Desalination 321 (2013) 3–8

Contents lists available at SciVerse ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

Removal of radioactive elements from aqueous solutions by adsorption onto polyacrylamide–expanded perlite: Equilibrium, kinetic, and thermodynamic study

Recep Akkaya *

Cumhuriyet University, Vocational School of Health Services, 58140, Sivas, Turkey

HIGHLIGHTS

- Adsorption capacities (X_L) of uranium and thorium ions were found to be 0.66 and 0.77 mol kg^{-1}.
- Adsorption data for uranium and thorium ions were well fitted by the Langmuir and D–R isotherms.
- Kinetic data corresponds well to the second order equation.
- Uranium and thorium ion adsorption onto P(AAm–EP) composite is an endothermic and spontaneous process.
- The composite is reused up to 5 times with no loss of removal efficiency.

ARTICLE INFO

Article history:
Received 28 June 2012
Received in revised form 8 September 2012
Accepted 17 September 2012
Available online 11 October 2012

Keywords:
Adsorption
Composite
Expanded perlite
Synthesis
Thorium
Uranium

ABSTRACT

In this research, a novel composite, poly(acrylamide-expanded perlite) [P(AAm–EP)], was synthesized and its adsorptive features were investigated for UO_2^{2+} and Th^{4+} ions. The composite's adsorptive features were evaluated for UO_2^{2+} and Th^{4+} ions in light of the dependency of the ion concentration, pH, temperature, time, and reusability. The composite could bind UO_2^{2+} and Th^{4+} ions with strong chemical affinity. The correlation coefficients indicate that the Langmuir model fits better for the UO_2^{2+} and Th^{4+} onto P(AAm–EP) composite with adsorption capacities as 0.66 and 0.74 mol kg^{-1}, respectively. Adsorption equilibrium of UO_2^{2+} and Th^{4+} ions was achieved in about 34 and 32 min, respectively. The kinetic data conformed better to the pseudo-second order equation. The adsorption of UO_2^{2+} and Th^{4+} ions increased with increasing pH and reached a plateau value at around pH 3.0. Thermodynamic parameters ΔH and ΔS values showed that the sorption process was spontaneous ($\Delta G<0$), endothermic ($\Delta H>0$), and had increased entropy ($\Delta S>0$). It was also found that the adsorption kinetics followed the pseudo-second-order model and that the rate-controlling step was chemical adsorption. The reusability of the composites was confirmed for 5 sequential reuses.

1. Introduction

The presence of uranium and thorium ions in fresh water supplies has been of health concern due to their detrimental effects associated with radioactivity and/or toxicity to biological systems [1–5]. A considerable amount of work has been carried out regarding the extraction of uranium and thorium by solvent extraction techniques, using various composites; i.e., magnetic chitosan composite for extraction of thorium and uranium [6], carboxyl-terminated hybrid adsorbent composite [7], pass cement dust [8], solvent-impregnated foam [9], soils [10], activated carbon [11], zeolitic volcanic tuff [12], and unsaturated polyester–styrene polymeric beads [13].

The use of many of the solvent extraction techniques has been limited because they are expensive, often require long processing times, and cause the release of toxic materials. A physicochemical method, adsorption, on the other hand, that appears to be a much more cost-effective and environmentally friendly technique [14–17], has been used for the recovery of metal ions selectively in remediation processes [18,19].

Perlite is an amorphous volcanic glass that has relatively high water content and is typically formed through the hydration of obsidian [20,21]. It occurs naturally and has the unusual property of greatly expanding when heated sufficiently. A cross-linked polyacrylamide (PAAm) hydrogel polymer could also be used as a support material. A composite material, prepared by crosslinking perlite with PAAm and named as P(AAm–EP), appeared to have much improved adsorptive features [22,23].

