



Thorium removal by different adsorbents

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Abstract

The removal of radiotoxic Th^{4+} from aqueous solutions has been explored using two different groups of adsorptive materials (e.g. two activated carbons and four zeolites—two natural and two synthetic). The activated carbons were prepared from solvent extracted olive pulp (SEOP) and olive stone (OS) by a two-step physical activation method with steam. They were characterized by N_2 at 77 K adsorption, Hg porosimetry and by determination of their iodine number. All carbons prepared are of the H-type (e.g. contain mainly basic surface oxides) confirmed by the results of the Boehm's method. The natural zeolites, clinoptilolite (NaCLI) and mordenite (NaMOR), were pretreated with Na^+ before the adsorption experiments, while the synthetic ones, NaX and NaA, were provided in their commercial sodium form.

The natural zeolites, NaCLI and NaMOR, utilized 11.5 and 38.6% of the theoretical ion-exchange capacity, based on Al content, respectively, while NaX and NaA utilized 41.5 and 45.9%, respectively. The activated carbons showed better removal capability than NaCLI. NaMOR, showed comparable results to the carbon originated from OS, but lower removal capability than the carbon originated from SEOP. The synthetic zeolites showed the highest removal ability for thorium ions due to their increased ion-exchange capacity because of their cleaner and larger framework channels and their higher number of ion-exchange sites. The carbons adsorption capacity mainly depends on the content and nature of functional surface groups. The adsorption data were fitted to Langmuir and Freundlich models. The former achieved best fits and was further applied to obtain the respective Langmuir constant and maximum adsorption capacity for each system.

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1. Introduction

Since the last century, thorium has been extensively used in a variety of applications [1–3]. These applications produce various gaseous, liquid and solid wastes containing isotopes of uranium, thorium and the daughter ions of Rn, Po, Bi, Ra. Liquid wastes are freed into the surface or the underground waters of mines. Solid and liquid wastes are also produced during nuclear fuel production. Direct toxicity of thorium is low due to its stability at ambient temperatures, however thorium fine powder is self-ignitable to thorium oxide [3]. When thorium nitrate enters living organisms it is mainly localized in liver, spleen and marrow and it precipitates in a hydroxide form.

Zeolites are crystalline aluminosilicates from natural or synthetic source. Their structure consists of SiO_4 and AlO_4 tetrahedra arranged so that each oxygen atom is shared between two tetrahedra. Because aluminum has one less positive charge than silicon, the framework has a net negative charge of one at the site of each aluminum atom and is balanced by the exchangeable cation. Pore structures are well defined within crystalline zeolites; however, their pore diameters are mainly limited to the micropore region. The microporosity and relatively high surface area of zeolites are utilized extensively in applications as ion exchangers, adsorbents, catalysts and separation media.

Activated carbons are unique adsorbents because of their extended surface area, microporous structure, high adsorption capacity and high degree of surface reactivity. They have the ability to adsorb ionic species and the nature of this process is largely governed by electrostatic attraction or repulsion (e.g. ion exchange). In the case where electrostatic interaction cannot explain the adsorption mechanism, the role of specific interactions (e.g. complex formation) or even non-specific van der Waals interactions (dispersive forces) become reasonable alternatives [4,5]. A number of parameters such as specific ion properties, the kind and the concentration of adsorbent surface groups as well as its point of zero charge (pH_{pzc}) and the pH of the solution affect the nature of the ion adsorption process [4]. For the adsorption process the chemical nature of the carbon surface might be more important than its surface area and porosity [5,6].

The solvent extracted olive pulp (SEOP) is an abundant precursor resulting from the kernel-oil processing [5–8] and can be readily used for the preparation of activated carbons due to its lignocellulosic structure.

Although a lot of work has been carried out during the last decades on the removal of metal ions by various adsorbents such as activated carbons and zeolites, there is limited published work on the removal of thorium from contaminated environments [9,10].

The objective of this work was to investigate the ability of activated carbons, originated from agricultural byproducts, for thorium removal from aqueous solution and compare it with the removal ability of natural and synthetic zeolites.

