

Concentrator cell methodology in the regeneration and recycle of chromium etching solutions using membrane technology

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Abstract

The regeneration of chromium (VI) and the recovery of etched copper from chromium etching solutions by electro dialysis is improved by the addition of a concentrator cell, using ion exchange resins or activated carbon cloth as concentrator media, in the catholyte chamber. The maximum percentages for the regeneration of chromium and recovery of copper in these systems is however less than 80 and 90% respectively because of the competition between the processes of oxidation of Cr(III) and electrodeposition of copper. A novel combination of electrolysis with electro dialysis and concentrator cell technology is developed that achieves 92.1% chromium regeneration and 90.4% copper recovery.

Keywords: Electro dialysis, copper, concentrator cell technology, ion exchange, activated carbon cloth.

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1. Introduction

Chromium solutions are used by the electroplating and metal finishing industries as etchants and passivating solutions. These chromium etchants are used, for example, in the printed circuit board industry, where they are used to remove excess copper from the plated board, leaving the imprint of the circuit behind. During the etching process, Cr(VI) (in the form of $\text{Cr}_2\text{O}_7^{2-}$) is reduced to the Cr(III) ion and the copper metal is oxidised to Cu(II) and dissolved to give a mixed chromium - copper wastewater solution (Rajeshwar and Ibanez, 1997).

Due to the high toxicity of chromium and the fact that Cr(VI) is a known carcinogen, most water treatment authorities limit discharge concentrations to about 1ppm. Discharge consents are, however site specific and are dependent upon the dilution capabilities of the water body, into which the effluent is discharged (Chaudhary, 2003). These low discharge consents mean that for most operations, the levels of chromium in the effluent have to be reduced.

The commonest methods of removal of metal species from effluents including etching solutions are based on precipitation, coagulation and cementation (Lee et al., 2003) but this leads to solid wastes that are difficult to dispose of. Other methods that have been used to treat these etching solutions include electrodialysis, reverse osmosis, adsorption and absorption, liquid membranes and ion exchange. Electrodialysis has been used to investigate the transport of trivalent and hexavalent chromium through different ion selective membranes (Kizim et al., 1987; Dalla Costa et al., 1998) and the use of reverse osmosis for the removal of hexavalent chromium from solutions has also been described (Liu and Wu, 1987; Schoeman et al., 1992). Electrodialytic remediation was also used to

treat a soil polluted with copper and chromium from a wood preservation plant (Hansen et al., 1997; Ottosen et al., 1997). The use of a fibre sorbents (Borisenko, 1997) to remove Cr(VI) by ion exchange membranes (Van Andel, 2002) to regenerate the spent chrome etching solution have also been described. The removal and recovery of hexavalent chromium from wastewater has also been achieved using liquid membranes (Palanivelu et al., 1998). A tri-N-butyl phosphate (TBP) liquid membrane, for example, was reported to recover 98% of the Cr(VI) in the effluent with no reduction in efficiency of the recovered solution in etching processes after ten re-uses.

Although copper has been efficiently removed from solution by use of membrane technology, it has been reported that the recovery of copper and chromium from mixtures by this method is more complicated (Ogutveren et al., 1997). One method of overcoming the difficulty associated with the presence of both copper and chromium involved the preliminary adsorption of copper ions onto bentonite clay (Lebedeva et al., 1994). The use of single and double chamber electro dialysis cells for the regeneration of a spent chromium-containing decoppering solutions has been compared (Orekhova et al., 1996). In the single chamber set up, the cathodic deposition of copper was found to be prevented by the presence of Cr(VI) ions. In the double chamber set up, titanium-manganese dioxide anodes were used for simultaneous recovery of copper ions and the oxidation of Cr(III) to Cr(VI). This is, however, a time-consuming process and potentially reusable chromium is lost from the system because of codeposition of Cr on the cathode a process that also reduces the value of the copper recovered.

