Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.937757

55 (2015) 2209–2220
August

Taylor & Francis
Taylor & Francis Group

Adsorption of uranium in the presence of different ions, humic acid and effect of thorium on uranium adsorption by activated carbon

S.M. Yakout[a,b,*], A.A. Abdeltawab[c,d]

[a]*Biochemistry Department, College of Science, King Saud University, PO Box 2455, Riyadh 11451, Kingdom of Saudi Arabia, Tel. +966558448693; Fax: +96614675931; email: sobhy.yakout@gmail.com (S.M. Yakout)*
[b]*Hot Laboratories Center, Atomic Energy Authority, PO Box 13759, Cairo, Egypt*
[c]*Chemistry Department, College of Science, King Saud University, PO Box 2455, Riyadh 11451, Kingdom of Saudi Arabia*
[d]*Chemical Engineering Department, Tabbin Institute for Metallurgical Studies, Cairo 11413, Egypt*

Received 27 December 2013; Accepted 25 May 2014

ABSTRACT

In this study, rice straw-based carbon was prepared and then modified by two acidic and basic oxidizing agents. One oxidized by HNO_3, labeled as RSN, and other oxidized by KOH labeled as RSK. The modified carbons (RSN and RSK) were tested in two single-component systems: Removal of U(VI) using RSK and Th(IV) using RSN. Factors affecting U(VI) in three multi-component systems were examined: (i) Co-existing anions and cations, (ii) co-existing Th(IV), and (iii) presence of humic acid (HA). In this concern, different cations under investigation have marginal effect on the adsorption of uranium, except in case of iron ion. Co-existing of iron ions at high levels may compete strongly for the adsorption sites with uranium ions, resulting in a substantial reduction of uranium removal. The prepared carbon showed good selectivity in extracting uranium even in the presence of relatively high concentrations (100 mg/l) of anionic complexing agents and common electrolyte species. In case of multi-component system U(VI)/Th(IV), the capacity of each metal was reduced due to the competition between two ions for sorption sites on carbon surface. In presence of HA, the metal–humic interactions play a very important role in determining the extent of adsorption. It is concluded that multi-species adsorption can be significantly affected by adsorbate interactions and the understanding of these interactions needs great attention in adsorption study in the future.

Keywords: Humic acid; Uranium; Thorium; Activated carbon; Wastewater treatment

1. Introduction

Uranium and thorium are elements of considerable technological importance. For this reason, the recovery, concentration, and purification of uranium and thorium are of great importance. Because of the expected shortage of uranium and thorium in near future, further researches are to be directed to the recovery of uranium from nonconventional resources, such as natural waters, sea water, industrial wastewaters, mine wastewater, and other waste sources in relation to the pollution of the natural environment [1].

The preconcentration and separation procedures by adsorption are important in nuclear and radiation

---

*Corresponding author.

chemistry, industry, medicine, and daily life [2]. Interest in the adsorption of metal ions for recovery purposes has increased manifold in recent years, because of its simplicity, selectivity, and efficiency [3].

Many works have been published on the adsorption of various radioisotopes from aqueous solutions on different adsorbents. Among the numerous adsorbents, activated carbon is one of the most widely used and economic adsorbent in the separation and purification. Furthermore, high chemical radiation and thermal stability, rigid porous structure, and mechanical strength gave activated carbon considerable advantages over polymeric materials [4].

Adsorption of uranium onto various solids is important for purification, environmental, and radioactive waste disposal [2–4].

The presence of a single heavy metal in natural water and wastewater is a rare situation [5]. Industrial application of sorption process must deal with the fact that metal-bearing waste effluents often contain other innocuous ions that may interfere in the uptake of the heavy metal ions of interest. Multi-component competitive interactions in solution with the sorbent material are amongst the basic factors affecting the degree of metal removal by sorption. With the help of multi-component sorption studies, these complex systems and their behavior will be better understood.

Another major constituents commonly present in water that require removal are humic substances, such as humic acids (HAs) and fulvic acids, which are known to influence the speciation and thus, the mobility of radionuclides in the environment due to their strong complexing ability [6,7]. Therefore, basic knowledge of the interaction of humic substances with metal ions is required.

This paper presents data and discussion regarding the adsorption capacity of uranium and thorium using activated carbons, prepared from locally available rice straw, from aqueous solution in single-component systems. In this concern, the effects of common cations and anions on uranium uptake have been studied. Moreover, the competitive studies were focused on the effects of HA during U(VI) and Th(IV) sorption in multi-component systems. The mechanisms of sorption process and adsorbates multi-species effect were discussed.

2. Materials and methods

2.1. Chemical and reagents

All chemicals used in this study were prepared from analytical reagent grade chemicals. Reagent water was used for all solution preparation. Stock solutions (1,000 mg/l) of Uranium and thorium were prepared by dissolving 2.10 g of uranyl nitrate (BDH) and 2.46 g thorium nitrate (Merck) in 1 l distilled deionized water acidified by 2 ml nitric acid to prevent the hydrolysis. Various standard solutions were obtained by diluting stock solution with the addition of distilled deionized water daily as required. The stock solution of HA, (Fluka) was prepared by dissolving the required amount of HA (sodium salt) in a least amount of bi-distilled water, then transferred to 100 ml volumetric flask, and completed to the mark with bi-distilled water.

2.2. Preparation of activated carbon

Activated carbon was prepared by steam pyrolysis; briefly, 0.5 kg dried rice straw was fed into fluidized bed reactor, described elsewhere [8], at a heating rate 50°C/10 min in the presence of N_2 flow (300 ml/min). The steam entered the reactor at a rate of 5 ml/min. when the furnace reached 350°C, and the heating continued up to final temperature of 550°C. The hold time was 1 h and then, the furnace was switched off. The produced carbon was oxidized using HNO_3 and KOH to produce modified carbons according to the procedures described earlier [9,10] and denoted as RSN and RSK, respectively. The oxidization of activated carbon with HNO_3 and KOH can offer more hydrophilic surface structure and introduce adsorption oxygen-containing functional groups to the surface of carbon. These functional groups provide binding sites. The main physicochemical characteristics of oxidized and nonoxidized carbons were reported in detail in our earlier work [11]. The surface area of RSN and RSK was measured using N_2-BET method and found to be 87.2 and 143.3 m^2/g, respectively.

