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Application of a Low-Cost Material for Uranium Removal: Experimental Variables and Study of Concomitants

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Abstract

In the present work, the extent in which the presence of concomitant ions affects the removal capacity of uranyl ion by the natural mineral perlite was studied. By using synthetic solutions of uranyl nitrate in batch systems, the variables affecting the process, namely sorbent dose, contact time, pH and initial UO_2^{2+} concentration, were firstly investigated. The zeta potential and the sorption capacity of perlite, as well as relevant kinetics and thermodynamic parameters were measured.

Removals up to 90 % were achieved for a dose of 45 g of Pava L^{-1} and a concentration of U of 100 μg U L^{-1}, of 74 % when the concentration was 1 mg U L^{-1}, 60 % for 10 mg U L^{-1} and 25 % for a concentration of 50 mg U L^{-1}. The best linear correlations in the adsorption isotherms were achieved by applying the Langmuir and Dubinin-Radushkevich models with adsorption energy of 8.72 kJ mol^{-1}. The thermodynamic variables indicated the feasible, spontaneous and exothermic nature of the sorption of UO_2^{2+} by perlite.

The influence of concomitant ions, in decreasing order, was: $Cs^+ > Ba^{2+} > Mg^{2+} > K^+ \sim Na^+ > NH_4^+ > Ca^{2+}$. The results of these investigations will allow determining the best treatment, weather the solution is an effluent from a nuclear plant or in case of environmental contamination.

Keywords: Concomitant Ions, Low-Cost Mineral, Nuclear Effluents, Remediation, Uranyl Ion

Introduction

Uranium, a naturally occurring heavy metal, is found in various chemical forms in the environment. The U (IV) oxide (UO_2) is the raw material for manufacturing nuclear fuel of electric power generating reactors. In the nuclear industry, the management of effluents is a great and important challenge for the protection of human health and the environment. Diverse processes have been developed for their treatment, such as chemical precipitation [1], separation on membranes [2] and ion exchange [3]. Adsorption processes have been the most popular to eliminate radioactive ions from aqueous solutions due to their ease of operation, simplicity of design and great applicability to eliminate various types of contaminants, allowing the concentration of radionuclides in small volumes of solid waste. Krestou et al. studied the adsorption of U (VI) on hydroxyapatite [4], Olmez et al studied the adsorption of U on natural zeolite [5] and Fasfous et al. investigated Uranium (VI) sorption by multiwalled carbon nanotubes [6], Kornilovych studied uranium removal from groundwater and wastewater using clay-supported nanoscale zero-valent iron [7].

Perlite is a natural, abundant low-cost mineral that requires minimum processing before use either as raw or expanded perlite, resulting in a low-cost porous material. Its composition depends on the origin. Argentina has two important provinces with perlite deposits of economic interest, namely Catamarca and Salta [8]. If the perlite is heated quickly to 800-1200 ºC, it undergoes a process where it expands around 20 times its original volume and it reaches densities of 0.35- 0.8 g cm^{-3} [9]. Expanded perlite is an excellent insulator, both thermal and acoustical, it resists fire and is also used in horticulture and agriculture. Besides, it is an excellent filter aid and filler in various processes such as drinks clarification, and paint, enamels, glazes, plastics and resins formulation, since it is a good adsorbent and it is chemically inert in many environments [9]. In this work we used a type of mineral that was processed in the same way as the material used for horticulture. The process consists of a first grinding and subsequent thermal treatment, followed by a second grinding, where the desired particle diameter is obtained.

In the last years the use of perlite has been successfully applied for adsorption of metal ions, such silver, copper and mercury [9], lead and cadmium [10] and zinc [11], in all the works expanded perlite was used.

Few publications presented the removal of radioactive elements by perlite, either alone or in combination with other compounds. Rizk [12] investigated the selective sorption and separation of molybdenum by impregnated perlite. Recep Akkaya [13,14] investigated the process of elimination of uranyl and Talip et al. [15] investigated the capacity of expanded perlite modified with polyacrylamide to removal thorium ions. Another ion that has been studied was cesium from nuclear waste [16,17]. We also studied, in a previous work [18], the capacity of perlite to remove cesium ion, the material was characterized and the effects of different variables on removal efficiency were investigated. Very recently, Hussein et al. [19] studied the removal of uranium from radioactive liquid wastes using expanded perlite (EP) from Egyptian origin. Their promising results on the use of unmodified perlite for removal of uranyl ions encourages further research to be made, to allow more comprehensive conclusions on the characteristics and potential of this natural, low-cost material from different geographical origins.-

In the present work we studied, by batch tests, the capacity of perlite for removal of uranium (as uranyl nitrate species, $UO_2(NO_3)_2$) from aqueous solutions and thoroughly investigated the different variables affecting the adsorption process. Firstly, the zeta potential was studied, which allows determining the surface charge of the perlite and its effect on aggregation, flow, sedimentation and filtration, among other characteristics of the material [20]. In addition, the effects of adsorbent dose, contact time, pH and initial UO_2^{2+} concentration on the sorption capacity of perlite were studied. In order to understand the potential of the process to be applied in real case situations, the interference caused by other ions usually present in nuclear effluents and environmental samples (Mg^{2+}, Ba^{2+}, Cs^+, Na^+, K^+ Ca^{2+} and NH_4^+) was investigated.

Materials and Methods

Perlite

A perlite from a mine in Salta, Argentina, provided by the company Imerys Perlita Tucumán S.A., called Pava, was used. In a previous work we characterized the local material, Table 1 summarizes the results obtained by scanning electron microscopy, X-ray powder diffraction, thermal analysis and specific area analysis (BET) and from other sources [18].

Scanning Electron Microscopy	The perlite has a rough surface with spherical structures	
The main components	Silica (SiO_2)	74–79 %
	Aluminium (Al_2O_3)	13–17 %
	Potassium (K_2O)	0.5–5 %
	Sodium (Na_2O)	2–5 %
	Calcium (CaO)	0.4–0.6 %
	Iron (Fe_2O_3)	0.3–0.95 %
	Water (H_2O)	3–5 %
Crystalline components	Silicon oxides, Na, Ca and K aluminosilicates.	
BET	Area	1.309 $cm^2\ g^{-1}$
	Type isotherms	II (mono-multilayer physical adsorption)

Table 1: Results obtained by X-ray powder diffraction, thermal analysis and BET of perlite Pava from a mine in Salta, Argentina, provided by the company Imerys Perlita Tucumán S.A. [18]

Zeta Potential

The zeta potential was studied with a Zetasizer 2000 (Malvern Instruments Ltd., United Kingdom) with the software PCS: Zeta mode v1.52. The equipment has a 5-mW nominal neon-helium continuous power laser with a 633 nm output. It measures the electrophoretic mobility of the perlite particles and then the software determines the zeta potential by applying the Smoluchowski Eq. (1) which shows a direct relationship between zeta potential (□) and electrophoretic mobility (□□ at the working temperature (V_t is the viscosity and D_t is the dielectric constant of the solvent [20]):

$$\xi = [(4 \pi V_{t)} / D_{t]} \mu \quad (1)$$

The perlite was conditioned to analyze the zeta potential at different pH values. It was washed with nanopure water, left in contact for 2 h, centrifuged at 3400 rpm and allowed to dry at 30 °C. It was subsequently milled using an agate mortar, until particles with a diameter smaller than 105 μm were obtained.

