[ENV02] Treatment of hexavalent chromium using a galvanic flow cell with different flow configurations

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Introduction

Wastewater sources involve two general types, chromium-related and non-chromium wastewaters (Patterson, *et al.*, 1994). Although chromium is present in both the trivalent and hexavalent state in process solutions and wastes, the dominant species is hexavalent chromium (Pollution prevention and control technologies for plating operations, 2000). Hexavalent chromium exists primarily in two anion forms, $HCrO_4^{2-}$ and CrO_4^{2-}, in wastewaters (Aoki, 1982). The hexavalent chromium discharged into the rivers is very harmful for aquatic life and other living organisms (Upadhyay, 1992). It can produce serious hazardous effects like skin disorder, nose bleeding and perforation of nasal septum (Sankaranarayanan, *et al.*, 1985). Medical statistics indicate that the risk of lung cancer is greater for workers in the chromium industry than for the general public (Roe, 1977). USEPA has adopted a limit of 0.05 mg/L in public water supplies (Eckenfelder, 1970).
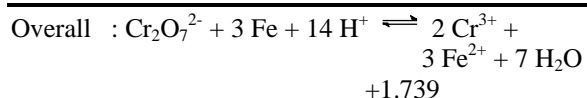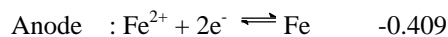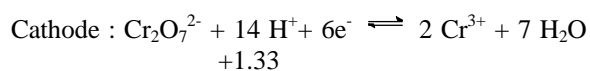
Waste waters polluted with toxic hexavalent chromium result from sources such as textile mills, the pigment industry, metal finishing industries, drug and organic chemical industries and plant cooling systems where chromate is used as a corrosion inhibitor (Radwan, 1992). Among the various treatment techniques available, the most commonly used are reduction and precipitation, ion exchange and adsorption (Sharma, 1993). Others treatment techniques for hexavalent chromium are extraction (Chu, *et al.*, 1996, Alonso, *et al.*, 1997, Palanivelu, *et al.*, 1998), biological treatment (Shen & Wang, 1994, Lee, *et al.*, 1995, Tobin & Roux, 1998, Aksu, *et al.*, 1999) and electrochemical treatment (Fleck & Bautista, 1991, Glikin, *et al.*, 1995, Zhang, *et al.*, 1998).

The present study reports work done on the reduction of hexavalent chromium indirectly with steel wood using a galvanic flow cell system represented as below:

$$Fe\,|\,Fe^{2+}\|Cr^{6+}, Cr^{3+}\,|\,C$$

The electrode reactions for the galvanic cell used in these studies are as follows: (Bard & Faulkner, 1980)

Reactions: E^o, V

Cathode : $Cr_2O_7^{2-} + 14\,H^+ + 6e^- \rightleftharpoons 2\,Cr^{3+} + 7\,H_2O$
              $+1.33$

Anode   : $Fe^{2+} + 2e^- \rightleftharpoons Fe$ -0.409

Overall : $Cr_2O_7^{2-} + 3\,Fe + 14\,H^+ \rightleftharpoons 2\,Cr^{3+} + 3\,Fe^{2+} + 7\,H_2O$
              $+1.739$

The positive overall cell potential indicates that the overall reaction is a spontaneous reaction. The galvanic flow cell was operated in a single pass mode as well as in recirculation mode. Studies were also carried out to study the effect of direction of flow of the electrolytes with respect to each other.

The apparent advantage of this technique is that it uses a cheap reducing agent. Besides, electrical energy is produced from the galvanic cell as a by-product. The advantage of the galvanic reduction of hexavalent chromium using a cell consisting of two compartments over the direct chemical reduction by iron scrap is that, in galvanic reduction, the resulting trivalent chromium is not mixed with iron ions and this makes it possible to recover trivalent chromium as pure $Cr_2(SO_4)_3$ after a preconcentration step (Abdo, 1998).

Materials and Methods

Setup of the cell system

The schematic diagram of the galvanic flow cell is shown in Figure 1. The cell consists of two compartments separated by a cation exchange membrane R4010 , which is sandwiched between the cathode and anode compartment to separate the catholyte and anolyte. The cathode was a graphite sheet of the dimensions 2 x 4 x 0.3 cm. The anode was steel wool. The catholyte used was potassium dichromate solutions prepared in 1 M sulphuric acid because the reduction efficiency is highly dependent on acid concentration (Ozer *et al*., 1997). The anolyte was 1 M NaCl solution. All solutions were prepared from analytical grade chemicals using deionised and distilled water. The current collectors were connected by an external conducting wire to complete the circuit.