2.3. Batch adsorption experiments

Batch sorption studies were performed to obtain both rate and equilibrium data. A known amount of RSK and RSN was added to 10 ml of U or Th solution followed by agitation for 3 h at 25°C. This time period was determined on the basis of preliminary studies and was found to be sufficient for the equilibrium uptake of metal ions [12]. After this period, the solution was filtered using a Whatman No. 42 filter paper and analyzed for the concentration of the metal ions remaining in the solution. Blank tests were performed without activated carbon to confirm that precipitation had not occurred during the period of investigation. The adsorption isotherms for multi-component systems were obtained at pH 4.5–5.0. This range is between the optimum adsorption pH for thorium (pH 4) and that for uranium (pH 5.5).

Sorption capacity of adsorbent was calculated by Eq. (1):

$$q_e = \frac{V(C_o - C_e)}{M} \tag{1}$$

Sorption efficiency based on the percentage of metal removal was calculated by Eq. (2):

$$R\% = \frac{C_o - C_e}{C_o} \times 100 \tag{2}$$

where C_o and C_e are the initial and equilibrium concentrations of metal ion (mg/l), respectively, M is the mass of dry carbon sample used (g), and V is the volume of the solution (ml).

2.4. Interference studies on uranium sorption

2.4.1. With cations and anions

Uranium sorption in the presence of other cations was tested in metallic combinations; 10 ml of 100 mg/l U(VI) with 10 ml of 10 or 100 mg/l concentration of each cation was mixed with 10 mg of RSK. Cations used were Na^+, K^+, Li^+, Ca^{2+}, Mg^{2+}, and Fe^{3+} (taken as chloride salts). For anionic interference, the adsorbent was placed in solutions containing equal quantities of uranium and the particular anions as their sodium salts (100 mg/l). The anions used are Cl^-, CO_3^{2-}, HCO_3^-, SO_4^{2-}, $S_2O_3^{2-}$, OH^-, NO_3^-, S^{2-}, and PO_4^{3-}.

2.4.2. Adsorption with HA

In order to gain better insight on the effect of HA on sorption capacity of uranium and thorium, three types of experiments were performed; (i) single HA species adsorption isotherm with fresh sorbent. The HA adsorption isotherm was conducted by the same procedure for metal adsorption isotherm with contact time 48 h, (ii) sequential adsorption of metal and HA (first HA adsorbed before metal ions are added), and (iii) simultaneous co-adsorption of metal ion and HA with clean sorbent (mixing HA with the solution that contains metal ions before the carbon is added. In (ii) and (iii), the same procedures described above were carried out using 100 mg/l HA solution instead of distilled water.

2.5. Analytical measurements

The concentrations of U(VI) and Th(IV) in the sample solutions were determined by measuring absorbance at 665 and 655 nm with Shimadzu model 160A double-beam UV spectrophotometer using Arsenazo III as color-producing reagent [13]. The concentration of uranium and thorium in mixture was determined by Arsenazo I method [14]. In this method, thorium forms a complex with Arsenazo I at $\lambda = 565$ nm, when pH of the solution is within the range 1.0–2.3 while uranium does not interfere with thorium at this pH. Otherwise, both uranium and thorium complexes exhibit strong absorbance at 596 nm within a pH range 8.0–9.0. The HA samples were analyzed at $\lambda = 420$ nm.

3. Results and discussion

Modification of the surface chemistry of porous carbons might be a viable attractive route towards novel applications of these materials. Surface area of our prepared carbon was lower than that of the commercial carbons. Therefore, surface modification was conducted for these carbons to obtain the highest adsorption capacity. The main physicochemical characteristics of RSK and RSN carbon were given in Table 1. The high-ash contents of RSK carbon (50%) and RSN carbon (54.1) can be explained by consumption of a considerable amount of carbon during activation which leads to high specific mineral content, especially its richness in silica. The results in Table 1 show the co-existence of acidic and basic surface sites in RSK and RSN carbon that indicate its amphoteric behavior. KOH oxidation increases the surface area on opposing of HNO_3 oxidation that decreases the surface area. It has been reported that metals, specially potassium, may be intercalated to the carbon matrix, resulting in increase in pore volume and alkali that might catalyze this process [15]. The potassium hydroxide is reduced by the carbon producing potassium metal which is removed by washing [16]:

Table 1
Characterization of prepared RS, and modified RSK and RSN carbons

Parameter	RS	RSK	RSN
S_{BET} (m^2/g)	71.35	143.3	87.2
Total pore volume (cc/g)	0.055	0.175	0.118
Pore volume fraction			
Micro-	0.55	0.25	0.18
Meso-	0.45	0.75	0.82
Pore radius (nm)	1.55	2.45	2.7
Basicity (meq/g)	6.22	10.1	2.79
Acidity (meq/g)	10.1	5.95	8.93
pH_{pzc}	9.2	10.25	3.23
Ash content (%)	49.0	50.5	54.1

$4KOH + C \leftrightarrow 4K + CO_2 + 2H_2O_2.$

Surface area reduction in case of HNO_3 may be due to presence of large amount of oxygen-functional groups located at the entrance of the pores, which hinder nitrogen molecules to go inside the pores [17]. It is clear that both RSK and RSN carbon has more mesopores than micropores. Mesopores volume is three and four times greater than micropores volume for RSK and RSN, respectively. This is good for our carbon as it was reported that the carbon mesopores enhanced its adsorption capacity for metals [18].