2. Experimental

2.1. Sample preparation

The activated carbons used in this study were prepared by the carbonization (850°C , heating rate $10^\circ\text{C}/\text{min}$, residence time 1.5 h) of solvent extracted olive pulp and olive

stone (carbons ACOP and ACO, respectively) followed by activation with a steam/nitrogen mixture (flow rate 100 ml/min, pure steam 4.5 l/h) until 18% burn-off (BO) for carbon ACOP and 28% BO for carbon ACO (800 °C, heating rate 10 °C/min). A horizontal furnace with a stainless steel tube was used for this purpose.

In all cases a portion of 4–7 g of sample was placed in a quartz boat within the furnace for the activation process [11]. The carbons used were moderately activated (low burn-off) and the selection of these was made among a series of carbons with different degrees of burn-off, which have already been tested for their ability to remove Zn^{2+} from aqueous solutions [5]. The results revealed that the adsorption of these ion species, on carbon surfaces, is independent of the porosity development.

The natural zeolites, NaCLI (clinoptilolite) and NaMOR (mordenite) were of Greek origin. Both zeolites were converted into the sodium homoionic form using 1 M NaCl solution (10 g zeolite/150 ml solution) at 70 °C under stirring for 12 days. The NaCl solution was replaced daily [10]. X and A zeolites were commercial (Carlo Erba) synthetic zeolites of sodium form.

2.2. Samples characterization

Activated carbons were characterized by N_2 at 77 K adsorption performed with an Autosorb 1 surface area and pore size analyzer, by mercury porosimetry performed with an Autoscan 25 Quantachrom porosimeter and by determination of their iodine number [12]. The ash content of the carbons was obtained by burning 1 g of carbon in air at 700 °C for 3 h. Surface oxides and pH_{pzc} of carbons were measured using the Boehm's method [13] and mass titration method [5], respectively.

Zeolites were analyzed in terms of metal content [14]. The determination was repeated five times.

2.3. Adsorption experiments

All adsorption experiments were obtained without adjusting the pH, which however, varied within narrow limits (2.8–3.6 for zeolites and 2.8–3.2 for carbons). Before each adsorption experiment, carbons were dried overnight at 110 °C. Determination of thorium concentration was performed by titrating an aliquot of the filtrate with EDTA, using xylenol orange, as the indicator and $LiNO_3$ as salt-out agent for undertaking of Al in the case of zeolites [11].

All adsorption experiments were performed in three replicates and the average was used in all cases. Standard deviation never exceeded 5% for each replicate.

2.3.1. Reagents

Analytical grade reagents were used. Stock solutions of the test metal, were prepared by dilution of the corresponding hydrated nitrate salts in distilled water.

2.3.2. Adsorption

Kinetic studies of adsorption were performed with 0.01N $Th(NO_3)_4 \cdot 5H_2O$ solution. Known portions of the adsorbent were mixed with 50 ml solution and placed in a thermostat

shaker at $25 \pm 0.5^\circ\text{C}$ for different time intervals. The adsorbent was finally removed by filtration and thorium concentration was determined as mentioned above. The isotherms were obtained at 48 h equilibration, with the same process as in the case of kinetics by varying the concentration of thorium in the range of 0.001–0.1N.

3. Results and discussion

3.1. Sample characterization

3.1.1. Activated carbons

The textural characteristics of the activated carbons ACOP and ACO are given in details elsewhere [5]. ACO carbon had a higher surface area, more developed micropore (DR method) and mesopore volume, but lower macropore volume than ACOP carbon (Table 1). On the basis of pH_{pzc} , the two carbons were of the H type being more basic. The ACOP carbon had significantly higher basic groups and higher pH_{pzc} if compared to the ACO carbon (Table 2).

3.1.2. Zeolites

The chemical composition of zeolites, in terms of moles of metal oxide per moles of Al, is given in Table 3. The natural zeolites had a Si/Al ratio higher than 5 (NaCLI: 5.12 and NaMOR: 5.11), which indicated the presence of non-framework elements [15]. On the other hand, the synthetic zeolites had a low Si/Al ratio (NaX: 1.18 and NaA: 1.02). Co-existing ions in the framework of synthetic zeolites were due to the binding agents, while in natural ones are due to the precursors.