Counter flow cell and parallel flow cell

The schematic diagram of the counter flow cell is shown in Figure 1 and the schematic diagram of the parallel flow cell is shown in Figure 2. The electrolytes were pumped into the cell by a peristaltic pump. In the counter flow cell, the direction of flow for the catholyte was opposite to that of the anolyte. In the parallel flow cell, the direction of flow is similar for both the catholyte and anolyte. Output from this cell was collected and the quantity of hexavalent chromium left in the electrolyte was determined with a spectrophotometeric method using 1,5-diphenyl carbazide (Greenberg, *et al.*, 1992). The experiment was carried out with different flow rates of electrolyte varying from 5 mL/min to 10 mL/min and different initial concentrations of hexavalent chromium solutions varying from 10 ppm to 500 ppm. The cell was operated as a single-pass reactor where the electrolyte was passed only once through the cell.
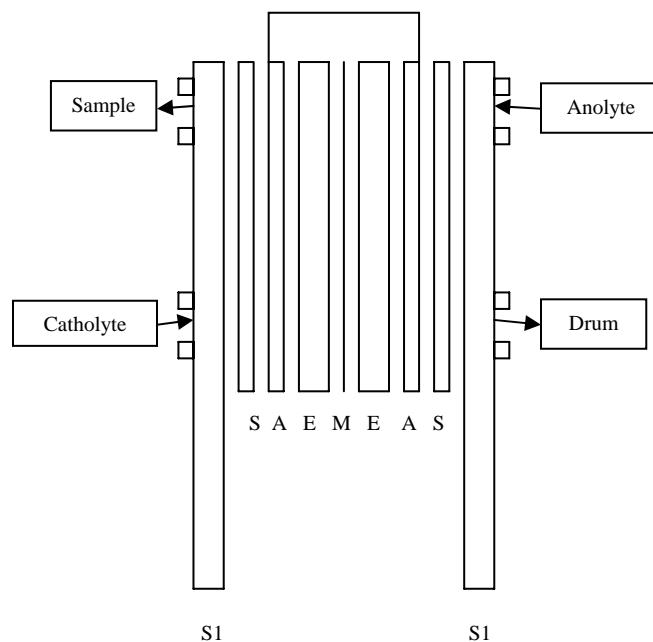

FIGURE 1 Schematic diagram of counter flow cell.(S1:stainless steel support, S: Teflon support, A: current collector, E: electrolyte compartment, M;membrane)

Recirculation flow cell

The schematic diagram of the recirculation flow cell is shown in Figure 3. The experiment was carried out with different flow rates of electrolyte varying from 21 mL/min to 300 mL/min and different initial concentrations of hexavalent chromium solutions varying from 10 ppm to 500 ppm. The cell was operated as a multiple-pass reactor where the electrolyte was passed through the cell and flowed back to the tank until the concentration of hexavalent chromium in the tank falls below the detection limit. Aliquots from the tank were obtained and the quantity of hexavlent chromium left in the catholyte was analyzed with the method mentioned earlier.

Real wastewater from electroplating company

Wastewater from an electroplating company was collected and the initial concentration of hexavalent chromium was determined. Sulfuric acid was added to increase the conductivity of the wastewater. Reduction of hexavalent chromium in wastewater carried out using the single-pass flow cell and recirculation flow cell.

