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U(VI) SORPTION FROM AQUEOUS SOLUTIONS ON NATURAL AND SYNTHETIC WAX

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The adsorbing properties of sorbents: beeswax, paraffin wax and polypropylenic wax were investigated for U(VI) concentration and separation from aqueous solutions. The optimum parameters which influence the equilibirum of the U(VI) sorption in the U(VI) sorbent-aqueous solution system, have been established: pH, concentration of the initial solution, sorbent amount, contact time were established. The study also developed a theoretical approach of the sorption process, involving identification of the model of the isotherm according to which sorption occurs. An optimum pH of 6.5-7.5 was established, and also a maximum sorption capacity – $\boldsymbol{q_{max}}$ *of 116.2 mg.g*$^{-1}$ *for beeswax, of 115.6 mg.g*$^{-1}$ *for paraffin wax and of 212.3 mg.g*$^{-1}$*, respectively, for polypropylene wax. The values of the separation factor* $\boldsymbol{R_L}$ *and of constant* ***b,*** *calculated from the linearized form of the Langmuir isotherm, as well as the values of constants* $\boldsymbol{K_F}$ *and* ***n,*** *calculated from the linearized form of the Freundlich isotherm, indicate that - in the three systems – sorption is favourable and reversible, as due to the bonding affinity of sorbents' sites to U(VI). The ratio of adsorbed U(VI) increases with the increase in the concentration of the initial solution and with that of the sorbent amount, varying between 78.2 % – for polypropylenic wax – and 98.7 % – for beeswax. The FTIR spectra show that sorption on beeswax is a complex chemosorption process, involving cationic exchange and complexation, combined with physical adsorption while, for the rest of the systems exclusively surface adsorption and – possibly - superficial layer adsorption will occur.*

Key words: Uranium (VI), sorption, isotherms, beeswax, paraffin wax, polypropylene wax.

INTRODUCTION

Analysis and separation of the metallic ion species has always represented a problem of the hour. In recent years, when the environment came to have an ever-increasing, special impact, the identification, concentration and separation of the ions of the heavy metals, especially of the radioactive ones, represent a special concern for science.

As to the concentration and separation of the species in which uranium occurs in different systems, the literature of the field provides numerous studies using as sorbents: natural zeolites (Al-Shaybe and Khalili, 2009; Krestou et al., 2003), natural minerals (Munoz et al., 2009), synthetic ion exchangers (Nascimento et al., 2004; Song et al., 1999; Raileanu, 2010; Ladeira and Morais, 2005), separation of U(IV) from U(VI) on synthetic resins (Raileanu, 2009; Raileanu and Cecal, 2008), and many other systems.

In this context, the present study discusses the utilization of some natural sorbents, of natural and synthetic type, for U(VI) concentration and separation from synthetic aqueous solutions.

Beeswax is a complex, highly stable substance, whose properties get modified in time, in contact with atmospheric air. It is resistant to hydrolysis and natural oxidation and insoluble in water. Its complex composition – still not fully elucidated – includes various substances, mainly esters of the superior fatty acids and alcohols, and pigments – most of them resulted especially from pollen (Tulloch, 1971).

Chemically, wax is composed of: esters of the ceric acids – 71%, free ceric acids – 13.5-14%, hydrocarbons – 10.5-13.5%, superior free acids – 1-1.25%, esters of cholesterol – 1%, humidity and impurities (pollen, resins, etc.) – 1-2% (Endlein and Peleikis, 2011). The content and some of its properties make it similar with the natural wax of vegetal origin (Kolattukudy, 1976; Puelo and Rit, 1992).

Paraffin wax is obtained from petroleum, in whose composition alkanes and isoalkanes are prevailing, while polypropylene wax is a synthetic substance, obtained from petroleum through cracking processes.

Selection of these three types of sorbents is not accidental, if considering their multiple utilizations in various domains, from which high amounts of wax-containing residues – which might be employed as sorbents – usually result.

MATERIALS AND METHOD

The reactives and sorbents employed, of high analytical purity, were: $UO_2(NO_3)_2.6H_2O$, from CAS Fluka Chemie AG, Darmstadt, Germany; beeswax, paraffin wax and polypropylene wax – obtained from Suppliers High Quality Technology Development Co., Ltd., China.

Devices: β and γ radiation TU 88 YCCP 245.006-89 GOST 27451-87 radiometer; IR spectra were recorded on a Perkin – Elmer FTIR 1650 spectrophotometer, in the 4000-400 cm^{-1} wavenumber region, by the KBr pellet technique; analytical balance and pH-meter Mettler Toledo.

