

Engineered Materials for the Containment of Uranium and Other Toxic Elements in Mine-polluted Water

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Abstract This study explored the potential of polymeric materials as adsorbents for contaminant removal from mine-polluted water. Polyethyleneimine was used as the core polymer and was modified on the surface using functional groups such as phosphate to target uranium. Adsorption capacities exceeding 90% were obtained for uranium, arsenic, zinc, copper and nickel at pH values as low as 3. Isothermic and kinetic models were used to describe the adsorption process. Desorption studies showed the potential regeneration of the materials.

Keywords uranium, polyethyleneimine, adsorption

Introduction

Water contamination is a global challenge and one that has led to some negative health effects. Water remediation and clean up has been central to most research work related to water. Several techniques have been proposed and used for the removal of metallic contaminants from water including precipitation, coagulation, reduction, neutralization, electrochemical separation through membranes, ion exchange and adsorption.

Several adsorbent materials have been used e.g. clays, zeolite (Bakatula et al., 2014), composite materials (Rosenberg and Fischer 2006), agricultural waste and polymers (Saad et al. 2011). Polymers are some of the most effective adsorbents for remediation of polluted water. They provide an opportunity for functionalization of the surface with reactive groups that can be used to target specific elements (Kaliyappan 2000).

In this study, a cross-linked polyethyleneimine (CPEI) was synthesized and functionalized with phosphate ligands to make it effective for uranium removal from polluted water. Several functional groups have been used to functionalize polymers to make them specific for uranium. These groups include sulphonates, imidazoles, glycolic acid and methylpropanesulphonic acid (Leroy et al. 2003).

Materials and methods

All chemicals were obtained from Sigma Aldrich (South Africa) without further purification. For functionalization, CPEI, H_3PO_3 , formaldehyde and 6 M HCl were used. Uranium solutions were prepared from the nitrate salt, $UO_2(NO_3)_2 \cdot 6H_2O$. Solutions of competing metal ions were also prepared from their nitrate salts and soluble oxides for As and Se. Deionized water was used for the preparation of all solutions.

CPEI was placed in 6 M HCl to which phosphorous acid was added and the mixture heated under reflux. Formaldehyde was then added and the reaction was left overnight. A pale yellow solid was obtained, washed with abundant deionized water before drying at 30°C in an oven. The solid, phosphonated CPEI (PCPEI), was then pulverized and sieved.

Batch adsorption studies were conducted using a 40 mg/L uranium solution. Adsorption at pH 3 and pH 8 was assessed. At equilibrium, the solutions were filtered and uranium concentrations determined using inductively coupled plasma optical emission spectroscopy (ICP-OES) (Spectro Genesis, Germany). The amount of ions adsorbed per unit mass of adsorbent was calculated using the equation:

$$q_e = \frac{(C_i - C_f) \times V}{1000 \times P}$$

where: q_e is the adsorption capacity (mg metal g^{-1} polymer); C_i is the initial concentration of the ion; C_f is the concentration of the ion in the filtrate; V (mL) is the volume of the initial solution; P (g) is the amount of polymer used.

The effect of contact time was assessed at various time intervals and fixed metal concentration. Metal concentrations were determined at the end of each time, allowing for kinetic models to be established.

The effect of competing ions was assessed using Cr, Mn, Fe, Hg, Zn, Pb, Ni, Se and Si. Desorption studies were conducted to assess the re-usability of the polymer. This was done by using HNO_3 at different concentrations (2, 3, 5 and 7 M).

Modelling of analytical results

The results from adsorption studies were modelled using kinetic (table 1) and equilibrium models (table 2).

Table 1 Kinetic models (Lagergren, 1898; Ho et al., 1999)

Model	Equations	linearized equation
Pseudo first-order model	$\log(q_e - q_i) = \log q_e - (k_1/2.303)t$	$\text{Log}(q_e - q_i)$ vs. t (to obtain k_1)
Pseudo second-order model	$1/q_t = (1/k_2 q_e^2) + (1/q_e)t$	t/q_t vs. t (to obtain k_2)

where: q_e and q_t are the amount of metal ions adsorbed (mg/g) at equilibrium and at any time t respectively, k_1 is the rate constant for the pseudo first-order adsorption and k_2 is the rate constant for the pseudo second-order adsorption.

Table 2 Langmuir (Eq. 3) and Freundlich (Eq. 4) isotherms

(Eq. 3)	(Eq. 4)
$\frac{C_e}{q_e} = \left(\frac{1}{q_{\max}} \right) C_e + \left(\frac{1}{K_L q_{\max}} \right)$	$\log q_e = \left(\frac{1}{n} \right) \log C_e + \log K_F$

where: q_{\max} is the maximum concentration of metal ions sorbed per unit weight of adsorbent (mg/g); K_L is the Langmuir constant for the reaction; K_F is the Freundlich constant; and $1/n$ describes the surface heterogeneity of the adsorbent.

Results and discussion

Effect of pH

The results for the adsorption of U from synthetic solutions are presented in table 3. The adsorption percentages showed high removal efficiency even at low pH. The elevated adsorption at pH 8 could be attributable in part to precipitation of U (Tutu et al. 2013).

Table 3 Removal of U at pH 3 and 8 from synthetic solutions by PCPEI

	Cf (mg/L)	RSD	Adsorption capacity (mg/g)	Adsorption efficiency (%)
pH 3	0.770	6.227	1.569	98
pH 8	0.600	0.333	1.576	99

initial concentration of $U = 40$ mg/L; C_f is the final concentration after adsorption; RSD is relative standard deviation ($n = 3$).

Effect of initial concentration

The results for the dependence of adsorption on U concentration showed a trend of increasing adsorption capacity with increasing U concentration. This could be attributed to the availability of active sites for adsorption as well as the possibility of clustering.

Effect of competing ions

The effect of Mn, Pb, As, Zn, Fe, Cr, Hg, Se and Ni on the adsorption of U was assessed. The results are presented in table 4 and point to an elevated adsorption capacity for U, similar to that observed for the single component system.

Table 4 Adsorption of U and competing ions

Element	Cr	Mn	Fe	Hg	Zn	Pb	U	Se	Ni	As
Removal (%)	68	90	62	57	71	61	98	26	84	76

Kinetic and isothermic models

The plot of the linearized form of the pseudo second-order model gave a good correlation ($R^2 = 0.998$), implying that adsorption occurred via a chemisorption process (Antunes et al., 2003). The Langmuir and Freundlich constants and coefficients are presented in Table 5. The results showed that the Freundlich model fitted the data best, implying adsorption on a heterogeneous surface.

Table 5 Langmuir and freundlich parameters for the adsorption of U

	b	Langmuir R^2	q_m	K_F	Freundlich R^2	n
U	0.220	0.942	15.00	4.317	0.957	0.222

Desorption studies

Optimal recovery and regeneration of PCPEI was achieved at a concentration of 7 M of the regeneration acid solution. The desorption percentage was 81%. The adsorption percentages of up to 95% were obtained at pH 3 and 8 for the regenerated PCPEI.

Conclusion

In this study, PCPEI was successfully employed for the removal of U from aqueous solutions. The removal mechanism of U hinges on the functional groups present in the polymer, largely the phosphate group. The fit of the adsorption data to the Freundlich model suggested that adsorption occurred on a heterogeneous surface. The kinetic results suggested that adsorption was via a chemisorption process. Competing ions were found not to have a significant effect on U adsorption. The possibility of regeneration of PCPEI is important and implies that the polymer can be used as a cost-effective adsorbent.

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