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# Uranium (VI) Sorption Using Functionalized-Chitosan Magnetic Nano-Based Particles

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**Abstract.** Hybrid materials were synthesized by chemical grafting of different compounds (diethylenetriamine DETA, cysteine, alanine and serine) on chitosan/magnetite nanoparticles. The sorbents were characterized by XRD and vibrating sample magnetometry (VSM) before being tested for uranium sorption. The nanometric size of sorbent particles reduces the impact of diffusion resistance and uptake kinetics are quite fast. Sorption isotherms are modeled by the Langmuir equation. The sorption is spontaneous and exothermic. Uranium is desorbed using acidic thiourea and the sorbent can be recycled for at least 4/5 cycles.

## Introduction

Chitosan can sorb metal ions through different mechanisms including chelation and ion-exchange depending on the pH and metal ions [1]. The main limitation in sorption properties is due to the poor porosity of chitosan that requires (a) using small-size particles at the expense of problems for their recovery at the end of the sorption process in batch systems or hydrodynamic constraints (head loss, clogging of column) when used in fixed bed systems, or (b) designing specific conditionings of the biopolymer (gel beads, hollow fibers, foams) with increased costs. Recently chitosan has been used for coating magnetic nanoparticles: the thin layer limits the diffusion resistance and the magnetic core allows readily recovering the spent particles by a magnetic field [2]. Chitosan being soluble in acidic solutions this limits the use of the sorbent for metal binding in acidic solutions or for desorption with acidic solutions. Chitosan cross-linking (for reinforcing its chemical stability) may strongly impact sorption performance by limiting the availability of amine groups. It can be useful grafting new functional groups on chitosan to increase its density of sorption sites, improve its selectivity. In this study chitosan was coated on *in situ* synthesized magnetic nanoparticles, before being treated with epichlorhydrin and further grafted with DETA and different amino acids. The sorbents were characterized (XRD spectrometry and VSM) and tested for uranyl sorption.

## Materials and methods

**Sorbents** Hybrid magnetic chitosan magnetic nano-based particles were prepared by chemical co-precipitation of Fe(II) and Fe(III) ions by NaOH in the presence of chitosan followed by hydrothermal treatment [3]. Chitosan (4 g) was dissolved in 200 mL (20 %, w/w) acetic acid solutions; FeSO<sub>4</sub>·7H<sub>2</sub>O (6.62 g) and FeCl<sub>3</sub> (8.68 g) salts were dissolved into the biopolymer solution. The metal-biopolymer was then precipitated with 2 M NaOH at 40 °C under continuous stirring (final pH 10). The resulting suspension was heated for 1 h at 90 °C. After recovery by settling and magnetic separation the solid was mixed with a 0.01 M epichlorohydrin solution (0.067 M NaOH): the mass ratio was 1:1 between epichlorohydrin and magnetic-chitosan composite. The

suspension was reacted at 40-50 °C for 2 hours under continuous stirring. Then the cross-linked chitosan-magnetite composite was rinsed to remove unreacted products. The grafting of diethylenetriamine (DETA) or amino acids was performed in two steps: (a) grafting of spacer arms, and (b) immobilization of the compound. The product was refluxed for 4 h in a mixture of epichlorohydrin (15 mL) and ethanol/water (1:1, 150 mL). After magnetic separation and alternated water and ethanol washing, the hybrid chitosan-magnetite material cross-linked and grafted with spacer arms was mixed with diethylenetriamine (or amino acid) (12 mL in 200 mL ethanol/water 1:1 or 16 g of amino acid in dioxane) under agitation and heating at 75-80 °C for 18 h. Finally the product was rinsed with water and ethanol before being freeze-dried for 24 h.

