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Uranium and neodymium biosorption using novel chelating polysaccharide

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A B S T R A C T

A direct reaction is described to prepare hydrophobic α -aminomethylphosphonic acid as a novel chitosan-based material. It exhibits chelating properties for polyvalent metal ions such as U(VI) and Nd(III) ions. The new sorbent was fully characterized using Elemental analysis, scanning electron microscope (SEM) and FTIR spectra. Different parameters were examined in order to evaluate the optimum conditions for U(VI) and Nd(III) ions biosorption. Sorption mechanisms of metal ions were investigated using kinetic and isotherm models. In addition, the sorbent selectivity was tested for both metal ions together in a binary solution.

Keywords:

Uranium
Biosorption
Chitosan

1. Introduction

Uranium is very essential element because of its strategic importance in the energy field [1]. Also, it is considered as a long-term potential environmental hazard as a result of its long half-life [2,3]. Because of its high radiological and biological toxicity, it is necessary reducing its discharge into the environment due to activities of nuclear industry [4,5].

Rare earth elements (REEs) are widely used in High-technology and nuclear power industries [6–8]. The trivalent state is the most thermodynamically stable form of these elements in aqueous solutions [9]. Their physical and chemical properties are very close because of their close electronic configurations. The slight differences among lanthanide elements are so weak where the separation requires numerous steps [10]. Nd(III) was selected as a representative of trivalent lanthanide family. Because an ever-increasing demand for REEs in the international markets and limited resources for their production, the recovery of these metals from non-conventional resources is a strategic target.

Many conventional metal ions removal processes such as precipitation or solvent extraction processes face economical or technical limitations for the treatment of contaminated solutions. Adsorption process using mineral, ion-exchange or chelating resins

may be more appropriate [11–13]. Recently, biosorbents as cheap materials have been employed as an alternative to conventional synthetic resins for the recovery of metal ions from contaminated solutions [14–16].

Chitosan is a promising polysaccharide resource due to its specific structure and properties [17]. Attention has been focused on chitosan and its derivatives because they are abundant biopolymers, renewable and biodegradable. Chitosan can be chemically modified using cross-linker to have better microbiological and chemical resistance [18].

Chelating resins with electron donor atoms are interesting materials for binding metal ions. Chitosan in base material form does not have significant affinity for Ln(III). The chemical grafting of chitosan was employed to increase the kind of sorption sites in order to increase sorption capacity and selectivity for target metals [19]. Chitosan is quite easily modified by chemical grafting where its backbone is associated to amine and hydroxyl groups.

A previous work has declared that the incorporation of methylene phosphonic groups into chitosan allowed solubility in water under neutral conditions [20]. To overcome this problem, a direct reaction was employed for fully substitution of hydrogen atoms of amino groups on chitosan by methylene phosphonic groups under drastic conditions. Abundant of methylene groups increases the hydrophobic property of modified chitosan and leads to its insolubility under a wide pH range. This resin was applied as a novel sorbent for uranyl and neodymium ions removal using batch

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processes. Kinetic and isotherm studies were investigated to understand the adsorption behavior of metal ions on the sorbent.

2. Experimental

2.1. Materials and methodology

A quantity of 5 g of crystalline phosphorous acid (Fluka) was dissolved in 100 ml of water and 100 ml of concentrated HCl (30%). After addition of 4 g of chitosan (M.Wt 138,000 g/mol, 94% deacetylation degree, Mahtani chitosan-India), the mixture was heated to reflux in 250 ml four-necked flask was fitted with thermometer, mechanical stirrer, condenser, and dropping funnel.

25 ml of aqueous formaldehyde solution (37%, Fluka) was added dropwise for 1 h and the reaction mixture was kept at reflux temperature for 20 additional hours. The mixture was neutralized using 100 ml of NaOH (10 M) and then precipitation of a brown product was obtained. The modified chitosan was filtrated and subjected to a series of intensive washing with water and dried at 30 °C then crushed and sieved to obtain a particle size of 500 μm.

2.2. Characterization of sorbent

Thermo Finnigan Elemental Analytical Instrument (Italy) was used to determine the chemical composition of resin represented by the percentages of C, H, N and S. FTIR spectra were carried out using a PerkinElmer BX series with a frequency range of 4000–400 cm⁻¹ after the samples were incorporated in KBr pellets. SEM/EDX analysis was performed on an environmental SEM (FEI Quanta 200 FEG) equipped with X-ray microanalyzer (OXFORD INCA ENERGY 350) to visualize surface morphology of sorbent and detect the elements and their semi-quantitative analysis.

2.3. Procedures

Adsorption behavior of metal ions on the sorbent was studied using batch experiments under different parameters. The resultant data is necessary for understanding the mechanisms of sorption and plays a fundamental role in assessing the suitability of sorbent for metal ions removal processes.

Batch experiments were performed by contact of 0.02 g sorbent with 25 ml of 55 mg L⁻¹ U(VI) or 57 mg L⁻¹ Nd(III) ions solution in a polypropylene centrifuge tube at 20 °C and agitation 150 rpm.