The full details of single-component adsorption of uranium and thorium on activated carbons RSK and RSN were described in our previous work [11]. In this concern, RSK was determined to be superior in removal of uranium while RSN for thorium than non-oxidized carbon. Uranium removal by RSK carbon showed that adsorption was maximum was pH 5.5 and equilibrium time of 40 min. with equilibrium adsorption capacity 100 mg/g. whereas thorium removal by RSN carbon maximum was at pH 4 and equilibrium time of 100 min. with equilibrium adsorption capacity 71 mg/g. The values of adsorption capacity for the removal of U(VI) were reported to be 58.43 mg/g onto mesoporous silica [19], 18.72 mg/g onto diarylazobisphenol modified carbon [20], 28.49 mg/g onto modified carbon [21], and 28.30 mg/g onto activated carbon [22]. On the other hand, for Th(IV), the values of adsorption capacity were 5.72×10^{-2} mg/g onto carbon nanotube [23], 1.1 mg/g onto olive pulp AC [24], 9.3 mg/g onto mangrove endophytic fungus biomass [25], 22 mg/g for Aspergillus niger biomass [26]. Therefore, it was clear that RSK and RSN carbon is more effective for this purpose. The efficiency of the RSK and RSN for the removal of uranium and thorium in the treatment of industrial or natural water is affected by the presence of various chemical species. As a continuation of this work, this study focused on U(VI) and Th(IV) adsorption in the presence of other competitive ions and HA.

3.1. Influence of co-existing cations

The effect of various cations such as Na^+, K^+, Li^+, Ca^{2+}, Mg^{2+}, and Fe^{3+} (taken as chlorides) on the adsorption of uranium onto RSK has been examined. The results of co-existing cations at two different initial concentrations (10; 100 mg/l) upon the removal percentage of uranium ($C_o = 100$ mg/l) is illustrated in Table 2.

Table 2
Effect of different cations (10 and 100 ppm) on uranium adsorption using RSK

Metal	Adsorption % at 10 mg/l	Adsorption % at 100 ppm
Nil[a]	84.2	84.2
Na^+	78.0	63.7
K^+	83.0	84.2
Li^+	77.8	85.7
Ca^{2+}	80.5	82.1
Mg^{2+}	82.2	79.8
Fe^{3+}	77.1	20.0

[a] Nil means no cation or anions present in the solution other than uranium.

It is obvious from Table 2 that the effect of different cations under investigation on the adsorption of uranium, in both lower and higher concentration, was marginal except in case of iron ion where the adsorption was significantly depressed by the addition iron ion (*R*% was 20% at 100 mg/l of iron). Muzzarelli and Tubertini showed that K^+, Na^+, and Mg^{2+} ions did not interfere with the removal of many metal ions from their solutions by chitin [27]. Hsi found that Ca^{2+} and Mg^{2+} at 10^{-3} M did not significantly affect uranyl adsorption onto ferric oxy hydroxides [28].

These results show that RSK has much higher relative affinity for uranium metal ions than for the light metal ions studied. RSK has low value of acidic groups, such as carboxyl, hydroxyl, and carbonyl [11] to which alkali ions can attach so that alkali metal ion didnot adsorb and didnot affect the uranium adsorption. The minor effect of light metals on the adsorption of uranium onto RSK indicates the selectivity of the uptake of uranium onto this carbon. It is therefore suggested that RSK could be used in the concentration, purification, and separation of uranium from other elements over a wide range of concentrations. Also, these observations point to a significant advantage in favor of RSK in industrial water treatment over the ion-exchange resins system since the binding of Ca^{2+} and Mg^{2+} with these resins limits their application for the sorption of other metals, as particularly both these divalent cations are present in high concentrations in wastewaters [29].

Dissolved iron is a natural component of most ground water and significantly affects the uranium adsorption. Fe^{3+} is considered as the most potent competitor of uranium for binding sorptive sites [30]. Such inhibition of U sorption by Fe^{3+} is a common phenomenon, and has been demonstrated in more than one study [30,31]. So, we studied the effect of different

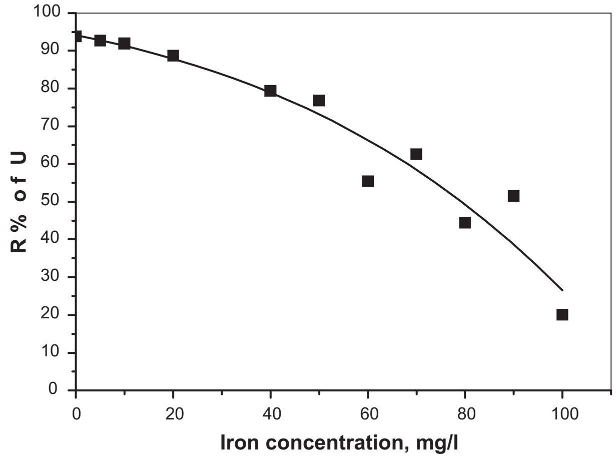

Fig. 1. Effect of iron concentration on uranium adsorption.

concentrations of iron on uranium adsorption in Fig. 1. It is clear that iron had a much stronger effect on the uptake of uranium, especially at concentration higher than 20 mg/l. The presence of iron has no significant detrimental effect on the removal of uranium until a concentration of about 20 mg/l, and as the iron concentration increased the removal decreased. Co-existing of iron ions at high levels may compete strongly for the adsorption sites with uranium ions resulting in a substantial reduction of uranium removal. Iron was therefore considered to control uranium adsorption on RSK. Ferric ion was a strong inhibitor of uranium binding, and then imposes serious restrictions on wastewater treatment by this sorbent. Ideally, iron should be removed from waste solution before treatment to remove uranium.

3.2. *Influence of co-existing anions*

The effects of various anions, commonly encountered in effluent streams, on uranium uptake capacity using RSK were studied. The adsorption behavior of uranium ions in the presence of Cl^-, CO_3^{2-}, HCO_3^-, SO_4^{2-}, $S_2O_3^{2-}$, OH^-, NO_3^-., S^{2-}, and PO_4^{3-} (taken as sodium) has been examined. The concentration of added anions was fixed at 100 mg/l and the pH of the solution was kept constant at 5.5 during these studies. The results are shown in Table 3. It may be inferred that RSK showed good selectivity in extracting uranium even in the presence of large concentrations (100 mg/l) of anionic-complexing agents and common electrolyte species. However, the presence of added anions sometimes, induced small positive effect on uranium adsorption (Table 3).