**Sorption tests** Solutions were prepared by dilution of uranyl acetate stock solutions ( $1 \text{ g L}^{-1}$ ) with MilliQ water. Batch experiments were carried out by contact of 0.02 g of sorbent with 100 mL of aqueous solution ( $C_0$ :  $100 \text{ mg U L}^{-1}$ ) in a stopper conical flask. The samples were agitated (at 200 rpm) for 2 h at 298 K. The residual uranium concentration ( $C_{eq}$ ,  $\text{mg U L}^{-1}$ ) was analyzed by the Arsenazo III method, whilst the concentration of metal ions sorbed onto functionalized chitosan (sorption capacity,  $q_{eq}$ ,  $\text{mg U g}^{-1}$ ) was obtained by the mass balance equation. The process optimization requires investigating the influence of parameters such as: (a) pH, (b) uptake kinetics, (c) sorption isotherms, and (d) regeneration/recycling of the resins. Standard experimental conditions were set at  $T$ :  $25 \pm 1^\circ\text{C}$  and  $\text{pH}$ :  $3.61 \pm 0.01$ ; the contact time was fixed to 40 min. When relevant these parameters were varied. In addition, the recycling of the sorbents was tested by comparing the sorption capacity at different successive steps in a series of 5 sorption/desorption cycles: using the same procedure for sorption while for the desorption, the metal-loaded sorbent (after being washed with demineralized water) was mixed with 50 mL of a 0.5 M urea solution (acidified at pH close to 3) for 30 min at 25 °C. Metal concentration in the eluate was used for calculating the desorption yield (by mass balance) at each step.

## Results and discussion

Fig. 1 shows the characterization of DETA sorbent (similar trends with other sorbents). FTIR analysis (not shown, [3]) confirmed the progressive increase of the density of amine groups in the sorbent (and for cysteine derivative the appearance of sulfur groups): as a confirmation of the efficient grafting of functional groups on cross-linked chitosan/magnetic nanoparticles.

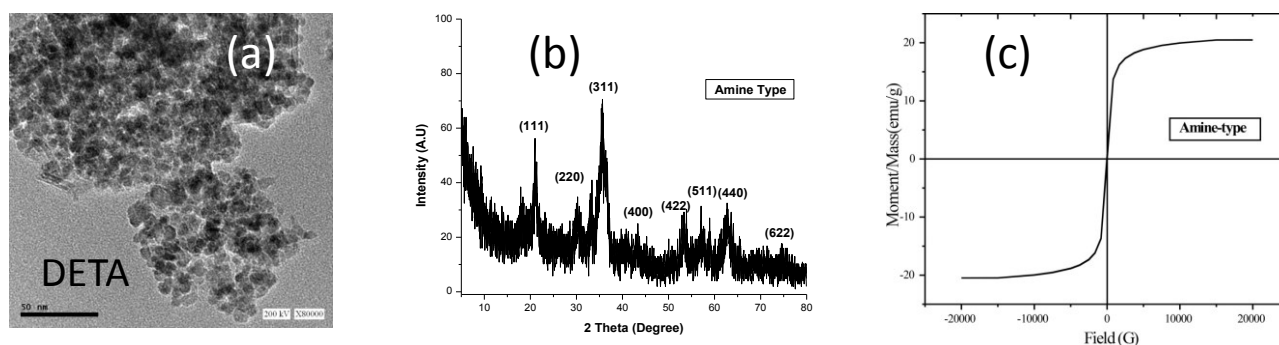


Figure 1. Characterization of DETA-chitosan magnetic nano-based particles: (a) TEM photograph, (b) XRD analysis, (c) VSM analysis (vibrating sample magnetometry) [3].

