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An innovative membrane method for the separation of chromium ions from solutions containing obstructive copper ions

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ABSTRACT

Chromium is one of the major pollutants of water and wastewater; this ion can be seen in different industrial effluents along with other metal ions such as Cu, As [E. Velizarova, A.B. Ribeiro, and L.M. Ottosen, A comparative study on Cu, Cr and As removal from CCA-treated wood waste by dialytic, Journal of Hazardous Material 94 (2) (2002)147–160]. In the current paper, experimental investigations have been done on the removal of the chromium ions from aqueous solutions which contain Cu^{2+} as obstructive ion. Electrodialysis is coupled with complexing to recommend a new technique for the elimination of chromium (III) ions. Ethylendiaminetetraacetate acid (EDTA) was used as the complexing agent. The effect of different operating conditions (feed flow rate, voltage or current density, the ratio of the chromium (III) concentration to the copper concentration, EDTA molar ratio to Cr (III) and pH of the feed) on the removal of chromium ions was investigated. The Taguchi method was implied to design the experiments. The optimum operating conditions were determined using the analysis of variance (ANOVA) method. The proposed method resulted in relatively high chromium removal (95% Cr (VI) and 87% Cr (III)) at the optimum operating conditions.

1. Introduction

Chromium is applied in different industries such as tanning factories, steel works, industrial electroplating, wood preservation, artificial fertilizers, paint and pigment manufacturing, corrosion control, textile and photography [1–4].

Chromium toxicity varies with the concentration and oxidation state. Hexavalent and trivalent chromium are two common oxidation states in nature. Although trivalent chromium is less toxic and similar to many other heavy metals, in small traces is necessary for life processes, the higher concentrations of it in the environment and consequently human intake cause many diseases [1,5,6].

Chromium (VI) is soluble in water over the entire pH range so it is mobile in nature. Because of its high mobility, Cr (VI) is able to easily permeate in to the biological membranes; therefore, it is highly toxic and known as a carcinogen material. Depending on the pH of the aqueous system, this ion is expected as anionic species such as $HCr_2O_7^-$, $HCrO_4^{2-}$, CrO_4^{2-} and $Cr_2O_7^{2-}$. According to the Environment Protection Agent (EPA), release of 1 ppm of Cr (VI) and 1–5 ppm of Cr (III) in the industrial effluents is permitted [2,7,8].

Methods such as chemical precipitation, ion exchange resin, foam flotation, adsorption, and solvent extraction are used for the removal of the chromium from industrial effluents. Membrane methods like ultrafiltration, nanofiltration, reverse osmosis, electrodialysis and liquid membrane may be suitable alternatives to the abovementioned methods [6,9–13].

The most widely applied method for the recovery of Cr (III) is precipitation with alkalis or sulfide; although this method is simple and inexpensive, it creates large loads of toxic waste sludge. The remaining sludge contains small suspended solids which have to be removed with filtration as a secondary method. The residue still contains trivalent chromium [5,8,14,15]. To remove Cr (VI), reduction is used prior to precipitation [16].

Another popular technique for the removal of chromium, especially chromium (VI), is ion exchange resins. This method has the advantage of treatment of huge quantities of wastewater. The drawback is the high cost of resins and their regeneration [15,17–19].

Electrodialysis (ED) is a proper alternative for the treatment of industrial effluents; it minimizes or prevents the production of the final sludge while still keeping high efficiency [20]. Many aspects of chromium removal from solutions using ED have already been studied; Rodrigues and his group investigated the separation of Cr^{+3} from Na^+ in aqueous solutions using modified cation exchange membranes. They used a two-step process; in the first step, the separation of Cr^{+3} and Na^+ was done by electrodialysis using a monovalent cation exchange membrane. In the second step, the optimum concentration of Cr (III) was achieved by electrodialysis using non modified membranes [21]. Cengeloglu et al. studied the transport of Cr (VI) ions in contact with different salt solutions from three different anion exchange membranes; their study showed that the transport of Cr (VI) ions is the highest when

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Table 1
Physical and chemical characteristics of ion exchange membranes.

Property	Membrane	
	AR204SXR412 CR67, MK111	CR67, MK111
Reinforcing fabric	Acrylic	Acrylic
Thickness (mm)	0.5	0.56–0.58
Specific weight (mg/cm^2)	13.7	13.7
Burst strength (kg/cm^2)	7	7
Water content (%)	46	46
Capacity (meq/g dry membrane)	2.8	2.4

there are no other salts available. For all three membranes, as the salt anion valence became higher the Cr (VI) anions separation was further reduced [22]. Tor et al. applied ED for the simultaneous recovery of Cr (III) and Cr (VI) ions from aqueous solution containing monovalent and divalent obstructive ions. Their investigation showed that the recovery of ions increased with the increase of current density and decreased in the presence of co-existent ions in the feed phase [23].

Although many original and modified methods for chromium ion removal are already recommended, there is still a need for innovating simpler and more efficient methods.