After equilibration and aqueous phase separation, the residual metal ions concentration in the aqueous phase was estimated by ICP-AES, while the concentration of adsorbed metal ions on the modified chitosan was estimated using the mass balance equation:

$$q = (C_i - C_e)V/W \quad (1)$$

where q (mg g⁻¹) is the amount of the adsorbed metal ions on the sorbent; C_i (mg L⁻¹) and C_e (mg L⁻¹) are the initial metal ion concentration and the residual metal ion concentration in the aqueous phase, respectively, V (L) is the volume of metal ions solution and W (g) is the weight of sorbent dosage.

3. Results and discussion

3.1. Preparation of the grafted biosorbent

The reaction of an amine, formaldehyde and phosphorous acid proceeds according to the following equation:

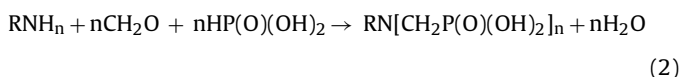


Table 1
Elemental analysis of chitosan and its derivative.

Sample	%C	%H	%N	C/N ^a	H/N ^a
Chitosan	40.17	7.19	8.9	5.27	11.31
Chitosan derivative	26.5	4.7	3.9	7.93	16.87

^a Molar ratio.

The acidic hydrogen in phosphorous acid has been found to undergo the mannich type reaction. The reaction with phosphorous acid requires a strong acidic medium and as a matter of fact, does not proceed in neutral or basic solution [21]. No special efforts have been made to separate the resulting aminomethylphosphonic acid from the reaction mixture. The grafted chitosan is soluble in concentrated hydrochloric acid but it is rather poorly soluble in water and to a great extent precipitate from the reaction mixture during the neutralization.

Chitosan has been employed successfully in the reaction of Eq. (2). The resulting chitosan derivative probably exists as zwitterion with three protons, a strongly dissociated proton and two weak ones, with the fourth available proton being coordinated to the central nitrogen atom [21].

3.2. Characterization of sorbent

Fig. 1 illustrates SEM photographs of the materials under study (magnification: ×100). The micrograph of chitosan shows irregular flakes morphology (Fig. 1a) while the grafted chitosan displays a rough surface contains small pores and interconnected macro-pores (Fig. 1b). The detection of elements and their semi-quantitative analysis were performed using SEM-EDX. The significant difference was represented in the presence of phosphorous element peak at 2 keV indicating the sharing of phosphorous acid in the chemical modification of chitosan.

More analyses were carried out to confirm the new structure such as elemental analysis and FTIR. The increasing of substitution degree into amine groups of chitosan was estimated by comparing the molar ratio of carbon or hydrogen and nitrogen between chitosan and the grafted chitosan using elemental analysis data from Table 1. The increase of molar ratio after modification indicates the increase of carbon and hydrogen in chitosan chain with taking into consideration the constancy of nitrogen percentage in chitosan and chitosan derivative.

On the other hand, the chemical modification of the chitosan was proved using FTIR spectra. From Fig. 2, the new structure displays some peaks are similar to the chitosan peaks but are different in terms of intensity. The band at 3428 cm⁻¹ due to contributions of stretching vibration of O–H group and stretching vibration of N–H group. The characteristic peak of C–H group appeared at 2933 cm⁻¹. The change of the peaks intensity can be attributed to the replacement of hydrogen atoms in amine groups with methylene phosphonic acid groups. A new band appeared at 1210 cm⁻¹ and represents a characteristic peak of P=O group. Fig. 3 shows the proposed structure of the new sorbent after chemical modification of chitosan using phosphorous acid and formaldehyde in a high acidic medium.

3.3. Adsorption study

3.3.1. Effect of pH and ionic strength

The pH of the contaminated solution may affect the charge of sorbent surface or the dissociation degree of functional groups such as hydroxyl, carboxyl and amino groups present on the sorbent surface [22]. It can also affect the aqueous chemistry of metal ions and their competition for binding with active sites on the sorbent surface.