The solutions of different pHs were prepared from KCl (1 mM), to maintain a constant ionic strength, and pH was adjusted either with HCl or KOH. Conditioned perlite (2 mg) was added to 20 mL of each solution, and equilibrated for three hours at room temperature. Before performing the zeta potential analysis, the pH value was measured again, noting a slight variation.

Sorption Experiments

Four working solutions of UO_2^{2+} of 0.1, 1, 10 and 50 mg L^{-1} were prepared by dilution of a stock solution of UO_2^{2+} in HNO_3 made from a uranium oxide pellet. The experiments were done in batch, at least in duplicate, at room temperature (21 Cº ± 1), except for thermodynamics measurements, where temperature was adjusted. The procedure consisted in placing a known mass of Pava in an Erlenmeyer flask, adding 40 mL of solution to be treated, stirring at 180 rpm to allow good contact of the material with the solution, leaving to settle for 30 min and then filtering the supernatant through nylon syringe filters of 0.45 μm.

Kinetic phosphorescence analysis (KPA), inductively coupled plasma optical emission spectrometry (ICP-OES), capillary zone electrophoresis (CZE) with diode array detection (DAD) and total reflection X-ray fluorescence (TXRF) were employed for remaining UO_2^{2+} measurement, for initial concentrations of 0.1, 1, 10 and 50 mg L^{-1}, respectively.

Results and discussion

Zeta Potential

The perlite Pava showed to have a negative surface charge in water at an unadjusted pH. This may be due to the isomorphic substitution of ions of the solid by others of different charge, to defects in the crystal lattice, broken edges of the particles, the presence of structural hydroxyl groups or some of them simultaneously [20].

The hydroxyl groups present in the silicates and aluminosilicates on the surface of the perlite are those that give it the adsorbent character. The groups formed by the silicon atoms tend to maintain their tetrahedral coordination with oxygen, completing their coordination by joining monovalent hydroxyl groups, forming silanol groups. Silanol groups can be protonated or deprotonated depending on the pH of the solution. At low pHs, the groups will be protonated and, at high pHs, they can deprotonate.

With this in mind, the pH of the solution is expected to influence the surface charge of the material, presenting a less negative surface charge at low pH values. As the pH increases, the negative charge will increase. In some cases, a surface charge of zero, called the isoelectric point, may be found at a certain pH value.

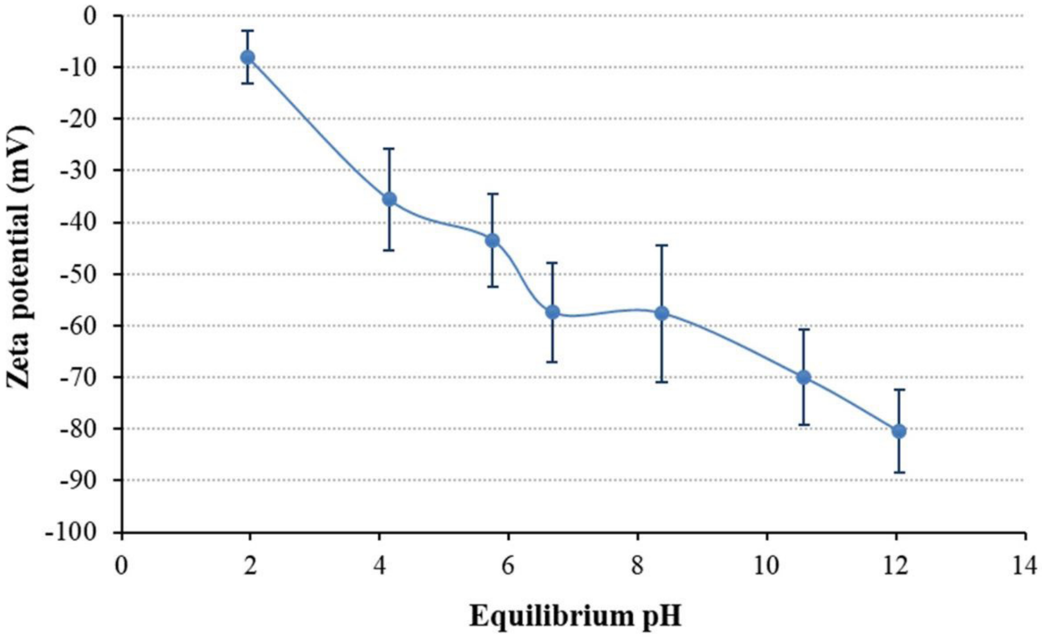

Figure 1: The effect of pH on the zeta potential of Pava samples

As can be seen in Figure 1, the perlite did not present an isoelectric point in the pH range studied. Showing negative zeta potential at all the pHs studied, as the pH increased, the negative zeta potential also did.

pH Effects on The Sorption of Natural Uranium

As the study of zeta potential suggests, the effect of pH is an important parameter to be investigated, since there is a dependence of complexation reactions and electrostatic interactions in the processes of physisorption of the perlite surface with pH [21,22,15]. In these experiments, a dose of Pava of 45 g L^{-1} was used and the initial uranium concentrations were 1 and 50 mg L^{-1}.

The pHs of the solutions were adjusted between 2 and 12 with HNO_3 or NH_4OH, as required. In order to detect possible variations in the concentration of uranium in solution due to other factors than sorption onto perlite (such for example potential precipitation, especially at alkaline pHs), control samples (without perlite) were also run at each pH. Variations in the concentration of the analyte were undetectable.

As can be seen in Figure 2, the effect of pH depends on the initial concentration of uranium in the solution. For a concentration of 1 mg L^{-1}, the elimination capacity was more affected at alkaline pHs than at acidic pHs. A maximum removal of 89 % was reached at pH 6 (natural pH of the solution), dropping to 51 % at pH 12. For solutions of 50 mg L^{-1}, the removal was always between 30 and 40 %, and no clear trend was found as a function of pH.