We now report on studies of the use of concentrator cell technology along with membrane dialysis to achieve the efficient simultaneous recovery of Cu(II) and regeneration of Cr(VI) etching solutions.

2. Experimental methodology

2.1 Chromium regeneration and copper recovery from a model waste solution

A model waste solution was prepared containing 100ppm Cu(II) and 100ppm Cr(III) by dissolving their sulphate salts in 0.02M H₂SO₄. This solution (15L) was placed in the anolyte chamber of an electro dialysis cell (Figure 1) with a 0.5M sulphuric acid solution (15L) in the catholyte chamber. The anolyte chamber contained a platinised titanium mesh anode with an overall surface area of 0.05m² and the catholyte chamber contained a stainless steel plate cathode with an overall surface area of 0.03m². Pumping systems permitted the circulation of the solutions in both chambers independently and the chambers were separated by a *Nafion* 450 perfluorosulphonic acid cation exchange membrane. Experiments were carried out with the cell as described in Figure 1 and with cells in which concentrator cells were added to the catholyte chamber. Two types of concentrator media for the cells was studied (i) ion exchange concentrators in which there is a narrow gap between the concentrator and the cathode as in Figure 2 and (ii) activated carbon concentrators in which the cathode is enclosed in the concentrator. Studies were carried on the dual chamber electro dialysis system alone and on a combination of an electrolytic cell with the dual chamber electro dialysis system. The electrolytic cell system consists of a reservoir tank of 15 litres capacity and an electrolytic chamber of 5 litres capacity. The electrolytic chamber contained two mesh anodes and a stainless steel plate cathode. A model waste solution (15L) containing 100ppm of chromium (III) as sulphate and 100ppm of copper (II) as sulphate was pumped through the

electrolytic chamber and back into the reservoir. In all experiments a current of 2A was applied to the membrane system and samples for analysis were taken from each chamber after 0, 2, 4, 6, 8 and 24 hours and the voltages at these stages recorded. The analysis for copper was carried out by atomic absorption spectroscopy and of chromium by colorometric methods.

3. Results & discussion

3.1 Comparison between electrodialysis systems with and without concentrator cell technology for the simultaneous recovery of copper and regeneration of chromium(VI) from etching solutions

For each of the dialysis systems (with and without concentrator technology), when the current is switched on, there is an immediate production of oxygen at the anode and hydrogen gas at the cathode. Since H^+ ions are also produced by the oxidation reactions at the anode and pass through the membrane to be reduced at the cathode. The ease with which cations are transported through the membrane is in the order $H^+ > Cu^{2+} > Cr^{3+}$ and for this reason, Cr(III) ions remain in the anolyte chamber for the longest time and have greatest chance of being anodically oxidised.

The transport of Cu(II) and Cr(III) from the anolyte to the catholyte chamber from model etching solutions are given in Table 1 for an electrodialysis system alone and for electrodialysis systems with two types of concentrator material, an ion exchange resin and an activated carbon cloth concentrator in the catholyte chamber. The data show that 90%, 93.5% and 94% Cu(II) is transported from the anolyte to the catholyte chamber respectively in these three systems. The data also show that the transport of Cr(III) from the anolyte chamber to the catholyte chamber is reduced from 43% to 21% and 23% in the presence of ion exchange and activated carbon concentrator systems. The high concentration of Cr(III) in the catholyte chamber means that the overall etching