A standard $UO_2(NO_3)_2.6H_2O$ solution with a concentration of 94.060 $mg.L^{-1}$ U(VI) and pH ranging between 6.5-7.5 was prepared. In the extraction cylinders, the corresponding amounts of wax are weighed, over which precisely measured volumes of standard solution are added, then diluted at 50 mL, the samples being intermittently stirred. Sample volumes are collected at 15 min intervals, and the U(VI) amount in solution is determined comparatively with the reference sample.

For each sorption system, the influence of the initial solution concentration, of the amount of sorbent and of the contact time upon sorption equilibrium was followed. Optimization of the parameters influencing sorption was performed experimentally, in a step-by-step system, each of system's parameters being analyzed and, once established, the optimum value was considered for subsequent experiments.

Interpretation of the data recorded at equilibrium and elucidation of the sorption mechanism made use of Langmuir sorption isotherm, which characterizes surface monofilm sorption, containing a finite number of sites. Langmuir equation, in its linearized form, is: $\mathbf{C_e/q_e = 1/K_L + b.Ce/K_L}$, where: C_e is U(VI) concentration at equilibrium ($mg.L^{-1}$); q_e is the amount of U(VI) adsorbed on unit of adsorbing mass ($mg.g^{-1}$) at equilibrium; K_L($L.g^{-1}$) is Langmuir constant, b ($L.mg^{-1}$) is a constant expressing sorbent's affinity; $\mathbf{K_L = q_{max} .b}$, where q_{max} ($mg.g^{-1}$) is the maximum amount that can be adsorbed by 1 gram of sorbent, at equilibrium; $\mathbf{R_L = 1/(1+b.C_0)}$, where R_L is an equilibrium parameter, C_0 ($mol.L^{-1}$) is the initial concentraton of the U(VI) solution in which sorption was performed.

Freundlich isotherm describes surface adsorption, followed by a condensation effect resulted from the sorbent – sorbate interaction. In its linearized form, Freundlich equation is the following: $\mathbf{lg\ q_e = lg\ K_F + lg\ (Ce/n)}$, where: K_F ($L.g^{-1}$) is Freundlich constant reflecting the sorption capacity; q_e is the amount of U(VI) adsorbed on unit of adsorbing mass ($mg.g^{-1}$) at equilibrium; C_e is U(VI) concentration in solution at equilibrium ($mg.L^{-1}$); n is a constant reflecting sorption's intensity.

RESULTS AND DISCUSSION

Fig. 1A plots graphically the data on the influence of the concentration of the initial solution upon sorption equilibrium, in the U(VI) – paraffin wax system. The observation was made that, at low concentrations, the rate for attaining sorption equilibrium is higher, which means that equilibrium is reached within a shorter time interval. With increasing concentration of U (VI) in the initial solution, the sorption is slow, the time necessary for attaining sorption equilibrium and the amount of U(VI) retained on the unit of adsorbing mass also increase.

Fig. 1B shows that the ratio of U(VI) retained when sorption equilibrium is attained increases with the increase of the amount of absorbing mass, the maximum value being of 82.202 %, for an initial concentration of 23.515 mg U(VI).L^{-1}.

Graph 1A shows that, over the whole concentration domain, sorption equilibrium is attainted after 60 minutes.

