



Electro-capture of heavy metal ions with carbon cloth integrated microfluidic devices



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ABSTRACT

A new multi-compartment microfluidic device was developed to simultaneously desalinate and recover valuable metal ions from aqueous streams mimicking metal plating and mining tailing wastewaters. Heavy and valuable metal ions including copper, zinc, nickel, silver and zinc/copper ionic mixtures were selectively transferred from the feed solution to a reduction chamber through ion-exchange membranes under the influence of an electrical field. A porous and conductive carbon cloth material was used as reduction platform, which led to improved desalination efficiencies, previously unachievable due to inevitable poisoning and degradation of the membranes at high current densities. The use of conductive carbon clothes enabled the recovery of the metal deposits, post reduction, through a simple electro-oxidation process. This novel microfluidic method, using ion-exchange materials as channel walls, has also the potential for the controlled decoration of materials with metal nanoparticle patterns and for the regeneration of rare earth trace contaminants by electro-sorption assisted electro-dialysis.

1. Introduction

Globally, large amounts of industrial tailing effluents containing toxic and valuable metal ions and metal oxide particles are continuously generated by numerous industrial activities including mining, textile, tanning, electroplating and metal finishing operations [1,2]. Valuable metals such as copper, zinc, iron, nickel, silver and many more are often discarded and sent to landfill or waterbodies due to the lack of effective, onsite separation and recovery methods [2,3].

In addition to partial economic loss, the inadequate release of heavy metal ions poses serious environmental and health risks particularly prevalent in developing countries where insufficient water purification systems still remain in operation [4,5]. Traces of heavy metal elements can now be detected in the vegetal biomass due to the use of contaminated water and polluted soils [2]. However, stricter legislations and environmental awareness are now pushing for the implementation of waste minimization and management solutions [2,5]. Chemical precipitation, solvent extraction, membrane separation, electro-chemical reduction, ion-exchange separation and adsorption are among the main methods used for the remediation of heavy metal ions from

diluted and concentrated solutions [2,3]. Each technique has specific advantages and limitations related to the durability, energy consumption and selectivity of the process [2,3]. Particularly, pressure-driven and electro-membrane separation processes such as electro-dialysis (ED), capacitive deionisation, nanofiltration, reverse osmosis and membrane distillation are proposed for the removal of heavy metal ions from liquid streams [6,7].

The advantages of membrane-based processes over traditional techniques include fewer chemical consumption, reduction of sludge volume, fast and limited materials regeneration as well as simpler and scalable module design [6]. Electro-separation and electro-membrane techniques used in electro-catalytic reactors offer additional advantages due to their ability to provide specific surfaces for the reduction or precipitation of the heavy metals in direct contact or through the membrane material [8,9]. ED is one of the most mature electro-membrane technologies widely used for the desalination of brackish water or for the pre-concentration of mineral salts [10,11]. During ED operation, ions and charged species are selectively separated from a feed to a concentrate solution across ion-exchange membranes (IEMs) under the influence of an electric potential gradient generated between two

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electrodes. Many successful ED applications associated with a variety of IEM brands can be found in the literature for the removal and concentration of heavy metal ions in aqueous solutions such as zinc, copper and silver [12–15]. However, one of the key limitations of ED process applied for the desalination of heavy metal streams remains the poisoning of the IEMs due to the precipitation of the metal cations across the ion-exchange polymer matrix [16].

In this research, a novel, portable and scalable microfluidic ED process is demonstrated for the one-step concentration of heavy metal ions from model wastewaters and their reduction to solid metal onto a protective, porous and electrically conductive carbon cloth. The use of microfluidic devices allowed to study the electro-diffusion and electro-reduction of ionic species in a controlled and optimized process environment. Real mining, tanning, textile or electro-plating industrial waste effluents often include a variety of organic molecule pollutants such as dyes, pesticides or resins residues [17]. However, due to the selectivity of the IEMs towards dissociated and charged species, model solutions composed of copper, zinc, nickel and silver as well as zinc/copper ionic mixtures were prepared to study the recovery of the metal ions within the microfluidics system and mimic specifically electroplating and mining effluents. Hydrophobic macro-porous carbon cloths inserted between the cation-exchange membrane (CEM) and the anion-exchange membrane (AEM), which formed the surface of the microfluidic device, were used as reducing platforms. The experimental conditions were systematically varied to optimise the metal ions transfer rates and understand the deposition kinetics of metal ions across the carbon cloths. The metal deposits were then isolated using thermal or electrolytic methods. This novel approach where, for the first time, the microfluidics device is composed of ion exchange materials offered a quick and easy way for the recovery of heavy metals, which may be applied to a very large range of industrial feed sources from which ionic species may be recovered.

2. Materials and methods

2.1. Materials and chemicals

Sodium chloride (NaCl, AR grade, > 99.7% purity, $M_w = 58.44 \text{ g}\cdot\text{mol}^{-1}$) and sodium sulphate anhydrous (Na_2SO_4 , analytical grade, > 99% purity, $M_w = 142.04 \text{ g}\cdot\text{mol}^{-1}$) were purchased from ChemSupply, SA, Australia. BioReagent grade copper sulphate pentahydrate ($\text{CuSO}_4\cdot 5\text{H}_2\text{O}$, > 98% purity, $M_w = 159.61 \text{ g}\cdot\text{mol}^{-1}$), zinc sulphate heptahydrate ($\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$, > 99% purity $M_w = 287.54 \text{ g}\cdot\text{mol}^{-1}$), silver nitrate (AgNO_3 , > 99%, $M_w = 169.87 \text{ g}\cdot\text{mol}^{-1}$), nickel sulphate heptahydrate ($\text{NiSO}_4\cdot 7\text{H}_2\text{O}$, purum grade, > 95%, $M_w = 280.86 \text{ g}\cdot\text{mol}^{-1}$) and magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, ACS reagent > 98%, $M_w = 256.41 \text{ g}\cdot\text{mol}^{-1}$) were sourced from Sigma-Aldrich, Castle Hill, NSW and used as received. The ionic solutions were prepared by dissolved a known quantity of salt crystals into deionized (DI) water under agitation.

