Desalination and Water Treatment
www.deswater.com

1944-3994/1944-3986 © 2012 Desalination Publications. All rights reserved
doi: 10.1080/19443994.2012.708566

50 (2012) 180–188
December

Taylor & Francis
Taylor & Francis Group

Separation of uranium and thorium in aqueous solution using polyhydroxyethylmethacrylate-hydroxyapatite novel composite

Recep Akkaya

Cumhuriyet Univ., Vocat. Sch. Hlth. Serv. TR. Sivas 58140, Turkey
Tel. +90 3462191010/1341; Fax: +90 3462191256; email: rakkaya@cumhuriyet.edu.tr

Received 27 March 2012; Accepted 21 May 2012

ABSTRACT

Poly(hydroxyethylmethacrylate-hydroxyapatite) [P(HEMA-Hap)] composite was synthesized by free radical polymerization in aqueous solution. The adsorptive features of P(HEMA-Hap) composite were investigated for UO_2^{2+} and Th^{4+} using a range of pH, concentration, time, temperature, and ionic strength values. It was observed that P(HEMA-Hap) composite had high affinity to uranium and thorium ions and that the adsorption capacity of the composite increased in proportion to the amount of Hap content. Adsorption data obtained fitted well into the classical Lagmuir, Freundlich, and Dubinin-Radushkevich sorption models. Changes in the enthalpy and entropy values showed that the overall adsorption process was endothermic and spontaneous ($\Delta G < 0$), as expected. The adsorption kinetics following the pseudo-second order model indicated that the rate-controlling step was chemical adsorption that occurred by ion exchange process. Reusability of the composite was also investigated, and it was found that the composite could be used at least five times.

Keywords: Adsorption; Composite; Hydroxyapatite; Polyhydroxyethylmethacrylate; Thorium; Uranium

1. Introduction

Groundwater and some surface water sources have often been polluted with radioactive uranium and thorium ions, and this causes serious environmental and health hazards [1,2]. Natural adsorbents such as cellulose [3], peat [4], chitosan [5], hydroxyapatite [6], activated carbon [7], or natural zeolites [8] have been used to remove uranium and thorium from aqueous solutions.

Poly(hydroxyethylmethacrylate), P(HEMA), is a non-adsorbent and hydrophilic polymer [9–11]. A wide range of studies on modified P(HEMA) have been reported [12]. The structure of the polymer could be modified by intra- or inter-chain reactions occurring between the side groups and resulting in crosslinking or cyclization. The polymer has many functional groups, such as OH, along its side chains [13]. P(HEMA) can be prepared in a variety of shapes and forms and has been known to be inert in biological processes and resistant to biodegradation and heat upon sterilization [14].

Use of composite materials can result in a dramatic change in properties such as mechanical behavior, solubility, absorbability, and swelling [15]. The polymer-based composite adsorbents have been used for recovery of metal ions in water, groundwater, wastewater, and sea water [16–22].

In a previous study, several polyacrylamide-based composite materials have been produced and used for the selective removal of heavy metal ions, UO_2^{2+}, Th^{4+}, and Pb^{2+}, from aqueous media [1,2,6,23,24]. The main aim of this study was to prepare a novel P(HEMA-Hap) affinity adsorbent composite for the removal of heavy metal ions. The adsorptive capacity of the composite was then tested with UO_2^{2+} and Th^{4+} ions, and many of the physicochemical parameters (pH, concentration, time, and temperature) for the adsorption were optimized.

2. Description of experiment

2.1. Reagents

HEMA, ethylene glycol dimethacrylate (EGDMA), N,N,N´,N´-tetramethylethylenediamine (TEMED), $UO_2(NO_3)_2{\cdot}6H_2O$, and $Th(NO_3)_4{\cdot}4H_2O$ were purchased from Sigma Aldrich. Arsenazo III (disodium salt) was obtained from Acros. Merck was the supplier of 4-(2´-pyridylazo)-resorcinol (PAR). Hydroxyapatite with 63–125 nm particle size and ammoniumperoxodisulfat; APS ($H_8N_2O_8S_2$) were obtained from Sigma Aldrich.

2.2. Preparation of P(HEMA-Hap)

Ten grams of P(HEMA-Hap) and 2 g of Hap were suspended in 20 mL of distilled water by stirring for 15 min. To the suspension, 4 mL of hydroxyethyl methacrylate monomer and 6 ml of EGDMA mixture, including 50 mg ammoniumperoxodisulfat (APS), were added, and the final mixture was stirred for 4 h. Polymerization was then propagated by adding 200 µL of TEMED. All manipulations and polymerization reactions took place at room temperature. The polymerization product, P(HEMA-Hap) composite, was washed with distilled water until the effluent attained a neutral pH. The composite was then dried, ground, sieved to a particle 25-mesh size, and stored in polypropylene containers.

2.3. The relationship between adsorption and pH

The effects of pH on UO_2^{2+} and Th^{4+} adsorption onto the composite were investigated at pH points ranging from 1 to 5 (1.0, 2.0, 3.0, 4.0, and 5.0). pH adjustments were performed using 0.1 mol L^{-1} HCl solution.