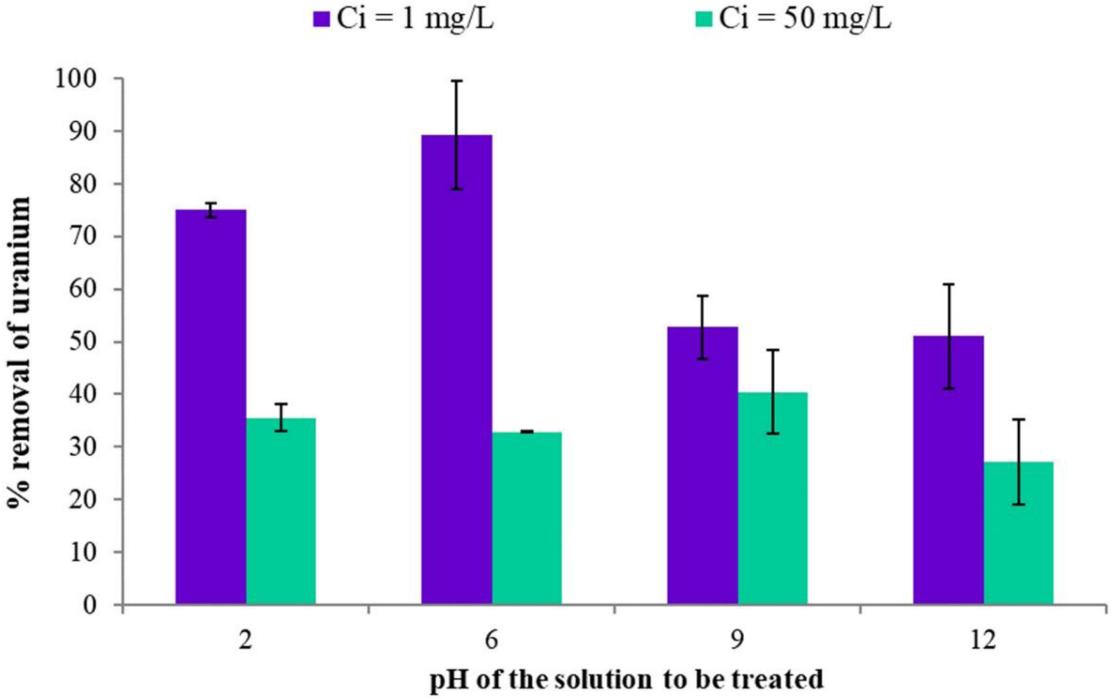

Figure 2: Comparison of the effect of pH on the removal of UO_2^{2+} for solutions of 1 and 50 mg L^{-1}. Perlite dose: 45 g L^{-1}, contact time: 40 min

Considering the results of increasing negative zeta potential with pH, uranium removal is expected to increase at high pH values. The removal behaviour observed can be explained by the presence of different mononuclear and polynuclear uranium (VI) hydrolysis complexes (see Figure 3 and 4). At pH values below 3, the predominant species is the uranyl ion (UO_2^{2+}). As the pH increases hydrolysis of the uranyl ion occurs, beginning to form other complexes such as $UO_2(OH)^+$, $(UO_2)_2(OH)_2^{2+}$, $(UO_2)_3(OH)_5^+$ and $(UO_2)_4(OH)_7^+$. From pH around 7, complexes with a negative charge begin to predominate, namely $(UO_2)_3(OH)_7^-$, $UO_2(OH)_3^-$ and $UO_2(OH)_4^{2-}$ [23,4]. These structural differences (hydrated radius) and charge (positive or negative) may explain the effect that was observed, where at high pH values the removal decreased, either due to steric and/or electrostatic repulsions.

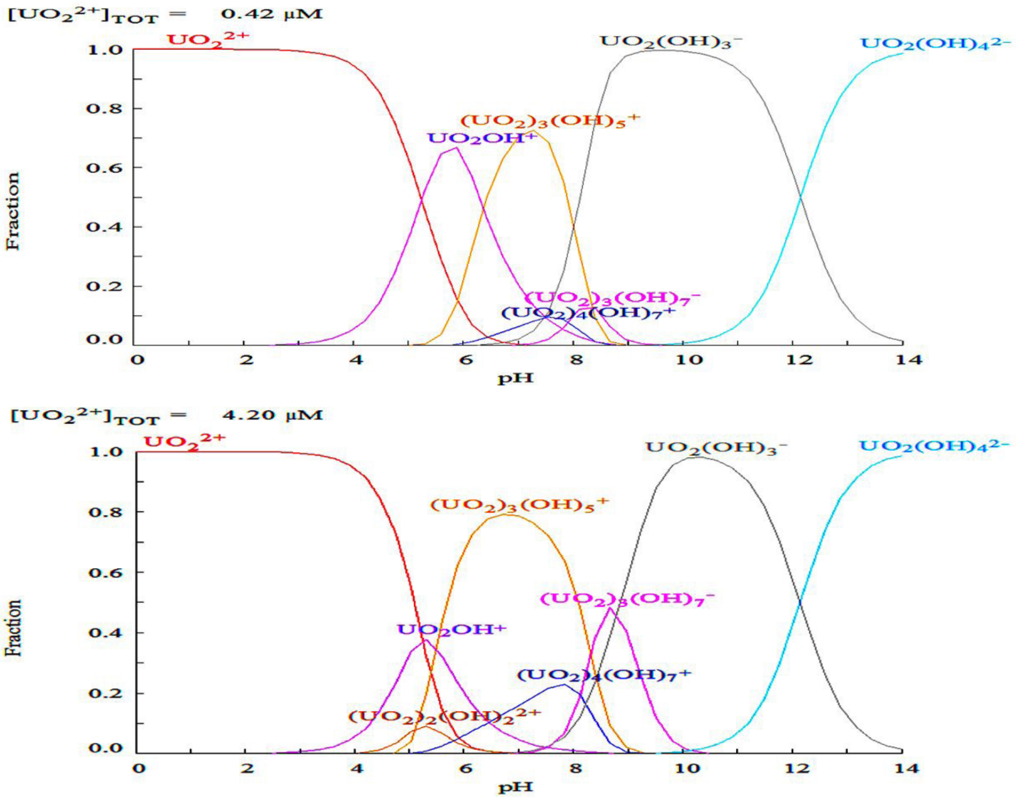

Figure 3: Graphs of the distribution of uranium (VI) species, for initial uranium concentrations of 100 µg L-1 (0.42 µM), 1 mg L-1 (4.20 µM). Obtained with the Medusa/Hydra Software (2010) of KTH Royal Institute of Technology of Stockholm