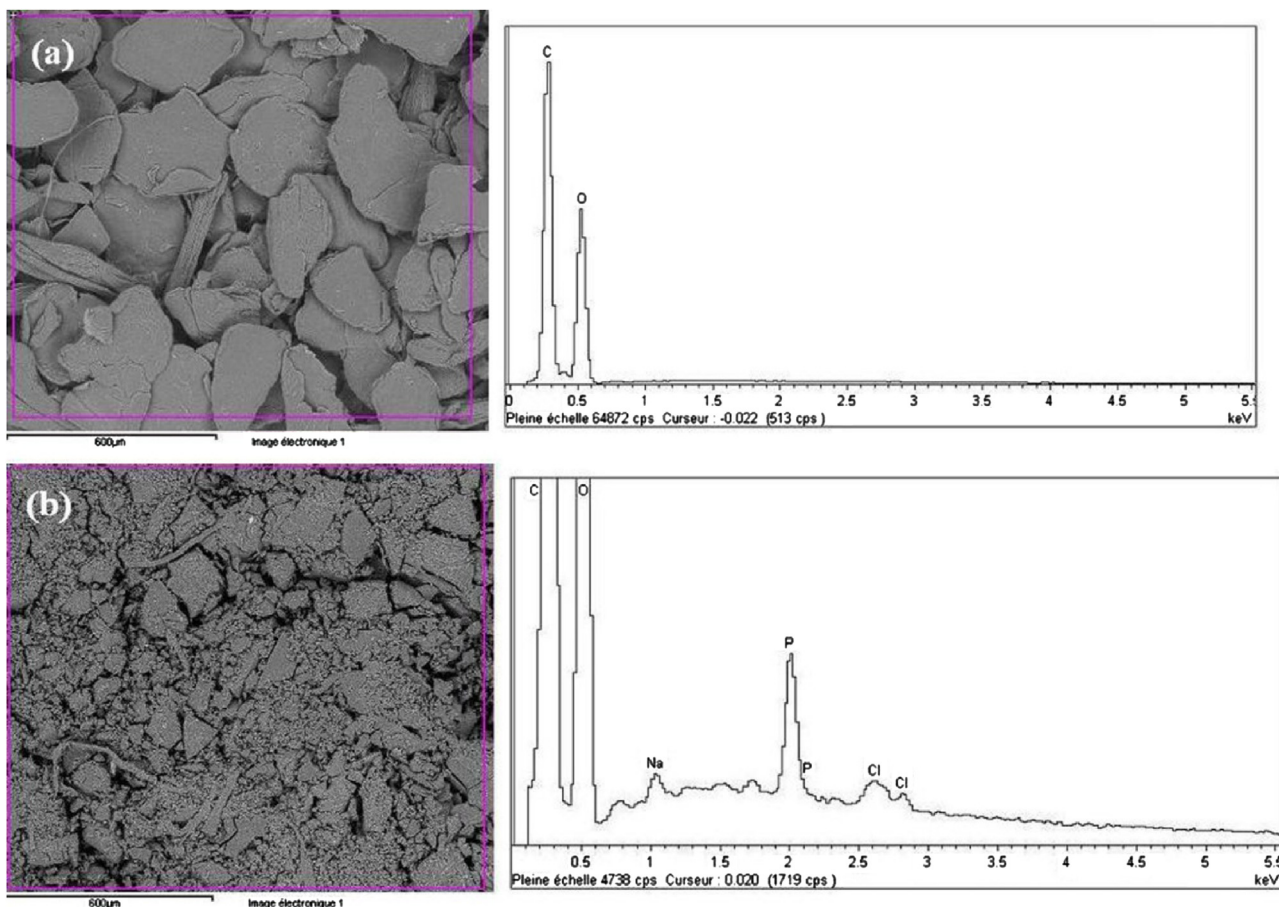


Fig. 1. SEM-EDX of (a) Chitosan and (b) Chitosan derivative (scale bar: 600 μm).

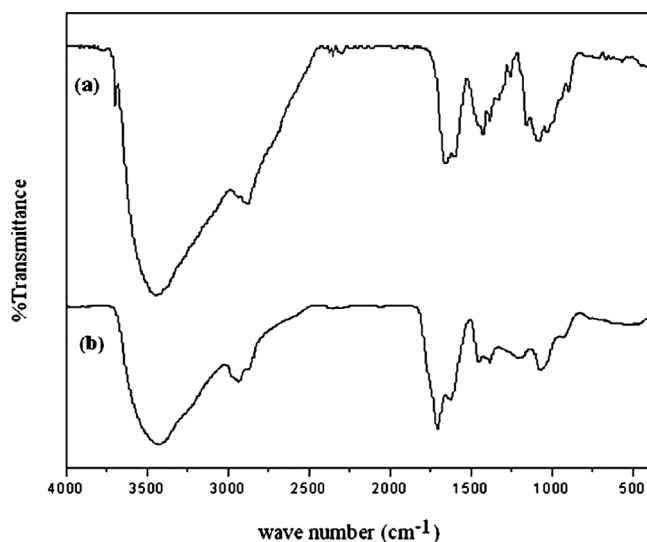


Fig. 2. FTIR spectra of (a) Chitosan and (b) Chitosan derivative.

The metal ions removal from aqueous solutions was studied under non-competitive conditions at different pH as shown in Fig. 4. The uranyl hydrolysis begins before pH 4 and other hydrolytic species are formed [23]. On the other hand, neodymium ions precipitate as neodymium hydroxide above pH 6.

Because of the donor effect of aminophosphonic acid group $-\text{N}(\text{CH}_2\text{PO}_3^{2-})_2$, the sorbent has the tendency to form chelates in a ring structure with the possibility of different conformations

