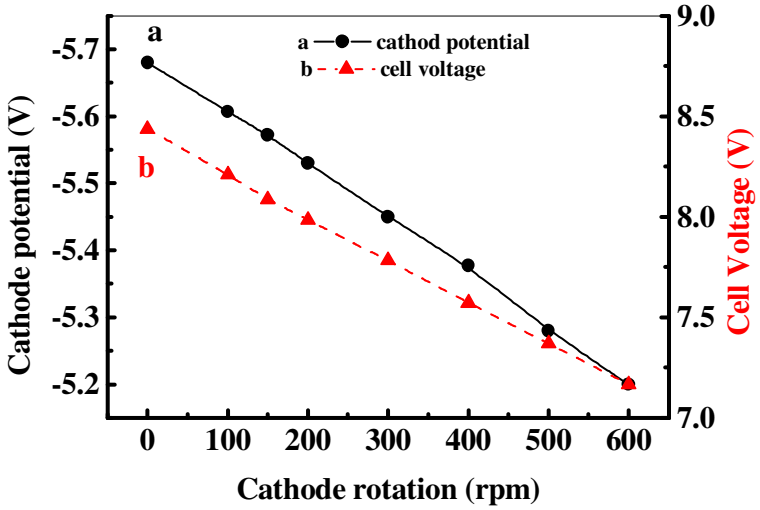

Figure 5. Effect of cathode rotation on cathode potential and cell voltage during chromium electroreduction in 1.5 g l^{-1} Cr^{6+} + 27.5 g l^{-1} H_2SO_4.

3.2.2. Effect of rotation of cathode

Figure 5 shows the effect of cathode rotation on cathode potential and cell voltage during chromium electroreduction from the aforementioned solution at 225 mA cm^{-2}. The rotation of the

cathode varied from 0.0 up to 600 rpm. The results show that the increase rotation of cathode causes a decrease in cathode potential (curve a) and cell voltage (curve b). This is ascribed to the increase in the electrode rotation. This increase in cathode speed leads to a greater uniform chromium concentration adjacent to the electrode surface, and thus decreasing the concentration potential difference [9]. The increase of cathode rotation repels the formed hydrogen gas bubbles from the cathode surface and increases its exposed active surface area.

3.2.3. Effect of sulphuric acid concentration

The effect of sulphuric acid concentration on the cathode potential in 1.5 g l^{-1} Cr^{6+} using different Cr^{6+} to H_2SO_4 molar ratios (1:10 to 1:60 chromium to sulphuric acid) are shown in Fig. 6.

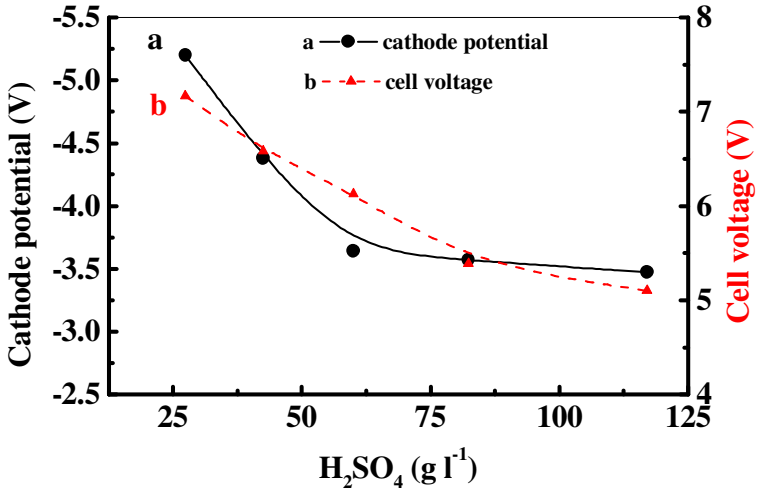

Figure 6. Effect of sulphuric acid on cathode potential and cell voltage during chromium electro reduction in 1.5 g l^{-1} Cr^{6+}, at 225 mA cm^{-2} and at 600 rpm.

