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Silica nanoparticles modified with a Schiff base ligand: An efficient adsorbent for Th(IV), U(VI) and Eu(III) ions

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Abstract−Modification of SiO_2 nanoparticles by salicylaldiminepropyl results in efficient adsorbents for removal of Th^{4+}, UO_2^{2+} and Eu^{3+} ions from aqueous solutions. The effect of parameters influencing the adsorption efficiency such as aqueous phase pH, contact time, initial metal ions concentration, adsorbent dosage and temperature dependency of the process was verified and discussed. Under optimal conditions (pH 5.5, adsorbent dosage 0.05 g, contact time 30 min. and 25 °C), thorium and uranyl ions (initial concentration 20 mg/*l*) were quantitatively removed from 20 ml of sample solution. Under such conditions 85% of europium ions was removed. Comparison of the adsorption efficiency of the studied modified nano-particles with those unmodified ones shows a shift for uptake of the metal ions vs. pH curves towards lower pH values by applying the modified adsorbents. In addition, a significant improvement of europium ions adsorption was observed by using the modified nanoparticles. Kinetics of the process was studied by considering a pseudo second-order model. This model predicts chemisorption for the adsorption mechanism. Freundlich, Langmuir and Temkin models were suitable for describing the equilibrium data of Th^{4+}, UO_2^{2+} and Eu^{3+} adsorption process, respectively. Thermodynamic investigation reveals the adsorption process of the studied ions is entropy driven.

Key words: Modified Silica Nano-particles, Schiff Base, Th(IV), U(VI), Eu(III), Removal, Separation

INTRODUCTION

Inter-group separation of actinides is a key step in the management and storage of radioactive waste [1,2]. Beside this, elimination of lanthanides from this waste enhances the efficiency of the converting process of long-lived radionuclides to short-lived elements via application of high energy neutrons [3,4]. In addition to their importance in production of nuclear energy, thorium, uranium and lanthanides are known as strategic elements in a variety of industries. Thorium occurs naturally in low concentrations (~10 ppm) in the earth's crust and has wide applications in various arrays of products and processes such as the production of ceramics, carbon arc lamps and alloys in mantles for lanterns [5]. Uranium finds extensive application as nuclear fuel in power plants [6]. Rare earth elements and their compounds have wide range of applications especially in metallurgy, ceramic industry and nuclear fuel control [7]. Considering these remarkable aspects of actinides and lanthanides, the separation of these ions has been extensively investigated. It is important to note that, in many investigations, Th(IV) is selected as a model for tetravalent actinides and due to its similarities with trivalent actinides, Eu(III) is used as a model for these ions.

Aforementioned industrial applications and their role in nuclear energy production of actinides and lanthanides show the importance of the studies concern on the separation and purification of these elements from their mixtures. Liquid-liquid extraction [8-11], super-critical fluid extraction [12], chromatographic methods [13,14] and application of various adsorbents such as organic chelating resins, silica gel, activated carbon, alumina, zeolites and microcrystalline materials [15-22] are among the techniques used for separation of these ions.

Nanometer materials play a substantial role in metal ion separation studies owing to their special physical and chemical properties. Although the potential of these materials in removal of various biomolecules [23,24], organic [25,26] and inorganic [27,28] species is widely investigated, such studies for actinides and lanthanides are rare [29-31].

Following our studies on separation of actinides and lanthanides [32], and investigations on the ionophore properties of Schiff base receptors [33], this report concerns the application of silica nanoparticles modified by a Schiff base ligand, named salicylaldiminepropyltriethoxysilane (Fig. 1) for removal and separation of Th^{4+}, UO_2^{2+} (shown also as U(VI)) and Eu^{3+} ions from aqueous solutions. The parameters affecting their adsorption properties have been investigated and discussed. The results were compared with those unmodified nanoparticles.

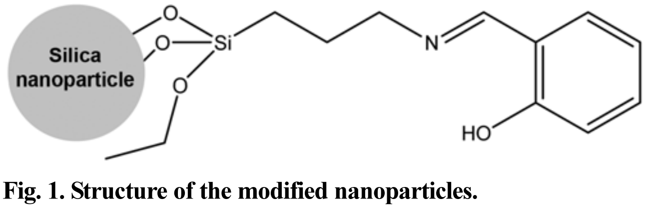

Fig. 1. Structure of the modified nanoparticles.