2.4. UO_2^{2+} and Th^{4+} adsorption

One hundred milligrams of the composite was equilibrated with 10 mL stock solutions containing UO_2^{2+} (between 5.6×10^{-3} and 1.9×10^{-4} mol/L) and Th^{4+} (6.4×10^{-3} and 2.2×10^{-4} mol/L) ions at concentrations [1,2, 25–27]. The adsorbent-solution systems were equilibrated at 298 K for 24 h in a thermostatic water bath. The suspensions were then centrifuged at 2,500 rpm for 5 min. The initial/final pH values of the solutions were 3.1/5 for UO_2^{2+} and 3.5/5 for Th^{4+}, respectively.

PAR was used as a complex-forming reagent to determine the concentration of UO_2^{2+} in the suspensions [1,2]. A solution of 3.5×10^{-3} mol L^{-1} of PAR in 0.7 mol L^{-1} Tris–HCl, pH 8.5 was prepared. A 50 µL fraction of the suspension was added to 3 mL of PAR solution. Absorbance of the formed reagent-ion complex was measured at 529 nm (Shimadzu-160A, Japan).

Arsenazo III was used as a dying reagent to determine the concentration of UO_2^{2+} or Th^{4+} [1,2]. Arsenazo III solutions were prepared at 0.04% concentrations, and their pH was adjusted to 1.5 or 2.0, with concentrated HCl, to determine the concentrations of UO_2^{2+} and Th^{4+}, respectively. A 50 µL fraction of the suspension was then added to 3 mL of Arsenazo-ion complex solution, and the absorbance was measured at 650 nm.

2.5. Time dependence of adsorption

One hundred milligrams of solid P(HEMA-Hap) was added to 10 ml solutions of each of the UO_2^{2+} and Th^{4+}. Fifty micromililiter aliquots of the reagent-ion complex solution were withdrawn, starting immediately after the solution-solid contact and continued at time intervals of 1, 2, 5, 10, 15, 30, 60, 120, 240, and 480 min. UO_2^{2+} and Th^{4+} contents of the fractions were determined as described above. To accommodate the fact that the suspension volume decreased after each of the aliquots was taken, a correction factor was applied to the calculated ion content values.

2.6. Temperature dependence of adsorption

One hundred milligrams of P(HEMA-Hap) equilibrated with UO_2^{2+} (3.7×10^{-3} mol L^{-1}) and Th^{4+} (4.3×10^{-3} mol L^{-1}) (1,000 mg L^{-1}) were incubated for 24 h at 5 different temperature points, 278, 288, 298, 308, and 313 K, to determine the effect of temperature on ion adsorption.

2.7. Reusability

The 100 mg of P(HEMA-Hap) was equilibrated with 10 mL of UO_2^{2+} (3.7×10^{-3} mol L^{-1}) and Th^{4+} (4.3×10^{-3} mol L^{-1}) solutions for 6 h (adequate period of time for completion of the adsorption after kinetic studies). The amount of adsorbed ions was derived from the contents of solutions at equilibrium. P(HEMA-Hap) composite material was precipitated after the adsorption procedure and was then placed in a column to remove the bound ions by washing with 15 mL of 1 mol L^{-1} HCl with a flow rate of 0.5 mL min^{-1}. The ion contents of the eluents were measured using the process described above. The columns were then reconstituted with distilled water until the effluents had a neutral pH. The reusability experiments were performed 5 times by using duplicate samples.

2.8. Competitive adsorption

Equivalent concentrations, 5×10^{-3} mol L^{-1}, of UO_2^{2+} and Th^{4+} were prepared and used for assessment of the ion selectivity of P(HEMA-Hap). Ten milliliter aliquots were taken from the suspension solution, and after 24 h of incubation, the ion contents were measured. The concentrations of UO_2^{2+} and Th^{4+} were determined with 0.04% Arsenazo III in HCl to provide a pH = 1.5 for UO_2^{2+} and in 2 molL^{-1} $HClO_4$ for Th^{4+} analysis [28,29]. To confirm the accuracy of the results obtained from the metal-dye detection, UO_2^{2+} and Th^{4+} in some of the samples were also determined by a Gamma spectrometry [NAI(Tl) detector combined with a EG&G ORTEC multi-channel analyzer and software, MAESTRO 32, MCA Emulator, USA].

2.9. The effect of ionic strength

The dependency of adsorption on ionic strength was performed using 10 mL 3.7×10^{-3} mol L^{-1} (1,000 ppm) of UO_2^{2+} and 4.3×10^{-3} mol L^{-1} (1,000 ppm) Th^{4+} ions solutions and in the presence of differing concentrations of $CaCl_2$, ranging from 0.01, 0.02, 0.04, 0.08, 0.10, 0.20, 0.25, to 0.30 mol L^{-1}. The samples were incubated for 24 h at room temperature. The concentrations of the equilibrated solutions were then assessed by spectrophotometry (Shimadzu 160A, Japan).

2.10. Evaluation of data

The adsorbed amounts of UO_2^{2+} and Th^{4+} (Q, mol kg^{-1}) were calculated using the formula $Q = [(C_i - C_e)V/w]$, in which C_i and C_e are the initial and equilibrium concentrations (mol L^{-1}), w is the mass of the adsorbent (kg), and V is the solution volume (L). Due to the inertness of P(HEMA), the values of Q were calculated with reference to the Hap content of adsorbents (0.035 g of 0.1 g P(HEMA-Hap).