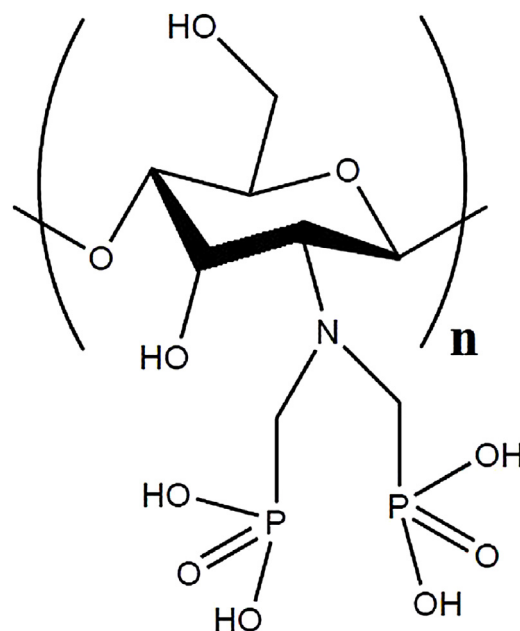


Fig. 3. The proposed structure of Chitosan derivative.

owing to the metal ion nature [24]. The sorption capacities of the grafted biosorbent increase significantly with increasing the initial pH range from 1 to 4.5 and 6 for uranyl and neodymium ions, respectively. The decreasing of final pH for both metal ions confirms the releasing of hydrogen ions during metal ions removal. The low

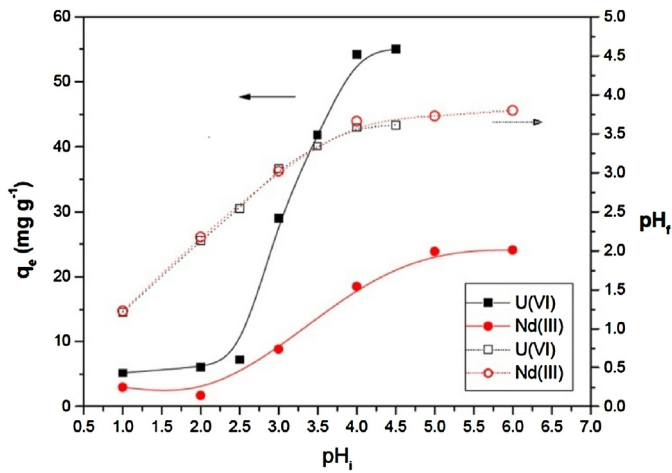


Fig. 4. Effect of pH on U(VI) and Nd(III) ions uptake using Chitosan derivative where $V/W = 1.25 \text{ L g}^{-1}$ and $C_i = 55 \text{ mg U L}^{-1}$ & 57 mg Nd L^{-1} at 20°C .

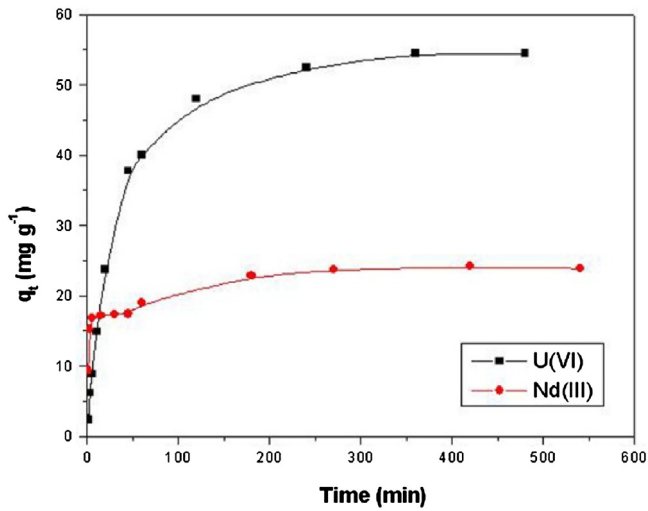


Fig. 5. Uptake kinetics of U(VI) at pH 4 and Nd(III) at pH 5 using Chitosan derivative where $V/W = 1.25 \text{ L g}^{-1}$ and $C_i = 55 \text{ mg U L}^{-1}$ & 57 mg Nd L^{-1} at 20°C .

adsorbed amounts for both metal ions at acidic media because the compensation of the negative charges on the sorbent by protons that suppress the biosorption process [25,26].

Batch experiments for both metal ions were conducted by adjusting ionic strength from 0.01 to 0.1 mol L^{-1} by addition of NaCl. It was found that ionic strength has no effect on the biosorption processes.

3.3.2. Kinetic study

Fig. 5 shows the kinetic profiles of U(VI) and Nd(III) ions sorption on the modified biosorbent in terms of adsorbed amount. Kinetic uptake was carried out under experimental conditions are comprised from optimum pH, an initial concentration of metal ions in the contaminated solution, 0.02 g of sorbent and agitation speed, 150 rpm at 20°C . For U(VI) ions, The initial pH and concentration were set to 4 and 55 mg L^{-1} , respectively. While pH of 57 mg L^{-1} Nd(III) ions solution was adjusted to 5.

The kinetic removal for both metal ions was initially rapid due to the greater concentration gradient and more available sites for adsorption. A slower removal stage comes after and gradually approaches equilibrium. U(VI) ions reached equilibrium in 6 h, while the kinetic profile of Nd(III) ions was slower and the equilibrium time was 7 h. Over 82 and 70% of total adsorption of uranyl

and neodymium ions occurred within the first 45 and 6 min, respectively.