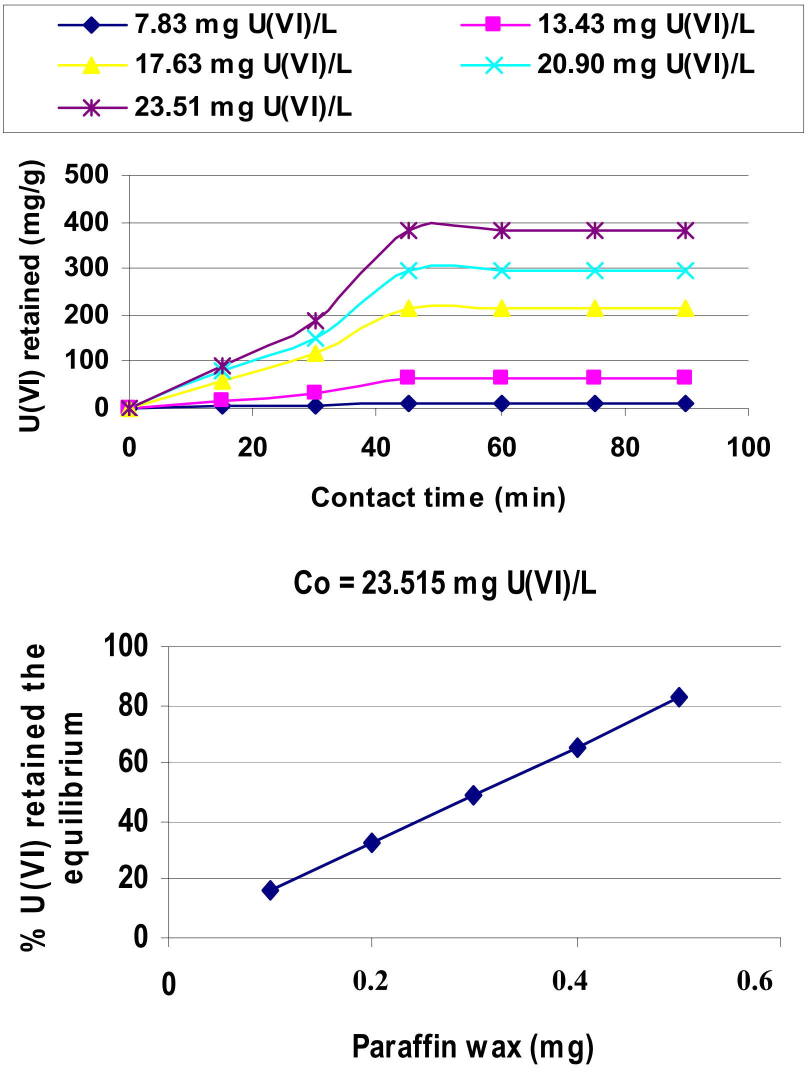

Fig. 1. Influence of concentration of the initial solution (upper panel) and of the amount of sorbent (lower panel) upon U(VI) sorption on paraffin wax.

The graphs plotted in Fig. 2A and 2B show that, in the U(VI)-beeswax sorption system, sorption is more rapid, the retained amount of U(VI) increasing considerably with the increase of the initial solution's concentration. Within 50 min, equilibrium is reached for any initial concentration of U(VI), the extraction ratio at equilibrium being of 98.84% for an initial concentration of 470 mg U(VI). L^{-1}.

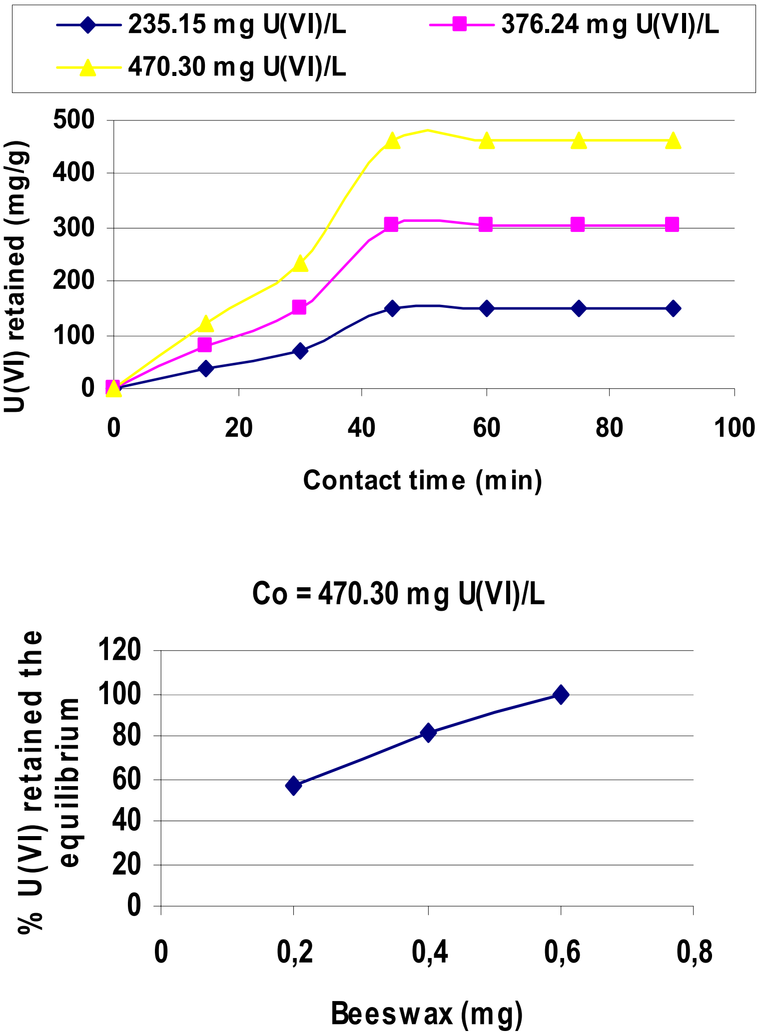

Fig. 2. Influence of concentration of the initial solution (upper panel) and of the amount of sorbent (lower panel) upon U(VI) sorption on beeswax.