In all experiments, sulphuric acid was added to support the electrolyte and to prevent chromium hydroxide formation [9, 22]. Increasing the sulphuric acid concentration up to 60 g l^{-1} shifts the cathode potential towards a more positive values (curve a) (chromium to sulphuric acid molar ratio 1:30). Further increase in sulphuric concentration causes a decrease in the cathode potential in its negative values. The increase in sulphuric acid concentration also decreases the cell voltage values (curve b). This is anticipated to the increase in the conductivity of the electrolyte. The conductivity increases with increasing sulphuric acid in the solution [23-24] which results in a decrease in the cell voltage and cathodic polarization values [11]. Moreover, increasing sulfate concentration prefers electro reduction of hexavalent chromium (reaction 1) rather than the reduction of hydrogen ions (reaction 2) [25- 27].

3.3. Current efficiency and energy consumption studies using rotating cylinder electrode cell

3.3.1. Effect of current density

The electrochemical factors displaying a role on the metal electro deposition are current efficiency and electrode potential. The electrode potential affects strongly in the cell voltage. It is seen that the electrode potential and the cell voltage are directly related to the energy consumption. The energy consumption calculated on the basis of the current efficiency and cell voltage data [11, 24].

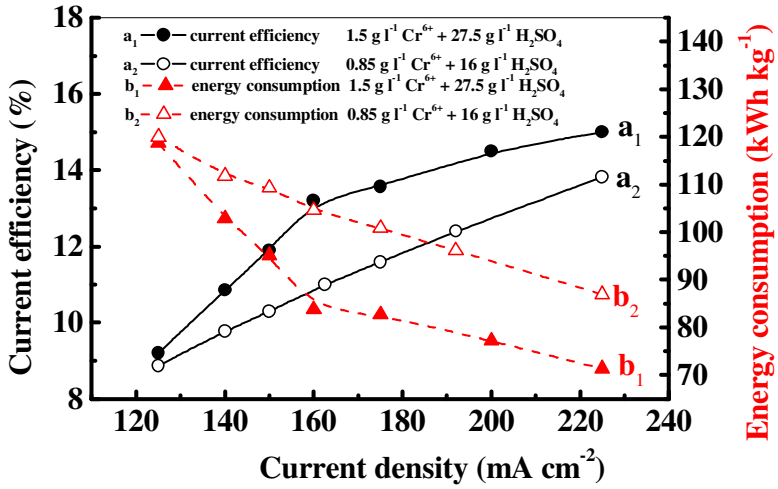

Figure 7. Effect of current density on current efficiency and energy consumption during chromium electro reduction from different concentrations.

Figure 7 shows the relation of current efficiency and energy consumption on the current density of reduction process. Experiments perform at rotation speeds 600 rpm. The cathodic current efficiency of the reduction process increases with increasing current density and chromium content in solution. The increase in the current density values from 125 to 220 mA cm^{-2} results in an increase in the current efficiency from 8.8 to 13.62% for solution containing 0.85 g l^{-1} Cr^{6+} (curve a1) and from 9.1 to 15% for the solution containing 15g $l^{-1}Cr^{6+}$ (curve a2). This behavior is in accordance with equation (1) where the increase in chromium ion concentration (in the left hand site) enhances the irreversible reduction reaction (in the right hand side) and trivalent chromium production [9, 22]. The energy consumption values decrease with increasing both current densities and hexavalent chromium concentration in solution (curve b1 and b2). This behavior agrees with the cell voltage and current efficiency results.

3.3.2. Effect of rotation of cathode

From the engineering point of view, energy consumption is an important factor in cell design and wastewater treatment reactors [11]. Figure 8 shows that the current efficiency increases with

increasing the speed of rotation up to 600 rpm after which a semi steady state behavior is approached (curve a). This is ascribed to the negative effect of stirring on the degree of cathode coverage by hydrogen gas bubbles. This consequently decreases cathodic polarization and increases the cathode effective area [26, 28-29].