The ion-exchange capacity was determined as the equivalent amount of cations, which could be replaced from a zeolites framework, without changing its total charge. Theoretically, this refers to the aluminum of the framework. In synthetic zeolites, ion-exchange

Table 1
Physicochemical characteristics of activated carbons [5]

Sample	Ash content (%)	S_{BET}	S_{DR}	Iodine number (mg/g)	Pore volume (cm^3/g)			
					$V_{\text{micro}} (t\text{-meth})$	$V_{\text{micro}} (\text{DR})$	V_{meso}	V_{macro}
ACO	6.9	474	646	574	0.16	0.23	0.22	0.42
ACOP	6.5	364	511	478	0.16	0.18	0.07	0.55

Table 2
Surface groups and pH_{pzc} of activated carbons [5]

Carbon	Total acidity NaOH (meq./g)	Total basicity HCl (meq./g)	pH_{pzc}
ACOP	0.76	2.73	11
ACO	0.52	1.76	10.2

Table 3
Chemical composition of zeolites in terms of moles of metal oxides per moles of Al

Adsorbents	Composition
Natural zeolites	
NaCLI	0.715Na ₂ O, 0.256K ₂ O, 0.315CaO, Al ₂ O ₃ , 10.247SiO ₂ , 4.412H ₂ O
NaMOR	0.714Na ₂ O, 0.348K ₂ O, 0.470CaO, Al ₂ O ₃ , 10.217SiO ₂ , 4.5142H ₂ O
Synthetic zeolites	
NaA	0.676Na ₂ O, 0.071K ₂ O, Al ₂ O ₃ , 2.037SiO ₂ , 1.507H ₂ O
NaX	0.728Na ₂ O, 0.071K ₂ O, Al ₂ O ₃ , 2.367SiO ₂ , 1.506H ₂ O

capacity can be based on the Al content. However, in natural zeolites, the co-existing ions in the framework may contribute to the ion-exchange process. This fact is not in disagreement to the requirement for counteracting of total lattice charge since there is a cation distribution in the lattice so as to minimize the free energy of the system. Subsequently there might be a partial or total coverage of cationic sites. In all four zeolites the sites of ion exchange, as determined by the Al content, were not fully covered by Na⁺. Thus, for comparative purposes, the ion-exchange capacity of zeolites was expressed based on both Al and Na as milli-equivalent per gram zeolite, since Na⁺ was the main exchangeable cation in the natural zeolites (Fig. 1).

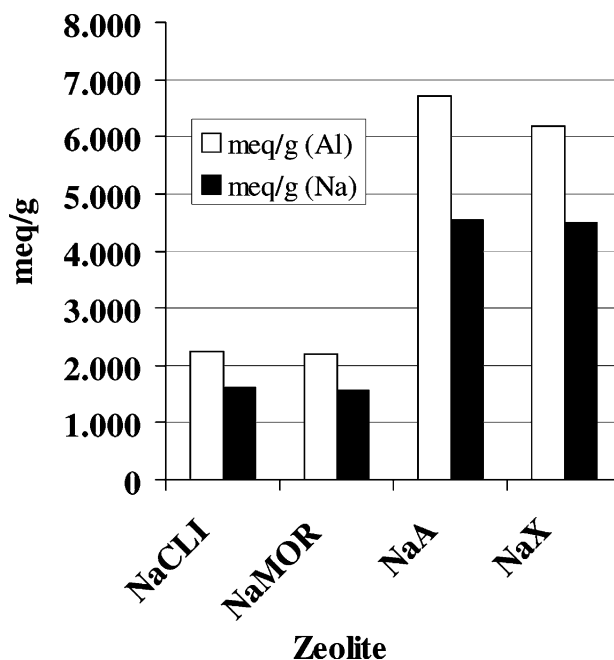


Fig. 1. Ion-exchange ability of zeolites based on Al and Na.

