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Separation and recovery of Cr(III) and Cr(VI) using electrodeionization as an efficient approach

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ABSTRACT

Cr(VI) is carcinogenic while Cr(III) is considered to be less toxic. Cr species with combined oxidation states are often found in industrial effluent. It is thus critical to develop techniques that have the capacity for the removal of both Cr(VI) and Cr(III). Here we report, for the first time, the continuous separation and recovery of Cr(III) and Cr(VI) using electrodeionization (EDI) as an advanced and efficient approach. Firstly, we have developed a new analytical method, which integrates UV–Visible spectroscopy and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), for determining the concentrations of both Cr(VI) and Cr(III) in a mixed solution, and for monitoring the EDI process. Secondly, we have determined the limiting current and systematically studied the effects of different applied currents on the removal of Cr(VI), as well as the recovery of Cr(III) and Cr(VI). Thirdly, the influence of the level of saturation of the ion-exchange resins was assessed in terms of both removal efficiency and energy consumption. It was revealed that the use of fresh ion exchange resins for the EDI process, initially exhibited the very effective removal of both Cr(VI) and Cr(III). Both resins became increasingly saturated subsequent to each cycle, resulting in a gradual lowering of the cell voltage. The continuous and highly efficacious removal of highly toxic Cr(VI) (>99%), and low energy consumption make the EDI process attractive for the separation and recovery of Cr(VI) and Cr(III).

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1. Introduction

Chromium is naturally occurring in soils, rocks, plants and animals and is of importance for the environment, human health, and in industry. However, it is also a waste product that is excessively generated by various industries, such as in stainless-steel production, leather tanning, paint and pigment fabrication [1–3]. The most useful form of chromium is metallic chromium, which is widely used to provide wear, abrasion and corrosion resistance for metals via the process of electroplating. For metallic chromium, chemically inert Cr_2O_3 forms on the surface, which is deemed as safe for the environment and human health. However, the remaining forms of chromium, subsequent to the electroplating process, are its only stable ions: Cr(III) and Cr(VI). Cr(VI) ions are extremely toxic, and have been classified as a carcinogenic agent in humans by the IARC (International Agency for Research of Cancer). Cr(VI) exists primarily as an anionic species in aqueous solutions such as $HCrO_4^-$, CrO_4^{2-}, $HCr_2O_7^-$ and $Cr_2O_7^{2-}$, contingent on pH [4]. In contrast, Cr(III) is less soluble and much less toxic than Cr(VI). One strategy that is utilized in industry to treat Cr(VI) involves its reduction to less toxic Cr(III), which is then precipitated out by forming $Cr(OH)_3$ at near neutral to high pH [5]. Other techniques for the treatment of chromium waste involve coagulation, ion exchange, reverse osmosis and solvent extraction. Both Cr(III) and Cr(VI) species may often be found in industrial effluents [6–8]. In addition, Cr(III) and Cr(VI) can be exchanged via oxidation and reduction [9]. It is therefore critical to develop a novel approach that can effectively treat both Cr(III) and Cr(VI).

Various techniques, for instance co-precipitation [10], solvent extraction utilizing different reagents [11], ion exchange [12], electrochemical reduction [13] and solid-phase extraction [14], have been used for the preconcentration, conversion and separation of Cr(III) and Cr(VI) species. Ion exchange resins have been employed for the removal of Cr(VI) from wastewater [15]; however, this is not a continuous process, as the resins may easily become exhausted (saturated). Therefore, they require the regeneration of its ion exchange sites with acids or bases, which creates a secondary chemical waste in the process [16]. Electrodialysis (ED) has been successfully utilized in the past as a method for the removal of metal ions from wastewater through the application of an electrical current or potential in conjunction with ion exchange membranes. The limitation of electrodialysis, however, is that once the ion concentration becomes low, higher levels of energy are

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consumed in conjunction with low ion removal efficiencies [17]. The synergistic combination of these two technologies is called electrodeionization (EDI) [18–22], which has been found to generally resolve issues that are inherent to these two technologies when they are applied on their own.

Electrodeionization has been used for the production of high-purity water, and it has also been investigated for the removal of heavy metals within diluted electroplating rinse waters [23–29]. The dual driving forces that have enabled this hybrid technology to outperform ion exchange resins and electrodialysis include the efficient regeneration of ion exchange sites, and the high level of conductivity that is maintained in the dilute compartment from the ion exchange resins, which leads to more rapid, energy efficient and extensive separation [30]. The regeneration of the ion exchange sites is accomplished through a process called electroregeneration, which electrically induces water splitting reactions via the formation of H^+ and OH^-, to regenerate the resins to their proton and hydroxide forms [31]. The water splitting reaction was found to be enhanced at the bipolar interfaces of ion-exchange materials (cationic resin – anionic resin, cationic resin – anionic membrane, anionic resin – cationic membrane) [32,33]. By virtue of having a mixed bed of ion exchange resins, water-splitting might theoretically be evenly dispersed across the entire dilute compartment, thus regenerating the ion-exchange resins in a uniform manner [34]. It was also experimentally discovered that mixed beds of resins in EDI were the most efficacious [18]. Although electrodeionization has an issue with metal hydroxide precipitation due to large OH^- ion populations that are formed as the result of water splitting, this might be avoided by lowering the pH to conditions where the precipitation does not occur [35].