Table 3
Effect of different anions on the adsorption of uranium using RSK

Anion	Adsorption % at 100 mg/l	Anion	Adsorption % at 100 mg/l
Nil[a]	84.2	$S_2O_3^{2-}$	93.8
Cl^-	91.0	OH^-	91.6
CO_3^{2-}	89.3	NO_3^-	85.9
HCO_3^-	88.8	S^{2-}	81.5
SO_4^{2-}	80.3	PO_4^{3-}	77.3

[a] Nil means no cation or anions present in the solution other than thorium.

The most adequate explanation, for the behavior of these anions, arises from the requirement for electroneutrality. Anions accumulate close to the surface, causing a localized net negative potential that attracts positively charged metal ions to the area close to the surface. The anions thus conduct metal ions to the negatively charged surface sites, enhancing the adsorption effect [32]. On the other hand, the anion can also enhance the adsorption capacity by pairing with the uranium species, hence, reducing the repulsion between adjacent uranium molecules adsorbed on the surface. This enables the carbon to adsorb more of the positive uranium ions, since the repulsive forces between the surface and uranium ions and repulsive force among positive uranium ions are reduced.

An alternative hypothesis would be due to the formation of some complex anions, which would be adsorbed on the activated carbons; hence, the metals will be adsorbed as anionic complex instead of cations. Since RSK is H-type carbon, that is it shows a positive charge potential at pH 5.5, it will have a higher tendency to adsorb anions than cations, thus, the adsorption of those complex anions will be favored with regard to U(VI).

It is good to note that the most known anion which interfered with sorption of U(V1) was carbonate due to the formation of stable tricarbonato complex, $UO_2(CO_3)_3^{4-}$ but we find that carbonate did not interfere with uranium adsorption at pH 5.5. As clear in Fig. 2 for uranium speciation, this behavior could be explained as follows: for pH higher than 7.5 and pH lower than 3.5, the uranium complexes with phosphates and carbonates predominate. In the region between 5.5 and 7.5, the predominant species are the polynuclear hydroxo-complexes while for $3.5 < pH < 5.5$ the uranyl ion is the major uranium species formed [32]. Hence, the noninterference of these ions is of interest for the application of RSK to the recovery

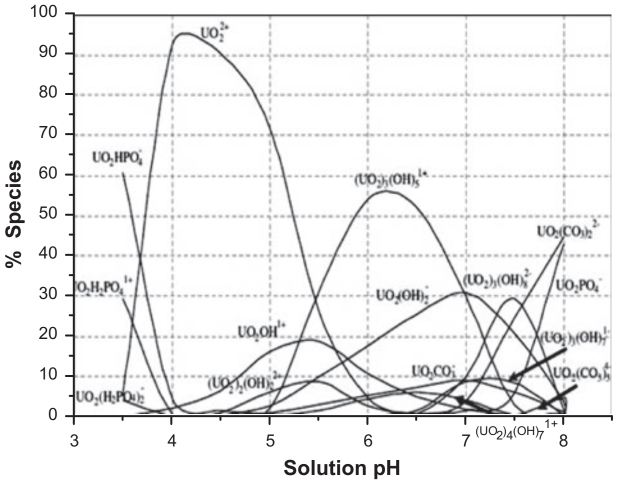

Fig. 2. Speciation diagram of uranium species in a solution at equilibrium with atmospheric CO_2 and $(UO_2)_3(PO_4)_2$.

of trace U(V1) from highly saline solutions such as uranium waste effluents.

3.3. Co-adsorption of uranium and thorium

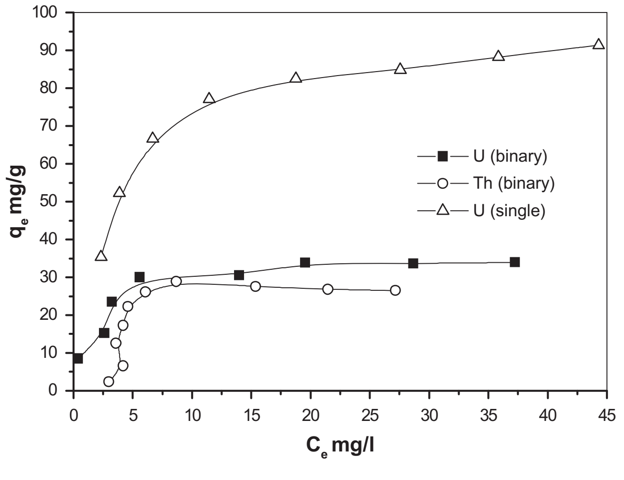

Fig. 3. Uranium and thorium sorption isotherms in single- and binary-component systems using RSK carbon.

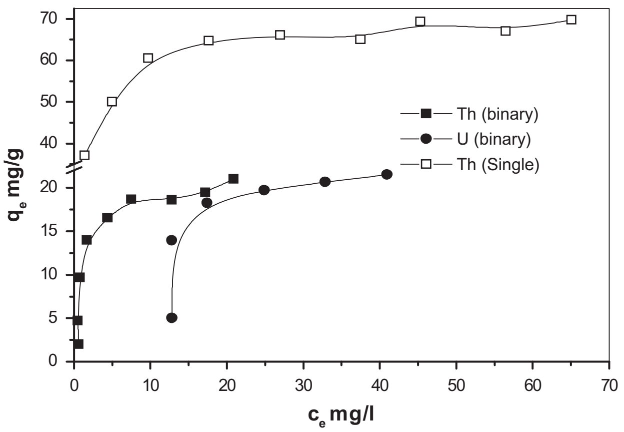

Fig. 4. Uranium and thorium sorption isotherms in single- and binary-component systems using RSN carbon.