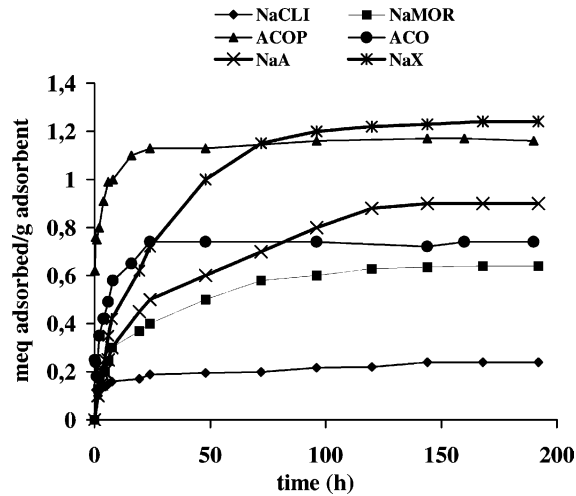


Fig. 2. Kinetics of thorium 0.01N adsorption for zeolites and activated carbons at $25 \pm 0.5^\circ\text{C}$.

3.2. Adsorption

3.2.1. Kinetics of adsorption

The kinetic curves for Th/zeolite and Th/carbon systems at $25 \pm 0.5^\circ\text{C}$, in 0.01N solution concentration, are given in Fig. 2. From these curves, the distribution coefficient k_d was estimated:

$$k_d = \frac{rV}{(100 - r)m} \quad (1)$$

where r is the percentage removal of Th, V the volume of solution and m is the weight of adsorbent.

The distribution coefficient k_d expresses the ratio of thorium in the solid phase over that in the liquid phase. It defines the selectivity of the adsorbents towards the radioactive element [16] and is depended on the ratio V/m . Changes in the ratio V/m affect the removal of thorium from solution and subsequently k_d values.

Other researchers [11,17] used simplified models described by Fick's 1st law. Studies on the distribution coefficient do not, in any case, substitute these attempts. However, it was chosen as a measure of the selectivity of zeolites and carbons and agrees quite well with the experimental data.

The respective values for all systems used were given in Table 4. The higher the maximum adsorption, expressed as percentage removal r , the greater the adsorption coefficient value (Table 4). The exchange capacity of zeolites on the basis of Al and Na content, along with the initial solution concentration, were given in Table 5. It was obvious that all zeolites did not reach their maximum ion-exchange capacity. This might be attributed to the reduced zeolites preference for Th^{4+} due to the steric effects.

Thorium removal, as indicated by k_d values (Table 4), was achieved to a higher extent by the synthetic zeolite NaX and by the SEOP activated carbon. ACO and mordenite

Table 4
Distribution coefficients and Lagergren constants of thorium removal for carbons and zeolites^a ($V/m = 167$ ml/g)

Adsorbents	K_{ads} (min^{-1})	r (%)	k_d (ml/g)
Activated carbons			
ACO	0.0023	42.5	123.4
ACOP	0.0039	70.3	395.3
Zeolites			
NaCLI	0.0061	14.55	28.50
NaMOR	0.0018	37.65	101.0
NaA	0.0250	50.39	169.3
NaX	0.0370	71.15	411.0

^a At temperature 25 ± 0.5 °C and 0.01N thorium nitrate solutions.

followed in this rank while the clinoptilolite had the lower removal capability. Comparing the synthetic zeolites, NaX showed higher values of percentage removal, coverage of the theoretical potential, percentage sodium replacement and binding rate than NaA. Although the natural zeolites had similar theoretical exchange capacities, the nature of the zeolite had a marked effect in Th^{4+} removal, leading to mordenite having higher exchange capacity than clinoptilolite. The selectivity of the six adsorbents based on k_d values followed the order:

$$\text{NaCLI} < \text{NaMOR} < \text{ACO} < \text{NaA} < \text{ACOP} < \text{NaX}$$

The higher distribution coefficient, k_d , number implied a higher selectivity or adsorption for synthetic zeolites and SEOP carbon, respectively.

