

# Sorption of toxic metal ions in aqueous environment using electrospun polystyrene fibres incorporating diazole ligands

Godfred Darko<sup>1</sup>, Samuel Chigome<sup>1</sup>, Stacy Lillywhite<sup>2</sup>, Zenixole Tshentu<sup>1</sup>,  
James Darkwa<sup>2</sup> and Nelson Torto<sup>1\*</sup>

<sup>1</sup>Department of Chemistry, Rhodes University, PO Box 94, Grahamstown 6140, South Africa

<sup>2</sup>Department of Chemistry, University of Johannesburg, PO Box 524, Auckland Park 2006, South Africa

## Abstract

Electrospun polystyrene fibres incorporating potassium salts of pyrazole-1-carbodithioate and imidazole-1-carbodithioate were employed as sorbents for heavy metals from aqueous environments. The equilibrating time, initial metal concentrations and sorbent mass for optimal adsorption were 40 min, 5 mg/l and 8 mg, respectively. The optimal pH for metal ion uptake was between 6.3 and 9.0 and was found to be dependent on the basicity of the ligands. Protonation constants for the ligands in aqueous solutions were determined potentiometrically; p*K* of the imidazole was 6.82 while that of the pyrazole was 3.36. The efficiencies of adsorption and desorption of metals on the imidazolyl-incorporated sorbents were more than 95%, up to the fifth cycle of usage. The limits of quantification were  $\leq 0.0145$  mg/l for all the metals. Accuracy of the determinations, expressed as relative error between the certified and observed values of certified reference groundwater samples was  $\leq 0.2\%$  with relative standard deviations  $< 3\%$ . Electrospun polystyrene fibres incorporating imidazoles proved to be efficient sorbents for divalent heavy metal ions in aqueous environments as their efficiencies exceeded those of chitosan microspheres, ion-imprinted composites, amino-functionalised mesoporous materials and most of the biomass-based sorbents previously reported on.

**Keywords:** electrospinning, polystyrene, heavy metals, diazole

## Introduction

Heavy metal ions are widespread in the human environment and very often occur, at low concentrations, in surface waters (Akoto et al., 2008). Although their concentrations in environmental samples are low, heavy metal ions tend to bioaccumulate through the food chain (Gundacker, 2000; Pourang, 1995) and exert various health effects in humans and animals. The direct determination of these metal ions in water samples has proven to be a challenge as their concentrations are usually too low for accurate detection on many analytical instruments (Mohammadi et al., 2010). There is therefore the need for a pre-concentration step to bring the concentrations of the ions to detectable levels for accurate measurements. The current practice of acid-digesting water samples prior to analysis is however cumbersome and renders the samples susceptible to cross-contamination, due to the multiple steps they are taken through. Therefore, a sample-handling methodology that allows for on-site sampling as well as enrichment of the analyte is preferred. Such a method reduces the number of analytical procedures associated with the handling of aqueous samples. For example, there will be no need for transporting large volumes of water samples from the sampling site (typically, 1 l per site) to the laboratory. The acid-digesting step will also be eliminated.

The ability of resins (Zhang et al., 2009; Vasiliev et al., 2009), porous materials (Heidari et al., 2009; Aguado et al., 2009), bentonite (Mishra and Patel, 2009), alumina (Ezoddin et al., 2010), biomass (Gundogdu et al., 2009; Hamissa et al., 2010;

Mapolelo et al., 2005; Miretzky et al., 2010; Sari and Tuzen 2009; Tang et al., 2010), sediments (Oh et al., 2009), substituted naphthalene (Rezaei et al., 2009), metal hydroxides (Bologo et al., 2012) and natural clinoptilolites (Mamba et al., 2009) to adsorb heavy metal ions from aqueous solutions has been reported. Most of the reported sorbents exhibited low loading capacities as well as sensitivities. In addition, some of them are not reusable (Zaman et al., 2009).

Sorbents developed from electrospun fibres have the potential to overcome these limitations as the fibres could be functionalised or incorporate moieties that can enhance their sorption abilities (Anderson and Long 2010; Zhang et al., 2009; Zhao et al., 2006). Electrospun polymer fibres with incorporated carbodithioate ligands, for example, can exhibit excellent adsorption capabilities owing to the strong affinity of their heteroatoms for metal ions (Change and Chen 2005; Rashchi et al., 2004; Qu et al., 2005; Samal et al., 2000). As bidentate ligands, the carbodithioates coordinate strongly with metal ions through their nitrogen and sulphur atoms (Bogdanovic et al., 2005). They could also act as bridging polydentate ligands when they have donor groups (Mukhopadhyay et al., 2001; Köysal et al., 2005; Szécsényi et al., 2006). Moreover, the benzene ring of the polymer can hold the ligand in place through hydrogen bonds (Tretinnikov, 2000; Vogler, 1998).

By virtue of their large specific surface areas and high porosities, the electrospun fibres have higher loading capacities for metal ions (Teo and Ramakrishna, 2006). The metal ions adsorbed could be released for quantification by placing the sorbent in an acidic solution. The desorbed sorbent could be generated for reuse after washing in ultrapure water and drying. The carbodithioates are stable in both acidic and basic conditions (Anderson and Long, 2010). The activity of the ligand could therefore be preserved during use. Electrospun polymer fibres incorporating carbodithioate ligands are,

\* To whom all correspondence should be addressed.

☎ +27 46 603 8924; fax: +27 46 622 8254;

e-mail: [n.torto@ru.ac.za](mailto:n.torto@ru.ac.za)

Received 8 March 2012; accepted in revised form 22 November 2012.