For the U(VI)-polypropylene wax system plotted in Fig. 3, sorption equilibirum is much slower than that of the U(VI) – beeswax and U(VI) – paraffin wax systems.

It results from here that sorption is favored by the complexity of beeswax sorbent's composition, which confers to it a higher affinity for U(VI) sorption. In the U(VI)-polypropylene wax system, the extraction ratio at low U (VI) concentrations and low sorbent amounts ranges between 60-70, the increase being significant at higher amounts of sorbent amounts – reaching up to 78.26% for an initial concentration of 35.272mgU(VI).L^{-1}.

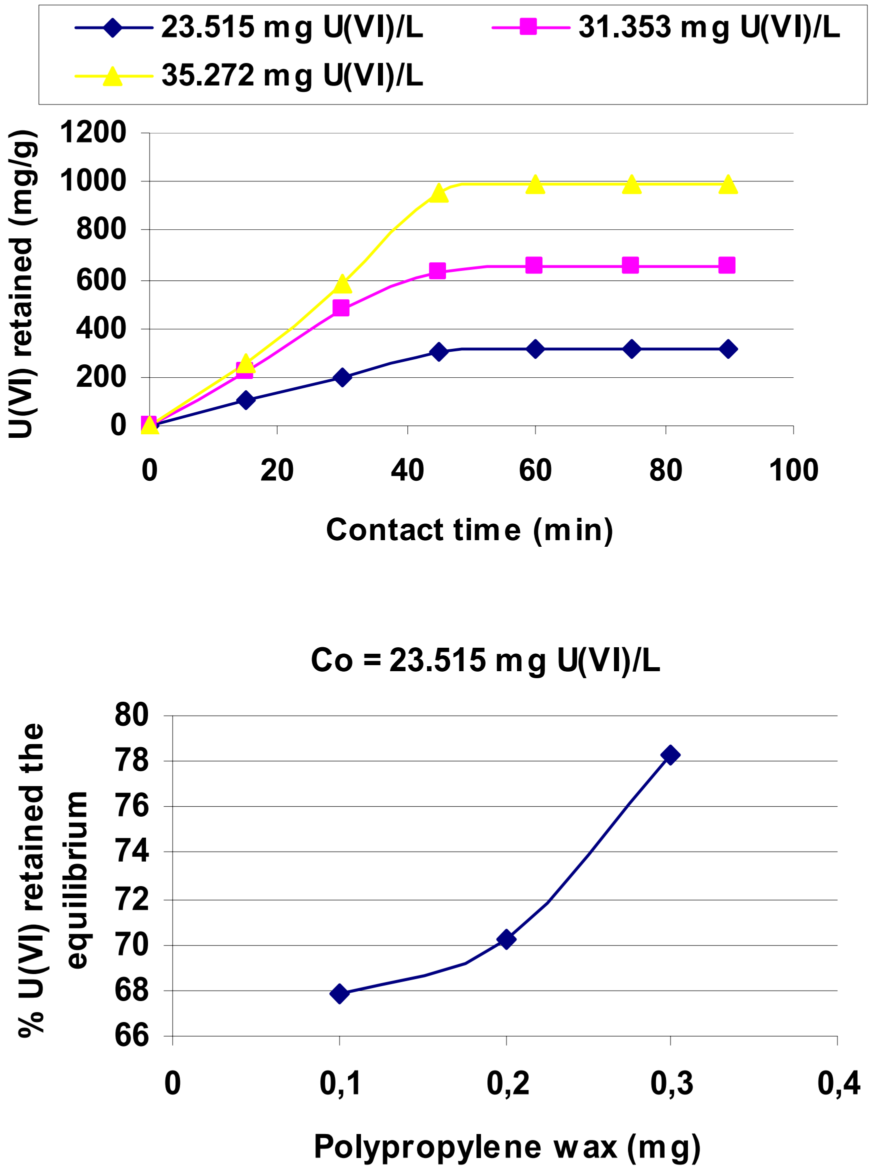

Fig. 3. Influence of concentration of the initial solution (upper panel) and of the amount of sorbent (lower panel) upon U(VI) sorption on polypropylene wax.