The Langmuir and Freundlich models, defined by $Q = (K_L X_L C_e)/(1 + K_L C_e)$, where C_e is the concentration at equilibrium, X_L is the monolayer sorption capacity (mol kg^{-1}), K_L is the adsorption equilibrium constant (L mol^{-1}) related to the adsorption energy, and $Q = X_F C_e^{\beta}$, X_F and 'β' are empirical Freundlich constants associated with the capacity and intensity of adsorption, fitted the experimentally obtained isotherms. The isotherms were also evaluated with reference to the Dubinin-Radushkevich (DR) model to determine K_{DR} ($mol^2 K J^{-2}$) related to the sorption energy from $Q = X_{DR} e^{-K_{DR} \varepsilon^2}$, where X_{DR} is the sorption capacity (mol kg^{-1}) and ε is the Polanyi potential, given with $\varepsilon = RT \ln(1 + 1/C_e)$, in which R and T represent the ideal gas constant (8.314 J $mol^{-1} K^{-1}$) and absolute temperature (298 K). The free energy change (E; J mol^{-1}) required to transfer one mole of ion from the infinity in the solution to the solid surface was then derived from $E = (-2K_{DR})^{-1/2}$. Langmuir isotherms were further considered to predict whether the composite was "favorable" in view of the dimensionless factor (R_L) and to calculate the weight of the composite (w; kg) for removing UO_2^{2+} and Th^{4+} from hypothetic solutions with "V" (L) volume: $R_L = 1/(1 + K_L C_e)$ and $W/V = (C_i - C_e)/[K_L X_L C_e/(1 + K_L C_e)]$ as suggested [30].

To determine the temperature dependence of adsorption, the distribution coefficients (K_d) were derived from $K_d = Q/C_e$ for each temperature and "$\ln K_d$" was depicted against $1/T$ to provide adsorption enthalpy (ΔH, kJ mol^{-1}), and entropy (ΔS, J $mol^{-1} K^{-1}$) from the slopes ($\Delta H/R$) and intercepts ($\Delta S/R$) of the depictions with reference to $\ln K_d = \Delta S/R - \Delta H/(RT)$. After the ΔH and ΔS values were obtained, ΔG values were calculated using the formula $\Delta G = \Delta H - T\Delta S$ for 298 K. Equations related to the pseudo-second order kinetic and intra-particle diffusion models were $t/Q_t = 1/(kQ_e^2) + t/Q_e$ and $Q_t = k_i t^{1/2}$, where Q_t and Q_e are the adsorbed amounts (mol kg^{-1})

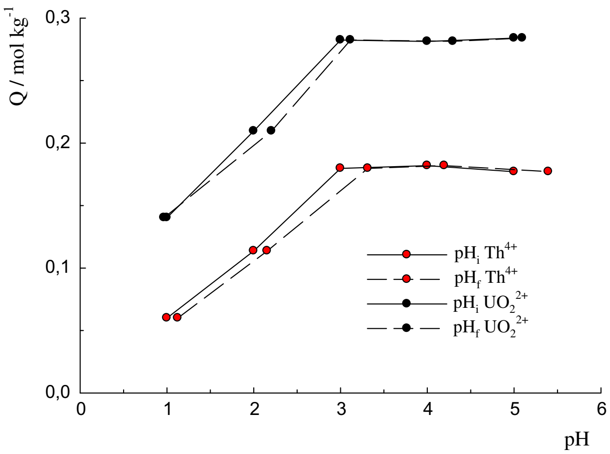

Fig. 1. The effect of initial and final solution pH on UO_2^{2+} and Th^{4+} adsorption onto the studied composite P(HEMA-Hap).

Table 1
The pH dependence of UO_2^{2+} and Th^{4+} adsorption

UO_2^{2+}			Th^{4+}		
pH_i	${}^a\Delta pH$	Q (mol kg^{-1})	pH_i	${}^a\Delta pH$	Q (mol kg^{-1})
1.0	0.03	0.14	1.0	0.13	0.06
2.0	0.20	0.20	2.0	0.16	0.11
3.0	0.12	0.28	3.0	0.32	0.18
4.0	0.30	0.28	4.0	0.20	0.18
5.0	0.10	0.28	5.0	0.40	0.18

Note: ${}^a\Delta pH = pH_f - pH_i$.

at time t, k and k_i are the rate constants applied to the results of kinetic studies to envisage the controlling mechanism of the adsorption process. The initial adsorption rate (H) was calculated by using the equation $H = kQ_e^2$, which relates to the time required for adsorption of half of the concentrations ($t_{1/2}$) given by $t_{1/2} = 1/(kQ_e) = Q_e/H$ [31,32].

A t-test was applied to obtain the significance of regression coefficients (R^2) for the compatibility of the present data with the Langmuir, Freundlich, and DR models, and for the linearity of kinetic equations [33].

3. Results and discussion

3.1. Adsorption-pH relationship

Adsorption of metal ions on composite material is pH dependent, and it is also one of the most important parameters for the removal of metal ions from aqueous solutions. Precipitation of the metal ions is affected by the concentration and their solubility. Hydrolysis of metal ions often takes place at a pH range between 7.5 and 8.5 [34]. The amounts of adsorbed UO_2^{2+} and Th^{4+} ions onto the P(HEMA-Hap) composite increased (from 0.18 mol kg^{-1} to 0.28 mol kg^{-1}) with increasing pH, and reached a plateau at around pH 3.0 (Fig. 1). As can be seen, the recovery of UO_2^{2+} and Th^{4+} ions from the P(HEMA-Hap) was strongly dependent on pH (Fig. 1).