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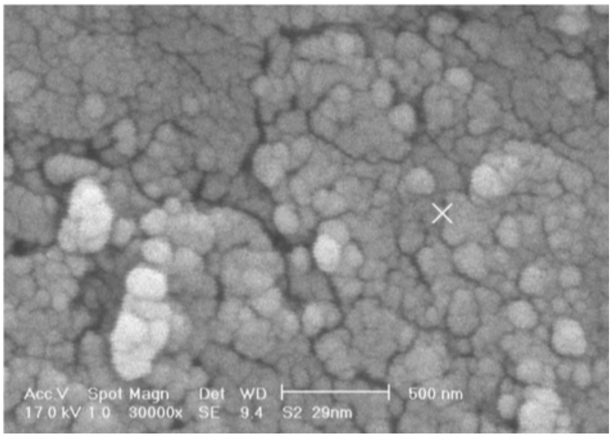

Fig. 2. Scanning electron micrograph (SEM) of the modified nanoparticles.

EXPERIMENTAL

1. Materials

Methanol, aminopropyltriethoxysilane and salicylaldehyde (Merck) were used as received. Unmodified nanoparticles were prepared by the reverse micelle method [34], in which they have smaller size (APS 29-30 nm) with respect to those purchased from the market (Iranian Nanomaterials Co., APS 20-30 nm). Both types of SiO_2 nanoparticles were modified and their adsorption efficiencies were compared towards the studied ions. Modification of silica nanoparticles was realized according to the procedure reported in the literature [34]. The SEM image of these particles (Fig. 2) shows the modified nanoparticles have rough structure. Bulk silica gel particles (0.063-0.200 mm) were purchased from Merck Chemical Company and were used as received. Stock solutions of thorium and uranyl ions (0.01 M) were prepared by dissolving a proper quantity of corresponding nitrate salts (Merck) in distilled water. For preparing the stock solution of europium, a weighed quantity of the corresponding oxide (Fluka) was dissolved in nitric acid (Merck). The stock solutions were standardized complexometrically [35]. Working solutions were prepared by suitable dilution of the stock solutions with distilled water.

2. Apparatus

^{1}HNMR and ^{13}CNMR measurements were performed on an FT-Bruker (AVC 250 MHz) spectrometer and data was referenced relative to residual protonated solvents (7.26 ppm for $CDCl_3$). FT-IR spectrum was recorded on a Unicam (Matson 1000) spectrometer.

The pH adjustments were performed by a Metrohm (model 780) digital pH-meter equipped with a combined glass electrode. A Heidolph magnetic stirrer (MR 3001K) was used for mixing sorbent and aqueous solutions. Temperature of the experiment vessels was controlled using a Julabo MP5 thermostate water circulator. A Varian ICP model Turbo AX 150 Liberty was used for ion measurements. A furnace (Exiton, model Atash-1200) was used for activation of the silica nanoparticle's surface before modification. Separation sorbent and aqueous solution was assisted by a high speed centrifuge (Sigma). Distilled water was passed through a filter model TKA-Gen Pure, before using for preparing aqueous solutions. The SEM photograph was taken with Philips XL30 scanning microscope to examine the morphology and surface structure of the adsorbent at the required magnification at room temperature.

3. Adsorption Procedure

The absorption experiments were carried out in stoppered glass tubes immersed in a thermostatted water bath (25±1 °C) using 0.05 g of the modified adsorbent in 20 ml of sample containing Th^{4+}, UO_2^{2+} and Eu^{3+} ions (20 mg/*l*). It is confirmed that the absorption equilibrium was reached after 30 min of magnetically stirring. After separation of the phases by centrifugation (at 5,000 rpm), the concentration of cations remaining in the aqueous phase was measured using inductively coupled plasma emission spectroscopy (ICP). The distribution coefficient, uptake and desorption percentage of the ions were calculated by Eqs. (1)-(3).

$$K_d = \frac{(C_0 - C_e)}{C_e} \times \frac{V}{M} \tag{1}$$

$$Up = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{2}$$

$$\text{desorption} = \frac{m_d}{m_a} \times 100 \tag{3}$$

where C_0 and C_e are the initial and equilibrium concentration of ions (mg/*l*), respectively, V (ml) is the volume of aqueous phase, M (g) is the mass of adsorbent, m_d and m_a are the desorption and absorption mass of ions from the adsorbent surface (mg), respectively.

RESULTS AND DISCUSSION

Condensation of aminopropyltriethoxysilane and salicylaldehyde in methanol produced salicylaldiminepropyltriethoxysilane $(EtO)_3SiCH_2CH_2CH_2N{=}C{-}C_6H_5(OH)$. Refluxing this product with silica nanoparticles in toluene results in modified nanoparticles as shown in Fig. 1. This product has been characterized by using its ^{1}H-NMR, ^{13}C-NMR and FT-IR spectra. The confirmation of the structure of the target adsorbent was realized by comparing of these data with those reported elsewhere [34]. The amount of grafted imine showed that the salicylaldimine loading in modified nanoparticles was 0.52×10^{-3} mol imine/g of nanosilica. These particles were used as adsorbent for Th(IV), U(VI) and Eu(III) ions.