Competitive adsorption of uranium and thorium ions from their binary solutions was investigated. Figs. 3 and 4 illustrate the adsorption isotherm of both uranium and thorium in mixture. The isotherms were obtained at pH 4.5–5.0 and 25˚C. The concentration range of 1–100 mg/l was investigated and a ratio of 1:1 was used to determine the effect on the adsorption of uranium and thorium. The result of single-metal isotherm was put in Figs. 3 and 4 for comparison. It is clear that the simultaneous adsorption of U and Th from U–Th solution produced an H-type isotherm according to Giles classification [33]. The initial linear part of the isotherms was shorter and the knee was steeper when compared with mono-metal sorption. The presence of equal concentrations of uranium and thorium in solution depressed the uptake capacity of each metal significantly, indicating marked competition between thorium (IV) and uranium (VI) ions for the active sites on the carbon surface.

Data obtained from single adsorption isotherms were fitted to linearized forms of Freundlich isotherm [34] and Langmuir isotherm [35] by Eqs. (3) and (4), respectively:

$$\log q_e = \log K + \frac{1}{n}\log C_e \quad \text{Freundlich} \tag{3}$$

$$\frac{C_e}{q_e} = \frac{1}{bq^o} + \frac{C_e}{q^o} \quad \text{Langmuir} \tag{4}$$

where K and n are the Freundlich constants, n gives an indication of favorability (adsorption intensity), and K the capacity of adsorbent (adsorption capacity). q^o and b are the Langmuir constants related to the maximum adsorption capacity corresponding to complete monolayer coverage and energy of adsorption respectively.

A detailed analysis of the regression coefficients showed that the data were best fitted by the Langmuir isotherm for all the metal ions in single as well as in multi-component systems as can be seen from Fig. 5. In single component system, Langmuir isotherm succeeds in describing the adsorption over the whole range of concentration more than Freundlich isotherm [11]. Therefore, Langmuir parameters of uranium and

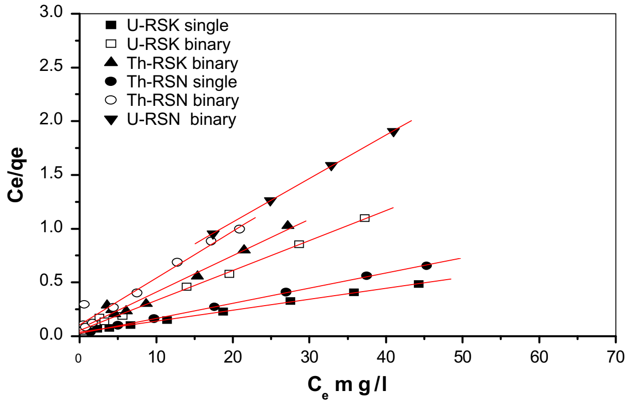

Fig. 5. Linear Langmuir plots of uranium and thorium isotherms in single- and binary-component systems.

thorium adsorption in the presence and absence of other metal ions are calculated and presented in Table 4. The correlation coefficient of Langmuir isotherms was almost higher than 0.998.

The high fit to the Langmuir model for both metal ions suggests that once metal ions occupies a site, no further adsorption can take place at that site, then the adsorption is limited with monolayer coverage and the surface is relatively homogeneous in terms of functional groups [36]. In other words, the Langmuir model is applicable when there is a strong specific interaction between the surface and the adsorbate so that a single adsorbed layer is formed due to chemisorption interaction [37].

As shown in Table 4, uranium still gives the best adsorption for RSK and thorium gives the best adsorption for RSN and therefore could be used to separate trace amount of metal-bearing solutions. It is inferred from this observation that the sites responsible for uranium adsorption on RSK are not available as those for thorium on RSN. In other words, there are at least two kinds of adsorption sites on two adsorbents which may be energetically or structurally different sites.

The langmuir bonding energy coefficient *b* for single- and binary-metal solutions varied with carbon type and metal solution. In binary system for RSK, the *b* value of uranium (0.52) is greater than that of thorium (0.48). Whereas, RSN has *b* value for thorium (0.41) greater than that of uranium (0.1). This can be attributed to the presence of at least some binding sites which are more specific for the different metal ions [38]. Thus, the results obtained for U–Th systems could not be explained on the basis of direct competition and it was suggested that preferential binding to different sites was involved. These observations conform again that RSK is selective to uranium and RSN is selective to thorium even in binary system.

Although the uranium capacity decreases in dual system from 100 to 35.9 mg/g, the *b* value increases from 0.28 to 0.52 l/g. The bimetal Langmuir isotherm *b* values may indicate that the competition for sorption sites promotes the retention of uranium on more specific sorption positions. As a result, although maximum sorption coefficient (q^o) decreases, uranium ions are held more strongly [39]. The value of *b* for Th adsorption decreases from 0.57 to 0.41. This indicates that the presence of co-ions decreased the binding levels of thorium.

The effect of ionic interaction on the sorption process may also be represented by the ratio of the sorption capacity for one metal ion in the presence of the other metal ions, q^o_{mix}, to the sorption capacity for the same metal when it is present alone in the solution, q^o [40,41].

$$\frac{(q^o_{\max})}{q^0} > 1 \quad \text{sorption is promoted by the presence of other metal ions;}$$

$$\frac{(q^o_{\max})}{q^0} = 1 \quad \text{no observable net interaction;}$$

$$\frac{(q^o_{\max})}{q^0} < 1 \quad \text{sorption is suppressed by the presence of other metal ion.}$$

Table 4
Langmuir parameters for single and multi-component systems of U(VI) and Th(IV) using RSK and RSN, respectively

Metal measured	System	q^o	*b*	R^2	$q^o_{\max}/q^o$
U	U: RSK	100	0.28	0.999	–
U	(U + Th): RSK	35.9	0.52	0.996	0.36
U	(U + Th): RSN	24.0	0.1	0.99	–
Th	Th: RSN	71.1	0.57	0.999	–
Th	(Th + U): RSK	29.5	0.48	0.97	–
Th	(Th + U): RSN	25.0	0.41	0.96	0.35

As presented in Table 4, the values of $q^o_{\max}/q^o$ are found to be <1 which are consistent with the sorption isotherms obtained for U(IV) and Th(IV) in the presence of other metal ions. These results suggesting that the simultaneous presence of both metals reduced sorption through competition for sorption sites in the solid phases. In addition, it was generally true that $q^o_{\max}/q^o$ for thorium $q^o_{\max}/q^o$ for uranium, suggesting that thorium sorption was more affected by the simultaneous presence of a competing metal than uranium [39]. The low interference of U with Th binding than vice versa can be attributed to a higher oxidation state of Th, along with additional bonding parameters [31].