The electrolyte flow rate for single-pass flow cell was 5.0 mL/min and the flow rate for recirculation flow cell was 300.0 mL/min. 1 M sodium chloride was used as anolyte.
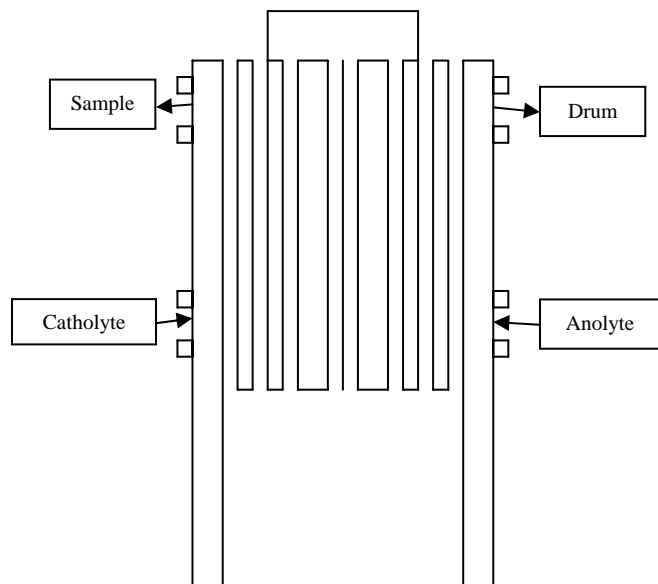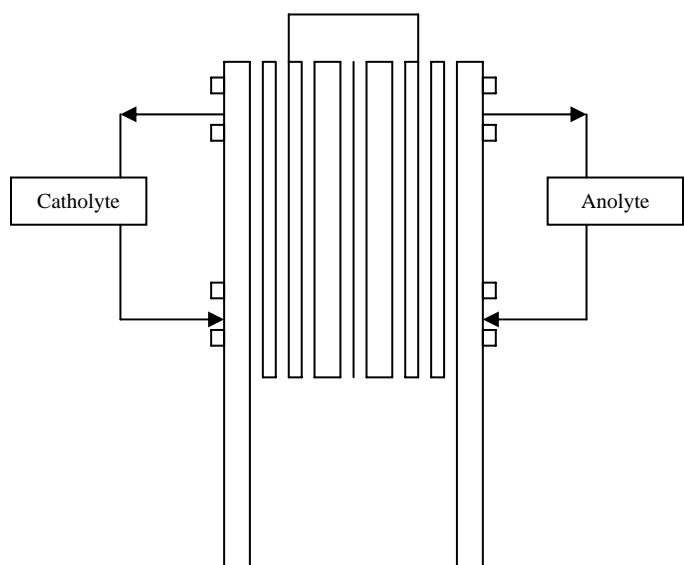

FIGURE 2   Schematic diagram of parallel flow cell.

FIGURE 3   Schematic diagram of recirculation flow cell

Results and Discussion

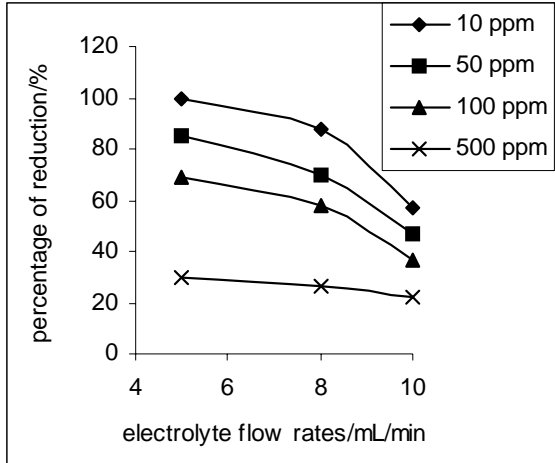### *Effect of flow rates of electrolytes*

Graph 1 and 2 show that the reduction percentage of hexavalent chromium increased when the flow rates of electrolyte were decreased. This indicates that the greatest reduction percentage of hexavalent chromium was achieved with the lowest flow rate of electrolyte. From the optimization process done by William (1999), it was shown that the highest reduction was achieved the lowest flow rate of catholyte. This is because the resident time for the catholyte to react in the cathode was increased at lower flow rates (Yiu, 2000).

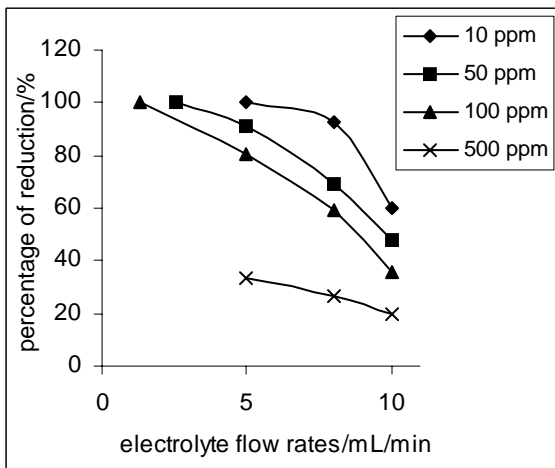### *Effect of initial concentration of hexavalent chromium solution*

The initial concentration of hexavalent chromium solution had a significant effect on the reduction percentage of hexavalent chromium on both cells used. The lower initial concentration of hexavalent chromium solution, the higher is the percentage reduction of hexavalent chromium as shown in graph 1 and 2. The studies done by Yiu (2000), William (1999) and Ozer (1997) had shown similar results using different systems. Because the aim is to reduce the hexavalent chromium completely, we need to use the lower flow rates of electrolyte for the higher initial concentration of hexavalent chromium solution for the single-pass flow cell.