Successive steps have been proposed in adsorption process such as bulk diffusion, film diffusion, intraparticle diffusion and adsorption uptake. The experimental data have been modeled using some conventional kinetic models in non-linear form to elucidate either the diffusion or adsorption is the rate limiting step.

Pseudo-first order rate equation (PFORE) [27]:

$$q_t = q_e [1 - \exp(-k_1 t)] \quad (3)$$

where q_e and q_t (mg g^{-1}) are the retention capacities at equilibrium and time t , respectively, and k_1 is the Pseudo-first order rate constant (min^{-1}).

Pseudo-second order rate equation (PSORE) [28]:

$$q_t = k_2 q_e^2 t / (1 + q_e k_2 t) \quad (4)$$

where k_2 is the Pseudo-second order rate constant ($\text{g mg}^{-1} \text{ min}^{-1}$).

The chemical adsorption processes between metal ions and active sites were described using Elovich model as follow [29]:

$$q_t = \ln(abt)/b \quad (5)$$

where b is constant related to the extent of surface coverage by metal ions and activation energy for chemisorption process (g mg^{-1}) and a is the initial adsorption rate ($\text{mg g}^{-1} \text{ min}^{-1}$).

The analysis of diffusion mechanisms was performed using Crank equation. It can be used for roughly evaluating the intraparticle diffusion coefficient, D_e [30]:

$$\frac{q_e}{q_\infty} = 1 - \sum_{n=1}^{\infty} 6\alpha(\alpha + 1) \exp(-D_e q_n^2 t / r^2) / 9 + 9\alpha + q_n^2 \alpha^2 \quad (6a)$$

where r is the radius of the particle, while q_n and α are the non-zero roots and the ratio of the volumes of solution and particles from the following equations:

$$\tan q_n = 3q_n / (3 + \alpha q_n^2) \quad (6b)$$

$$q_\infty / VC_i = 1 / (1 + \alpha) \quad (6c)$$

Uranyl ions reach the equilibrium faster than neodymium ions although the intraparticle diffusion coefficient value of neodymium ions, ($7.77 \times 10^{-11} \text{ m}^2 \text{ min}^{-1}$) is about two orders of magnitude larger than uranyl ions, ($6.44 \times 10^{-13} \text{ m}^2 \text{ min}^{-1}$). Therefore, the diffusion of metal ions does not control the rate limiting step.

All constants of the sorption kinetic models are estimated including rate constants and equilibrium adsorbed amounts of metal ions on the sorbent surface and listed in Table 2. It shows that the data are better simulated by PSORE in terms of a higher correlation coefficient value (R_{adj}^2) and an equilibrium adsorbed amount.

3.3.3. Sorption isotherm and thermodynamic study

Fig. 6 shows the adsorbed amount of metal ions on the sorbent increases with increasing the residual metal ions concentration till the maximum capacity of the sorbent is reached. To obtain isotherm data for U(VI) or Nd(III) removal, batch experiments were performed by equilibrating 0.02 g of the sorbent and 25 ml of different initial metal ions concentrations at optimum pH and 20°C . The experimental data were tested using various isotherm models to determine the binding nature between metal ions and the sorbent surface [31]. The constants were evaluated by non-linear regression method and reported in Table 3.

Freundlich model:

$$q_e = K_F C_e^{1/n} \quad (7)$$

where K_F and n are constants related to the adsorption capacity and the intensity of adsorption, respectively.

Table 2
Kinetics parameters for U(VI) and Nd(III) ions sorption.

Metal	q_{exp} ($mg\ g^{-1}$)	PFORE			PSORE			Elovich equation		
		q_e ($mg\ g^{-1}$)	k_1 (min^{-1})	R^2_{adj}	q_e ($mg\ g^{-1}$)	k_2 ($g\ mg^{-1}\ min^{-1}$)	R^2_{adj}	a ($mg\ g^{-1}\ min^{-1}$)	b ($g\ mg^{-1}$)	R^2_{adj}
U(VI)	54.52	51.92 ± 1.23	0.0289 ± 0.002	0.99	58.96 ± 0.59	0.00061 ± 0.00003	0.9989	7.08 ± 1.16	0.099 ± 0.006	0.9659
Nd(III)	24.17079	20.06 ± 1.07	0.4973 ± 0.16	0.5834	21.01 ± 1.01	0.035 ± 0.013	0.71	421.29 ± 30.43	0.473 ± 0.055	0.6506

Table 3
Isotherm constants for U(VI) and Nd(III) ions sorption.

Metal	q_{exp} ($mg\ g^{-1}$)	Ferundlich equation			Langmuir equation			(D-R) equation		
		$1/n$	K_F	R^2_{adj}	q_{max} ($mg\ g^{-1}$)	K_L ($L\ mg^{-1}$)	R^2_{adj}	q_{max} ($mg\ g^{-1}$)	E_{DR} ($kJ\ mol^{-1}$)	R^2_{adj}
U(VI)	114.12	0.29 ± 0.03	25.61 ± 3.67	0.966	115.37 ± 5.05	0.09 ± 0.02	0.9678	276.13 ± 19.39	13.37 ± 0.43	0.9498
Nd(III)	30.32	0.33 ± 0.05	5.5 ± 1.29	0.9216	32.59 ± 0.25	0.054 ± 0.002	0.9991	73.62 ± 9.26	12.16 ± 0.73	0.9539

Table 4
Comparison of sorption capacities of different sorbents for U(VI) and Nd(III) ions.