Although EDI has been widely investigated for the removal of Cr(VI) from wastewater [36–39], to the best of our knowledge, there is no report on the simultaneous separation of Cr(III) and Cr(VI). In the present study, we have explored EDI as an advanced approach for the continuous separation and recovery of Cr(III) and Cr(VI). A new analytical method, which integrates UV–Visible spectroscopy and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) has been developed for monitoring the concentrations of both Cr(VI) and Cr(III) in a mixed solution. We have also determined the limiting current and systematically studied the effects of different applied currents of EDI on the removal of Cr(VI), as well as Cr(III). Moreover, the influence of the level of saturation within the ion-exchange resins has been assessed in terms of both removal efficiency and energy consumption. The improved configuration of the EDI membrane stack described in this study may also be employed to simultaneously separate other anions and cations.

2. Experimental

2.1. Materials

The cationic exchange membranes (CMI-7000S) and anionic exchange membranes (AMI-7001S) were purchased from Membranes International Inc. As for the AMI-7001S, the polymer structure was comprised of cross-linked gel polystyrene and DVB (Divinylbenzene), with $-N^+(CH_3)_3$ functional groups and a total exchange capacity of 1.3 Eq/L. The polymeric structure of the CMI-7000S was also cross-linked gel polystyrene and DVB (Divinylbenzene), with $-SO_3^-$ functional groups and a total exchange capacity of 1.6 Eq/L. A strong basic macroreticular anion exchange resin (Amberlite® IRA900RF Cl) and a strong acidic macroreticular cation exchange resin (Amberlite® 200C Na) were purchased from Rohm and Haas Co. The matrix of IRA900RF Cl was a styrene DVB (Divinylbenzene) copolymer, with $-N^+(CH_3)_3$ functional groups and a total exchange capacity of >1.0 Eq/L (Cl^- form). The matrix of 200C Na consisted of a styrene DVB (Divinylbenzene) copolymer, with $-SO_3^-$ functional groups and a total exchange capacity of >1.7 Eq/L (Na^+ form). Solutions containing Cr(VI) were prepared from analytical grade $K_2Cr_2O_7$ (99.5% purity; Sigma Aldrich). Solutions containing Cr(III) were prepared from 'Baker Analyzed' Reagent $Cr_2(SO_4)_3{\cdot}nH_2O$. The 0.1 M H_2SO_4 electrolytes were prepared from ACS reagent grade H_2SO_4 (95.0–98.0% purity; Sigma Aldrich). The water used in the preparation of all the solutions was purified by a Nanopure® Diamond Water System (18 MΩ cm). All of the experiments were carried out at 20 ± 2 °C.

2.2. Ion exchange resin and membrane pre-treatment

The anion exchange resin (Amberlite® IRA900RF Cl) and a strong acidic macroreticular cation exchange resin (Amberlite® 200C Na) were treated with 0.1 M H_2SO_4 for 60 min, rinsed with Nanopure water for 30 min, treated with 0.1 M KOH for an additional 60 min, rinsed once again with pure water for 30 min, and then dried at 60 °C. The membranes were immersed in 0.1 M KOH for 24 h prior to use, and subsequently rinsed with deionized water to remove any excess KOH just prior to their installation into the electrochemical cell system.

2.3. Analysis of Cr(III) and Cr(VI)

The total Cr(VI) and Cr(III) concentrations in solutions were determined by ICP-AES (Varian Vista Pro). The Cr(VI) for the Cr mixture experiments was analyzed using a UV–Visible spectrophotometer (Cary 50). The pH of the aqueous solutions was measured with an Oakton Acorn® pH meter.

2.4. Electrochemical set-up

Our previous studies have shown that Ta_2O_5–IrO_2 coatings possess robust electrocatalytic activity and stability as an anode material [40,41]. The ED and EDI were carried out in an electrochemical cell utilizing a stainless steel plate (5 cm × 8 cm) as the cathode, and Ti/Ta_2O_5–IrO_2 as the anode, whereas Ti mesh was employed as the substrate. To determine the optimized current for the EDI process, a polarization curve was recorded using a Voltalab (PGZ 402 Universal Potentiostat).

2.5. Preparation of the Ti/Ta_2O_5–IrO_2 electrode

A thermal decomposition technique was employed in the preparation of the Ti/Ta_2O_5–IrO_2 anode. A Ti mesh substrate (5 cm × 8 cm) was immersed in acetone in an ultrasonic bath for 15 min. Subsequently, the mesh was etched in 32% HCl at 85 °C for 15 min and rinsed with ultrapure water. The Ta_2O_5–IrO_2 coating was prepared by combining iridium and tantalum precursor solutions, according to an established protocol [42]. The precursor solution was prepared by mixing the iridium precursor solution (dissolution of 0.30 g of $IrCl_3{\cdot}3H_2O$ in 2.5 mL of ethanol) and the tantalum precursor solution (0.13 g $TaCl_5$ dissolved in 7.5 mL of isopropanol). The coating solution was painted manually onto the Ti substrates using a brush technique. This process was repeated until an oxide coating load of 30 g/m^2 was attained. The electrode then underwent thermal treatment under 450 °C for 1 h.

2.6. ED and EDI treatment of Cr(VI) and a mixture of Cr((III) and Cr(VI)

The ED stack setup, as shown in the top of Scheme 1 (designated as "unexpanded cell"), was configured by using two acrylic sheets of 18 mm in thickness, which housed the two electrodes as well as the electrodic compartment solution, and by integrating three

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