Figs. 4, 5 and 6 plot the Langmuir and Freundlich isotherms for the three sorption systems: U(VI)-paraffin wax; U(VI)-beeswax; U(VI)-polypropylene wax.

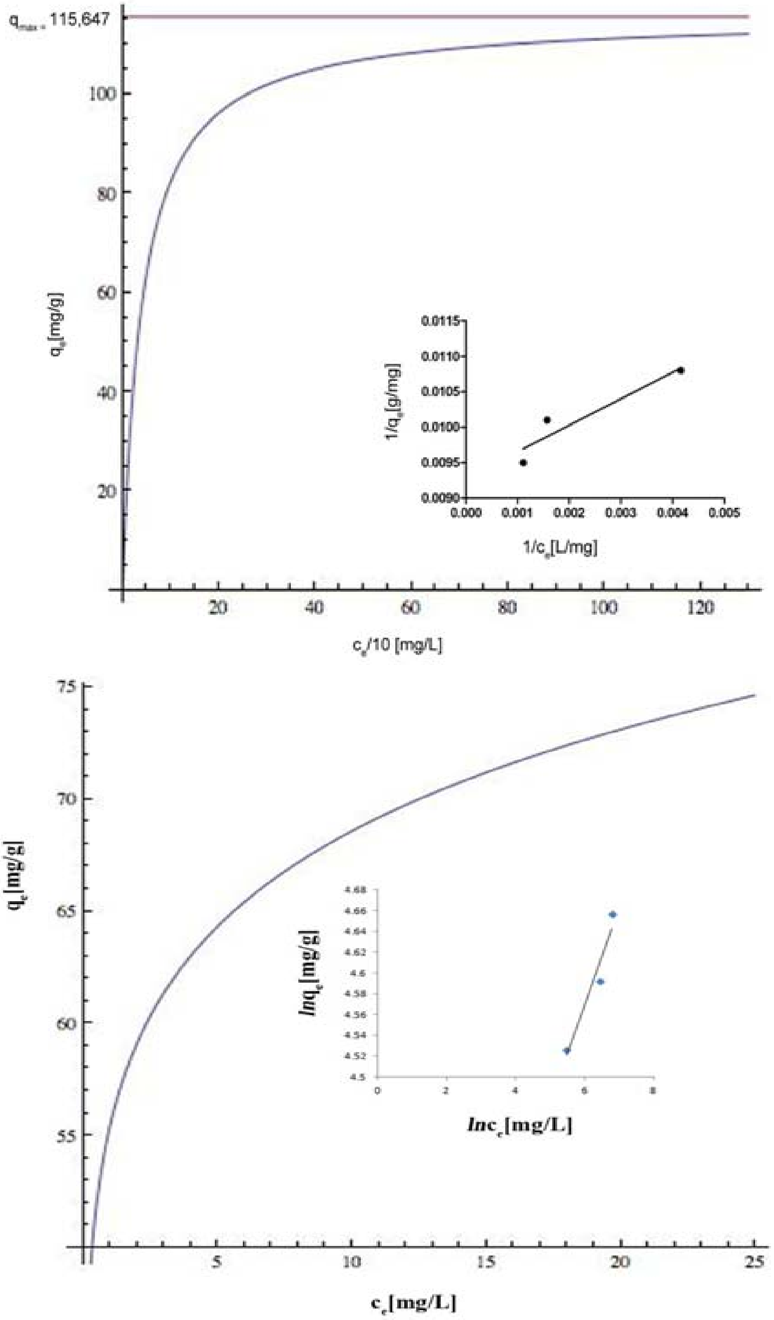

Fig. 4. Langmuir (upper panel) and Freundlich (lower panel) isotherms of U(VI) sorption on paraffin wax.