The purpose of this study was therefore to prepare a novel, low-cost, polyacrylamide–expanded perlite [P(AAm–EP)]-affinity adsorbent composite for the removal of UO_2^{2+} and Th^{4+} ions from aqueous solution in a batch system. In our previous work, we reported the sorption of uranium, thorium, and lead ions through P(AAm)-based composite under

Abbreviations: EP, expanded perlite; P(AAm), polyacrylamide; [P(AAm–EP)], polyacrylamide–expanded perlite; D–R, Dubinin–Radushkevich; PAR, [4-(2′-pyridylazo)-resorcinol].

* Tel.: +90 3462191010/1341; fax: +90 3462191256.
E-mail address: rakkaya@cumhuriyet.edu.tr.

0011-9164/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.desal.2012.09.020

different conditions [24,25]. This study investigated the composite's adsorptive features depending upon concentrations, initial pH, and temperature of uranium and thorium ions.

2. Experiment

2.1. Reagents

Expanded perlite (EP) was obtained from a local source (Etibank, Izmir, Turkey). The mineral was first washed with water to remove fine grains and water-insoluble particles. It was then dried for 24 h at 110 °C. Then the dried EP samples were mechanically sieved at 100 mesh. Before each adsorption experiment, the expanded perlite samples were kept at 110 °C for 1 h and stored in a desiccator before use [26].

Acrylamide monomer, N,N′-methylenebisacrylamide crosslinker, N,N,N′,N′-tetramethylethylenediamine accelerator, initiator ammonium peroxide disulfate ($H_8N_2O_8S_2$), $UO_2(NO_3)_2{\cdot}6H_2O$, and $Th(NO_3)_4{\cdot}4H_2O$ were purchased from Sigma Aldrich-Germany. Arsenazo III (disodium salt) and 4-(2′-pyridylazo)-resorcinol (PAR) were obtained from Merck (Germany). All of these materials were analytical grade.

2.2. Preparation of PAA-EP composite

P(AAm–EP) was prepared by direct polymerization of AAm monomer in expanded perlite suspensions [22–25]. Two grams of EP and 1 g of AAm were mixed in 10 mL water [22–25]. The composite was synthesized with 98% efficiency, which was determined by weighing. The composite was then washed with distilled water until neutral pH was attained, dried at ambient temperature, ground, sieved to a particle size of −50 mesh, and stored in a container. One batch for each of P(AAm–EP) sample was prepared simultaneously to conduct the overall investigation.

2.3. The relationship between adsorption capacity and pH

The effect of pH on the adsorption of UO_2^{2+} (3.7×10^{-3} mol L^{-1}) and Th^{4+} (4.3×10^{-3} mol L^{-1}) onto P(AAm–EP) composite was investigated for 24 h using a pH range – 1.0, 2.0, 3.0, 4.0, and 5.0 – at 298 K in 5 mL final adsorption volume [22–25]. PAR was used as a complex forming reagent to determine the UO_2^{2+} and Th^{4+} ions in the supernatants [22–25]. Solutions of 3.5×10^{-3} mol L^{-1} of PAR in 0.7 mol L^{-1} of Tris/HCl at pHs 8–9 were prepared. Fifty microliter aliquots of the supernatant were added to 3 mL of the reagent, and the absorbance of the formed metal complex was measured at 510 nm (Shimadzu-160A, Japan).

2.4. Influence of ion concentration on adsorption

The adsorptive capacity of the adsorbent was investigated using 0.1 g of P(AAm–EP), equilibrated in a thermostatic water bath for 24 h with 10 mL UO_2^{2+} and Th^{4+} ion solution containing 1.2×10^{-4}–9.6×10^{-3} mol L^{-1} (25–2000 mg L^{-1}) at 298 K. The pH of the equilibrated solutions was 3.5. The suspensions were then centrifuged for 5 min at 2500 rpm. Ion contents of the supernatants were assessed using the procedure described above.