Sorbent	Metal	pH	Adsorption capacity ($mg\ g^{-1}$)	Reference
Magnetite nanoparticles	U(VI)	7	5	[33]
Magnetic chitosan	U(VI)	5	42	[34]
Cross-linked chitosan with epichlorohydrin	U(VI)	3	70	[35]
Ethylenediamine-modified magnetic chitosan	U(VI)	2–7	82.83	[18]
Magnetic Schiff base	U(VI)	6	94.3	[36]
Amberlite IRA-910 resin	U(VI)	1	64.26	[37]
This work	U(VI)	4	114.12	
Mordenite containing tuff	Nd(III)	3	11.77	[38]
Yeast cells	Nd(III)	1.5	10–12	[39]
microorganisms	Nd(III)	1.5	6–25	[40]
This work	Nd(III)	5	30.32	

Langmuir model:

$$q_e = q_{max} K_L C_e / [1 + K_L C_e] \quad (8)$$

where K_L is Langmuir adsorption constant ($L\ mg^{-1}$).

Dubinin–Radushkevich (D–R) model:

$$q_e = q_{max} \exp(-K_{DR} \varepsilon^2) \quad (9a)$$

ε ($J\ mol^{-1}$) is the Polanyi potential:

$$\varepsilon = RT \ln(1 + (1/C_e)) \quad (9b)$$

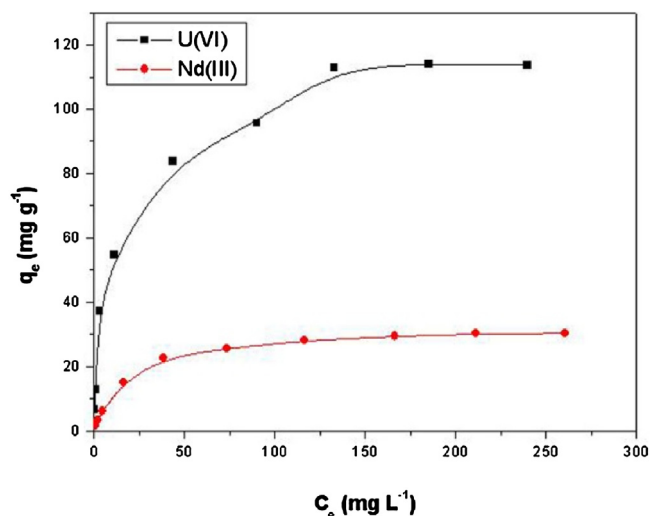


Fig. 6. Sorption isotherms of U(VI) at pH 4 and Nd(III) at pH 5 using Chitosan derivative where $V/W = 1.25\ L\ g^{-1}$ at $20\ ^\circ C$.

The mean-free sorption energy per molecule of adsorbate, E_{DR} ($kJ\ mol^{-1}$) is related to K_{DR} ($mol^2\ J^{-2}$) and can be calculated from the following equation:

$$E_{DR} = 1/(2K_{DR})^{0.5} \quad (10)$$

E_{DR} gives information about the nature of sorption process of metal ions on the surface of sorbent. E_{DR} for uranyl and neodymium ions is 13.37 ± 0.43 and $12.16 \pm 0.73\ kJ\ mol^{-1}$, respectively; this indicates that interaction between both metal ions and active sites comes through a chemisorption mechanism [32].

According to the obtained results, sorption isotherm data are more fitting with Langmuir model compared with the other models. Table 4 shows that the experimental maximum capacities of the sorbent for both metal ions could be competitive when compared to some other previously prepared sorbents.

Thermodynamic behavior of the sorption processes for metal ions was evaluated using batch experiments under the same conditions in the range of temperatures from 20 to $50\ ^\circ C$. It was found that there is no significant variation in the sorption capacities of the new sorbent for both metal ions.

3.4. Sorbent selectivity

The uptake of metal ions was performed under non-competitive conditions to obtain the optimum parameters for removal processes. The sorbent selectivity was tested for both U(VI) and Nd(III) ions together in a binary solution at pH 4. The initial concentrations of U(VI) and Nd(III) ions were $0.47\ mmol\ L^{-1}$ and $0.64\ mmol\ L^{-1}$, respectively. After the equilibrium was reached, the residual concentration of Nd(III) ions about $0.59\ mmol\ L^{-1}$ was higher than U(VI) ions, $0.21\ mmol\ L^{-1}$. This indicates that the sorbent has a high affinity toward U(VI) ions and the higher initial concentration of

Nd(III) ions confirms it. It could be explained that the 4f orbital of neodymium is effectively shielded from the strong interaction with ligand orbitals by electrons in the 5S and 5P orbitals [41].