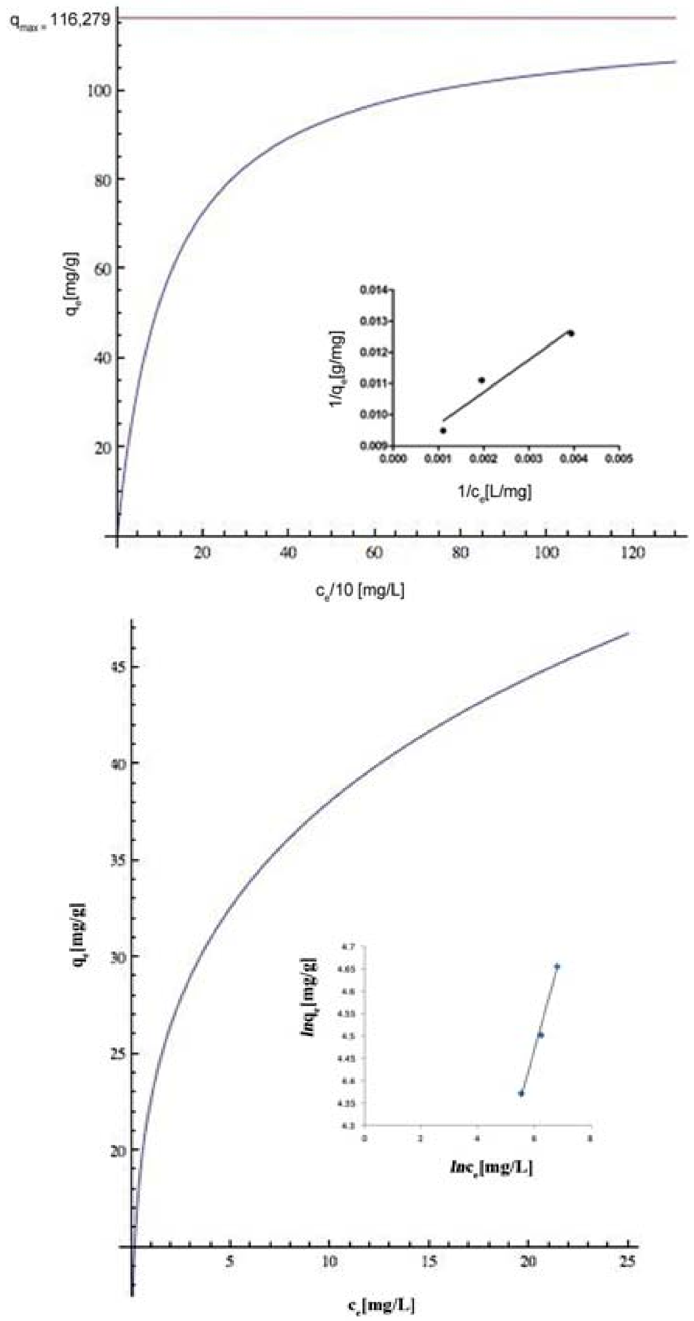

Fig. 5. Langmuir (upper panel) and Freundlich (lower panel) isotherms of U(VI) sorption on beeswax.

