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Short Communication

The regeneration and recycle of chromium etching solutions using concentrator cell membrane technology

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Abstract

The regeneration of chromium (VI) and the recovery of etched copper from chromium etching solutions by electrodialysis is improved by the addition of a concentrator cell in the catholyte chamber. The concentrator media used are ion-exchange resins or activated carbon cloth. 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 electrodialysis and concentrator cell technology is developed that achieves 92% chromium regeneration and 90% copper recovery.

Keywords: Electrodialysis; Copper; Concentrator cell technology; Ion exchange; Activated carbon cloth

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, 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 $Cr_2O_7^{2-}$) is reduced to Cr(III) 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 1 ppm. 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 these lead to solid wastes that are difficult to dispose of. Other methods that have been used to treat 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

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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 fibre sorbents (Borisenko et al., 1997) to remove Cr(VI) by ion-exchange membranes (Van Andel and Janssen, 2002) to regenerate the spent chrome etching solution have 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 liquid membrane, for example, was reported to recover 98% of the Cr(VI) from etching effluent with no reduction in efficiency of the recovered solution in etching processes after ten reuses.

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 electrodialysis 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) species. 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). The process is, however, time-consuming and potentially reusable chromium is lost from the system because of codeposition of Cr on the cathode a factor 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 100 ppm Cu(II) and 100 ppm Cr(III) by dissolving their sulphate salts in 0.02 M H_2SO_4. This solution (15 l) was placed in the anolyte chamber and in the reservoir (A) of an electrodialysis cell (Fig. 1) with a 0.5 M sulphuric

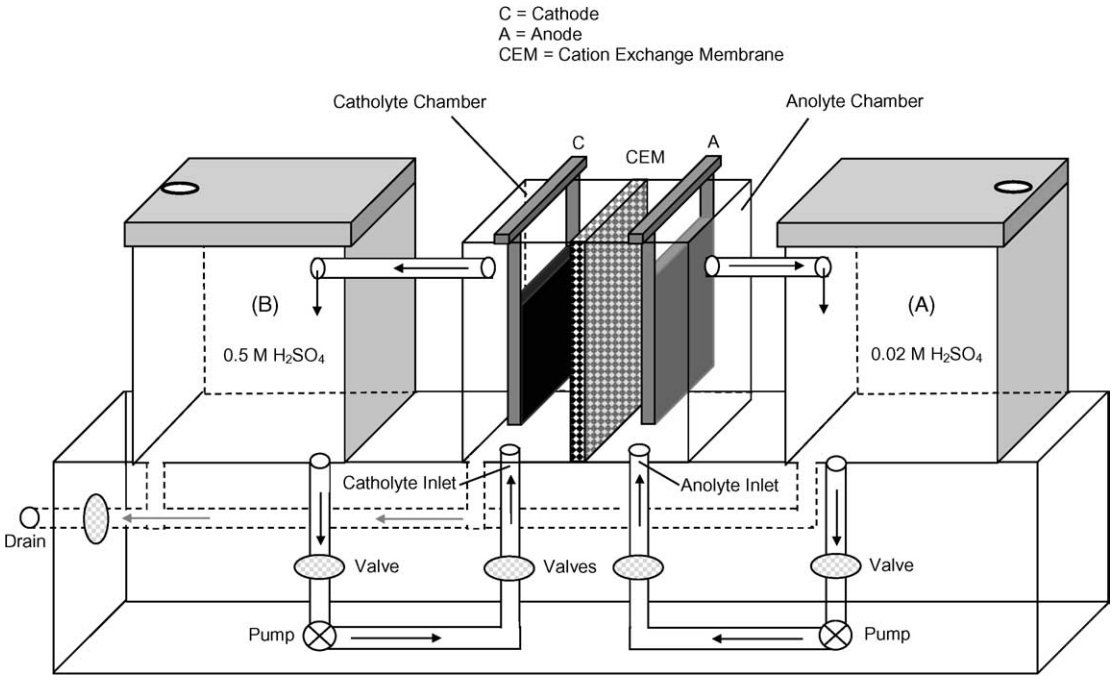

Fig. 1. A standard electrodialysis cell system.