1. Effect of pH on the Adsorption Process

Competitive adsorption of Th(IV), U(VI) and Eu(III) ions (initial concentration 20 mg/*l*) on unmodified and modified SiO_2-O_2(EtO)Si-LH nanoparticles was studied at different pH values in the range 2-6. The results show the pH dependency of adsorption process with both types of adsorbents (Fig. 3). The selectivity of adsorption in both adsorbents varies as Th(IV)>U(VI)>Eu(III). Although the higher selectivity presented towards thorium ions can be attributed to the high charge to size ratio of these ions, in this stage of study we cannot give a clear reason for the higher affinity of the adsorbents towards uranyl ions with respect to europium ions.

It is noteworthy that whereas the modification of nanoparticles affects slightly the removal of thorium ions, a remarkable enhancement in uptake of U(VI) and Eu(III) ions is presented by the modified nanoparticles. In fact, a shift of the uptake percentage towards lower pH values, and considerable augmentation of removal of uranyl and europium ions has resulted by replacing unmodified nanoparticles by modified one. At pH 4, the quantitative removal of thorium ions by the both adsorbents was achieved. Such conditions for

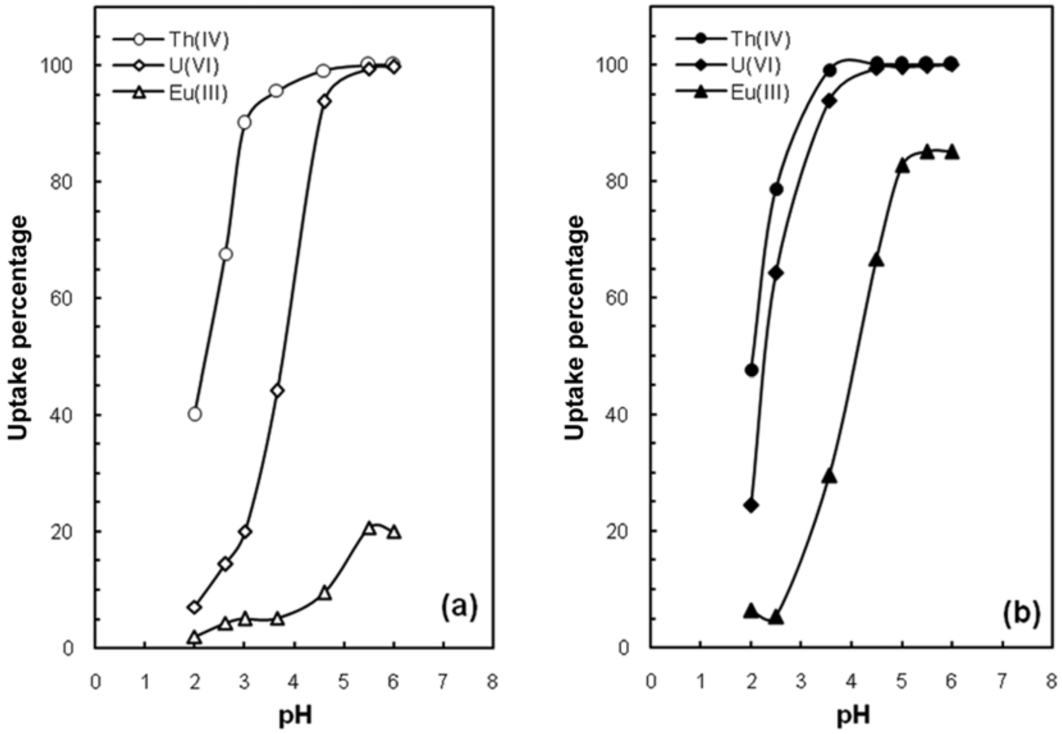

Fig. 3. Effect of pH on the competitive sorption of the studied ions onto (a) unmodified and (b) modified silica nanoparticles. Experimental conditions: initial concentration of the metal ions 20 mg/*l*; adsorbent amount 0.05 g; stirring time 60 min.; temperature 25 °C.

U(VI) ions are reached at pH values higher than 5 and 4 with unmodified and modified nanoparticles, respectively. A maximum value of Eu(III) ions uptake (~85%) was observed by using modified nanoparticles at pH values higher than 5. Thus, pH 5.5 was selected for further experiments.