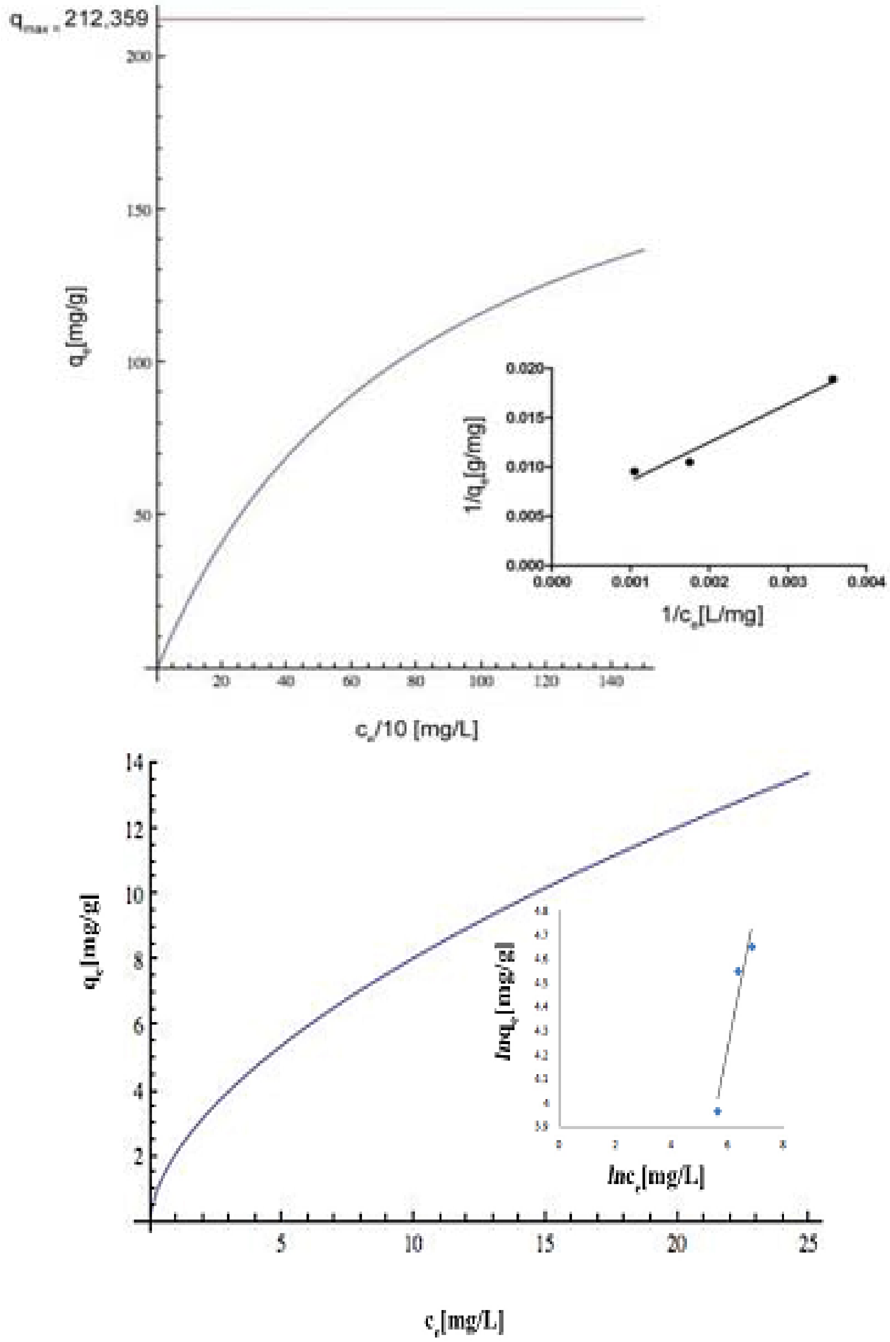

Fig. 6. Langmuir (lower panel) and Freundlich (lower panel) isotherms of U(VI) sorption on polypropylene wax.

The experimental data obtained, at an equilibrium time of 12 hours, at 25°C, under intermittent stirring, were processed for the identification of the type of isotherm to which U(VI) sorption on the three sorbents obeys.

The parameters of Langmuir and Freundlich isotherms for the three sorption systems are comparatively centralized in Table 1.

A comparison between the results obtained on linearization according to the pattern of Langmuir isotherm with those attained on linearization according to the Freundlich model shows that, for beeswax sorbent, a better superposition is observed in the case of Langmuir isotherm while, for the systems with paraffin wax and polypropylene wax as sorbents, a better superposition occurs in the case of Freundlich isotherm.

The values of the coefficient of linear regression (R^2) also show that the model of Langmuir isotherm is best superposed on the experimental data of the system with sorbent beeswax, while the model of Freundlich isotherm is best superposed on the experimental data of the systems with paraffin wax and polypropylene wax as sorbents.

The values of the separation factor $\mathbf{R_L}$ and of constant **b,** calculated from the linearized form of Langmuir isotherm, as well as the values of constants $\mathbf{K_F}$ and **n,** calculated from the linearized form of Freundlich isotherms, indicate that, in the three systems, sorption is favourable and reversible due to the bonding affinity of the sorbent sites to U(VI).

Table 1

Parameters of Langmuir and Freundlich isotherms for U(VI) sorption on the wax-type sorbents under analysis

Sorbent / T=298 K	Langmuir parameters					Freundlich parameters		
	K_L (L.g^{-1})	q_{max} (mg.g^{-1})	b (L.mg^{-1})	R_L	R^2	K_F (L.g^{-1})	n	R^2
Beeswax	8.34	116.279	0.071	0.0137	0.9411	22.739	4.46	0.9885
Paraffin wax	19.08	115.647	0.164	0.0060	0.8895	55.456	9.83	0.9342
Polypropylene wax	24.87	212.359	0.117	0.0084	0.9683	2.127	1.72	0.9184

The FTIR spectra plotted in Figs. 7 and 8 show that sorption on beeswax represents a complex chemisorption process involving cationic exchange and complexation, combined with physical adsorption while, for the rest of the systems, it is only a physical adsorption developed at surface and, possibly, in the superficial layers.

Chemosorption on beeswax is determined/induced by the presence – in the sorbent – of polyfunctional natural compounds with COOH; -OH (alcoholic and phenolic); >C=O; -CH=O; -COOR; -NH_2; >C=N-OH groups etc., which may form heterocycles of 5-6 atoms with the UO_2^{2+} ion – namely, complex stable combinations. Out of the natural compounds present in beeswax, (special) mention should be made of those capable of forming stable complex combinations with UO_2^{2+}: the citric, lactic, pyruvic, pyroglutamic, malic, mandelic acids; lactones (cyclic esters); aminoacids and proteins; oximes, enzymes; pigments.