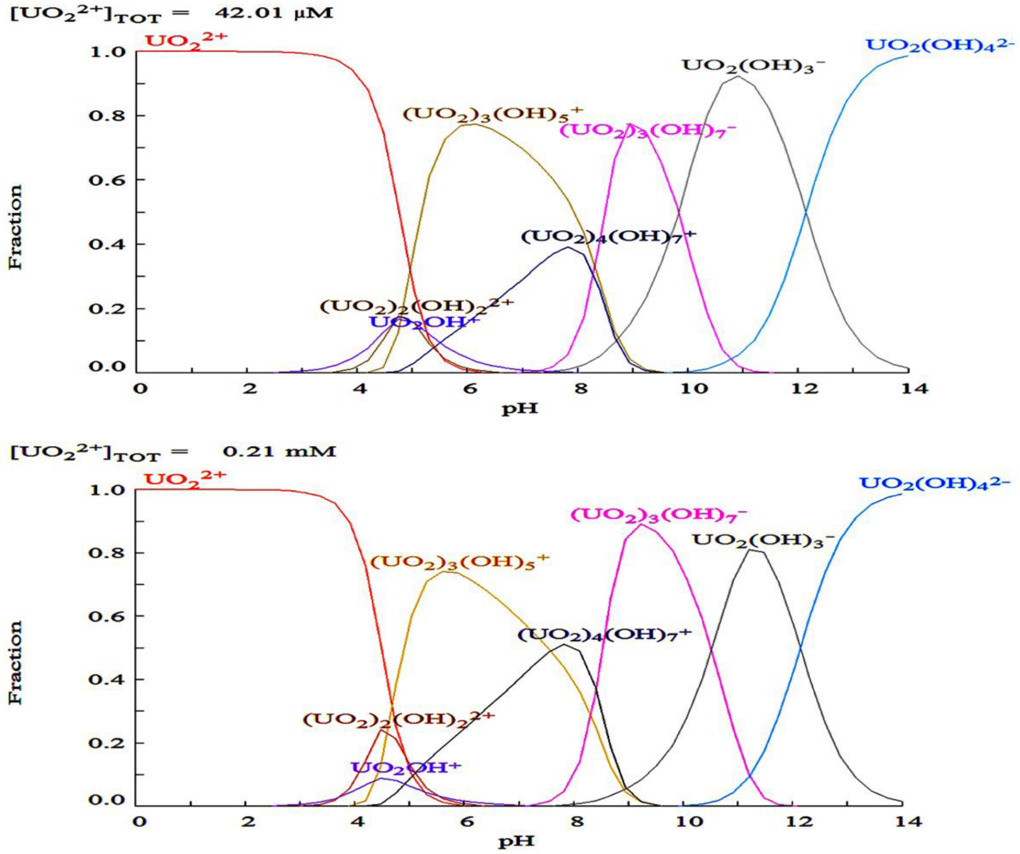

Figure 4: Graphs of the distribution of uranium (VI) species, for initial uranium concentrations of 10 mg L-1 (42.01 µM) and 50 mg L- 1 (0.21 mM). Obtained with the Medusa/Hydra Software (2010) of KTH Royal Institute of Technology of Stockholm

Consistently, when Hussein et al. studied the effect of pH for a solution of 70 mg L^{-1} of U (VI) from nuclear waste liquor using expanded perlite at a dose of 1 mg L^{-1}, their results showed that uranium adsorption efficiency increased from 35 to 83% as the pH increased from 0.5 to 5 and at higher pHs the efficiency decreased significantly, obtaining for the highest studied pH value of 7 a removal value close to 30 % [19].

The Effect of the Variation of the Substrate Mass

These experiments were carried out for solutions with initial uranium concentrations of 0.1, 1, 10 and 50 mg L^{-1}, with an unadjusted pH of 4-5, at room temperature (25 ± 1 °C), with a contact time of 40 min, 180 rpm agitation speed and a decantation time of 30 min.

As can be seen in Figure 5 as the dose of perlite increased the percentage of uranium removal also increased, up to a perlite dose around 30 g L^{-1}, from which the removal remained constant. Increasing the concentration of uranium caused a depletion in removal, for instance, for a dose of 30 g L^{-1}, when uranium concentration was 0.1 mg L^{-1}, the percentage removal was 83 %, while for 1 mg L^{-1} it was 70 %, followed by 50 % for 10 mg L^{-1} initial concentration and finally, 20 % for an initial concentration of 50 mg L^{-1}.

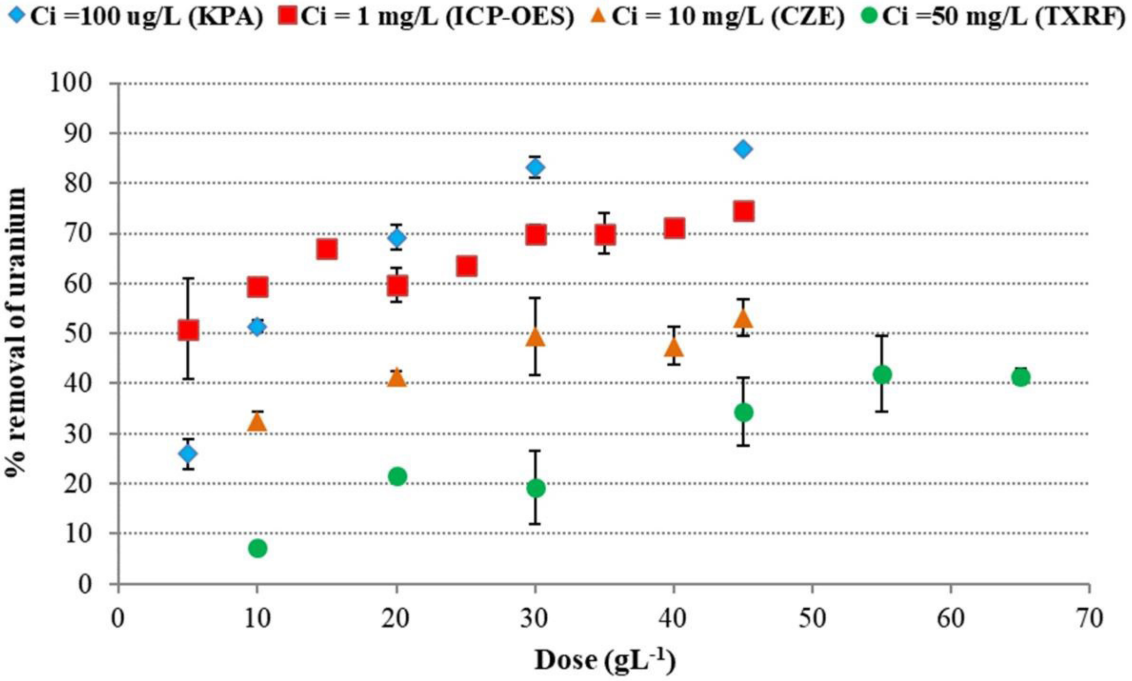

Figure 5: Variation of uranium removal for different masses of perlite, for four different initial concentrations of uranium

Hussein et al., in contrast, observed that as the mass/volume ratio increased from 0.25 to 4 g L^{-1}, the uranium sorption efficiency decreased from 94 to 77 % while shaking the perlite with 10 mL of 70 mg L^{-1} uranium solution in a test tube, attributing this result to the fact that the available adsorbent capacity was not fully used at the higher adsorbent amounts [19]. The differences found with our results could be ascribed to the different experimental setup adopted, in our case using larger masses and volumes and stirring at high speed in an Erlenmeyer flask, thus allowing good contact between the perlite and the solution.

The Effect of Contact Time

For the three different uranium concentrations studied, the equilibration time and the maximum removal achieved can be seen in Table 2 and Figure 6. In general terms, the times in which the equilibrium was reached and the maximum removals were obtained, ranging from 10-40 min, can be considered short times. In this work, we chose 40 min contact time for the experiments with the other studied variables, to assure enough robustness without enlarging too much the duration of the experiments.