Table 1 reports the main characteristics of sorbent particles in terms of composition (reactive groups; i.e., amine and sulfur groups), magnetic properties, size of crystals and particles. XRD diffraction analysis (Fig. 1b for DETA derivative) confirmed the presence of iron oxide particles with a spinel structure, which is characteristic of magnetite (the peaks observed  $2\theta$ : 18.0, 30.1, 35.4, 43.0, 53.5, 57.0, 62.5 and 74.4 correspond to (111), (220), (311), (400), (422), (511), (440), and (622) diffraction planes). The Scherrer equation was used for calculating the size of crystals [4]. Nanoparticles of less than 14 nm were obtained; due to dipole-dipole attraction they tend to form

stable agglomerates of 15-40 nm, and superstructures of several hundred of nanometers (which can disperse under strong agitation) (Figure 1a for DETA derivative). VSM analysis showed that DETA and cysteine derivatives have a higher saturation magnetization (Cysteine > DETA >> Alanine > Serine) (Fig. 1c, for DETA derivative).

Table 1. Main characteristics of composite magnetic nano-based particles coated with chitosan and modified by grafting DETA, alanine, cysteine and serine.

Characteristics	DETA	Alanine	Cysteine	Serine
Saturation magnetization (emu g <sup>-1</sup> ) (Fig. 1c)	20.5	14.0	21.5	10.6
Crystal size (nm) (XRD analysis) (Fig. 1b)	6.5	13.0	13.5	11.6
"Agglomerate" size (nm) (TEM analysis) (Fig. 1a)	10-30	15-40	15-40	15-40
N (%)	4.8	3.5	3.1	3.3
S (%)	-	-	2.3	-

Sorption studies have shown that the optimum pH is close to 4 to reach high sorption capacities and prevent precipitation phenomena (associated to pH increase during sorption; equilibrium pH was systematically below 5.5) (Fig. 2a). Fig. 2 also reports some data obtained with alanine and serine derivatives of chitosan coated on magnetic nanoparticles; similar results were obtained with other systems and Table 2 summarizes the principal results. The sorption isotherms have been modeled using different equations (such as Langmuir, the Freundlich and Dubinin-Radushkevich equations [3]). Best results were obtained with the Langmuir equation (Eq. 1) that assumes an asymptotic trend as it was observed on experimental data (Fig. 2b). Sorbents can be ranked according to their maximum sorption capacities: DETA > Serine > Cysteine > Alanine. This may be due to the density of reactive groups but also to the affinity of additional functional groups according to Pearson's theory (Hard and Soft Acid Base theory) [5].

$$q = (q_m b C_{eq}) / (1 + b C_{eq}) \quad (\text{Eq. 1})$$

With  $q$  and  $q_m$  the sorption capacities at equilibrium with residual concentration  $C_{eq}$  (mg U L<sup>-1</sup>) and at saturation of the monolayer, respectively. The coefficient  $b$  (L mg<sup>-1</sup>) is the affinity coefficient.

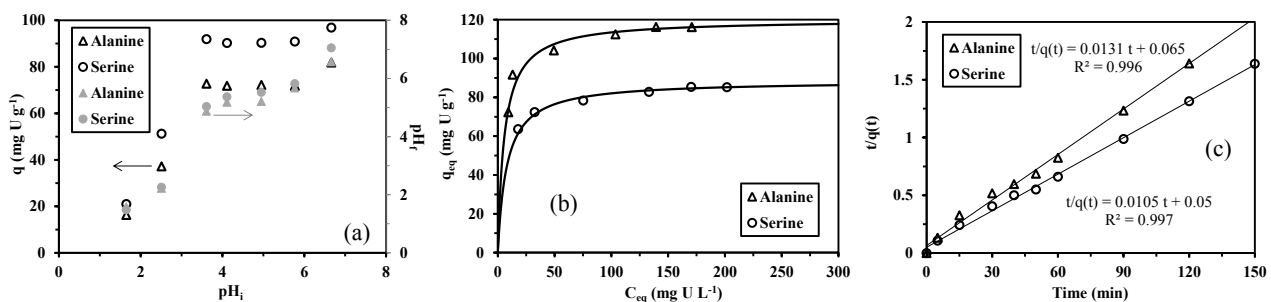


Figure 2. Uranium sorption using alanine and serine functionalized chitosan/magnetic nanobased particles: (a) pH effect on sorption and pH variation, (b) sorption isotherms (and Langmuir modeled curves as solid lines), and (c) modeling of uptake kinetics with PSORE.