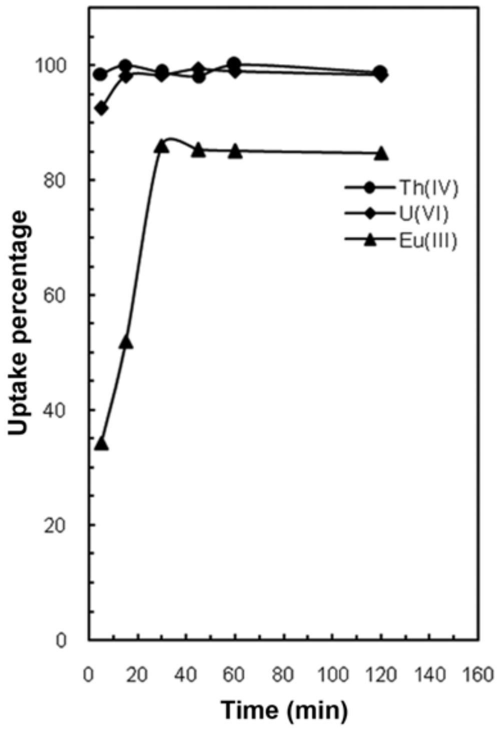

Fig. 4. Time dependency of the adsorption process of a mixture of Th(IV), U(VI) and Eu(III) by the modified nanoparticles. Aqueous phase pH 5.5; other experimental conditions are as shown in the legend of Fig. 3.

2. Shaking Time

The adsorption of Th(IV), U(VI) and Eu(III) ions from aqueous solutions adjusted at pH 5.5m on the modified nanoparticles (0.05 mg) was studied at different shaking time in the range 5-120 min (Fig. 4). The results indicate that within 15 min of shaking, Th(IV) and U(VI) ions were totally removed from aqueous solution. In similar experimental conditions, 85% of Eu(III) ions was removed after 30 min of shaking. This shows more rapid adsorption kinetics of thorium and uranyl ions with respect to that of europium ions. Therefore, a shaking time of 30 min was selected for following the experiments.

3. Amount of Adsorbent

To test the effect of amount of adsorbent on the process a series of experiments was performed by using 0.005-0.1 mg of the modified adsorbent (Fig. 5). A quantitative uptake (>95%) was attained for Th(IV) and U(VI) ions by using >0.025 mg of the studied adsorbent. A maximum adsorption (85%) of europium ions was observed by using higher than 0.05 mg of the modified nanoparticles.

4. Initial Concentration of Metal Ions

The capacity of the process can be monitored by a study of amount of maximum metal ions adsorbed by a given amount of the adsorbent. This variable was tested by removal of the studied metal ions from their mixture (initial concentration of each in the range 10-100 mg/*l*) by 0.05 mg of adsorbent at pH 5.5 (Fig. 6). The results show a decrease in the percentage removal of Th(IV), U(VI) and Eu(III) ions beyond 20, 50 and 20 mg/*l*, respectively, of their initial concentrations. This observation can be attributed to the relative decrease in adsorbing sites by increasing the amount of metal ions.

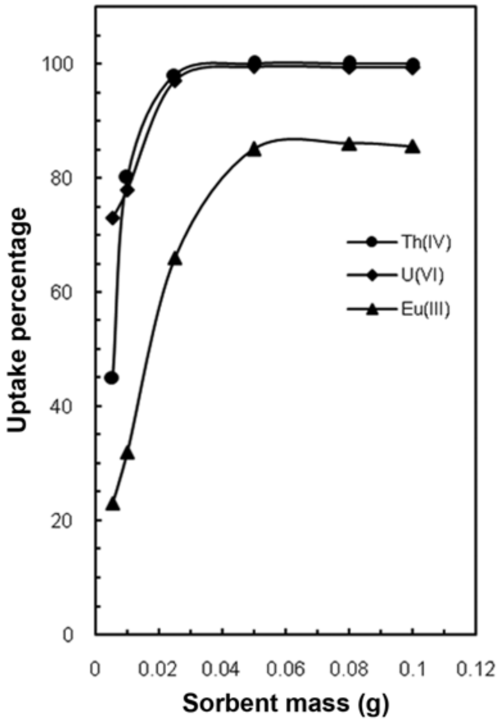

Fig. 5. Effect of the amount of modified nanoparticles on sorption efficiency. Stirring time 30 min; other experimental conditions are as shown in the legend of Fig. 3.

5. Temperature Dependency of the Process

Depending on the adsorption mechanism, the processes can be affected by temperature. To assess the effect of this parameter, the removal of Th(IV), U(VI) and Eu(III) ions from their mixture by the modified nanoparticles was examined in the range 10-35 °C. As shown in Fig. 7, the process efficiency is augmented by increasing temperature up to 25 °C. Beyond this temperature a decrease in adsorption is observed. These observations can be explained by considering both chemical and physical adsorption mechanisms for the proposed process. However, a further conclusion based on these results can be given by considering the rate of decrease of the adsorption amount of Th(IV) and U(VI) ions with respect to that of Eu(III) ions. In fact, one can conclude that the extent of chemical adsorption for the two former ions is more pronounced with respect to that for europium ions.