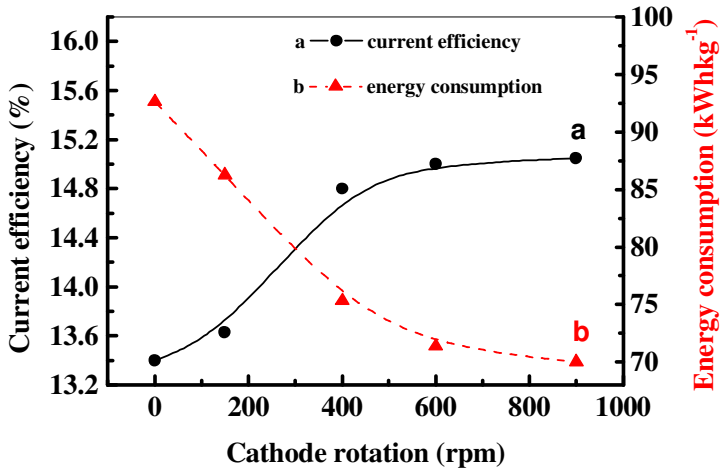

Figure 8. Effect of cathode rotation on current efficiency and energy consumption during chromium electroreduction in 1.5 g l^{-1} Cr^{6+} + 27.5 g l^{-1} H_2SO_4, at 225 mA cm^{-2}.

Figure 8 also shows the effect of cathode rotation on the current efficiency and energy consumption values (curve a, b). Increasing cathode rotation from 0.0 to 900 rpm results in a decrease in energy consumption value from 92.63 to 70 kWh kg^{-1} (curve b). Previous study aimed toward achieving decreased electrical energy consumption is reported [30]. The investment cost of the used Pt anode in these previous studies should be borne in mind and the energy consumption requirement for chromium electrolysis notably higher (137-93 KW h kg^{-1}). In our paper, the energy consumption requirement for reduction process notably lower (92.6 - 70 kW h kg^{-1}). Moreover, the lower investment cost due to the cost of graphite anodes should be borne in mind.

3.3.3. Effect of sulphuric acid concentration

The pH of the solution changes adjacent to the electrode surface during electro reduction of hexavalent chromium to the trivalent state. This favors the precipitation of the formed trivalent chromium to the insoluble hydroxide on the cathode surface. This precipitation increases the electrode passivity and blocks the electrode active sites. So that sulphuric acid supports the electrolyte pH change and prevents chromium hydroxide formation.

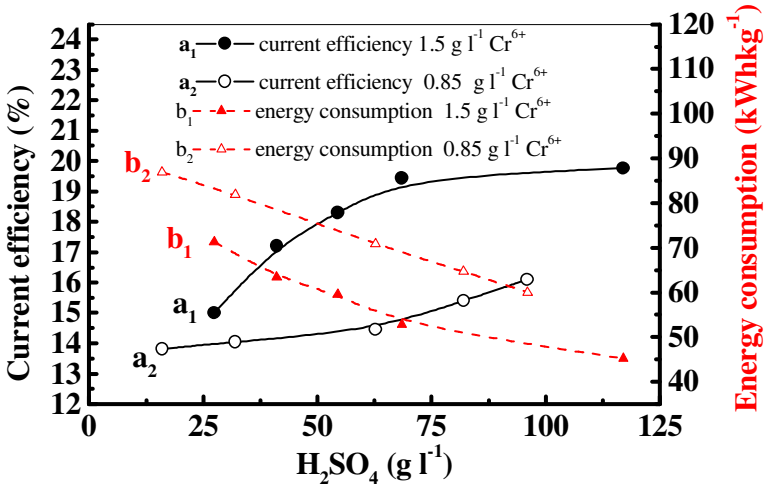

Figure 9. Effect of H_2SO_4 on current efficiency and energy consumption during chromium electroreduction from different concentrations.

Figure 9 represents the effect of sulphuric acid concentration on the current efficiency in 1.5 Cr^{6+} and 0.85 g l^{-1} Cr^{6+} solution. Experiments occur at 225 mA cm^{-2} and at 600 rpm. The molar ratios of chromium to sulphuric acid are ranged from 1: 10 to 1: 60 for both tested solutions (27.5 to 117.5 gl^{-1} H_2SO_4 (0.2 to 1.2 M) for 1.5 g l^{-1} Cr^{6+} (0.02M) and 16 to 96 gl^{-1} H_2SO_4 (0.16 M to 0.98 M) for 0.85 gl^{-1} Cr^{6+} (0.016 M), respectively). These results show that reduction current efficiency increases with the increase in sulphuric acid content in the solution up to about 60 g l^{-1} H_2SO_4 (0.61 M, curve a1) (chromium to sulphuric acid molar ratio 1: 30). With the lower chromium content, the current efficiency increases with the sulphuric acid up to 100 g l^{-1} acid (1.02 M, curve a2). Increasing the acid content in the tested two solutions, results in a limited increase in the current efficiency. This revealed that the reduction products depend on the acidity of the solution [8].