3.4. Effect of HA

3.4.1. Adsorption of HAs

HAs are polyelectrolytic macromolecules that are widely distributed in natural waters [42]. On one hand, it is well known that humic substances possess a substantial capacity to complex dissolved species such as metal ions. Their role in natural waters has gained importance because of these interactions that control the behavior and the mobility of metals [42]. On the other hand, adsorption of HAs by activated carbon is of particular interest, as they may change the surface charge and surface properties in general significantly [43].

The adsorption isotherm of HA on RSK at pH 5.5 (optimum pH of uranium adsorption onto RSK) was given in Fig. 6. It is clear that the isotherm showed an initial steep slope, indicating a relatively high affinity between HAs and carbon surface (L-shape). Similar results were observed by other researchers studying the sorption of humic substances onto aluminum and iron oxide surfaces [44]. Ochs et al. (1994) proposed that polydispersity of humic substance was partly responsible for the initial fast sorption [45]. Nonlinear isotherms suggest that the dominant force for HA sorption onto carbon is by a specific interaction that involves presumably the polar and ionizable groups of the HA [46]. The Freundlich and Langmuir isotherms of humic adsorption were presented in Fig. 7 and their constants were listed in Table 5. It is clear that the isotherm follows Langmuir equation (Eq. (4)) due to the large electrostatic attraction between the adsorbed HA molecules and carbon surface, which has positive charge at this pH. As the HA quickly saturates the more energetic sites of carbon, fewer active sorption sites are available and/or the affinity of remaining HA to carbon surface became less due to the fractionation, resulting in a Langmuir-type isotherm [43,46].

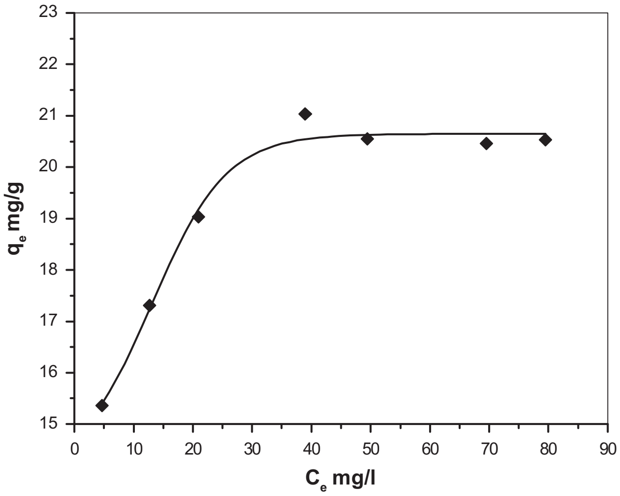

Fig. 6. Equilibrium adsorption isotherm of HA adsorption using RSK carbon.

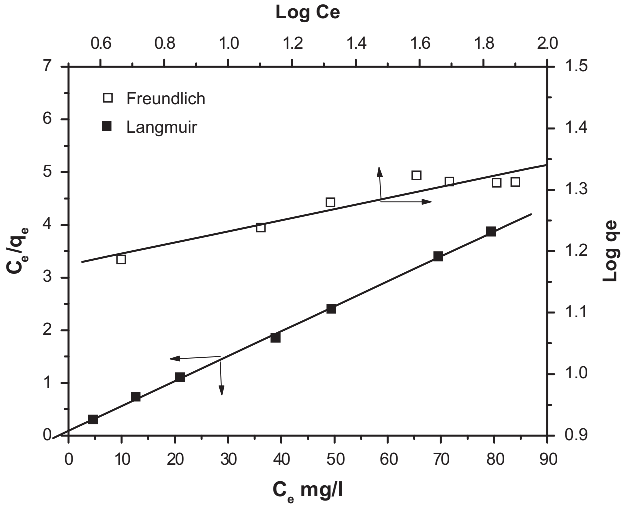

Fig. 7. Freundlich and Langmuir adsorption isotherms of HA using RSK carbon.

As anticipated, the large HA molecules will be adsorbed essentially on the external surface or in wider pores, and thus upon covering the surface a second layer is not favorable. The HA molecules will favorably go into solution instead of forming a second layer over the already adsorbed layer [8].

3.4.2. Uranium and thorium adsorption in presence of HA

The nature of the interactions between metal ions and carbon adsorbent may depend on the presence or

Table 5
Freundlich and Langmuir parameters HA adsorption using RSK carbon

Freundlich			Langmuir		
K (mg/g)	*n*	R^2	q^{o} (mg/g)	*b* (1/mg)	R^2
13.3	9.3	0.9	21.14	0.53	0.999

Table 6
Langmuir parameters of uranium and thorium adsorption with/without HA

System	q^{o} (mg/g)	*b* (g/l)
U single	100	0.28
U/HA simultaneous	11.85	0.18
U/HA sequential	41.5	0.14
Th single	71.1	0.57
Th/HA sequential	88.0	1.47

absence of HA. Similarly, the nature of the interactions between HA and adsorbent may vary with the presence or absence of metal ions.

Three types of experiments were performed: single species (metal or HA) adsorption with fresh sorbent; sequential adsorption of metal and HA (first HA adsorbed before metal ions are added); and simultaneous co-adsorption of metal ion and HA with clean sorbent (mixing HA with the solution that contains metal ions before the carbon is added).