solution regeneration will increase when the membrane system is used in combination with the concentrator cell technology. The data in Figure 3a show that the use of concentrator cell technology increases the conversion of Cr(III) to Cr(VI) after 24 hours from 45.8% for electro dialysis alone to 78.4% for the ion exchange concentrator and 61.9% for the activated carbon cloth concentrator. The data in Figure 3b show that the copper recovery is low, at the initial stages of the reaction, for electro dialysis alone compared to the combined electro dialysis and concentrator cell systems. After 24 hours, copper recoveries are over 80% for all three systems with the best recovery (91.6%) being achieved with an activated carbon cloth concentrator. The energy consumptions in the three systems are shown in Figures 4a and 4b for chromium regeneration and copper recovery respectively. The results show that less energy is required to oxidise Cr(III) to Cr(VI) with the use of combined dialysis – concentrator systems. This decrease in energy consumption in the combined electro dialysis – concentrator cell systems is due to the fact that a high concentration of Cr(III) remains in the anolyte chamber rather than being transported to the catholyte chamber. In the case of copper recovery, more energy is required for electro dialysis system compared to the combined electro dialysis – concentrator systems. The results in Figure 4b show that there is an initial increase in energy consumption for all three systems. This can be explained by the delay in the rate of copper recovery over the first two hours due to the preferential selectivity of H^+ across the membrane. At this point there are very few copper ions moving across the membrane to be recovered at the cathode. In the combined systems, a sufficient number of Cu(II) ions have transported across the membrane after 4 hours so that less energy is required to plate out at the cathode surface.

3.2 Combined electrolytic – dialysis system (with concentrator technology)

Although the dialysis system using concentrator cell technology in the catholyte chamber does lead to an improvement in the percentage regeneration of the Cr(VI) etching solutions, the maximum recovery is still less than 80% because some Cr(III) is transported through the membrane to the catholyte chamber with the Cu(II) ions. To improve the percentage regeneration of Cr(VI), studies were carried out on the combined electrolytic – dialysis (with concentrator cell) technology (Figure 5). This system is designed to achieve the maximum oxidation of Cr(III) to Cr(VI) in the electrolytic cell prior to treatment in the dialysis/concentrator cell.

The data obtained for the pH dependence of the regeneration of chromium and recovery of copper in an electrolytic cell alone show that the optimum pH for chromium regeneration is 2.5, that good regeneration is achieved in the pH range 2.5 to 4.5, and that the greater the percentage regeneration of chromium the lower the percentage recovery of copper. The lower copper recoveries occur because, as the strength of the Cr(VI) increases it begins to leach the deposited copper from the electrode. The purpose of the combined system is to separate the processes of oxidation of Cr(III) from the deposition of copper on a cathode.

The results obtained show that a substantial increase in the rate of chromium regeneration and copper recovery from a Cu(II)/Cr(III) waste model solution can be achieved by the synergistic combination of electrolysis and the electro dialysis/concentrator cell system. This increase in regeneration is due to the fact that more than 87% of Cr(III) is oxidised to Cr(VI) in the electrolytic cell system (Stage – 1). The transport of Cr(VI), in the form of $\text{Cr}_2\text{O}_7^{2-}$, from the anolyte chamber to

the catholyte chamber cannot occur through the cation exchange membrane., whereas maximum transport of Cu(II) ions occurs in the dialysis system (Stage - 2).

The energy consumption for the oxidation of Cr(III) to Cr(VI) in the electrolytic cell system is lower than the electro dialysis system alone. For all pH values tested, the overall energy consumption for chromium regeneration is lower than the electro dialysis cell system (Figure 6). The greatest energy consumption is required at pH 1.5 when the chromium regeneration is low. The energy consumption is minimum at pH 2.5 which is an optimum pH for the regeneration of chromium etching solution.

4. Conclusion

Regeneration of Cr(VI) from copper etching solutions requires both the oxidation of the Cr(III) (formed as the copper is etched) to Cr(VI) and the removal of etched copper from solution. Although the results of this work show that a combination of electro dialysis and concentrator technology, increases the rate of chromium regeneration, the optimum process to regenerate the maximum amount of Cr(VI) and recover the maximum amount of copper is shown to be a novel combination of electrolysis, dialysis and concentrator cell technologies. Optimum regeneration of chromium occurs at pH 2.5 – 4.5 where an average of 92.1% chromium regeneration and 90.4% copper recovery is achieved in the combined electrolysis – dialysis with concentrator technology. The energy consumption for the oxidation of Cr(III) to Cr(VI) is also low compared to the standard electro dialysis system.