Moreover, Fig. 9 represents the effect of sulphuric acid on energy consumption for 1.5 and 0.85 g l^{-1} Cr^{6+} concentration (curve b1, b2). The energy consumption values decrease with increasing sulphuric acid concentration in both tested chromium solutions. The lowest energy consumption value is achieved with the highest sulphuric acid content 45 kW h kg^{-1} (curve b1) and 60 kW h kg^{-1} (curve b2*)* are obtained for the two tested solutions containing 1.5 and 0.85 g l^{-1} Cr^{6+}, respectively.

3.4. Application on industrial disposal waste solutions

Based on the previous results, the optimum electroreduction conditions achieve at 225 mA cm^{-2}, time 80 min, and at cathode rotation 600 rpm. The performance of the RCE cell in the treatment of industrial wastewater was tested. Industrial samples are delivered by chromium plating and rinse baths companies. A continuous experiment of chromium electroreduction from these samples containing 1.5 g l^{-1} Cr^{6+} dissolved in 75 g l^{-1} H_2SO_4 under the above mentioned conditions. The results show that the

current efficiency for the reduction process is 16 %, the energy consumption is 58 kW h kg^{-1} and the resulted solution is completely depleted from Cr^{6+} ions (Cr^{6+} free solution).

4. CONCLUSIONS

The electroreduction of hexavalent chromium to trivalent chromium was successfully achieved using RCE cell. Electrolysis of hexavalent chromium solution containing chromium to sulphuric acid molar ratio 1: 10 using a lead rotating cathode produced exclusively trivalent chromium. A set of LSV curves of hexavalent chromium from acidic solutions containing 1.5, 0.85 and 0.5 g l^{-1} Cr^{6+} were tested. The curves were displayed two regions. The first region was described as the reduction of Cr^{6+} to Cr^{3+}. The second region was ascribed to the reduction of both Cr^{6+} to Cr^{3+} and hydrogen ions. The limiting current density of hexavalent chromium reduction to trivalent chromium in the first region increased with the increase in the cathode rotation that indicates its diffusion-limited nature.

The cathode potential and cell voltage were increased with increasing current density in acidic solution containing 1.5 g l^{-1} Cr^{6+}. Moreover, the cell voltage decreased with the increase in sulphuric acid concentration from 25 to 160 gl^{-1} H_2SO_4 in solution containing 1.5 Cr^{6+} (chromium to sulphuric molar ratios 1:10 -1: 60). This was ascribed to the increase in solution conductivity. The cell voltage and cathodic polarization decreased with increasing cathode rotation speed up to 600 rpm.

The current efficiency of hexavalent reduction increased with increasing current density from 120 to 240 mA cm^{-2} for the same tested solution. In addition, the efficiency increased with increasing chromium to sulphuric acid molar ratios from 1:10 to 1:60 in the tested chromium solutions, while the energy consumption values decreased. Moreover, the current efficiency results of the acidic solution containing 1.5 g l^{-1} Cr^{6+} were higher than that of 0.85 g l^{-1} Cr^{6+} (of the same chromium to acid molar ratio 1:10), while the energy consumption of the acidic solution containing 1.5 g l^{-1} Cr^{6+} is lower than that of 0.85 g l^{-1} Cr^{6+} (of the same chromium to acid molar ratio 1:10). This data reflects that the current efficiency of Cr^{6+} reduction is catalyzed by the presence of hexavalent chromium and sulphuric acid concentration in wastewater solution. The current efficiency increased with the increase in cathode rotation speeds up to 600 rpm. The performance of the cell in industrial wastewater treatment was tested and hexavalent chromium could be completely reduced to trivalent chromium and removed with a good reduction current efficiency.

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