The amounts of adsorbed ions were close to the maximum adsorption capacity of P(HEMA-Hap) at pH 3.0. The pH dependence of adsorption also confirmed that UO_2^{2+} and Th^{4+} ions were adsorbed via an ion-exchange mechanism. The pH ($\Delta pH = pH_i - pH_f$) values were always $\Delta pH > 0$ and as expected for the basic contribution of the adsorption (Table 1). It has been shown that P(HEMA-Hap) was able to form complex ion associations with uranium at pH 3. This result was also consistent with those of literature where it has been demonstrated that both precipitation and hydrolysis occurred at (for thorium) pH > 4.7 $K_{solubility} = 4 \times 10^{-45}$ [27,35]. In the present work, the

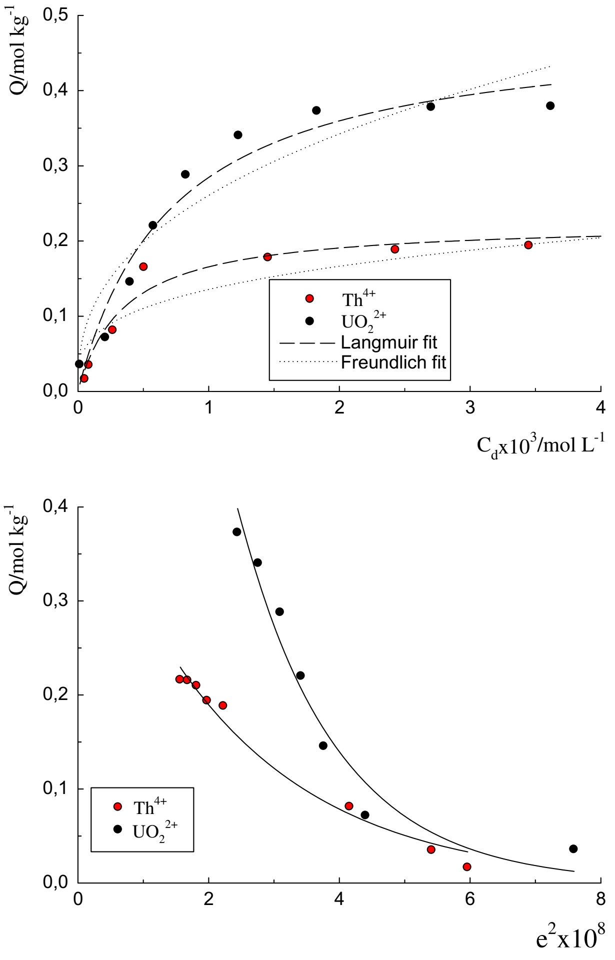

Fig. 2. Experimentally obtained isotherms and their compatibility to Langmuir, Freundlich and DR models for adsorption of UO_2^{2+} and Th^{4+} onto the studied composite P(HEMA-Hap).

Table 2
Langmuir, Freundlich and DR parameters for UO_2^{2+} and Th^{4+} adsorption on to P(HEMA-Hap)

	Langmuir			Freundlich			DR		
	${}^{a}X_L$	${}^{b}K_L$	${}^{c}R^2$	X_F	β	${}^{c}R^2$	X_{DR}	$-K_{DR} \times 10^9$	${}^{c}R^2$
UO_2^{2+}	0.489	1,392	0.967	3.96	0.39	0.913	2.07	6.74	0.960
Th^{4+}	0.225	2,799	0.967	1.05	0.30	0.887	0.46	4.40	0.983

Note: ^{a}mol kg^{-1}, ^{b}L mol^{-1}, ^{c}statistically significant correlation ($p < 0.05$).

Table 3
R_L values from sorption isotherm for UO_2^{2+} and Th^{4+} sorption onto P(HEMA-Hap)

Concentration (ppm)	UO_2^{2+}	Th^{4+}
100	0.24	0.47
500	0.12	0.34
750	0.07	0.21
1,000	0.05	0.14
1,500	0.02	0.07

optimum adsorption value was obtained at pH 3, at which no precipitation and hydrolysis were observed.

3.2. Concentration dependence of adsorption

The adsorption isotherms obtained were of *L* or *H* types, specified in Giles classification (Fig. 2).

These findings indicated that P(HEMA-Hap) displayed higher adsorption capacity to UO_2^{2+} and Th^{4+}. The parameters derived from the Langmuir, Freundlich, and D-R models are shown in Table 2. The amounts of ion recovery for the P(HEMA-Hap) composite were 0.489 μmol g^{-1} of composite for UO_2^{2+} and 0.225 μmol g^{-1} of composite for Th^{4+}, respectively (Table 2). The X_L value of the composite was higher than Hap, indicating that the encapsulation with P(HEMA) increased the adsorption of Hap. The increase in adsorption could be attributed to catalytic contribution of P(HEMA) in the adsorption process, and the fine dispersion of mineral particles in P(HEMA) could be accounted for by the high adsorption capacity.

