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ORIGINAL ARTICLE

Synthesis and characterization of ion imprinted polymeric adsorbents for the selective recognition and removal of arsenic and selenium in wastewater samples

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Abstract Arsenic (As) and selenium (Se) ion imprinted polymers, As-IIPs and Se-IIPs, were synthesized via bulk polymerization. The prepared materials were then characterized using Fourier Transform Infrared (FT-IR), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). These characterization methods confirmed the difference between IIPs and non-imprinted polymers (NIP). From the adsorption studies done IIPs did not only show better adsorption than NIPs but also better selectivities as well. As adsorption using As-IIPs (AsAsIIPs) reached a maximum of 482 μg g^{-1} whilst Se adsorption using Se-IIPs (SeSeIIPs) reached a maximum of 447 μg g^{-1} after optimization of the sample pH, adsorption time and sample temperature. However these adsorption capacities were increased to 568 μg g^{-1} and 530 μg g^{-1} for As and Se respectively when column experiments were done at the same sample temperature and pH. Against Pb, Cd and Hg, As-IIPs and Se-IIPs showed selectivity towards As and Se, respectively.

1. Introduction

The supply of clean and safe water for human consumption has been viewed to be heavily dependent on the cleanliness of waste water effluents of late [1–3]. It has been established that most wastewater effluents are having toxic materials in amounts exceeding permitted levels as per the dictates of the World Health Organisation (WHO), United States Emergency Protection Agency (USEPA) and the Department of Water and Environmental Affairs of South Africa (DWEA-SA) [4,5]. Making the list of these toxic materials includes trace metals and heavy metals such as arsenic (As), selenium (Se), copper (Cu), lead (Pb) and cadmium (Cd) amongst others [6–11]. Transition metals such as mercury [12,13] and some actinides [14] and lanthanide [14–16] series species have also been detected in previous studies.

Arsenic and selenium find their way into the environment via their usage in medicine, agriculture, steel industry as well

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as the rubber industry [17–19]. Both arsenic and selenium have been labelled as very notorious because their toxic and essential levels are in close proximity and they are also known for bioaccumulation. As a result, if these are ingested in low quantities by organisms of the early stages in a food web, they may still be very harmful as they may exceed toxic levels when detected at the higher levels of the same food web [17,20–22].

As such, various ultrasensitive methods that may enhance both the determination and removal of these metals have been developed and improved with much success. These include the use of natural adsorbents such as eggshell membranes [23,24], orange peels [25–27], activated alumina [28] as well as scientifically advanced methods like hollow fibre supported liquid membranes [1,3], exfoliated graphite electrodes [11], melt-mixed polypropylene zeolite blends and many more [29] whereby high adsorption efficiencies and better selectivities were achieved. Drawbacks such as reusability, periodicity and highly toxic waste sludge disposal pose a bigger threat if not carefully looked into.

One mitigation tool that comes across as a better alternative to the 'traditional' water treatment methods, in as far as metal remediation is concerned, is the synthesis of adsorbents on the basis of ion imprinting. This produces polymers (IIPs) with specialized cavities which mostly recognize the analytes of interest [30–32]. These polymers are either used as a column packing or as adsorbents via batch adsorption recording high selectivities as well as removal efficiencies [33,34]. They have been used for numeral pollutants in a wide variety of samples including both waste water and drinking water which include, but not limited to, cadmium [33,35], copper [36–38] and zinc [39].

This study reports on the synthesis, characterization and application of arsenic-ion imprinted polymers (AS-IIPs) and selenium-ion imprinted polymers (Se-IIPs) by bulk polymerization for use in the removal of As and Se from wastewater samples. The effect of the template molecule in the selectivity of the polymers is reported and various factors that influence the removal or adsorption efficiencies of the IIPs are also reported.

2. Experimental

2.1. Materials

Sodium arsenate dibasic heptahydrate (AR), styrene, acetic acid, methanol, ethylene glycol dimethacrylate (EGDMA), 2,2′-Azobis (cyclohexylcarbonitrile), selenium dioxide, 4,7-Dichloroquinoline, nitric acid, hydrochloric acid, sodium hydroxide and acetonitrile were supplied by Merck (Darmstadt, Germany). Calibration standards were prepared by dissolving arsenic and selenium metals in 10 mL of 15 M aqua regia and subsequent dilutions were done using deionized water (18.4 MΩ conductivity) from an in-house reverse osmosis water purification set-up.

2.2. Instrumentation

The determination of metal concentrations before and after extraction, during the template removal was performed using inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Wirsam Scientific, GBC Quantima Series ICP connected to a GBC SDS 720 auto sampler). Scanning electron microscopy (SEM) analyses were carried out using SEM (Tescan) for the surface morphology studies whilst for functional group analyses, a Thermo Scientific (Nicolet IS 10) Fourier Transform Infrared (FT-IR) spectroscopy was used. The thermogravimetric analysis was done using a Perkin Elmer TGA 400.

2.3. Ion imprinted polymer synthesis

To synthesize IIPs, 0.5 g of sodium arsenate dibasic heptahydrate and 1 mL of styrene were homogenized in a reaction vessel and dissolved in 10 mL of 25:75 (v/v) acetic acid/methanol. 6 mL of ethylene glycol dimethacrylate and 100 mg of 2,2′-Azobis (cyclohexylcarbonitrile) were added with stirring. This solution was then frozen with liquid nitrogen and polymerization was triggered thermally at 70 °C and left to polymerize overnight with slow stirring. For selenium polymers, the template used was a complex of 0.2 g SeO_2 and 0.05 g 4,7-Dichloroquinoline dissolved in 15 mL methanol and 6 mL ethylene glycol dimethacrylate and 110 mg of 2,2′-Azobis (cyclohexylcarbonitrile) added to the homogenous solution. Again polymerization was triggered thermally at 70 °C after purging with nitrogen for 5 min and allowed to go for completion overnight.

Solid polymer was ground and sieved through a 45 μm sieve, numerously washed with methanol and finally water to remove unreacted reagents. Template removal was done using 3 M HNO_3 after which the polymers were washed with deionized water until a constant pH of 7 was reached then polymers were oven dried at 80 °C. Control polymers, referred to in this communication as non-imprinted polymers (NIP) were also prepared the same way but without the involvement of the template molecules.

2.4. Adsorption–desorption studies

2.4.1. Batch experiments

Polymer concentration was fixed at 50 mg/100 mL and was suspended in sample solution of known concentration for 30 min except for time optimization experiments. The polymer-sample mixture was stirred at 200 rpm, centrifuged and syringe-filtered for analysis with ICP-OES. The initial and final sample concentration was determined against known arsenic and selenium standards. The adsorption capacity and extraction efficiency were calculated using Eqs. (1) and (2).

$$\mathrm{AC} = \frac{(C_\mathrm{i} - C_\mathrm{f})V}{m} \tag{1}$$

$$\%R = \frac{C_\mathrm{i} - C_\mathrm{f}}{C_\mathrm{f}} * 100 \tag{2}$$

where,

- AC is adsorption capacity,
- C_i the initial concentration of analytes before adsorption,
- C_f the final concentration of analytes after adsorption,
- V the sample volume,
- m the mass of polymer and
- $\%R$ the extraction percentage.

The pH was adjusted by drop wise addition of concentrated NaOH or HNO_3, and desorption studies were carried out by shaking the used polymer materials in a desorption solvent,