Comparison between counter flow cell and parallel flow cell

Graphs 3 and 4 show that the percentage of reduction for hexavalent chromium using the counter flow cell was higher 2.1% than the parallel flow cell at flow rates of electrolyte at 10 mL/min and the percentage of reduction for hexavalent chromium using the counter flow cell was 3.4% lower than the parallel flow cell at lower flow rates of electrolyte. The corrosion that occurs at the steel wool anode indicates that most of the reactions occur at the electrolyte inlet at lower flow rate. The percentage of reduction is higher using the parallel flow cell
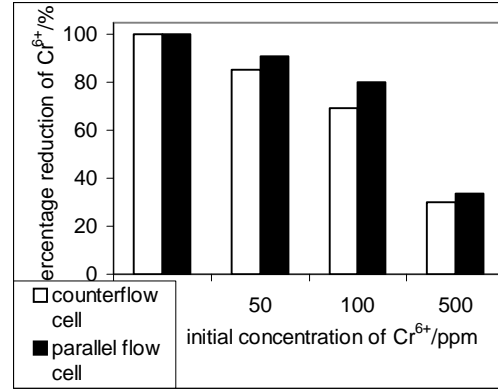
GRAPH 1 Effect of electrolyte flow rates and initial concentration of hexavalent chromium using a counter flow cell.
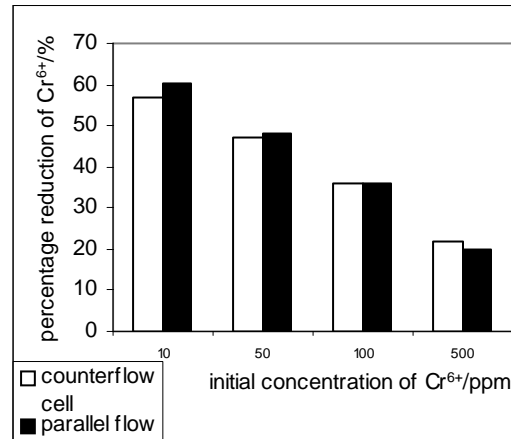

GRAPH 2 Effect of electrolyte flow rates and initial concentration of hexavalent chromium using a parallel flow cell.

because the reactions in the catholyte compartment and anolyte compartment occur at the same place. At higher flow rates of electrolyte, corrosion of steel wool occurs in the whole compartment. The percentage of reduction is higher using the counter flow cell because the pressure was higher when the electrolyte flows opposite to each other.

GRAPH 3 Comparison between counter flow cell and parallel flow cell for electrolyte flow rate of 5 mL/min.

GRAPH 4 Comparison between counter flow cell and parallel flow cell for electrolyte flow rate of 10 mL/min.

Comparison between single-pass flow cell and recirculation flow cell

The data in Table 1 shows the time needed for the single-pass flow cell and recirculation flow cell to reduce 500mL of hexavalent chromium with similar concentration to below the detection limit. The flow rate of electrolyte for the recirculation cell was 300 mL/min and the flow rate of electrolyte for the single-pass flow cell to reduce hexavalent chromium to below detection limit is also shown in Table 1.

TABLE 1 Comparison between single-pass flow cell and recirculation flow cell.

Initial concentration of Cr^{6+}	Electrolyte flow rate of single-pass flow cell	Recirculation flow cell (minutes)	Single-pass flow cell (minutes)
10 ppm	5.00 mL/min	18	100
50 ppm	2.55 mL/min	26	196
100 ppm	1.31 mL/min	36	382
500 ppm	-	66	-

The time needed for the single-pass flow cell was calculated using the equation below:

$$\text{Time (min)} = \frac{500\text{mL}}{\text{Flow rate of electrolyte (mL/min)}}$$

It is also shown that the recirculation flow cell needed less time compared to the single-pass flow cell. The recirculation flow cell will be more suitable for industrial use because it saves time that will be used for wastewater treatment.

Wastewater from electroplating company

Initial concentration of hexavalent chromium for wastewater that was collected from an electroplating company was 312.2 ppm. Results showed a 73.6% reduction of hexavalent chromium using the single-pass flow cell. With the recirculation flow cell, 28 minutes was required to reduce 500 mL of the wasterwater sample to hexavalent chromium levels below the detection limit. It shows that it is feasible to treat hexavalent chromium wastewater with this system in terms of cost and efficiency if this system.

Acknowledgements

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