Functionalisation of cross-linked polyethylenimine for the removal of As from mining wastewater

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ABSTRACT

Cross-linked polyethylenimine (CPEI) was phosphonated by reaction with phosphorous acid and formaldehyde. The functionalised polymer was used as an adsorbent for the removal of arsenic as an oxo-anion. The binding affinity of the synthesised polymer to abstract As from synthetic solutions and wastewater samples was assessed, as well as its ability to be regenerated for re-use. The PCPEI demonstrated an elevated loading capacity, removing up to 88% of As. The kinetic rates were modelled using pseudo first-order and pseudo second-order equations. The pseudo second-order equation was found to explain the adsorption kinetics most effectively, implying chemisorption. The Langmuir and Freundlich isotherms were used to interpret the adsorption of As onto PCPEI. The Freundlich isotherm was found to best fit and describe the experimental data. The thermodynamic study of the adsorption process indicated high activation energies (55.91 kJ mol^{-1}) which confirms chemisorption as a mechanism of interaction between As and PCPEI.

Keywords: Adsorption; arsenic; phosphonated cross-linked polyethylenimine, functionalisation

INTRODUCTION

Water pollution is an increasingly pressing problem. The world is facing a challenge in meeting rising demands for unpolluted water, since the available supplies of freshwater are decreasing due to population growth, extended droughts, extensive industrialisation and improper disposal. Water contamination by trace elements is a global environmental concern as it affects the quality of drinking water and hence human health. Although some elements are natural nutrients at trace level, they become very toxic at high concentrations. High concentrations of toxic elements result from intensive anthropogenic activities, including mining, agriculture, and disposal of industrial waste materials (Akpor and Muchie, 2010; Liu et al., 2008; Savage and Diallo, 2005; Ruparelia et al., 2008; Ahmed et al., 2008; Madoni and Giuseppa, 2005; Bhattacharya et al., 2007). Arsenic (As) is one of the most toxic elements. It is a naturally occurring metalloid and a micronutrient in small quantities. Elevation of As concentration in natural water is a major concern because of its toxicity, posing a threat to aquatic life if left untreated. Long-term drinking of arsenic-polluted water causes bladder, kidney, skin, and lung cancer, as well as other effects such as loss of appetite, muscular weakness, pigmentation changes, and nausea. Arsenic is mobilised naturally by weathering reactions, biological activity, geochemical reactions and volcanic emissions, as well as anthropogenic activities. Mining activities account for some of the most serious additional sources (Carvalho and Martin, 2001; Mohan and Pittman, 2007).

Several different methods have been reported to remove toxic elements from wastewaters, such as chemical-, physical-, and bio-remediation (Sauer et al., 2004). Among the remediation techniques for metal ion removal, polymeric adsorbents are some of the more efficient in terms of technical and economic efficiency, feasibility, and environmental impact.

Polyethylenimine (PEI) is one of the most popular polymeric adsorbents and well-known for its metal-chelating properties (Leroy et al., 2003). It has been widely applied for the retention of toxic elements. PEI is more effective for the removal of metals than metalloids (Saad et al., 2011). The aim of this study, therefore, was to develop a water-insoluble form of polyethylenimine with suitable functionality to facilitate selective removal of As. The insoluble property of PEI was achieved by cross-linking, as reported in a previous study by the authors (Saad et al., 2011).

MATERIALS AND METHODS

Materials

All chemicals were obtained from Sigma Aldrich (South Africa) without further purification. Cross-linked polyethylenimine (Saad et al., 2011), phosphorous acid, formaldehyde 38% (CH_2O), and 6 mol·ℓ$^{-1}$HCl were used. The solutions were prepared from $NaAsO_2$. Adjustments of pH for the adsorption experiments were conducted using 1 mol·ℓ$^{-1}$ solutions of HNO_3 and NaOH. Deionised water was used for the preparation of all solutions.

Synthesis of PCPEI

The synthesis of PCPEI was carried out according to the method reported by Saad et al. (2012a); cross-linked polyethylenimine, 2.5 g, was placed in 80 mℓ of 6 mol·ℓ$^{-1}$ HCl. Phosphorous acid, 19.31 g, was added and the mixture was heated under reflux at 90°C. Formaldehyde, 38 mℓ, was added drop-wise over a period of an hour, and the reaction was left overnight. A pale powdery yellow solid was obtained, and was washed with abundant deionised water before drying in an air oven at 30°C. The solid was then pulverised and sieved.

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