The values of "R_L" were always found to be $0 < R_L < 1$, indicating that P(HEMA-Hap) could be suggested for UO_2^{2+} and Th^{4+} adsorption (Table 3). The calculated mass of P(HEMA-Hap) composite for the removal of 50% of UO_2^{2+} and Th^{4+} from a hypothetical solution containing 100 mgL^{-1} UO_2^{2+} and Th^{4+} was found to be 0.17 mgL^{-1} and 0.24 mgL^{-1}. Such low amounts appeared to be sufficient for uranium and thorium removal/recovery procedures (Table 4). The low amounts should also be considered evidence for the effectiveness of the proposed adsorbent.

3.3. Adsorption kinetics

The compatibility of UO_2^{2+} and Th^{4+} adsorption data with the pseudo-second order kinetics and intra-particle diffusion (Weber–Morris) models was also evaluated (Table 5) with reference to the linearity obtained from "$t - t/Q_t$" and "$t^{0.5} - Q_t$" plots (Fig. 3).

Statistical significance of the regressions coefficients indicated that the pseudo-second order model was the fitted kinetic model of adsorption ($p < 0.05$). Furthermore, the identical nature of the values of the adsorbed amounts at equilibrium, obtained from

Table 4
Mass of composite for 50, 90 and 95% extraction of UO_2^{2+} and Th^{4+} from the hypothetical solutions containing 4.8×10^{-4}, 2.4×10^{-3} and 4.3×10^{-3} UO_2^{2+} and Th^{4+} (100, 500 and 1,000 mg L^{-1})

Concentration/ppm	[m/V] mg L^{-1}					
	UO_2^{2+}			Th^{4+}		
	50%	90%	95%	50%	90%	95%
100	0.17	1.07	2.71	0.24	2.04	3.21
500	0.32	1.25	3.24	1.24	2.45	4.25
1,000	1.12	2.17	4.51	2.43	3.24	5.46

Table 5
Kinetic parameters, for UO_2^{2+} and Th^{4+} adsorption on to P(HEMA-Hap), derived from the second order and Weber-Morris models and coefficients of regression (R^2) for the compatibilities

	Pseudo-second order model						Weber-Morris model	
	^{a}k	$^{b}Q_{mod}$	^{b}Q	^{c}H	$^{d}t_{1/2}$	$^{f}R^2$	$^{e}k_i \times 10^3$	$^{f}R^2$
UO_2^{2+}	0.209	0.259	0.265	0.0147	17.62	0.999	5.71	0.887
Th^{4+}	0.523	0.371	0.374	0.0732	5.15	0.999	8.71	0.995

Notes: $^{a}mol^{-1}\,kg\,min^{-1}$, $^{b}mol\,kg^{-1}$, $^{c}mol\,kg^{-1}\,min^{-1}$, ^{d}dk, $^{e}mol\,kg^{-1}\,min^{0.5}$, ^{f}Statistically not significant ($p > 0.05$).

the model (Q_{mod}) and from the experiment (Q) confirmed that the nature of adsorption was concentration dependent [36]. Q_t values plotted as a function of $t_{0.5}$ (Weber and Morris model) did not provide intercepts at the origin, defining the adsorption process controlled by diffusion (Fig. 3), but it was a curve that could be evaluated in two linear parts [37]. The adsorption appeared to occur in two steps: The first step was very rapid in which the ions bound to the surface of the composite particles and saturated the adsorption capacity; the second step was much slower as it involved intra-particle diffusion. This behavior of the composite was concordant with the results of the Weber-Morris model. Therefore, the overall adsorption process was concentration-dependent.

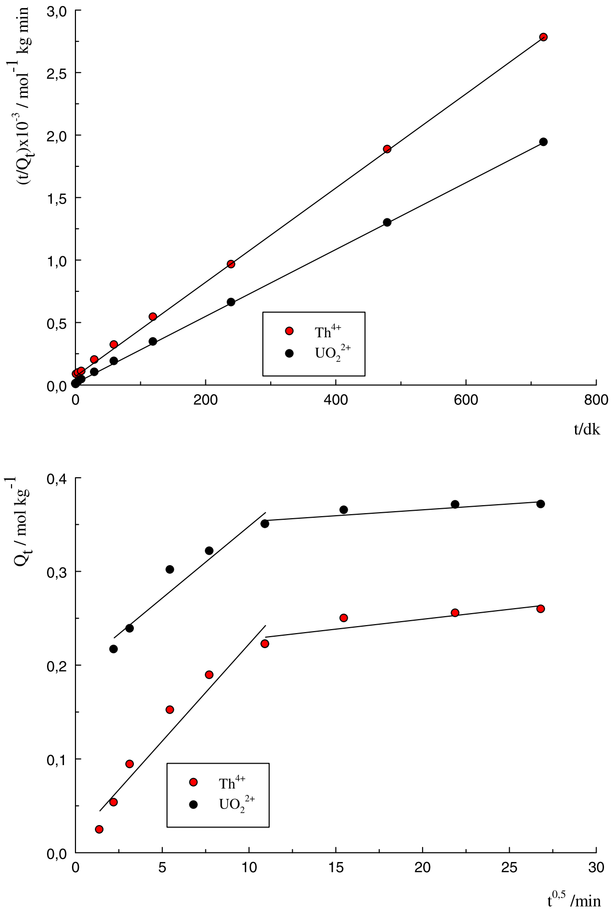

Fig. 3. The compatibility of UO_2^{2+} and Th^{4+} adsorption kinetics to pseudo-second order model and Weber-Morris model.