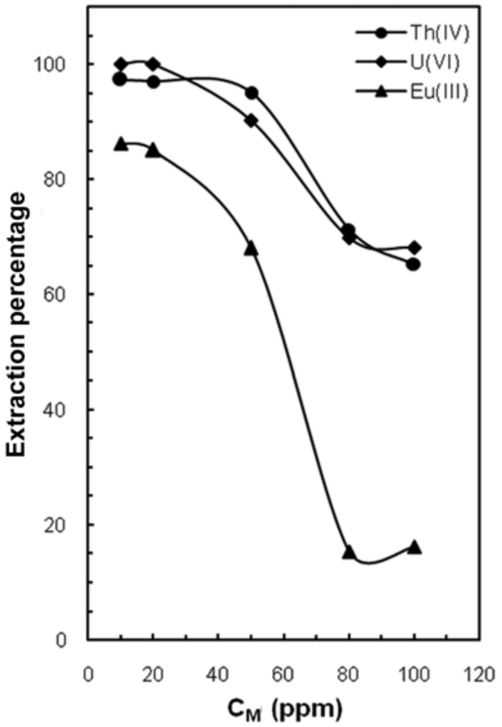

Fig. 6. Effect of metal ion concentration on the adsorption of Th(IV), U(VI) and Eu(III) ions onto modified silica nanoparticles. Stirring time 30 min., pH 5.5; other experimental conditions are as shown in the legend of Fig. 3.

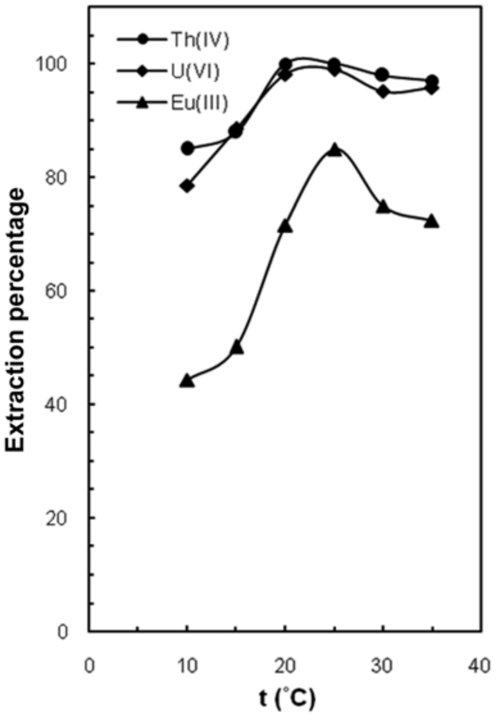

Fig. 7. Effect of temperature on sorption efficiency of metal ions onto modified silica nanoparticles. Stirring time 30 min; other experimental conditions are as shown in the legend of Fig. 3.

6. Comparison of Adsorbents

Taking the selected experimental conditions, i.e., initial concentration of Th(IV), U(VI) and Eu(III) in mixture 20 mg/*l*, sample solution pH 5.5, amount of adsorbent 0.05 g, equilibration time 30 min and temperature 25 °C, the adsorption efficiency of the studied modified nanoparticles (A_1) was compared with those obtained by their unmodified nanoparticles (A_2), unmodified commercial nanoparticles (A_3) and commercial bulk unmodified silica (A_4). It is shown in Fig. 8 that, although the adsorption of europium ions is comparable for A_1, A_2 and A_3, the lowest adsorption efficiency towards Th(IV) and U(VI) ions is achieved by bulk unmodified adsorbents. The improvement in adsorption of thorium and uranyl may be attributed to the smaller size of the particles used in this work (A_1) with respect to the commercial one (A_3). However, the main advantage of the modified nanoparticles used in this work is the significant improvement in the uptake of europium ions.

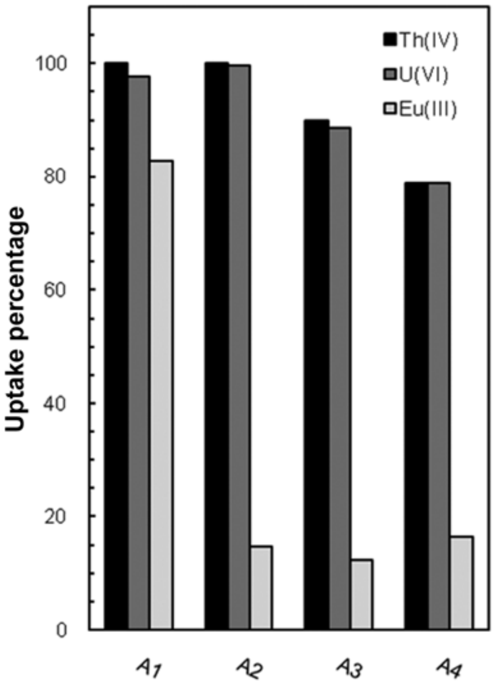

Fig. 8. Comparison of the performance of different sorbents in uptake of Th(IV), U(VI) and Eu(III) ions, under selected experimental conditions. Stirring time 30 min., pH 5.5; other experimental conditions are as shown in the legend of Fig. 3.