In this respect, the literature of the field provides data on: HPLC determination of U(VI), with the mandelic acid as a complexation reactive (Jaison et al., 2011); U(VI) separation with poly(amidoamines) and poly(propyleneimines) as chelating agents (Mamadou et al., 2008); U(VI) extraction from aqueous solutions with chelating agents of the HCMAOX and HCMBOX oximes (Punita and Bharadwaj, 2012) and ortho-aminophenol type (Raileanu and Grigoriu, 2012).

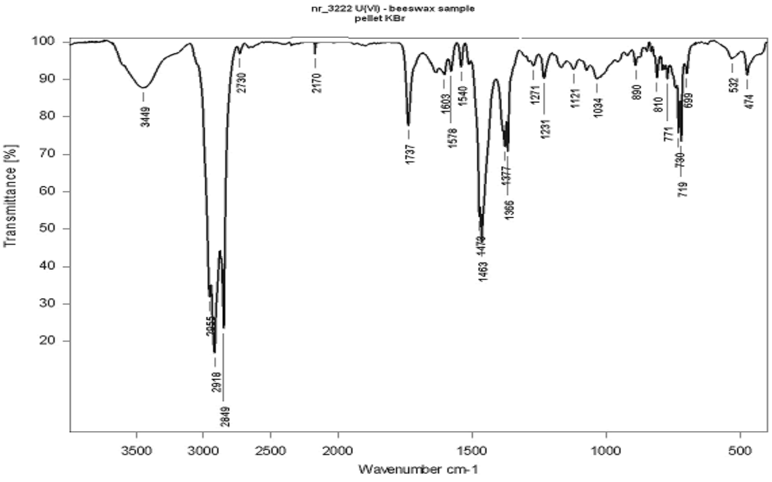

Fig. 7. The IR spectra of uranium’s compound with beeswax.

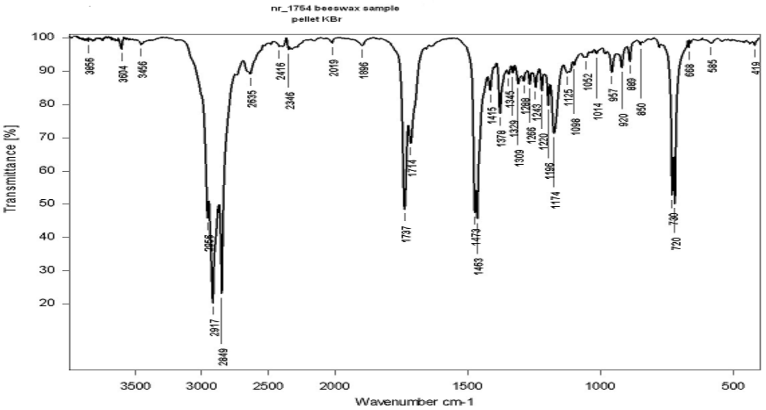

Fig. 8. The IR spectra of beeswax.

To assess and complete the data obtained in the distribution study with other data, referring to the structure of some possible complexes formed during sorption with the compounds of sorbent beeswax, after sorption, the sorbent was isolated and studied in solid state.

The IR spectra of uranium's compound with beeswax and the IR spectra of beeswax was plotted in Figs. 7 and 8. An adsorption band may be observed at 950 cm^{-1}, attributed to the asymmetrical vibration specific to UO_2^{2+}, as well as a band at 414 cm^{-1} and another one at 533 cm^{-1}, specific to U-N, the 669 cm^{-1} band specific to the U-O from the complex, and the 1214 cm^{-1} band specific to the C-O-U from the complex.

A comparison between our data and those offered in the literature on the analogous complexes of the uranyl ion (Raileanu and Grigoriu, 2012; Jaison et al., 2011; Mamadou et al., 2008; Punita and Bharadway, 2012) permits the conclusion that the N and O atoms bound to either U(VI) or U(IV) form chelatic cycles of 5 atoms, and that the O atoms from the neutral ligands are placed in the equatorial plane, occupying the corners of a pentagon. The linear uranyl group occurs perpendicularly to the equatorial plane.

CONCLUSIONS

The high affinity of the beeswax, paraffin wax and polypropylene wax sorbents for U(VI) indicate a high sorption ratio and a high stability rate of sorption equilibrium. The present study recommends the utilization of natural and synthetic waxes for eliminating U(VI) from ore solutions, and also for its separation/recovery from effluents.

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