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C = Cathode
A = Anode
CEM = Cation Exchange Membrane

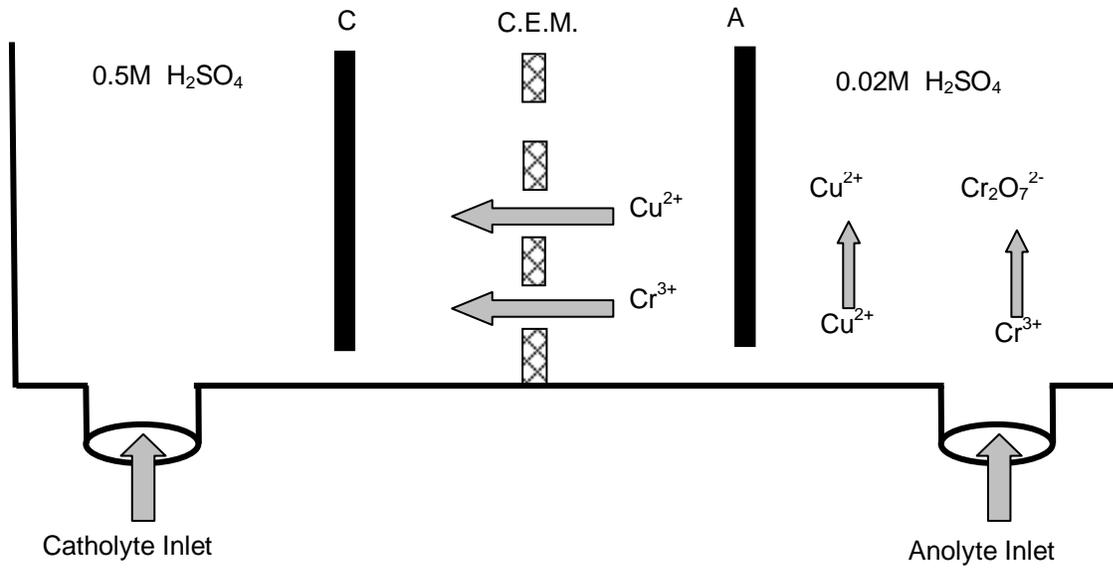