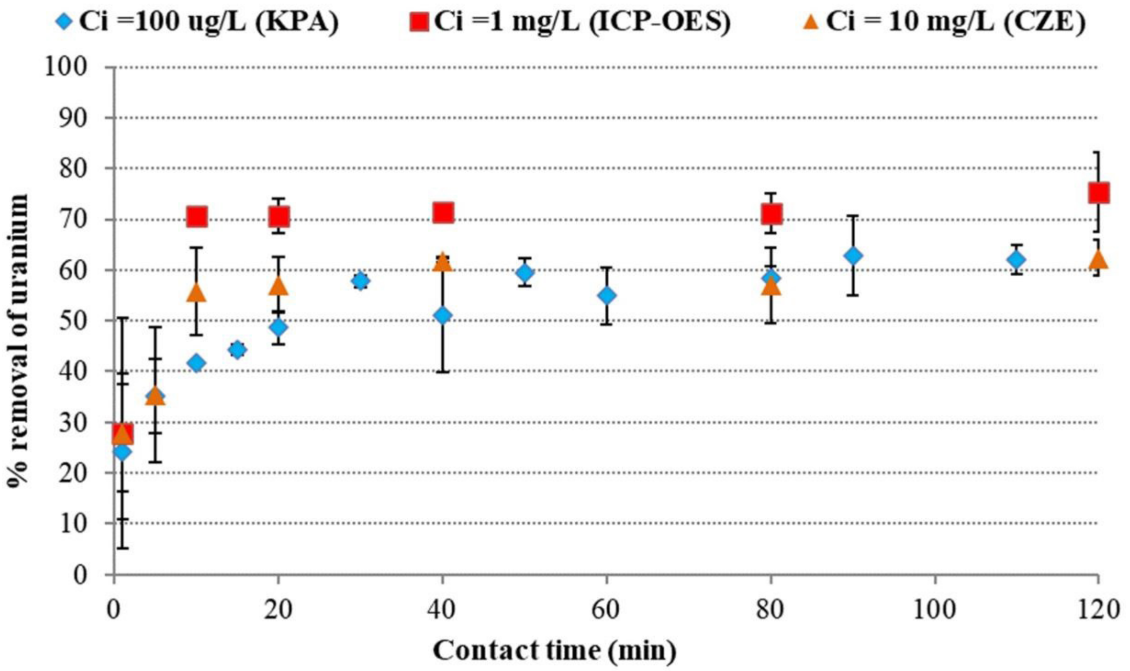

Figure 6: Uranium removal as a function of contact time at three different initial concentrations. The pH of the solution was around 4-5. Stirring speed was 180 rpm at room temperature of 25 °C. Perlite doses are as in table 1

Concentration of uranium	Perlite dose	Equilibration time	% Removal of uranium
0.1 mg L^{-1}	20 g L^{-1}	30 min	58 %
1 mg L^{-1}	30 g L^{-1}	10 min	71 %
10 mg L^{-1}	30 g L^{-1}	20 min	56 %.

Table 2: Maximum removal obtained for different initial ionic concentration at pH unadjusted (4-5), stirring speed 180 rpm and room temperature (25 ± 1 °C)

Variation of UO_2^{2+} Concentration - Adsorption Isotherms

In order to understand the mechanism involved in the sorption of uranium by the perlite, the adsorption processes in monolayer (Langmuir, Dubinin-Radushkevich (D-R) and Frumkin) and in multilayer (physisorption) due to weak interactions (Freundlich, Temkin and Harkins-Jura), were studied.

The kinetics of uranium removal was analysed using a sorbent dose of 50 g L^{-1}, a contact time of 40 min and a temperature of 21 ± 1 °C. Synthetic solutions were prepared using a salt of uranyl nitrate ($UO_2(NO_3)_2.6H_2O$), with uranium concentrations up to a maximum of 500 mg L^{-1}. The pH of the solutions was not adjusted and it was close to 6.0. Figure 7 (a) shows the experimental isotherm. The parameters for constructing the adsorption isotherms were calculated as:

Q_e = mass of adsorbed UO_2^{2+} (mg)/ sorbent mass (g)
C_e = mass of remaining UO_2^{2+} (mg) / solution volume (L),
being Ce the concentration of UO_2^{2+} in equilibrium and Qe the maximum amount of UO_2^{2+} per perlite mass to form a complete monolayer on the surface of the mineral particles.

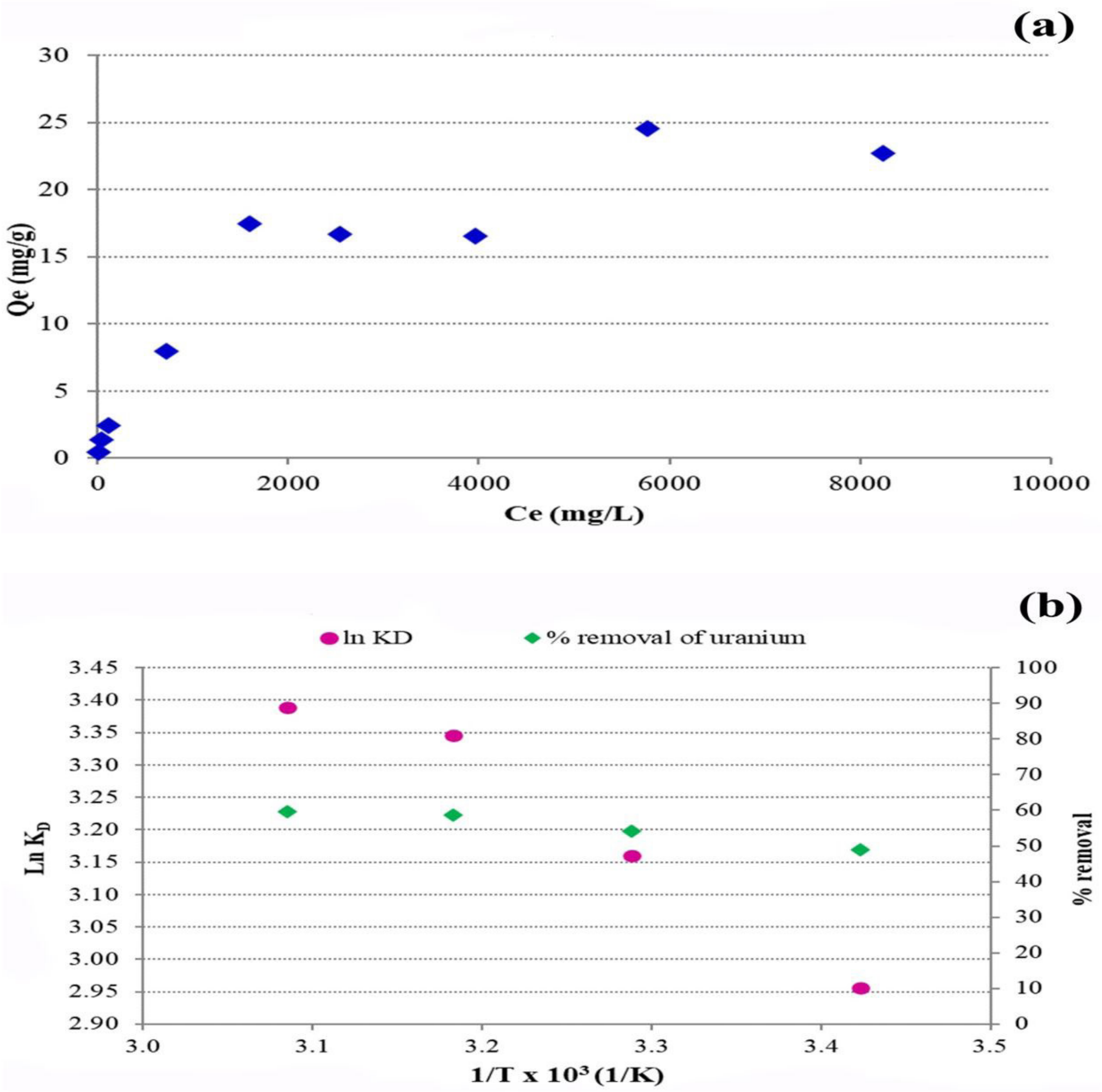

Figure 7: (a) Variation of the concentration of UO_2^{2+}. q_e = mass of adsorbed UO_2^{2+} (mg)/perlite mass (g), Ce = mass of remaining UO_2^{2+} (mg)/solution volume (L). Experimental conditions: perlite dose 50 g L^{-1}, contact time 40 min, temperature 21 °C.
(b) Plot of ln K_D versus 1/T x10^3 for uranium adsorption in Pava perlite, and the variation of the percentage removal