3.4. Temperature dependence of adsorption

Temperature dependence of the adsorption was represented as a function of $\ln K_d$ (Fig. 4). Thermodynamic parameters, derived from the depictions and free energy change (E_{DR}), derived from DR model are presented in Table 6.

The enthalpy and entropy changes were $\Delta H > 0$ and $\Delta S > 0$ for P(HEMA-Hap), indicating that the overall process was endothermic in the solid-solution interface, which increased during the later stages of the adsorption process. The Gibbs free enthalpy change, $\Delta G < 0$, was always negative during the spontaneous adsorption process. The E_{DR} value for both

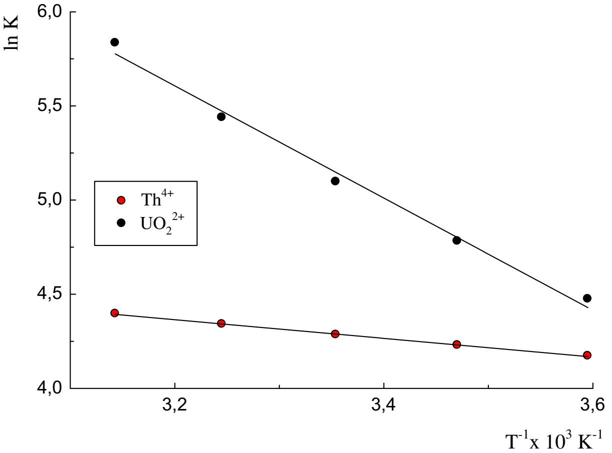

Fig. 4. Temperature dependence of UO_2^{2+} and Th^{4+} adsorption and its compatibility to linearity.

Table 6
Thermodynamics parameters obtained from Vant-Hoff and D–R models

	Vant-Hoff				D–R	
	$\Delta H/\mathrm{kJ\,mol^{-1}}$	$\Delta S/\mathrm{J\,mol^{-1}K^{-1}}$	$-\Delta G/\mathrm{kJ\,mol^{-1}}$	${}^{a}R^2$	$E/\mathrm{kJ\,mol^{-1}}$	${}^{a}R^2$
UO_2^{2+}	24.8	125.9	37.5	0.992	9.6	0.960
Th^{4+}	4.1	49.5	14.7	0.998	10.7	0.983

Note: [a]Statistically significant, $p < 0.05$.

Table 7
Reusability of the composite for adsorption of UO_2^{2+} and Th^{4+}

Reuse no Eluents →	UO_2^{2+} $1\,\mathrm{mol\,L^{-1}}$ HCl	Th^{4+} $1\,\mathrm{mol\,L^{-1}}$ HCl
1	78.2 (100)[a]	52.7 (100)[a]
2	76.5 (98)	51.3 (97)
3	75.3 (96)	48.7 (92)
4	74.4 (95)	48.0 (91)
5	73.5 (94)	48.0 (91)
Mean ± SEM	75.6 ± 1.2 (97 ± 1.8)	49.7 ± 0.7 (94 ± 1.4)

Note: [a]Values of % adsorption with reference to the first use assumed to be 100%.

Table 8
Metal selectivity of P(HEMA-Hap) from solutions containing possible combinations of studied ions at equivalent concentrations ($5\times10^{-3}\,\mathrm{mol\,L^{-1}}$)

Combinations (binary)	Adsorption %
UO_2^{2+}	85[a] (72)[b]
Th^{4+}	33 (28)

Note: [a]As percentage of the amount of ion added to the solution. [b]As percentage of total ion adsorption onto the adsorbent.

the ions was > 8 kJ mol^{-1}, clearly demonstrating that the nature of the adsorption process was chemical [38,39].

3.5. Reusability

The reusability of P(HEMA-Hap) was tested for UO_2^{2+} and Th^{4+} five times, one initial and four regenerations, and the resulting adsorption percentages were calculated (Table 7). The adsorption means of the four regenerations and their ± SEM values were

Table 9
Ion strengths of the composites for adsorption of UO_2^{2+} and Th^{4+} from solution

$[CaCl_2]/\mathrm{mol\,L^{-1}}$	Adsorption/%	
	UO_2^{2+}	Th^{4+}
0	77.7 (0.29)[a]	43.7 (0.19)[a]
0.01	77.3	43.3
0.02	76.5	42.3
0.04	76.2	40.8
0.08	75.6	32.8
0.10	74.9	30.0
0.20	73.7	27.5
0.25	72.6	21.2
0.30	72.5	18.6
Ort ± SS($n = 8$)	75.2 ± 0.4 (0.28)[a]	33.35 ± 1.4 (0.11)[a]

Note: [a]Adsorption (mol kg^{-1}).

found to be 97 ± 1.8% for UO_2^{2+} and 94 ± 1.4% for Th^{4+}, respectively. The mean values were found not to be significantly different from that of the initial adsorption experiment ($p < 0.05$).

3.6. Competitive adsorption

The ion selectivity of P(HEMA-Hap) was tested for a mixture solution of UO_2^{2+} and Th^{4+} ions (5×10^{-3} mol L^{-1}) (Table 8).