The CEM and AEM, Selemion® (CMV and AMV brand names), were purchased from AGC Asahi Glass, Japan. Before starting the experiments, the membranes were first converted to Na^+ form for the cation-exchange type membranes and to Cl^- form for the anion-exchange type membranes using 0.5 M NaCl aqueous solutions. The membranes were immersed for 48 h under stirring in the NaCl solution, which was refreshed twice a day to ensure proper and complete exchange [18]. The properties of the Selemion® membranes are shown Table S2. A plain carbon cloth composed of woven carbon fibers was used as heavy metal ions collector. The plain carbon cloth (AvCarb 1071 HCB, 356 μm thickness) was ordered from FuelCellStore, TX, USA and used without any further modifications.

2.2. Characterization of materials and membranes

The morphology of the carbon cloths and membranes was studied

by scanning electron microscopy (SEM) on a Jeol JSM 7800F. The elemental distributions on the surface of the carbon cloth samples were evaluated by Electron Dispersive X Ray Spectroscopy (EDS) analysis with an Oxford detector. SEM imaging was performed at 10 keV with a 10 mm working distance while elemental mapping was performed at 20 keV and with a 10 mm working distance.

The thicknesses of the IEMs and carbon cloths were measured using a digital micrometer (ProScitech, model SUM2-025). The average pore size distribution of the plain carbon cloths was measured using a capillary flow porometer (3–6 mbar pressure range, Porometer 3GZH Quantachrome Instruments, USA) after wetting the samples with Porofil® wetting solution (16.00 $\text{dyn}\cdot\text{cm}^{-1}$ surface tension).

The nature of the metal deposits on the carbon cloth was assessed by XRD measurements on a X'pert Pro (Panalytical, USA) equipped with a copper X-ray tube using $\text{Cu K}\alpha$ radiation. The voltage and current were set to 40 kV and 30 mA during the experiments. Low background noise holders were used during the measurements.

The amount of deposited metal onto the carbon cloth was measured by weight difference of the carbon cloth before and after experiment on an AES 200-4C scale instrument with a precision of $\pm 0.2 \text{ mg}$. The carbon cloth was first dried in an oven at 80 °C for 30 min. The measurements were performed three times and the average values were reported. In addition, Thermogravimetric Analysis (TGA) tests were performed under air atmosphere using a Q50 TGA (TA instrument, USA) to assess the thermal stability of the samples and the amount of inorganic elements present across the carbon cloth. The experiments were performed with a fixed heating rate of 10 °C $\cdot\text{min}^{-1}$, while the gas flow was maintained at 60 $\text{cm}^3\cdot\text{min}^{-1}$.

Water contact angle measurements were performed with 4 μL DI water drops on the carbon cloth surface with a goniometer (KSV instruments model CAM 101). The tests were performed at three random locations on the surface of the sample. The images were acquired 5 s after the water drop impacted the membrane surface. The contact angles were calculated by fitting the image of the drops to the Young-Laplace equations and averaging with the obtained values on both sides of the drop using the optical tensiometer software, OneAttension Theta Lite.

2.3. Advanced electro-dialysis microfluidics set-up

Advanced ED tests were performed in a modified laboratory scale ED module fitted with microfluidics spacers set as a four-compartment stack made up of two AEMs and one CEM separated by spacers with specifically designed hydraulic pathways with effective transfer area of 4.60 cm^2 [19]. The width and depth of the channels across the spacers were 3.4 and 2 mm, respectively. Gold electrodes (40 \times 40 mm^2) were used as cathode and anode materials to complete the ED stack. In a typical heavy metal recovery experiment, a carbon cloth piece (40 \times 40 mm^2) was inserted between the pair of CEM and AEM facing the cathode in order to collect the heavy metal ions and protect the AEM from poisoning and degradation mechanisms (Fig. 1(a)). In addition, the desalination performance of the advanced ED process concept was compared to the desalination rates of metal ions by conventional ED process without carbon cloth present in the module. The experiments were carried out across a range of current densities (i) varying from 6.25 to 43.75 $\text{mA}\cdot\text{cm}^{-2}$ and performed at room temperature (20 °C). The flow rate across the spacers was set at 18 $\text{mL}\cdot\text{min}^{-1}$, which represented a fluid flow velocity across the spacers of 4.3 $\text{cm}\cdot\text{min}^{-1}$. Each test lasted for 30 min while a minimum of two sets of experiments were carried out in order to assess the reproducibility of the experiment.

The diluate compartment was fed with 250 mL of aqueous metal salt solutions. The concentrate and electrode compartments were fed with 250 and 500 mL of 0.1 M sodium sulphate aqueous solutions, respectively (Fig. 1(b)). The metal salt concentration in the feed solution was fixed at 0.1 M for copper and zinc sulphate salts and 0.05 M for nickel sulphate and silver nitrate. Magnesium nitrate was used as electrolyte

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