7. Desorption Process

Three aqueous solutions (each 20 ml) containing mixture of Th(IV), U(VI) and Eu(III) ions (20 mg/*l*) were magnetically stirred with 0.05 g of the modified nanoparticles, for 30 min, at 25 °C. The uptake of the ions was 100% for Th(IV) and U(VI) ions and 85% of Eu(III) ions. The loaded adsorbents were filtered-off and then were contacted with 5 ml of nitric, hydrochloric and sulfuric acids (0.1 M), separately. It was found that the adsorbed ions can be quantitatively stripped by contacting two times the loaded adsorbents with two volumes of 5 ml of sulfuric or hydrochloric acids.

8. Reusability of the Adsorbent

The reusability potential of an adsorbent is one of the important parameters from an economical point of view. To check this, a given amount of the adsorbent (0.05 g) was contacted with an aqueous solution (20 ml) containing a mixture of the studied ions (each 20 mg/*l*). After equilibration, the adsorbent was stripped with sulfuric acid solution (0.5 ml of 0.1 M, two times) based on the aforementioned procedure. The adsorbent was contacted again with a fresh sample solution containing the studied ions. It was observed that, although the reused adsorbent removes thorium ions quantitatively, its adsorbent capacity diminishes to nearly 70 and 50 percent of uranyl and europium ions, respectively.

9. Competitive Uptake of Thorium, Uranyl and Lanthanides

The investigation hitherto performed was with a scope of separation of Th(IV), U(VI) as representative ions actinides and Eu(III) as a symbol of not only a lanthanide, but also as trivalent actinides [32]. Considering the presence of lanthanides other than europium ions in the nuclear wastes, a competitive uptake of Th(IV), U(VI), La(III), Ce(III), Sm(III), Eu(III), Dy(III), Ho(III) and Er(III) by 0.05 g of the adsorbent was performed (Table 1). The results were compared with those using unmodified adsorbents. Although the modification of the nanoparticles influences their adsorption capacity towards lanthanides, the selectivity remains unchanged. And although the presence of other lanthanides affects the uptake efficiency of europium ions, the adsorption of Th(IV) and U(VI) ions was not significantly altered.

Table 1. The effect of interfering ions in adsorption of Th(IV), U(VI) and lanthanide ions onto modified silica nanoparticles[a]

Metal ions	Unmodified nanoparticles[b]	Modified nanoparticles[b]
Th(IV)	96.7	96.8
U(VI)	90.0	91.0
La(III)	5.3	16.3
Ce(III)	7.6	21.2
Sm(III)	6.8	26.5
Eu(III)	7.0	28.1
Dy(III)	6.2	23.5
Ho(III)	6.6	23.7
Er(III)	5.1	22.5

[a] Experimental conditions: initial concentration of each metal ions, 20 mg/*l*; aqueous sample pH, 5.5; amount of adsorbent, 0.05 g; temperature, 25 °C

[b] In percent and s_{n-1}, <±0.5 for three replicate experiments

10. Applications

According to the obtained data a three-step procedure was designed for separation of thorium, uranyl and europium ions by using the unmodified and modified nanoparticles. This procedure was as follows. At the first step, adsorption of ~98% of thorium ions and 12% of uranyl at pH 3.5 by 0.05 g of unmodified nanoparticles from a 20 ml sample solution was achieved after 30 min mixing of the adsorbent/sample solution mixture. By adjusting the pH of the solution resulting from the first step at 4.5 and contacting it with a new portion of unmodified nanoparticles (0.05 g), 85% and 10% of UO_2^{2+} and Eu^{3+} ions were adsorbed, respectively. At the end, the pH of the solution was increased to 5.5. To this solution a portion of the modified nanoparticles (0.05 g) was added. After 30 min mixing the analysis of the solution showed 85% of Eu(III) ions had been adsorbed.

It is also tested the removal efficiency of the proposed method from a tap water sample. A given amount of Th(IV), U(VI) and Eu(III) ions (each 20 mg/*l*) was added to a tap water sample. The pH of this solution was adjusted to 5.5, and 0.05 g of modified nanoparticles was added. This mixture was magnetically stirred for 30 minutes. The analysis of the solution showed the removal of 97, 95 and 78% of thorium, uranyl and europium ions. This reveals that the matrix of the selected sample does not affect the process efficiency.