The new adsorbent was found to be more selective toward UO_2^{2+}, even in the presence of Th^{4+}. This can be explained by the magnitude of the ionic diameter and by the parameters specified for UO_2^{2+} adsorption (K_L and β, see Table 2).

3.7. The effect of ionic strength

The influence that the ionic strength of UO_2^{2+} and Th^{4+} exerted on the adsorption capacity of P(HEMA-Hap) was investigated in the presence of $CaCl_2$ at 10×10^{-3}–300×10^{-3} mol L^{-1}. The variations in the adsorption values in the absence and presence of $CaCl_2$ were calculated (Table 9). As can be seen, ion adsorption was inversely proportional to the ionic strength, and the presence of $CaCl_2$ did not change the adsorption capacity of the composite.

4. Conclusion

A novel composite, P(HEMA-Hap), was synthesized by polymerizing a non-adsorbent material, P(HEMA), with an adsorbent component, Hap. By using a number of differing physiochemical conditions such as temperature, kinetics, and pH, it was demonstrated that the resulting composite displayed higher adsorption capacity than Hap alone. The adsorption kinetics for UO_2^{2+} and Th^{4+} were found to be compatible with the pseudo-second order model, and the adsorption process was chemical. The adsorption capacity appeared to increase at elevated temperatures. Changes in the values of enthalpy and entropy were also found to be positive. The regeneration tests showed that P(HEMA-Hap) could be used at least five times. Selectivity studies also showed that P(HEMA-Hap) had higher selectivity for UO_2^{2+}.

Acknowledgment

The author is grateful to Dr. Birnur AKKAYA for her valuable insights and contributions. This work was supported by The Research Fund of Cumhuriyet University (CÜBAP) to which the author is grateful.

References

[1] U. Ulusoy, R. Akkaya, Adsorptive features of polyacrylamide–apatite composite for Pb^{2+}, UO_2^{2+} and Th^{4+}, J. Hazard. Mater. 163 (2009) 98–108.

[2] R. Akkaya, U. Ulusoy, Adsorptive features of chitosan entrapped in polyacrylamide hydrogel for Pb^{2+}, UO_2^{2+} and Th^{4+}, J. Hazard. Mater. 151 (2008) 380–388.

[3] M. Tabakci, S. Erdemir, M. Yimaz, Preparation, characterization of cellulose-grafted with calix[4]arene polymers for the adsorption of heavy metals and dichromate anions, J. Hazard. Mater. 148 (2007) 428–435.

[4] N.G. Rachkova, I.I. Shuktomova, A.I. Taskaev, The state of natural radionuclides of uranium, radium, and thorium in soils, Eurasian Soil. Sci. 43 (2010) 651–658.

[5] V.N. Tirtom, A. Dinçer, S. Becerik, T. Aydemir, A. Çelik, Removal of lead (II) ions from aqueous solution by using cross-linked chitosan-clay beads, Desalin. Water Treat. 39 (2012) 76–82.

[6] R. Akkaya, Thermodynamic parameters of TI^{+}, Ra^{2+}, Bi^{3+} and Ac^{3+} adsorption onto polyhydroxyethylmethacrylate-hydroxyapatite composite, J. Radioanal. Nucl. Chem. 292 (2012) 771–775.

[7] T.E. Kose, H. Demiral, N. Ozturk, Adsorption of boron from aqueous solutions using activated carbon prepared from olive bagasse, Desalin. Water Treat. 29 (2011) 110–118.

[8] R. Akkaya, Synthesis and characterization of poly (2-hydroxyethylmethacrylate-hydroxyapatite) a novel composite for the removal of lead (II) from aqueous solutions, Clean-soil air, Water, (in press), doi: http://dx.doi.org/10.1002/clen.201200053.

[9] A. Saglam, S. Bektas, S. Patır, O. Genc, A. Denizli, Novel metal complexing ligand: Thiazolidine carrying poly (hydroxyethylmethacrylate) microbeads for removal of cadmium(II) and lead(II) ions from aqueous solutions, React. Funct. Poly. 47 (2001) 185–192.

[10] A. Denizli, B. Garipcan, A. Karabakan, H. Senöz, Synthesis and characterization of poly(hydroxyethyl methacrylate-N-methacryloyl-(L)-glutamic acid) copolymer beads for removal of lead ions, Mat. Sci. Eng. B-Solid. 25 (2005) 448–454.

[11] A. Denizli, R. Say, B. Garipcan, S. Patır, Methacryloylamidoglutamic acid functionalized poly(2-hydroxyethyl methacrylate) beads for UO_2^{2+} removal, React. Funct. Poly. 58 (2004) 123–130.

[12] B. Salih, A. Denizli, P. Kavaklı, R. Say, E. Piskin, Adsorption of heavy metal ions onto dithizone-anchored poly (EGDMA-HEMA) microbeads, Talanta. 46 (1998) 1205–1213.

[13] B.H. Samia, L. Bousselmi, E.M. Rezrazi, P. Berçot, E. Triki, Comparative study of protective magnesium deposit behaviour obtained by continuous and pulsed currents from methylmagnesium chloride solution, Surf. Coatings Tech. 202 (2008) 3579–3584.

[14] M.H. Casimiro, J.P. Leal, M.H. Gil, Characterisation of gamma irradiated chitosan/pHEMA membranes for biomedical purposes, Nucl. Instrum. Meth. B. 236 (2005) 482–487.