Figure 1: A standard electro dialysis cell system

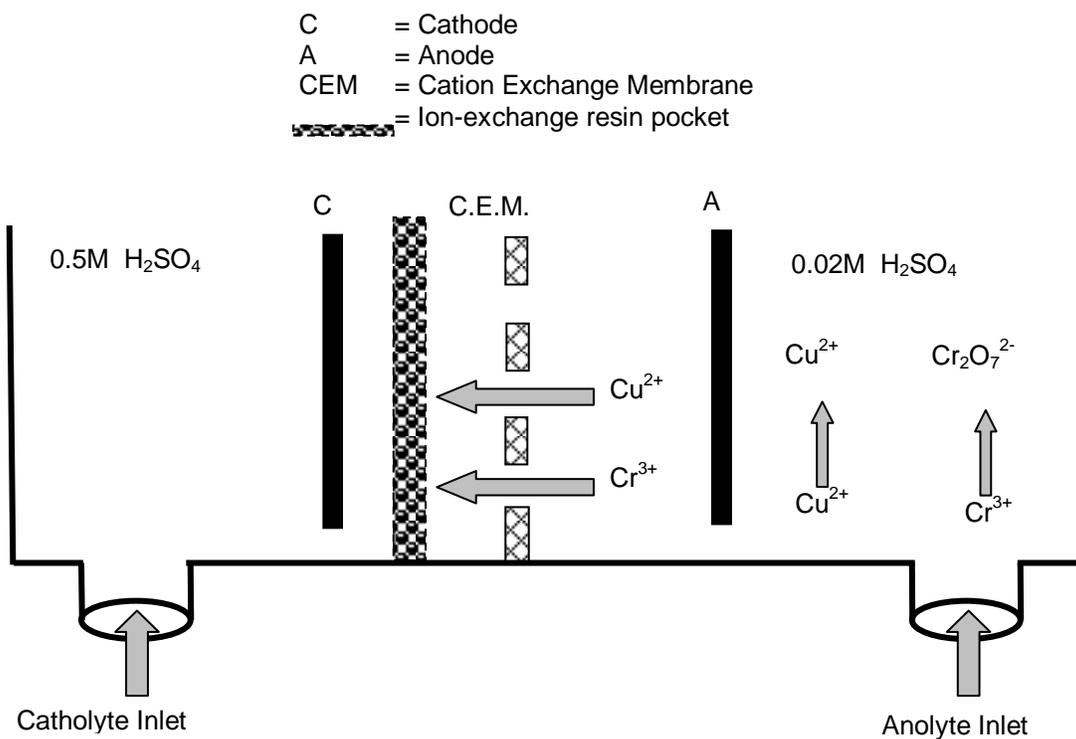


Figure 2: A combined electro dialysis – ion-exchange concentrator cell system

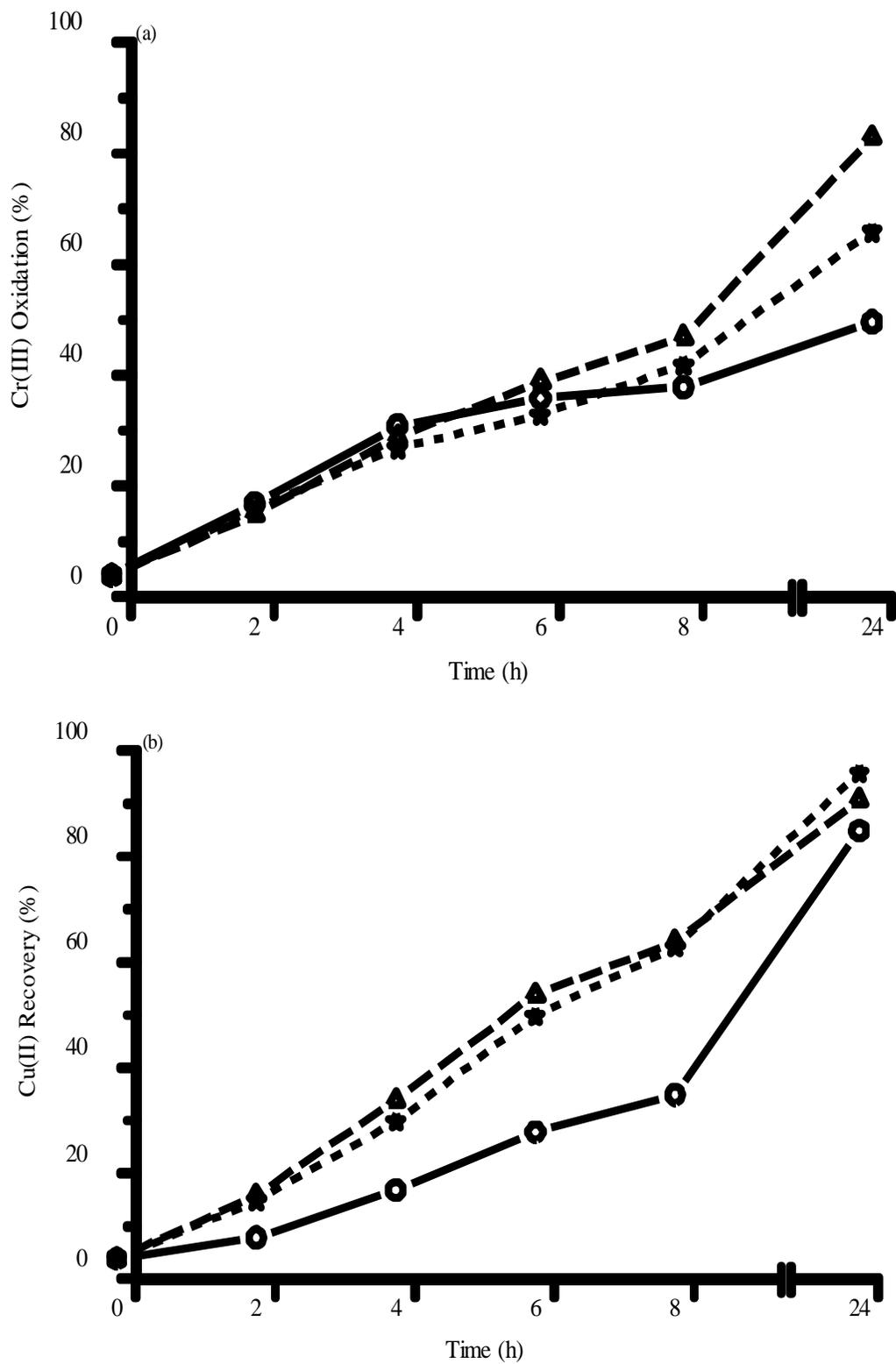