Additionally the kinetic data was treated with the following first-rate Lagergren equation [18] (Fig. 3):

$$\log(q_e - q_{\text{ads}}) = \frac{1}{2.303} \log q_e - (K_{\text{ads}} t) \quad (2)$$

where q_e and q_{ads} are the amount of total thorium adsorbed per gram of adsorbent at the equilibrium and at any time t , respectively, and K_{ads} is the adsorption rate constant.

Table 5
Thorium removal for the kinetic experiments^a

Adsorbents	Thorium removal (meq./g)	r^b (%)	r^c (%)	r^d (%)
Zeolites				
NaCLI	0.25	10.92	15.27	14.55
NaMOR	0.64	28.80	40.00	37.65
NaA	0.85	12.67	18.75	50.40
NaX	1.20	19.42	26.70	71.15
Activated carbons				
ACOP	–	–	–	70.30
ACO	–	–	–	42.5

^a At temperature 25 ± 0.5 °C and 0.01N thorium nitrate solutions.

^b Percentage removal based on Al.

^c Percentage removal based on Na.

^d Percentage removal based on the concentration of the initial solution.

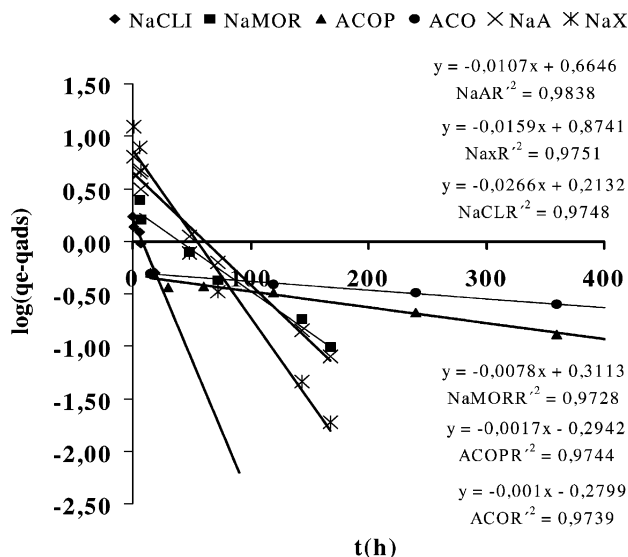


Fig. 3. Lagergren plots of thorium adsorption for zeolites and activated carbons.

All systems used attain satisfactory fit to the model. The K_{ads} values are given in Table 4. The adsorption rate constant increases irrespectively to the maximum adsorption q_e since it is related to the first stages of the adsorption process [7].

3.2.2. Adsorption isotherms

The adsorption isotherms of Th^{4+} at $25 \pm 0.5^\circ\text{C}$ for all systems used were obtained in an attempt to get a more thorough insight to the adsorption mechanism of thorium onto the activated carbons and the zeolites. The isotherms for carbon/Th and zeolite/Th systems were given in Fig. 4. They were both classified as H_2 isotherms showing a high affinity, commencing at a positive value [19]. This is a special case of the L curves of Giles' classification, in which the solution has such a high affinity for the solute that in dilute solutions it is, completely, adsorbed resulting in a vertical initial part of the isotherm. The H_2 isotherm has been appeared for single ions, which either exchange with others of much lower affinity or adsorbed by ion attraction or even chemisorbed. The activation energy E_A for lifting a molecule already adsorbed on the surface is quite high so that dy/dC_A (where y is the amount of substance in the adsorbed monolayer and C_A is the solute concentration) has a very high value. The shape of the isotherms of Th^{4+} removal for zeolite/thorium systems indicates that there is selectivity for the zeolites towards the incoming ion compared to the ions already bind in its lattice. In other words the zeolites favored the replacement of its ions (especially Na) by the solute (Th^{4+}).