Table 3 shows all the parameters determined for the different models. The highest linear correlation values were reached with the Langmuir model (R^2= 0.948). R_L indicates that the adsorption on the surface is initially homogeneous, with Qm of 7.32 mg U L^{-1} [12]. After the saturation of the monolayer, the formation of a multilayer occurs, this is indicated by the parameters obtained by the Freundlich model where (n) was a value above unity, indicating that adsorption in multilayers is favourable. In the case of Hussein et al., the value of n was greater than that determined in this work [19]. These differences may be due to variations in the composition and/or structure of the material, since it is a natural mineral. For the Dubinin-Radushkevich model, the adsorption energy value indicates that two processes coexist in the removal of uranium: an ion exchange process, together with weak force adsorption of the Van der Waals type.

Isotherm	Linearized equation	Parameters and results
Langmuir	$\frac{1}{q_e} = \frac{1}{Q_m\,K}\frac{1}{C_e} + \frac{1}{Q_m}$ $R_L = \frac{1}{1 + KC_e}$	$^{a)}$ $Q_m = 7.32$ mg L^{-1} $^{b)}$ $K = 0.02$ L mg^{-1} $R^2 = 0.948$ $^{c)}$ $R_L = 0.948$
Freundlich	$\ln q_e = \ln K_f + \frac{1}{n}\ln C_e$	$^{d)}$ $K_f = 0.27$ Lg^{-1} $^{e)}$ $n = 2.02$ $R^2 = 0.853$
Dubinin-Radushkevich	$\ln q_e = \ln q_{DR} - K_{DR'}\varepsilon^2$ $\varepsilon = RT\ln(1 + \frac{1}{C_e})$ $E = \frac{1}{\sqrt{2K}}$	$^{f)}$ $q_{DR} = 1.65x10^{-4}$ mol g^{-1} $^{g)}$ $K_{DR'} = 6.58x10^{-9}$ mol^2 J^{-2} $^{h)}$ $E = 8.72$ kJ mol^{-1} $R^2 = 0.939$
Temkin	$q_e = B\,ln\,A + B\,lnC_e$ $B = \frac{RT}{b}$	$A = 1.15_x10^{-2}$ $B = 19.23$ kJ mol^{-1} $b = 127.16$ j mol^{-1} $R^2 = 0.562$
Harkins-Jura	$\frac{1}{q_e^2} = \frac{B}{A} - \frac{1}{A}logC_e$	$A = 14.71$ $B = 4.04$ $R^2 = 0.606$
Frumkin	$ln\left[\left(\frac{\theta}{1-\theta}\right)\frac{1}{C_e}\right] = \ln k + 2a\theta$ $\theta = \frac{q_e}{q_m}$ $\ln k = \frac{-\Delta G}{RT}$	$a = -2.60$ $k = 2.07_x10^{-4}$ $\Delta G^0 = 20.74$ kJ mol^{-1} $R^2 = 0.699$

Table 3: The six models of isotherms analyzed with their respective linearized equations, and corresponding results at 21 ºC for adsorption of UO22+ by the perlite Pava.

a) Qm = Maximum adsorption

b) K = Affinity constant

c) RL = Separation factor or equilibrium parameter

d) Kf = Adsorption capacity

e) n= Adsorption intensity (n)

f) qDR = Saturation capacity of the monolayer

g) KDR´ = Activity coefficient

h) E = Adsorption energy

Adsorption Thermodynamics

Thermodynamics can be used to characterize differences in the physical properties of various states of equilibrium and the driving forces towards equilibrium. The determination of enthalpy (ΔH), entropy (ΔS) and Gibbs free energy (ΔG) changes allow us to know the interaction that takes place.

These studies were carried out with a dose of perlite of 50 g L^{-1} and a uranium solution of 10 mg L^{-1}, prepared from the salt. The pH was around 6 (not adjusted). The samples were placed in a thermostated bath, stirred for 40 min at 120 rpm and allowed to settle for 30 min. The supernatants were filtered, HNO_3 was added and they were analysed by TXRF.

The distribution coefficient (K_D), in mL g^{-1}, was determined by Eq. (2):

$$K_D = [(C_o - C_i) / C_i] - (V / m) \quad (2)$$

Being C_0 the initial concentration of uranium in solution (mg L^{-1}), Ci the concentration of uranium in solution after adsorption (mg L^{-1}), V the volume of the solution (mL) and m the mass of perlite used (g).

The Van't Hoff Eq. (3) allowed determining the thermodynamic parameters of enthalpy (ΔH^0) and entropy (ΔS^0) changes, when making a graph of ln K_D vs 1/T (see Figure 7 (b)) [15].

$$\text{Ln } K_D = (\Delta S^0 / R) - (\Delta H^0 / R\, T) \quad (3)$$

Where R is the universal gas constant and T is the absolute temperature.

It can be seen in Table 4 a positive ΔS^0, indicating an increase in the solid interface/solution randomness during adsorption. Regarding the negative value of ΔH^0, it indicates that the adsorption of the uranyl ion on perlite is an exothermic process. Changes in enthalpy may be associated with the forces of attraction ($\Delta H<0$) or repulsion ($\Delta H>0$) between the analyte and the sorbent.

R^2	ΔS^0 (J $K^{-1}mol^{-1}$)	ΔH^0 (kJ mol^{-1})	ΔG^0 (kJ mol^{-1})			
			292 K	304 K	314 K	324 K
0.962	62.88	-11.15	-29.52	-30.27	-30.90	-31.53

Table 4: Thermodynamic parameters obtained for the adsorption of uranium on perlite Pava

The free energy change of the specific adsorption (ΔG^0) was determined using Eq. (4):

$$\Delta G^0 = \Delta H^0 - (T\, \Delta S^0) \quad (4)$$

The negative value of ΔG^0 demonstrate that the adsorption of the uranyl ion by perlite is thermodynamically feasible and naturally spontaneous in the range of 19 to 51 °C. As the temperature increases, a slight increase in the absolute value of ΔG^0 is noticed, indicating that the viability of the adsorption is greater at higher temperatures.