Figure 3: (a) Oxidation of Cr(III) to Cr(VI) and (b) recovery of Cu(II) using three different systems

○ Electrodesialysis system alone, △ Electrodesialysis + Ion-exchange concentrator and
 ☆ Electrodesialysis + Activated carbon concentrator system

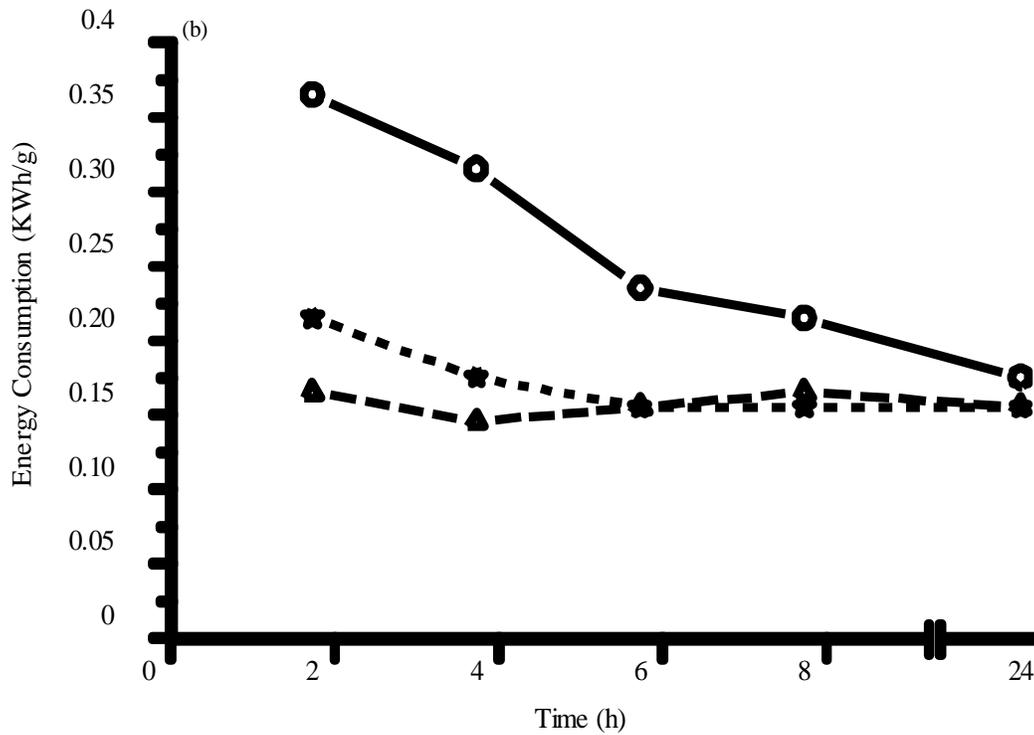
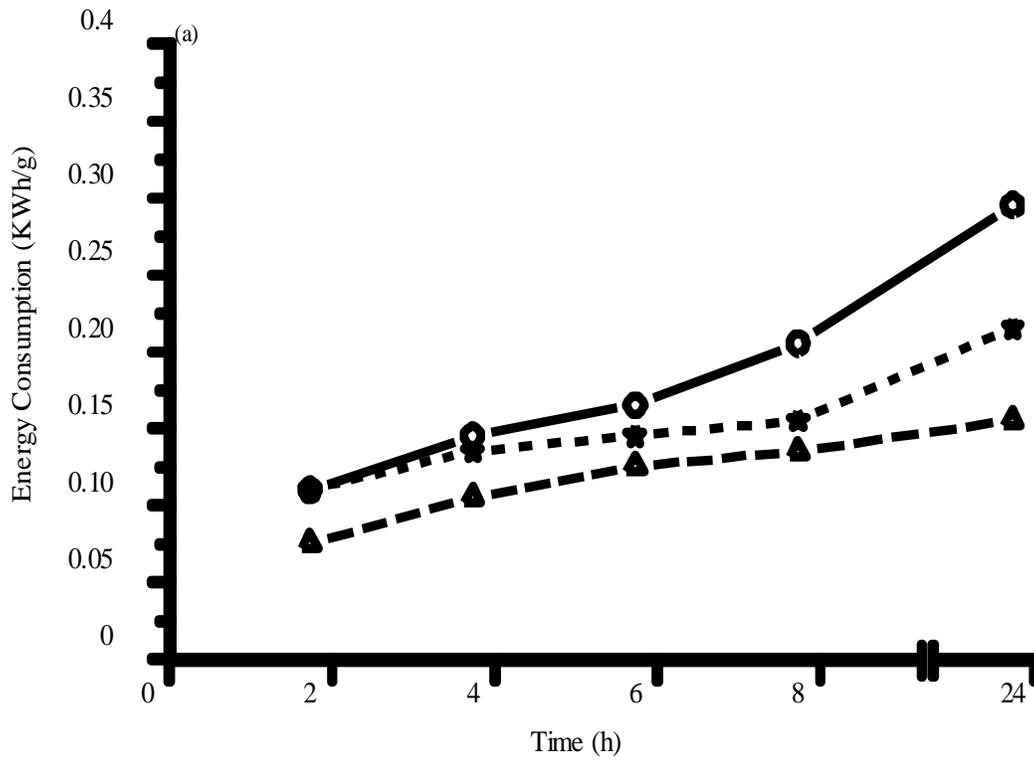