Uptake kinetics may be controlled by different mechanisms including the proper reaction rate, the resistance to film diffusion, the resistance to intraparticle diffusion. Several models such as the pseudo-first order rate equation, the pseudo-second order rate equation (PSORE), the simplified model for resistance to intraparticle diffusion (the so-called Weber & Morris equation) have been tested, the best results were obtained with the PSORE (Eq. 2a, and Eq. 2b for its linearized form, Fig. 2c): the contribution of the resistance to diffusion was negligible due to the small size of sorbent particles and the equilibrium was systematically reached within 1 hour of contact.

$$q(t) = \frac{q_{eq}^2 k_2 t}{1 + k_2 q_{eq} t} \quad (\text{Eq. 2a})$$

$$\frac{t}{q(t)} = \frac{1}{k_2 q_{eq}^2} + \frac{1}{q_{eq}} t \quad (\text{Eq. 2b})$$

With  $q(t)$  and  $q_{eq}$  are the sorption capacities at time  $t$  and at equilibrium ( $\text{mg U g}^{-1}$ ), respectively,  $k_2$  is the pseudo-second order rate coefficient ( $\text{mg g}^{-1} \text{min}^{-1}$ ).

Table 2. Uranium sorption properties: sorption isotherms (Langmuir constants), thermodynamics parameters and uptake kinetics (pseudo-second order rate equation parameters, PSORE).

	DETA	Alanine	Cysteine	Serine
$q_m$ ( $\text{mg U g}^{-1}$ ) (Langmuir)	185.0	88.5	101.0	120.5
$b$ ( $\text{L mg}^{-1}$ ) (Langmuir)	0.093	0.127	0.132	0.17
$\Delta H^\circ$ ( $\text{kJ mol}^{-1}$ )	-12.45	-10.0	-11.85	-9.5
$\Delta S^\circ$ ( $\text{J mol}^{-1} \text{K}^{-1}$ )	62	64	59	70
$\Delta G^\circ$ ( $\text{kJ mol}^{-1}$ )	-30.8/-32.3	-29.0/-30.6	-29.5/-31.0	-32.9/-34.0
$K_2 \times 10^3$ ( $\text{mg g}^{-1} \text{min}^{-1}$ ) (PSORE)	3.66	1.94	3.11	2.19
$q_{eq}$ ( $\text{mg U g}^{-1}$ ) (PSORE)	161.3	77.5	82.6	95.2

The thermodynamics of the sorption process shows that uranium uptake was systematically exothermic (negative value of enthalpy change) and spontaneous (negative value of Gibbs energy) and that the randomness of the system increases after sorption (positive value of entropy change).

The sorption properties have been compared for a series of 5/6 cycles of sorption/desorption using acidified urea (pH close to 3): the sorption capacity progressively decreases along the successive steps; however, this decrease did not exceed 13-15 % at the sixth cycle. The metal can be easily recovered and the sorbent can be readily recycled for a minimum of 5 cycles.

## Conclusions

Magnetic nanoparticles coated with chitosan and chemically modified by grafting of DETA and amino-acids are very efficient for the recovery of uranyl ions from slightly acidic solutions: fast kinetics are obtained (equilibrium reached within 1 hour of contact) due to the reduction in diffusion resistance. Sorption reaction is spontaneous and exothermic, regardless of the sorbent. The maximum (experimental) sorption capacity ( $\text{mg U g}^{-1}$ ) for uranium decreases for the different substituents according: DETA (178) > Serine (116) > Cysteine (96) > Alanine (85). Uranium can be desorbed using acidified urea solutions and the sorbent can be recycled for a minimum of 4/5 cycles.

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