Effect of the Presence of Concomitants

For these studies, the cations were selected taking into account their possible presence in the effluents to be treated and their potential to compete with UO_2^{2+}, focusing on a possible adsorbate/adsorbent interaction mechanism by ion exchange [20]. Their radii are shown in Table 5. Due to similarities in both the ionic charge and the hydrated ion radius, it was expected that barium, calcium and uranyl compete for sorption sites with similar strengths. The concentrations of the cations were close to and higher than those of uranium. In the case of potassium, sodium and ammonium, their effect was analyzed for even higher concentrations, taking into account the high levels expected in the effluents. The perlite dose was 45 g L^{-1} and the pH was around 4 (not adjusted). The temperature was 25 ± 1 ^{o}C, the contact time 40 min, the stirring speed 180 rpm and the settling time 30 min.

Cation	**10^8r_i**
Cs^+	1.044
Ba^{2+}	2.572
K^+	1.114
Na^+	1.624
Ca^{2+}	2.750
Mg^{2+}	3.088
NH_4^+	1.104
UO_2^{2+}	2.54

Table 5: Hydrated ionic radii ri (in cm) of the selected inorganic cations [24,25]

As shown in Figure 8 (a), in the presence of Ba^{2+} at a level 10 times higher than that of uranium (0.05 mM Ba^{2+}), removal was 82 %, which means a decrease of only 6 %. In the case of Mg^{2+}, uranium removal was 86 % when the concomitant was present in a concentration 19 times higher (0.08 mM Mg^{2+}), which led to a decrease in removal of 9 %. In the case of Ca^{2+} (Figure 8 (b)) its presence did not cause a significant effect, obtaining a removal of 93 % for Ca^{2+} concentration of 20 mM, a decrease of only 1.5 %. These results suggest that there are prevalent factors affecting sorption on the perlite sites, other than charge and radii of the competing ions.

In the case of NH_4^+ (Figure 8 (c)), in the presence of a concentration 1.1 mM in the effluent, uranium removal was 86 % (a 5 % drop). Because very high concentrations of this concomitant were expected in some currents of the nuclear fuel cycle, where UO_2^{2+} solutions are treated with NH_3 (c), higher concentrations were investigated. For an ammonium concentration of 2.39 x 10^3 mM, removal was 32 %, that is, the removal only dropped a 59 % when NH_4^+ concentration was almost 5.7 x 10^5 times higher than that of UO_2^{2+}.

In the case of Cs^+, K^+ and Na^+, not only the variation in the removal of uranium for different concentrations of the concomitants was investigated, but also the variation in the removal of each concomitant ion in the presence of uranium 4.2 x 10^{-3} mM was evaluated. In Figure 9 (a) it can be seen that uranium removal was 66 % for a Cs^+ concentration of 0.05 mM. It can also be seen that the presence of UO_2^{2+} does not affect the removal of Cs^+ by the perlite, which shows that this material has more affinity for Cs^+ than for UO_2^{2+}, anyway, the presence of a concentration of Cs^+ 12 times greater than that of uranium only produced a 22 % decrease in uranium removal. The competition of Cs^+ can be attributed to its high polarizability, which could be playing an important role in the sorption process.

In the case of K^+ (Figure 9 (b)), for a concentration of 51.2 mM, the removal of UO_2^{2+} was 58 % and that of K^+ was only 2 %, which shows that perlite has a marked preference for UO_2^{2+} against K^+. Finally, when studying the effect of Na^+ (Figure 9 (c)), a removal of 63 % for UO_2^{2+} and 5 % for Na^+ was observed, when the initial concentration of Na^+ was 87 mM, a concentration 20,000 times higher than that of UO_2^{2+}, thus showing a similar behavior to the one of K^+.

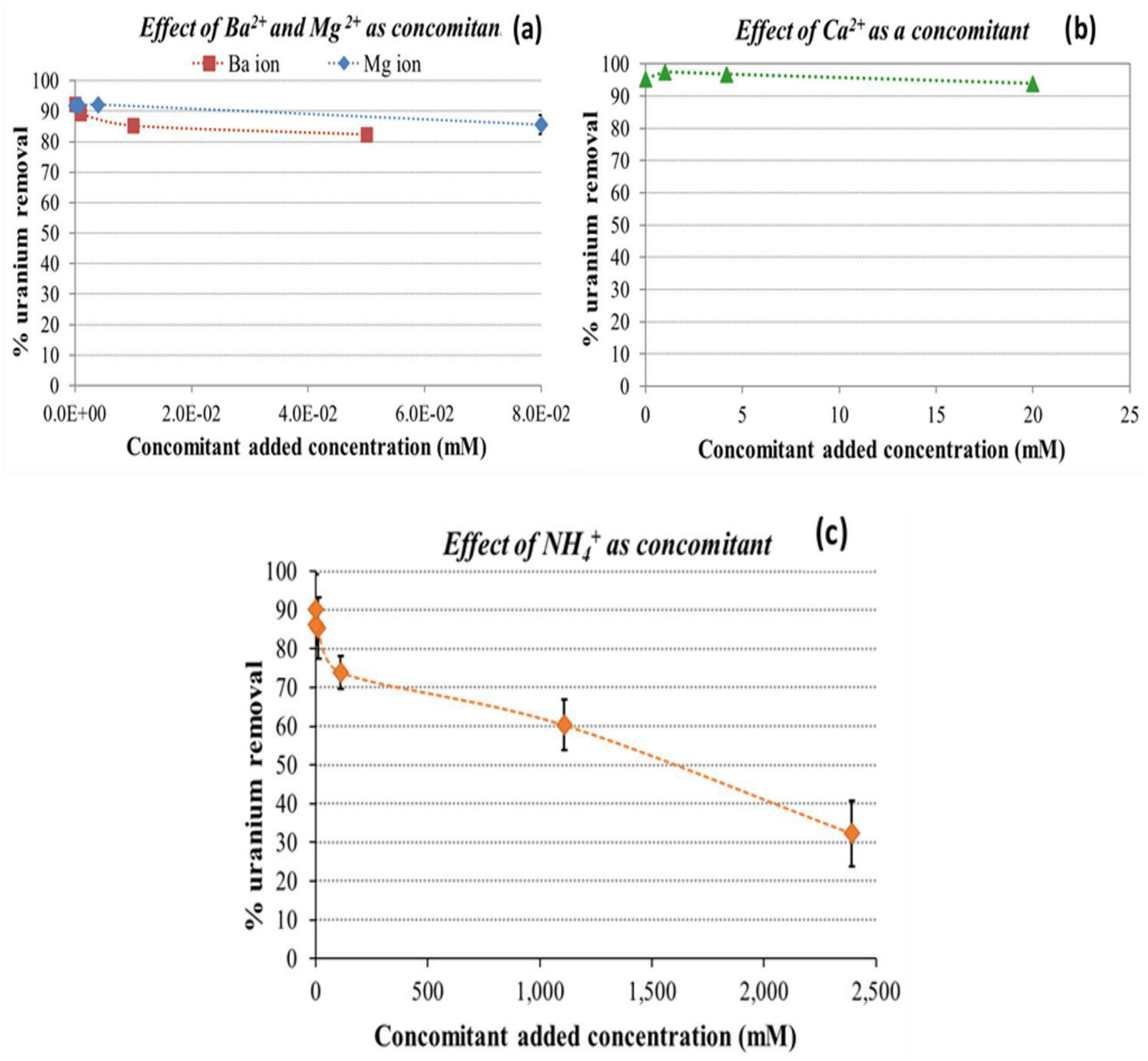

Figure 8: Variation in the removal of UO_2^{2+} as a function of the concentration of concomitants: (a) Ba^{2+} and Mg^{2+}, (b) Ca^{2+} and (c) NH_4^+, for a dose of Pava of 45 g L^{-1} and an initial uranium concentration of 4.2 x10^{-3} mM