11. Kinetics of the Adsorption Processes

To investigate the mechanism controlling the adsorption processes, pseudo first-order, pseudo second-order, power function and simple Elovich kinetic models [36-38] were examined. Considering the evaluated values of correlation coefficients (Table 2), the experimental results were well described by the pseudo second-order kinetic model. This model provided an impressive and comparable corre-

Table 2. Pseudo second-order kinetic model parameters of the adsorption process

Ion	R^2	K_2 (mg/g·min)	h_0 (mg/min)	q_{exp} (mg/g)	q_e (mg/g)
Th^{4+}	0.998	1.18	76.66	8.000	8.060
UO_2^{2+}	0.999	0.32	20.42	8.040	8.000
Eu^{3+}	0.995	0.02	0.93	6.860	7.690

lation for the adsorption of ions with respect to the other models.

The pseudo second-order model is an empirical model describing the relation between mass of the sorbate per unit mass of the adsorbent and time. A mathematical expression of the model is shown in Eq. (4):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} = \frac{t}{q_e} \tag{4}$$

where "t" is time (min), "q_t" and "q_e" are the quantity of adsorbed ions on the surface of sorbent (mg/g) at time "t" and at equilibrium, respectively, "k_2" denotes the pseudo second-order rate constant (g/mg·min). In this model the initial rate of sorption can be evaluated as q_t/t approaches to zero:

$$h_0 = k_2 q_e^2 \tag{5}$$

where "h_0" is the initial rate of sorption (mg/g·min).

The comparison of the evaluated adsorption capacity considering the pseudo second-order equation (q_e) and that found experimentally (q_{exp}) also confirms the validity of the proposed model.

12. Sorption Isotherms

Adsorption isotherm studies allow describing solute/adsorbent interactions. These investigations are also useful for designing adsorption systems in practical and technological goals. Furthermore, adsorption isotherms are applicable for evaluating adsorption capacity, allowing one to examine the feasibility of an adsorption process and to assign the appropriate amount of adsorbent in such process [39].

To specify the models characterizing the sorption isotherm, three conventional models, Langmuir, Freundlich and Temkin [40], were used and applied to the experimental data. The Langmuir model assumes that the uptake of metal ions occurs on a homogeneous surface by monolayer adsorption without any interaction between adsorbed species. The Freundlich isotherm considers the uptake of metal ions occurs on a heterogeneous surface by multilayer adsorption. The Temkin model assumes that the fall in heat of sorption is linear rather than logarithmic, as given in the Freundlich equation. Due to sorbate/sorbent interaction the heat of sorption of all the molecules in adsorbed layer would decrease linearly with coverage.

The Langmuir model is mathematically presented in Eq. (6):

$$\frac{C_e}{q_e} = \frac{1}{q_{max} b} + \frac{C_e}{q_{max}} \tag{6}$$

where q_{max} the maximum sorption capacity (mg/g) and b is a constant related to binding energy of the sorption system (l/mg). Furthermore, in the Longmuir isotherm the favorability of adsorption can be tested by evaluating a dimensionless constant called the separation factor (R_L). This factor is calculated by Eq. (7):

$$R_L = \frac{1}{1 + bC_0} \tag{7}$$

Based on the R_L values the adsorption process is categorized as unfavorable (>1), linear (=1), favorable ($0<R_L<1$) and irreversible (=0) [38].

The Longmuir model on the experimental data of the adsorption process was applied by drawing C_e/q_e versus C_e. This allows evaluating parameters q_{max} and b. Table 3 contains the evaluated R^2, R_L, q_{max} and b based on the Longmuir isotherm model.

The logarithmic presentation of the equation describing the Freundlich model is given in Eq. (8),

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{8}$$

where K_f and n are the Freundlich constants. They are relative indicators for adsorption capacity and adsorption intensity, respectively. A plot of $\log q_e$ versus $\log C_e$ results these constants (Table 3). A favorable adsorption conditions, is achieved when n>1. As an indicator for suitability of this model for describing the experimental data, R^2 values are also evaluated and are given in Table 3.

The Temkin equation has the form:

$$q_e = \frac{RT}{b} \ln(aC_e) \tag{8}$$

where R is the gas constant (0.0083 kJ/K·mol) and T is the absolute temperature (K), b is the Temkin constant related to heat of sorption (kJ/mol), a is the Temkin isotherm constant (l/g). Drawing q_e versus $\ln(aC_e)$ allows evaluating a, b and the corresponding R^2 of the resulted (Table 3).

Comparison of the R^2 values (Table 3) results in selecting the appropriate adsorption isotherm model describing the adsorption process of the studied ions by the modified nanoparticles. This comparison reveals the adsorption process isotherms of thorium, uranyl and europium ions to be more suitably described by the Langmuir, Freundlich and Temkin models, respectively. In addition the evaluated R_L (0.002), in the Langmuir model, confirms the favorable uptake of thorium ions by the examined sorbent.