2.5. Time dependence of adsorption

A composite suspension was prepared in 50 mL water using 0.4 g composite and 3×10^{-3} mol L^{-1} of UO_2^{2+} (3.7×10^{-3} mol L^{-1}) and Th^{4+} (4.3×10^{-3} mol L^{-1}) [1000 mg L^{-1}]. Fifty microliter aliquots were then taken at 0, 1, 2, 5, 10, 15, 30, 60, 120, 240, and 480 min, and the ion content was determined as described above. A correction factor was used in the measurements by taking the volume decrease in equilibrium solutions, during sampling, into consideration.

2.6. Temperature dependence of adsorption

Duplicate suspension samples, containing 0.1 g P(AAm–EP) and UO_2^{2+} (3.7×10^{-3} mol L^{-1}) and Th^{4+} (4.3×10^{-3} mol L^{-1}) [1000 mg L^{-1}], were incubated for 24 h at 278, 288, 298, 308, or 313 K. One hundred milligrams of P(AAm–EP) was equilibrated with 10 mL stock UO_2^{2+} or Th^{4+} solutions. Free-ion contents were determined as described above.

2.7. Reusability experiments

Ten milliliter solutions of UO_2^{2+} and Th^{4+} ions (1000 mg L^{-1}) were added to 0.1 g P(AAm–EP), and the mixture was incubated for 24 h. The mixture was then passed through 10-mL columns, 0.5 cm in diameter. UO_2^{2+} and Th^{4+} ions that were retained in the column were recovered by washing with 15 mL of 1 mol L^{-1} HCl at 0.5 mL min^{-1}. The adsorbent in the column was regenerated by washing with water until a neutral pH was reached. This adsorption/desorption and regeneration procedure was repeated five times.

3. Results and discussion

3.1. Influence of pH on adsorption

Fig. 1 shows that final pH was almost the same as shown and that the complexation behavior of UO_2^{2+} and Th^{4+} ions is sensitive to pH changes, especially at lower pH levels [21]. UO_2^{2+} and Th^{4+} ion adsorption is pH dependent. The amounts adsorbed onto the P(AAm–EP) composite increased with increasing pH for both ions and reached a plateau around pH = 3.5 for UO_2^{2+} and Th^{4+} ions. The Q values for studied ions in the pH range of 1–5 were presented in Table 1. Ion diameter influenced the adsorption efficiency as it appeared that uranium binding was lower than that of thorium probably because of the steric hindrance caused by two oxygen atoms bound to uranium. Steric hindrance could result from the ionic charge (radii/ionic charge; UO_2^{2+}: 253 pm/2, Th^{4+}: 94 pm/4) [24,25].

3.2. UO_2^{2+} and Th^{4+} ion adsorption

The extent of UO_2^{2+} and Th^{4+} ion adsorption (Q, mol kg^{-1}) was determined by means of the following formula:

$$Q = [(C_i - C_e)V/w] \quad (1)$$

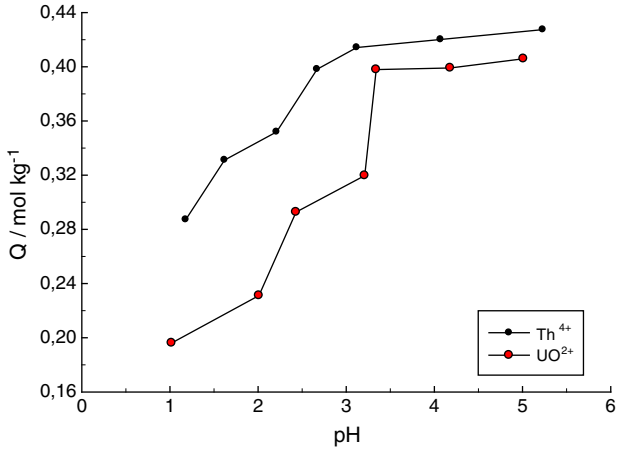

Fig. 1. Effect of final solution pH for adsorption of UO_2^{2+} and Th^{4+} ions onto the composite.