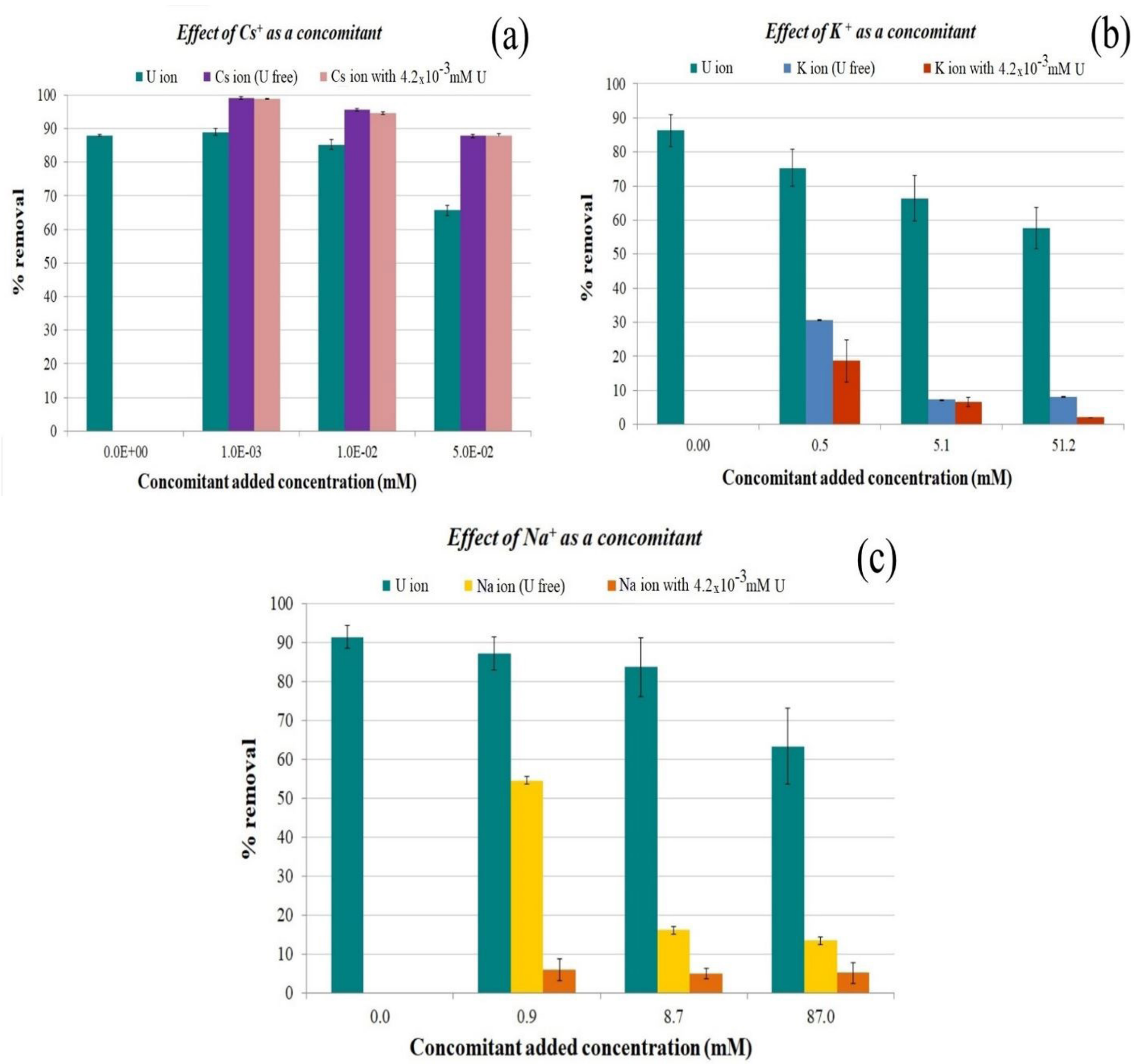

Figure 9: Removal of uranium as a function of the concentration of concomitants: (a) Cs^+, (b) K^+ and (c) Na^+, for an initial concentration of uranium of $4.2x10^{-3}$ mM (green bars). Also, variations in the removal of the concomitant ions in the presence of 4.2×10^{-3} mM U(VI) (violet bars for Cs^+, blue bars for K^+ and yellow bars for Na^+) and in the absence of uranium (pink bars for Cs^+, red bars for K^+ and orange bars for Na^+) are depicted. Perlite dose: 45 g L^{-1}

Concluding Remarks

Perlite Pava can be considered a material capable of removing uranium. The removal capacity will depend on the dose of adsorbent and the concentration of the analyte. pH is a parameter to consider because it is related to the net surface charge of the material, observing a decrease in zeta potential as the pH increased.

Removals up to 90 % were achieved for doses of 45 g Pava L^{-1} for low concentrations of U (100 µg L^{-1}), of 74 % when the concentration was 1 mg L^{-1}, 60 % for 10 mg L^{-1} and 25 % for a concentration of 50 mg L^{-1}.

Optimum contact time will depend on the initial concentration of uranium, but the maximum removal percentages are reached in a few minutes.

The best linear correlations were achieved by applying the Langmuir and Dubinin-Radushkevich adsorption models. Adsorption energy of 8.72 kJ mol^{-1} was determined, a result that falls within the range of energies characteristic of the chemical ion exchange process and Van der Waals type bonds. Through the Frumkin isotherm, a Gibbs free energy of 20.74 kJ mol^{-1} was determined, characteristic of strong bonds forces such as ion exchange, in addition to the presence of weak forces of physical nature.

The analysis of the thermodynamic process indicated the feasible, spontaneous and exothermic nature of the adsorption of UO_2^{2+} by perlite.

The presence of concomitants affected the removal of uranium to a different extent, in decreasing order: $Cs^+ > Ba^{2+} > Mg^{2+} > K^+ \sim Na^+ > NH_4^+ > Ca^{2+}$. Cs^+ was the one that caused the greatest effect. K^+, Na^+ and NH_4^+ presented effects very similar to each other, and together with Ca^{2+} they are the concomitants that caused the least depletion on the removal of uranium, even when the concentrations were 1000 times higher than those of uranium. All in all, the material investigated showed to have a robust performance even in the presence of a variety of potential concomitant ions.

Declarations

Ethics Approval and Consent to Participate: Not applicable

Consent For Publication: Not applicable

Availability of Data and Materials

All data generated or analysed during this study are included in this published article [and its supplementary information files].

Competing Interests

The authors have declared no conflict of interest. This is a mandatory requirement for all articles.

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Authors' Contributions

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by MC, SGM, AGL and PAB. The first draft of the manuscript was written by MC and PAB, and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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