[15] E. Karadag, O.B. Uzum, D. Saraydin, Swelling equilibria and dye adsorption studies of chemically crosslinked superabsorbent acrylamide/maleic acid hydrogels, Eur. Polym. J. 38 (2002) 2133–2141.

[16] D. Ozer, T. Kutsal, A. Caglar, A staged purification process to remove heavy metal ions from wastewater using *Rhizopus arrhizus*, Process Biochem. 32 (1997) 319–326.

[17] N. Sahiner, N. Pekel, O. Guven, Radiation synthesis, characterization and amidoximation of N-vinyl-2-pyrrolidone/acrylonitrile interpenetrating polymer networks, React. Funct. Polym. 39 (1999) 139–146.

[18] N. Pekel, O. Guven, Synthesis and characterization of poly(N-vinyl imidazole) hydrogels crosslinked by gamma irradiation, Polym. Int. 51 (2002) 1404–1410.

[19] S. Erdogan, M. Merdivan, C. Hamamci, O. Akba, A. Baysal, Polymer supported humic acid for separation and preconcentration of thorium (IV), Anal. Lett. 37 (2004) 2565–2575.

[20] O. Ozay, S. Ekici, Y. Baran, N. Aktas, N. Sahiner, Removal of toxic metal ions with magnetic hydrogels, Water Res. 43 (2009) 4403–4411.

[21] T.S. Anirudhan, S.S. Sreekumari, Synthesis and characterization of a functionalized graft copolymer of densified cellulose for the extraction of uranium(VI) from aqueous solutions, Colloid. Surface A. 361 (2010) 180–186.

[22] S.S. Bozkurt, Z.B. Molu, L. Cavas, M. Merdivan, Biosorption of uranium (VI) and thorium (IV) onto Ulva gigantea (Kutzing) bliding: Discussion of adsorption isotherms, kinetics and thermodynamic, J. Radioanal. Nucl. Ch. 288 (2011) 867–874.

[23] R. Akkaya, U. Ulusoy, Tl-208, Pb-212, Bi-212, Ra-226 and Ac-228 adsorption onto polyhydroxyethylmethacrylate—bentonite composite, Nucl. Instrum. Meth. A. 664 (2012) 98–102.

[24] B. Akkaya, A.F. Yenidunya, R. Akkaya, Production and immobilization of a novel thermoalkalophilic extracellular amylase from bacilli isolate, Int. J. Biol. Macromol. 50 (2012) 991–995.

[25] C. Degueldre, A. Kline, Study of thorium association and surface precipitation on colloids, Earth Planet. Sc. Lett. 264 (2007) 104–113.

[26] R. Akkaya, Synthesis and characterization of a new low-cost composite for the adsorption of rare earth ions from aqueous solutions, Chem. Eng. J. 200–202 (2012) 186–191.

[27] V. Neck, R. Muller, M. Bouby, M. Altmaier, J. Rothe, M.A. Denecke, J.I. Kim, Solubility of amorphous Th(IV) hydroxide - application of LIBD to determine the solubility product and EXAFS for aqueous speciation, Radiochim. Acta. 90 (2002) 485–494.

[28] H. Rohwer, N. Rheeder, E. Hosten, Interactions of uranium and thorium with arsenazo III in an aqueous medium, Anal. Chim. Acta. 341 (1997) 263–268.

[29] M. Khan, H. Ali, N.N.A. Khan, Spectrophotometric determination of thorium with disodium salt of Arsenazo-III in perchloric acid, J. Radioanal. Nucl. Chem. 250 (2001) 353–357.

[30] M. Dogan, M. Alkan, Removal of methyl violet from aqueous solution by perlite, J. Colloid Interf. Sci. 267 (2003) 32–41.

[31] S. Sun, A. Wang, Adsorption kinetics of Cu (II) ions using N, O-carboxymethyl-chitosan, J. Hazard. Mater. 131 (2006) 103–111.

[32] S. Basha, Z.V.P. Murthy, Kinetic and equilibrium models for biosorption of Cr(VI) on chemically modified seaweed, Cystoseira indica. Process Biochem. 42 (2007) 1521–1529.

[33] J.C. Miller, J.N. Miller, Statistics for Analytical Chemistry, Wiley, New York, NY, 1989.

[34] P. Sharma, R. Tomar, Synthesis and application of an analogue of mesolite for the removal of uranium(VI), thorium (IV), and europium(III) from aqueous waste, Mıcropor. Mesopor. Mat. 116 (2008) 641–652.

[35] C.F. Baes-J.R., R.E.N. Mesmer, The Hydrolysis of Cations, Wiley-Interscience, New York, NY, 1976.

[36] W.J. Weber, J.C. Morris, Kinetics of adsorption on carbon from solution, J. Sanit. Eng. Div. Am. Soc. Civ. Eng. 89 (1963) 31–60.

[37] S.Y. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451–465.

[38] A.R. Cestari, V.F. Eunice, C.R.S. Mottos, Thermodynamics of the Cu (II) adsorption on thin vanillin-modified chitosan membranes, J. Chem. Thermodyn. 38 (2006) 1092–1099.

[39] M. Mahramanlioglu, K. Guclu, I. Kizilcikli, Adsorption of uranium by adsorbents produced from coal mining waste, Fre. J. Anal. Chem. 16 (2007) 988–1004.