4. Conclusion

A direct reaction was employed for the optimization of the sorption performance of chitosan. A novel chitosan-based material exhibits a good affinity for binding uranium and neodymium ions from aqueous solutions. It is attributed to the chelating effect of aminomethylphosphonic acid group owing to the donor effect of nitrogen atom and electrostatic attraction of phosphonate group. For all studied systems, the kinetic and isotherm sorption data follow pseudo-second order rate equation and Langmuir equation, respectively.

The maximum sorption capacities were 114.12 and 30.32 mg g⁻¹ for U(VI) and Nd(IV) ions, respectively. The temperature has no a significant effect on the variation in sorption capacities of the sorbent for both metal ions. Selectivity study indicates that the chitosan-based material has high affinity to stabilize uranyl ions over Nd(III) in a binary solution.

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References

- [1] A. Kumar, R.K. Singhal, S. Rout, U. Narayanan, R. Karpe, P.M. Ravi, Adsorption and kinetic behavior of uranium and thorium in seawater-sediment system, *J. Radioanal. Nucl. Chem.* 295 (2013) 649–656.
- [2] K.Z. Elwakeel, A.A. Atia, E. Guibal, Fast removal of uranium from aqueous solutions using tetraethylenepentamine modified magnetic chitosan resin, *Bioresour. Technol.* 160 (2014) 107–114.
- [3] X. Zhang, C. Ding, H. Liu, L. Liu, C. Zhao, Protective effects of ion-imprinted Chitooligosaccharides as uranium-specific chelating agents against the cytotoxicity of depleted uranium in human kidney cells, *Toxicology* 286 (2011) 75–84.
- [4] G. Meinrath, Aquatic chemistry of uranium, *Geoscience* 1 (1998) 1–101.
- [5] T.P. Rao, P. Metilda, J.M. Gladis, Preconcentration techniques for uranium(VI) and thorium(IV) prior to analytical determination—an overview, *Talanta* 68 (2006) 1047–1064.
- [6] A.A. Galhoum, M.G. Mahfouz, S.T. Abdel-Rehem, N.A. Gomaa, A.A. Atia, T. Vincent, E. Guibal, Diethylenetriamine-functionalized chitosan magnetic nanobased particles for the sorption of rare earth metal ions [Nd(III), Dy(III) and Yb(III)], *Cellulose* 22 (4) (2015) 2589–2605.
- [7] T. Xu, H. Peng, Formation cause, composition analysis and comprehensive utilization of rare earth solid wastes, *J. Rare Earth* 27 (2009) 1096–1102.
- [8] J. Zhou, W. Duan, X. Zhou, C. Zhang, Application of annular centrifugal contactors in the extraction flowsheet for producing high purity yttrium, *Hydrometallurgy* 85 (2007) 154–162.
- [9] V. Diniz, B. Volesky, Biosorption of La, Eu and Yb using sargassum biomass, *Water Res.* 39 (2005) 239–247.
- [10] T.S. Martins, P.C. Isolani, Rare earths: industrial and biological applications, *Quím. Nova* 28 (2005) 111–117.
- [11] A.M. Donia, A.A. Atia, A.M. Daher, O.A. Desouky, E.A. Elshehy, Synthesis of amine/thiol magnetic resin and study of its interaction with Zr(IV) and Hf(IV) ions in their aqueous solutions, *J. Dispers. Sci. Technol.* 32 (2011) 634–641.
- [12] J. Roosen, K. Binnemans, Adsorption and chromatographic separation of rare earths with EDTA- and DTPA-functionalized chitosan biopolymers, *J. Mater. Chem. A* 2 (2014) 1530–1540.
- [13] H. Wang, L. Ma, K. Cao, J. Geng, J. Liu, Q. Song, X. Yang, S. Li, Selective solid phase extraction of uranium by salicylideneimine-functionalized hydrothermal carbon, *J. Hazard. Mater.* 229 (2012) 321–330.
- [14] E. Guibal, C. Roulph, P. Le Cloirec, Uranium biosorption by a filamentous fungus *Mucor miehei*: pH effect on mechanisms and performances of uptake, *Water Res.* 26 (1992) 1139–1145.
- [15] G. Haferburg, D. Merten, G. Büchel, E. Kothe, Biosorption of metal and salt tolerant microbial isolates from a former uranium mining area. Their impact on changes in rare earth element patterns in acid mine drainage, *J. Basic Microb.* 47 (2007) 474–484.
- [16] G. Naja, C. Mustin, B. Volesky, J. Berthelin, Biosorption study in a mining wastewater reservoir, *Int. J. Environ. Pollut.* 34 (2008) 14–27.
- [17] S.K. Shukla, A.K. Mishra, O.A. Arotiba, B.B. Mamba, Chitosan-based nanomaterials: a state-of-the-art review, *Int. J. Biol. Macromol.* 59 (2013) 46–58.