Data obtained from adsorption isotherms was fitted to linearized forms of Freundlich, Eq. (3) and Langmuir, Eq. (4) [20–22]:

$$\ln C_{\text{ads}} = \ln k + n \ln C_e \quad (3)$$

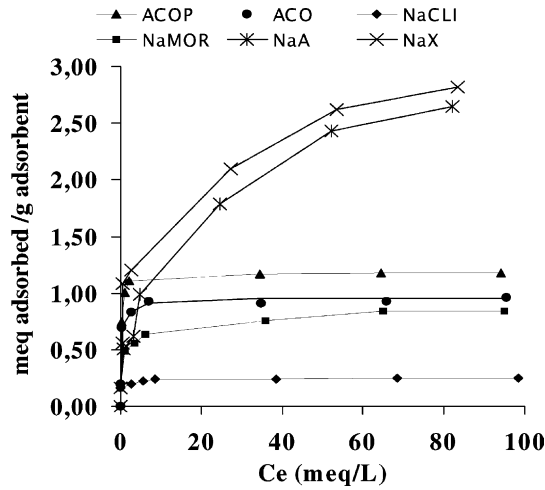


Fig. 4. Adsorption isotherms of thorium for zeolites and activated carbons at 25 ± 0.5 °C.

$$\frac{C_e}{C_{ads}} = \frac{1}{k C_{max}} + \frac{C_e}{C_{max}} \tag{4}$$

where C_{ads} is the amount adsorbed per gram of adsorbent, C_e the adsorbate equilibrium concentration, k and n the isotherm constants (k differs for each model) and C_{max} is the maximum amount adsorbed per gram of adsorbent.

The Langmuir model assumes that the energy of adsorption is the same for all surface sites and not dependent on the degree of coverage indicating monolayer adsorption of the adsorbate. The Freundlich model assumes that the frequency of sites associated with free energy of adsorption decrease exponentially with increasing free energy and that the energy of adsorption may vary because real surfaces are heterogeneous.

The calculated correlation coefficients, R' , for each model (Table 6) indicated that best fits were achieved for Langmuir model. The Langmuir isotherms for activated carbons and

Table 6
Adsorption isotherm coefficients for each model applied

Adsorbents	Correlation coefficient (R'^2)	
	Langmuir	Freundlich
Activated carbons		
ACO	0.999	0.643
ACOP	0.998	0.935
Zeolites		
NaCLI	0.999	0.937
NaMOR	0.996	0.956
NaA	0.979	0.958
NaX	0.990	0.953

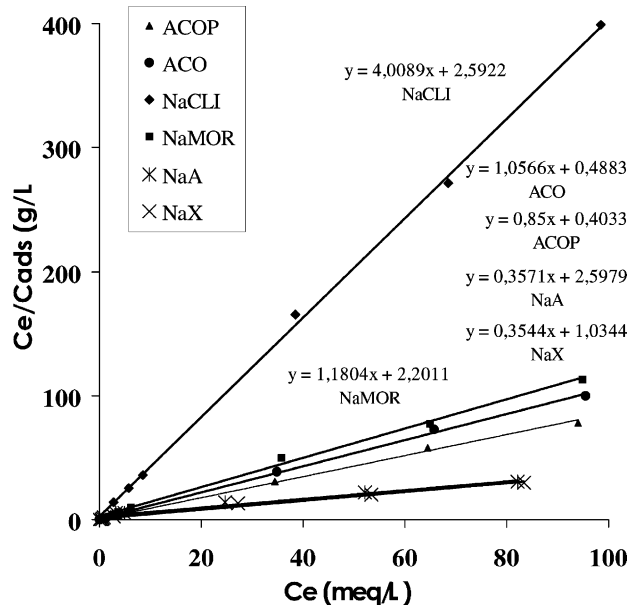


Fig. 5. Langmuir plots of thorium adsorption for zeolites and activated carbons.

zeolites are given in Fig. 5. The values of maximum adsorption and Langmuir constants were calculated by the slope and intercept of Langmuir equations (Table 7).

The results of Langmuir analysis indicated that the maximum adsorption for all six materials follow the order:

$$\text{NaCLI} < \text{NaMOR} < \text{ACO} < \text{ACOP} < \text{NaA} < \text{NaX}$$

The synthetic zeolites (Table 7, Fig. 5) removed higher quantities of thorium because of their cleaner and larger framework channels and their higher number of ion-exchange sites.