A Fig. 8 shows that the equilibrium isotherm of U was affected by the manner in which HA was added to the solution. Namely, U showed a decreased absorbability when it co-existed with HA from the start, compared with the case when U was added after equilibrium adsorption of HA on activated carbon occurred. This is also clear from Langmuir q^{o} value in Table 6. The reason for this phenomenon was that the difference in the extent of complexibility of U with free HA ion and adsorbed HA on RSK, i.e. U made a complex more easily with HA which exists as a free ion in solution than the one in the adsorbed state. Complexes that remain in solution will prevent a fraction of the uranium from adsorbing [47]. The interactions between uranium ions and HA before the adsorption caused the formation of U–HA complexes that changed the surface interactions of both uranium ions and HA with carbon surface. In co-adsorption, three substances were present in the aqueous phase (carbon, uranium ions, and HA), and may interact each other. In the absence of metal ions, the negative electrostatic charges on HA macromolecules repel one another, keeping HA in dispersed colloid-like state [48]. When cations such as uranium ions are added, they complex with HA and neutralize its surface charges. As a result, the U–HA complex may have a more compact coil-like structure with less surface groups exposed to the carbon surface. In such a state, the probability for a HA molecule to be adsorbed by carbon surface can be reduced. On the other hand, uranium ions complexed with HA would have less opportunity to be adsorbed.

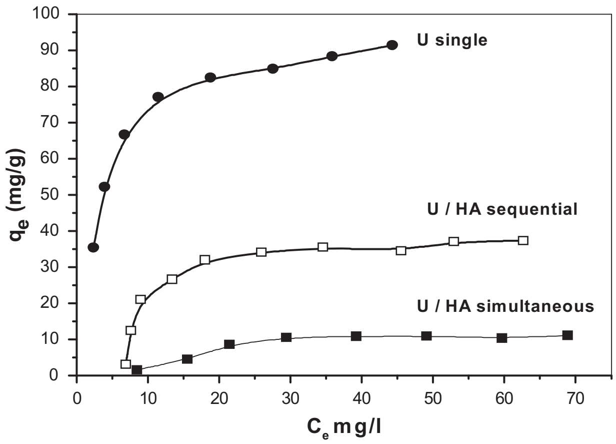

Fig. 8. Effect of presence HA on uranium isotherms using RSK (i) sequentially and (ii) simultaneously.

The effect of HA on metal adsorption by activated carbon is not easily generalized. Although sequential adsorption of HA acid increases the uranium adsorption on RSK than simultaneous adsorption of HA and uranium, the adsorption capacity of single uranium is higher in solution (Fig. 8). However, thorium showed opposite trend i.e. the sequential adsorption of HA increases the thorium adsorption capacity on RSN than single thorium system as shown in Fig. 9 and from q^{o} values in Table 6.

Previously adsorbed HA on the surfaces of adsorbent may affect metal adsorption through one of the following mechanisms [48]. (i) HA binds to the same sites on carbon surface as metal ions and hence previously adsorbed HA reduces metal adsorption subsequently due to site blockage. (ii) HA attaches to carbon surface through a mechanism different from that of metal ions, and the total sites available for subsequent metal adsorption remain the same, but a layer of HA adsorbed on the surface of carbon may create a steric barrier for metal to approach to the available adsorption sites. (iii) The attached HA through either mechanism of (i) or (ii) or both provides additional sites for metal adsorption, and, as a result, causes increased adsorption of metal ions. Although the three adsorption mechanisms may exist together, the

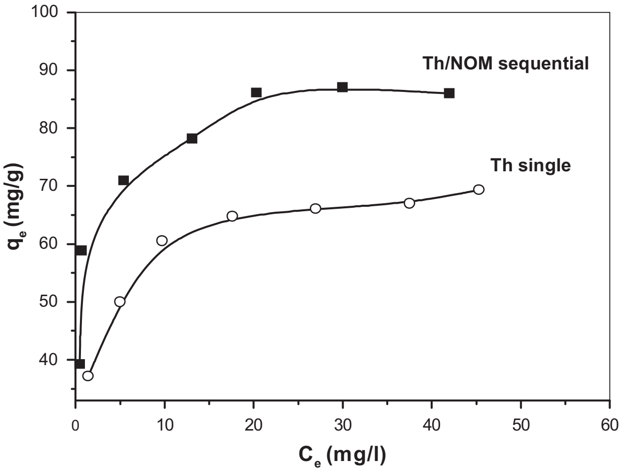

Fig. 9. Effect of presence HA sequentially on thorium isotherms using RSN.

increased thorium adsorption by RSN with previously adsorbed HA in the experiments suggest that at least mechanism (iii) was operative and played a role in the sequential adsorption of thorium ions. On the other hand, mechanism (iii) was less important than mechanisms (i) and (ii) in this case of RSK with previously adsorbed HA. It adsorbed less uranium than clean carbon surface. Similar results were reported [49].

These observations confirm the difference in mechanism controls of uranium and thorium removal in single-component systems. As HAs adsorb and cover the carbon surface, they significantly alter the characteristics of the surface with respect to metal uptake. HA molecules contain many functional groups (carboxyl and phenolic groups). The functional groups of an adsorbed HA may provide other new HA adsorption sites for trace metals which may be more reactive than isolated carbon surface sites. The adsorption of thorium ions may be dominated by the exposed functional groups of the adsorbed HA, which is similar to its adsorption sites on carbon surface. That means, the number of binding sites blocked by sorbed HA is overcompensated by additional binding sites stemming from the HA itself. Thus, many thorium ions were bound to the HA, which were themselves previously bound to RSN surface. These are in accordance with the high stabilities of Th–humate complexes [50] which evidenced by high Langmuir b value in Table 6. This behavior is not predominant in uranium adsorption. Schmeide et al. (2003) reported that the loading of HA with uranyl ions in the uranyl humates was between only 15 and 22% of the carboxylic group capacity of the HA [51]. These results are conformed by that obtained by Szalay that thorium enrichment by HAs is greater than uranyl ion [52].