- [18] J.S. Wang, R.T. Peng, J.H. Yang, Y.C. Liu, X.J. Hu, Preparation of ethylenediamine-modified magnetic chitosan complex for adsorption of uranyl ions, *Carbohydr. Polym.* 84 (2011) 1169–1175.
- [19] R. Jayakumar, M. Prabakaran, R.L. Reis, J.F. Mano, Graft copolymerized chitosan—present status and applications, *Carbohydr. Polym.* 62 (2005) 142–158.
- [20] V.M. Ramos, N.M. Rodriguez, M.F. Diaz, M.S. Rodriguez, A. Heras, E. Agullo, N-Methylene phosphonic chitosan—effect of preparation methods on its properties, *Carbohydr. Polym.* 52 (2003) 39–46.
- [21] K. Moedritzer, R.R. Irani, The direct synthesis of α -aminomethylphosphonic acids—Mannich type reactions with orthophosphorous acid, *J. Org. Chem.* 31 (1966) 1603–1607.
- [22] G. Crini, H.N. Peindy, F. Gimbert, C. Robert, Removal of C.I. Basic Green 4 (Malachite Green) from aqueous solutions by adsorption using cyclodextrin-based adsorbent: kinetic and equilibrium studies, *Sep. Purif. Technol.* 53 (2007) 97–110.
- [23] S. Berto, F. Crea, P.G. Daniele, A. Gianguzza, A. Pettignano, S. Sammartano, Advances in the investigation of dioxouranium(VI) complexes of interest for natural fluids, *Coord. Chem. Rev.* 256 (2012) 63–81.
- [24] H.S. Hendrickson, Comparison of the metal binding of nitrilotri(methylenephosphonic)acid and nitrilotriacetic acid: calcium (II), Ni(II), iron (III) and thorium (IV) complexes, *Anal. Chem.* 39 (1967) 998–1000.
- [25] V.A. Drits, E. Silvester, A.I. Gorshkov, A. Manceau, Structure of synthetic monoclinic Na-rich birnessite and hexagonal birnessite: I—results from X-ray diffraction and selected-area electron diffraction, *Am. Mineral.* 82 (1997) 946–961.
- [26] C.L. Peacock, D.M. Sherman, Sorption of Ni by birnessite: equilibrium controls on Ni in seawater, *Chem. Geol.* 238 (2007) 94–106.
- [27] S. Lagergren, About the theory of so-called adsorption of soluble substances, *Vetenskapsakademiens Handlingar* 24 (1898) 1–39.
- [28] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, *Process Biochem.* 34 (1999) 451–465.
- [29] K.Z. Elwakeel, M.A. Abd El-Ghaffar, S.M. El-Kousy, H.G. El-Shorbagy, Synthesis of new ammonium chitosan derivatives and their application for dye removal from aqueous media, *Chem. Eng. J.* 203 (2012) 458–468.
- [30] J. Crank, *The Mathematics of Diffusion*, 2nd ed., Oxford University Press, London, 1975.
- [31] K.Y. Foo, B.H. Hameed, Insights into the modeling of adsorption isotherm systems, *Chem. Eng. J.* 156 (2010) 2–10.
- [32] A.R. Elsalamouny, O.A. Desouky, S.A. Mohamed, A.A. Galhoum, Evaluation of adsorption behavior for U(VI) and Th(IV) ions onto solidified Mannich type material, *J. Dispers. Sci. Technol.* 38 (2017) 860–865.
- [33] D. Das, M.K. Sureshkumar, S. Koley, N. Mithal, C.G.S. Pillai, Sorption of uranium on magnetite nanoparticles, *J. Radioanal. Nucl. Chem.* 285 (2010) 447–454.
- [34] L.C.B. Stopa, M. Yamaura, Uranium removal by chitosan impregnated with magnetite nanoparticles: adsorption and desorption, *Int. J. Nucl. Energy Sci. Technol.* 5 (2010) 283–289.
- [35] G. Wang, J. Liua, X. Wang, Z. Xiea, N. Dengb, Adsorption of uranium (VI) from aqueous solution onto cross-linked chitosan, *J. Hazard. Mater.* 168 (2009) 1053–1058.
- [36] X. Zhang, C. Jiao, J. Wang, Q. Liu, R. Li, P. Yang, M. Zhang, Removal of uranium(VI) from aqueous solutions by magnetic Schiff base: kinetic and thermodynamic investigation, *Chem. Eng. J.* 198 (2012) 412–419.
- [37] A. Rahmati, A. Ghaemi, M. Samadfam, Kinetic and thermodynamic studies of uranium(VI) adsorption using Amberlite IRA-910 resin, *Ann. Nucl. Energy* 39 (2012) 42–48.
- [38] N.M. Kozhevnikova, N.L. Tsybikova, Sorption of neodymium(III) ions by natural mordenite-containing tuff, *Russ. J. Appl. Chem.* 81 (2008) 42–45.
- [39] A. Vlachou, B.D. Symeopoulos, A.A. Koutinas, A comparative study of neodymium sorption by yeast cells, *Radiochim. Acta* 97 (2009) 437–441.
- [40] M. Palmieri, O. Garcia Jr., P. Melnikov, Neodymium biosorption from acidic solutions in batch system, *Process Biochem.* 36 (2000) 441–444.
- [41] R.K. Tak, B.D. Gupta, P.D. Sobhash, A. Sharma, S.P. Mathur, Some rare earth chelates on N-thioacetyl-N-phenylhydroxylamine, *Asian J. Chem.* 2 (1990) 132–135.