13. Thermodynamics of the Process

To identify the effect of temperature on the adsorption of thorium,

Table 3. Sorption isotherm parameters for thorium, uranyl and europium ions onto modified silica nanoparticles

Metal ions	R^2	Langmuir model			Freundlich model			Temkin model		
		R_L	q_{max} (mg/g)	b (*l*/mg)	R^2	K_f (mg/g)	n	R^2	a (*l*/g)	b (kJ/mol)
Th(IV)	0.999	0.002	34.500	29.000	0.672	12.000	2.830	0.601	0.291	0.511
U(VI)	0.841	0.055	52.600	0.864	0.897	18.300	1.840	0.876	0.385	0.242
Eu(III)	0.009	0.890	200.000	0.006	0.733	1.410	1.120	0.899	−1.390	0.318

uranyl and europium ions by the studied nanoparticles, a series of adsorption experiments were performed in the range of 283-298 K, under experimental conditions noted in section 3.7. For the adsorption process at the tested temperature, the corresponding distribution coefficient (K_d) was calculated.

The evaluated distribution coefficients allow determining the free-energy changes (ΔG^o) by using the Gibbs-Helmholtz equation (Eq. (9)):

$$\Delta G^o = -RT\ln K_d \tag{9}$$

The relation between the free-energy changes with enthalpy (ΔH^o) and entropy changes (ΔS^o) is shown in Eq. (10):

$$\Delta G^o = \Delta H^o - T\,\Delta S^o \tag{10}$$

Combining Eqs. (9) and (10) results in Eq. (11) describing the variation of K_d as a function of temperature:

$$\ln K_d = \frac{1}{R}\left(\Delta S^o - \frac{\Delta H^o}{T}\right) \tag{11}$$

Plots of the $\ln K_d$ values as a function of the inverse temperature in the range 283-298 K gave straight lines (Fig. 9). The calculated thermodynamic parameters are presented in Table 4.

The positive values of ΔH^o suggest the endothermic nature of adsorption of the Th(IV), U(VI) and Eu(III) ions onto the modified nanoparticles. The positive values of entropy show the increasing randomness at the solid/solution interface during the adsorption process. Also, the positive entropy of adsorption reflects the affinity of the adsorbent for these ions.

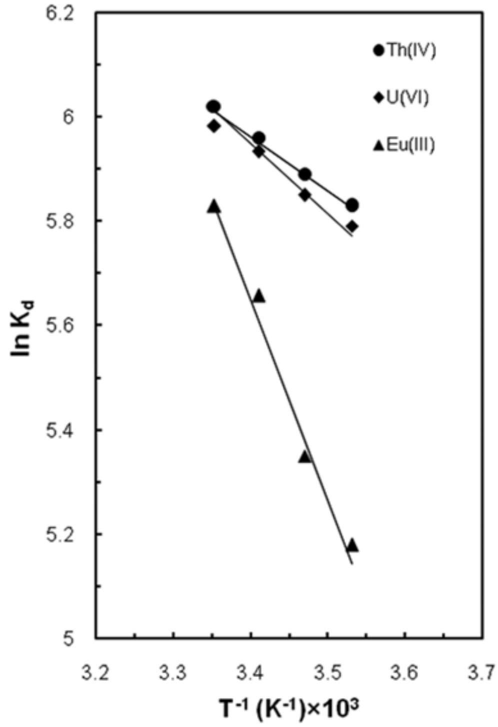

Fig. 9. Variation of ln K_d vs T^{-1} for the sorption of Th(IV), U(VI) and Eu(III) ions from aqueous medium onto modified silica nanoparticles (concentration 20 mg/*l* Th(IV), U(VI) and Eu (III); adsorbent amount 0.05 g; stirring time 30 min; pH= 5.5).

Table 4. Thermodynamic parameters for Th(IV), U(VI) and Eu(III) ions sorption on modified silica nanoparticles, at 298 K

Cation	ΔG^o (kJ/mol)	ΔH^o (kJ/mol)	$T\Delta S^o$ (kJ/mol·K)
Th(IV)	−14.89	8.65	23.54
U(VI)	−14.88	11.22	26.10
Eu(III)	−14.25	30.11	44.41

CONCLUSIONS

Modified silica nanoparticles with salicylaldimine are able to be used as efficient adsorbent for removal-separation of actinides and lanthanides from aqueous solutions. With respect to those unmodified nanoparticles, the modified ones particularly improve the uptake of europium ions. The experimental data was well described by considering the pseudo second-order kinetic model of the adsorption of Th(IV), U(VI0 and Eu(III) ions. Thermodynamic study of the processes reveals the adsorption of all studied ions is entropy driven with positive enthalpy changes.

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