Figure 4: Energy consumption for a) the oxidation of Cr(III) to Cr(VI) and b) recovery of Cu(II) using three different systems. ○ Electrodesialysis system alone, △ Electrodesialysis + Ion-exchange concentrator and ☆ Electrodesialysis + Activated carbon concentrator system

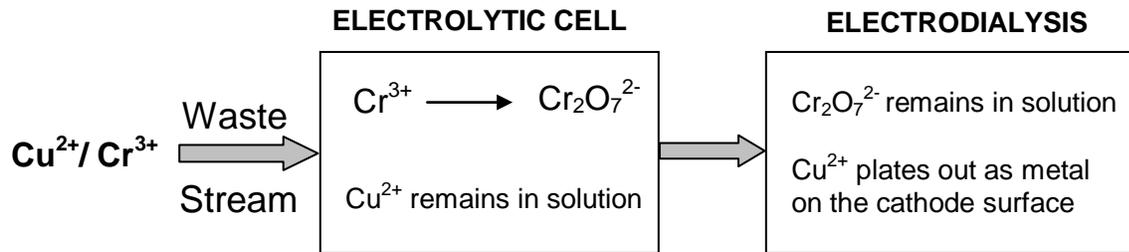


Figure 5: A combined electrolytic - electro dialysis cell system

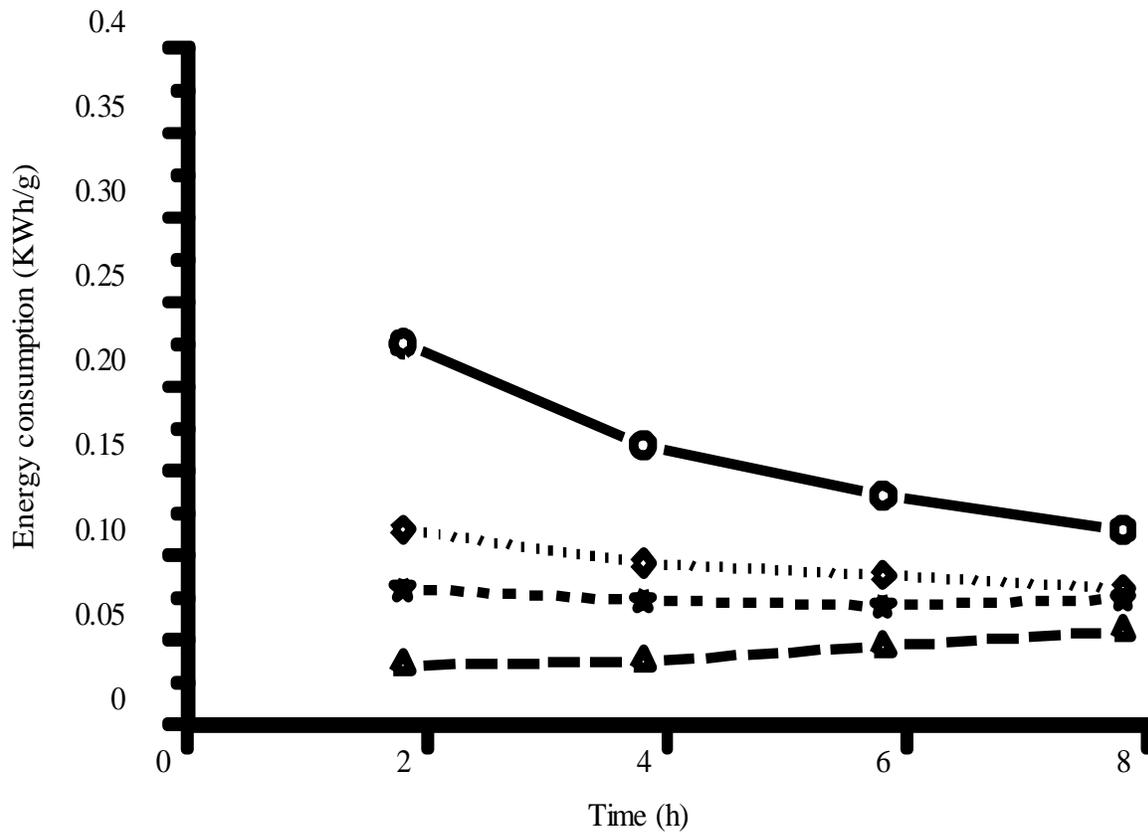


Figure 6: Effect of pH on the energy consumption for the oxidation of Cr(III) to Cr(VI) using an electrolytic cell system. ○ pH 1.5, △ pH 2.5, ☆ pH 3.5 and ◇ pH 4.5

Table 1: Transport of Cu(II) and Cr(III) from the anolyte chamber to the catholyte chamber in three different systems

Time (Hours)	Average anolyte metal concentration (ppm)					
	Electrodialysis alone		Electrodialysis + ion exchange resin		Electrodialysis + activated carbon cloth	
	Cu	Cr	Cu	Cr	Cu	Cr
0	100	100	100	100	100	100
2	82.6	92.0	85.3	96.7	85.2	97.8
4	60.5	86.2	63.1	93.5	62.5	92.3
6	38.2	75.9	56.3	87.0	53.1	89.9
8	24.2	69.0	49.1	82.5	42.4	84.3
24	10.2	57.9	6.5	79.1	5.9	77.4