The activated carbons showed much higher adsorption than the natural zeolite NaCLI (Fig. 4). An important factor, controlling the acid–base behavior of surface oxides and the

Table 7
Langmuir constants and maximum adsorption for Th^{4+} by activated carbons and zeolites

Adsorbents	C_{max} (meq./g)	k (l/g)
Activated carbons		
ACO	0.95	2.15
ACOP	1.18	2.11
Zeolites		
NaCLI	0.25	1.54
NaMOR	0.85	0.54
NaA	2.82	0.14
NaX	2.80	0.34

activity of delocalized π -electron system of graphene layers of activated carbons, was the pH of the solution. Depending on their pK_a values, surface oxide might act either as acids or as bases, affecting the mechanism of adsorption of metal ions on carbon surfaces [23]. As shown in another work [5], ACO carbon gave lower adsorption values for zinc than ACOP although it had a more developed porosity and a higher surface area. The basicity of ACO and ACOP activated carbons, which had high pH_{pzc} (Table 2) and consequently low [O] content [24], arised from their ability to form EDA complex. ACOP carbon had a higher number of basic groups than ACO (Table 1) and this might be the reason for its higher removal capability [5]. The significant amount of the metal removal observed, might be attributed mainly to the EDA complexation between the cations and the delocalized π -electron system of activated carbons graphene layers by dispersive forces [4,5].

In other words the surface chemistry of carbon and the pH of the solution were the key factors in the adsorption of metal ions from aqueous solutions and might be able to control the adsorption process in a higher extent than the pore size distribution. In addition both carbons had a considerable amount of ash (Table 1) that might enhanced the adsorption of cations via ion exchange [25].

Comparing the kinetic data shown in Table 4 with the isotherm adsorption data, an alteration in the adsorption order for the synthetic zeolite NaA and the carbon ACOP was observed. This would be attributed to the high ion-exchange affinity of the zeolites while regarding the carbons there might be a saturation of the active sites of adsorption preventing from further adsorption at higher concentration values.

Comparison of synthetic zeolites and activated carbons indicated that the zeolites had a higher selectivity for Th^{4+} removal. Additionally since both synthetic zeolites and activated carbons undergo a certain process to get into the final form, the cost-effectiveness of using each of these groups of adsorbents is also related to the economics of their production.

Comparison of activated carbons to the natural zeolites should be made on the basis of the raw material (olive stone and solvent extracted olive pulp before the carbonization/activation process). Taking into account the yield of the latter processes for each carbon (Table 1) the maximum adsorption for each carbon lowered down to 0.27 meq./g raw material for ACOP and 0.21 meq./g raw material for ACO. However, carbon raw material was readily used while the recovery of natural zeolites required a certain cost so as the economics of using each group of materials is under investigation.

4. Conclusions

Activated carbons prepared from agricultural wastes (solvent extracted olive pulp, olive stone) had satisfactory removal ability for radiotoxic thorium. Although both carbons were moderately activated, they adsorb effectively thorium ion. The higher maximum adsorption of ACOP carbon compared to the activated carbon prepared from olive stone might be attributed to its higher number of basic groups.

The adsorption capacity of these activated carbons for thorium was higher than the ion-exchange capacity of natural zeolite NaCLI. NaMOR, showed comparable results to the carbon originated from OS, but lower removal capability than the carbon originated from SEOP. Although the natural zeolites had comparable Si/Al ratio and theoretical exchange

capacity, they showed significant variation in the removal of thorium. The latter might be attributed to their different origin (impurities, different structure).

At higher concentration values of Th^{4+} , NaX and NaA showed a significantly increased adsorption, due to their cleaner and larger framework channels and their higher number of ion-exchange sites. Furthermore, the low Si/Al ratio of the synthetic zeolites favored the Th^{4+} exchange process.

However, at low concentration values of Th^{4+} , the SEOP activated carbon and the synthetic zeolites have similar removal capacities.

Consequently, low-cost moderate activated carbons, originated from inexpensive agricultural wastes (SEOP), could be more preferable than the synthetic zeolites in Th^{4+} removal from aqueous solutions at low concentrations values, and better than the natural zeolites NaMOR, NaCLI over the whole concentration range.

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