Many researchers applied complexing agents along with the separation processes such as ultrafiltration and electrodialysis to increase the efficiency of the ion removal. Addition of a complexing agent resulted in higher selectivity and permeation fluxes, lower energy costs and high rejection coefficients [24–27]. EDTA as an organic chelating agent has high selectivity and creates stable complexes with most of the metal ions [25,28,34]. In the current study, with the complete attention to the advantages of EDTA as a complexing agent, complexing was combined with ED method to enhance the removal of chromium ions in co-existence with the copper ions. The purpose of the EDTA addition is to engage the copper ions and prevent their immigration from cation exchange membrane in order to reach high removal of chromium ions.

2. Material and methods

2.1. Experimental set up

A 150 × 150 mm^2 three-compartment ED cell made from Plexiglas was used. Plexiglas was chosen to be able to observe the inside of the cell and wash the membranes in the case of precipitation; Plexiglas also resisted against the corrosion in contact with acids. Because electrical resistance adversely changes with distance, thin Plexiglas frames were used (thickness of dilution chamber was 7 mm). Smaller compartments cause high turbulence of the feed flow; turbulence in the compartments prevents the formation of concentration polarization inside the cell. The ED cell was packed with a pair of ion exchange membranes (AR204SXR412 as anionic and CR67, MK111 as cationic both manufactured by Ionics Resources Conservation Co.). The effective area of membranes was 95 × 95 mm^2. The membranes' physical and chemical properties are given in Table 1.

The cathode was chosen from stainless steel and the anode was made of titanium coated with platinum. 0.05 M nitric acid and 0.05 M hydrochloric acid were used alternately, as the anode and cathode cleansing solutions. The electrodes were washed to avoid the accumulation of the produced gasses on them; the consequent result of gas accumulation is the increase of the cell electric resistance. All the experiments were done at room temperature (20–22 °C). To reach steady state, runs were continued for at least 20 min before sampling the dilute (discharge). A complete schematic of the experimental set up is illustrated in Fig. 1.

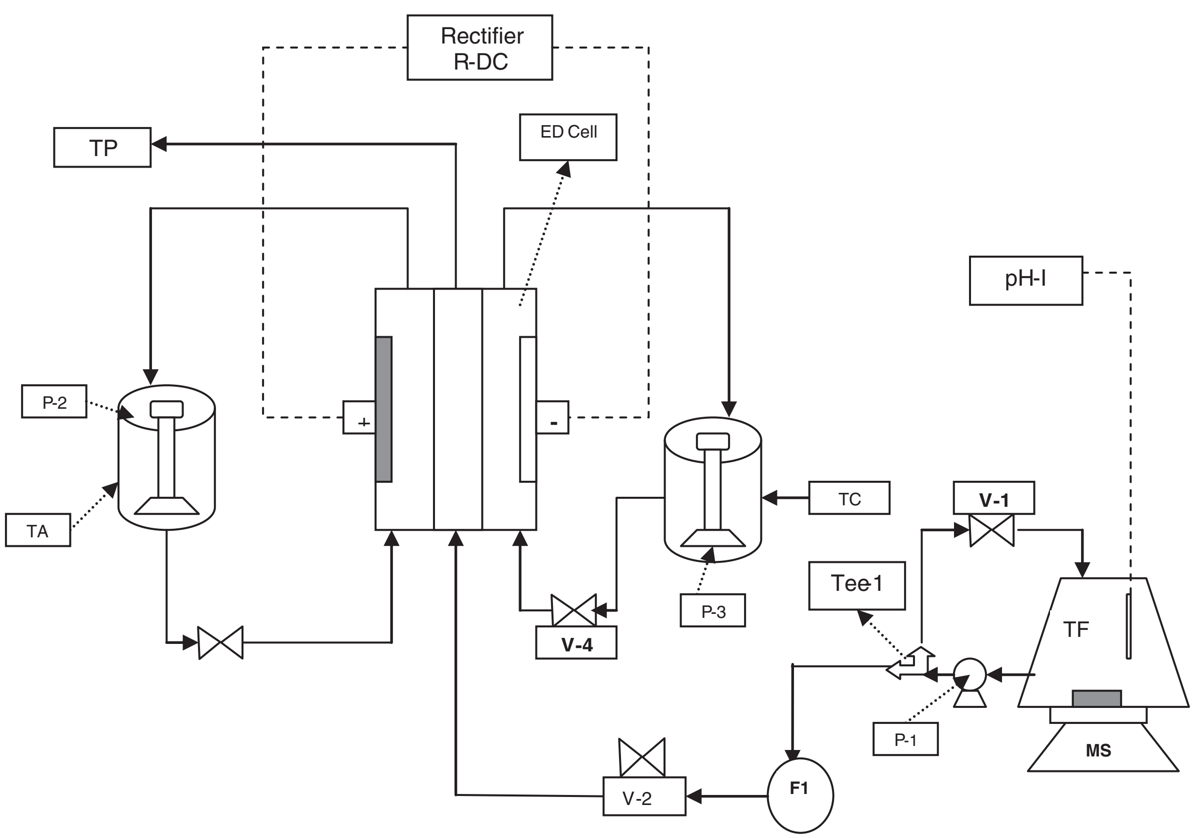

Fig. 1. Experimental set up.