The difference between sequential adsorption of U and Th can be related to the difference in pH, under which the experiments were conducted. It is well known that the sorption of HA decreases with increase in pH [49]. Thorium adsorption occurs at pH value (4.0) lower than adsorption of uranium (5.5). So, those free HA or humic–metal complexes tend to remain in solution in case of uranium than in case of thorium. This leads postulate mechanism for HA adsorption onto activated carbon similar to that proposed by Lai et al. (2002) for the adsorption of HA onto goethite-coated sand [53]. This pattern was consistent with ligand exchange between carboxylate groups in HA and carbon hydroxyls.

$$-\mathrm{C}-\mathrm{OH}+\mathrm{H}^{+} \Leftrightarrow -\mathrm{C}-\mathrm{OH}_2^{+}$$

$$-\mathrm{C}-\mathrm{OH}_2^{+}+\mathrm{Hu}-\mathrm{COO}^{-} \Leftrightarrow -\mathrm{C}-\mathrm{OH}_2^{+}\mathrm{O}^{-}\mathrm{CO}-\mathrm{Hu}$$

$$-\mathrm{C}-\mathrm{OH}_2^{+}\mathrm{O}^{-}\mathrm{CO}-\mathrm{Hu} \Leftrightarrow -\mathrm{C}-\mathrm{OCO}-\mathrm{Hu}+\mathrm{H_2O}$$

where –C–OH represents carbon carboxyl group and Hu–COO– represents a HA. It is clear that the above mechanism is favorable at lower pH values.

4. Conclusion

The prepared RSK carbon showed good selectivity in extracting uranium even in the presence of large concentrations (100 mg/l) of anionic- and cationic-complexing agents and common electrolyte species. Co-existing of iron ions at high levels may compete strongly for the adsorption sites with uranium ions resulting in a substantial reduction of uranium removal. Preferably, iron should be removed from waste solution before treatment to remove uranium.

Capacity of each metal in binary U and Th system was reduced due to competition between two ions for sorption sites on carbon surface.

In presence of HA, the metal–humic interactions play a very important role in determining the extent of adsorption. U(VI) showed an increased absorbability when U(VI) was added after equilibrium adsorption of HA on activated carbon occurred compared with the case when it co-existed with HA from the start The increase of sorption is explained by the sorption of HA on the carbon surface followed by the interaction of the uranium ion with surface-sorbet HA, whereas the reduction of sorption is explained by the formation of soluble U–HA complexes which stabilize the metal ion in aqueous solution.

It could be concluded that iron and HAs were strong inhibitor of uranium binding, thus limits the wastewater treatment by this sorbent. Therefore, iron and humic substance should be removed from waste solution before treatment to remove uranium.

Acknowledgement

This project was supported by King Saud University, Deanship of Scientific Research, College of Science Research Centre.

References

[1] T. Sakaguchi, A. Nakajima, Recovery of uranium by immobilized polyhydroxyanthraquinone, Sep. Sci. Technol. 21 (1986) 519–534.

[2] M. Saleem, M. Afzal, R. Qadeer, J. Hanif, Selective adsorption of uranium on activated charcoal from electrolytic aqueous solution, Sep. Purif. Technol. 27 (1992) 239–253.

[3] R. Qadeer, J. Hanif, Kinetics of uranium (VI) ions adsorption on activated charcoal from aqueous solutions, Radiochim. Acta 65 (1994) 259–263.

[4] W.A. Abbasi, M. Streat, Adsorption of uranium from aqueous solutions using activated carbon, Sep. Sci. Technol. 29 (1994) 1217–1230.

[5] S.-Y. Kang, J.-U. Lee, S.-H. Moon, K.-W. Kim, Competitive adsorption characteristics of Co^{2+}, Ni^{2+}, and Cr^{3+} by IRN-77 cation exchange resin in synthesized wastewater, Chemosphere 56 (2004) 141–147.

[6] G.R. Choppin, The role of natural organics in radionuclide migration in natural aquifer systems, Radiochim. Acta 58/59 (1992) 113–120.

[7] R.J. Silva, H. Nitsche, Actinides environmental chemistry, Radiochim. Acta 70/71 (1995) 377–396.

[8] A.A.M. Daifullah, Removal of 226Ra, Fe^{3+} and Mn^{2+} from ground water using modified activated carbon, Isot. Radiat. Res. 35 (2003) 77–93.

[9] A.W. Heinen, J.A. Peters, H.V. Bekkum, Competetive adsorption of water and toluene on modified activated carbon supports, Appl. Catal. A: General 194–195 (2000) 194–195.

[10] J.-W. Shim, S.-J. Park, S.-K. Ryu, Effect of modification with HNO_3 and NaOH on metal adsorption by pitch-based activated carbon fibers, Carbon 39 (2001) 1635–1642.

[11] S.M. Yakout, M.A. Rizk, Adsorption of uranium by low-cost adsorbent derived from agricultural wastes in multi-component system, Desalin. Water Treat. (2013) 1–6, doi: 10.1080/19443994.2013.860625.

[12] A.A. Daifullah, S.M. Yakout, S.A. Elreefy, Adsorption of fluoride in aqueous solutions using KMnO4-modified activated carbon derived from steam pyrolysis of rice straw, J. Hazard. Mater. 147 (2007) 633–643.

[13] Z. Marczenko, Spectrophotometric Determination of Elements, Wiley, New York, NY, 1986.

[14] H.P. Holcomb, J.H. Yoe, Spectrophotometric determination of uranium and thorium with arsenazo, Microchem. J. 4 (1960) 463–480.

[15] I. Martin-Gullon, J.P. Marco-Lozar, D. Cazorla-Amorós, A. Linares-Solano, Analysis of the microporosity shrinkage upon thermal post-treatment of H_3PO_4 activated carbons, Carbon 42 (2004) 1339–1343.

[16] M.A. Lillo-Ródenas, D. Cazorla-Amorós, A. Linares-Solano, Understanding chemical reactions between carbons and NaOH and KOH, Carbon 41 (2003) 267–275.

[17] B.K. Pradhan, N.K. Sandle, Effect of different oxidizing agent treatments on the surface properties of activated carbons, Carbon 37 (1999) 1323–1332.

[18] S.M. Yakout, S.S. Metwally, T. El-Zakla, Uranium sorption onto activated carbon prepared from rice straw: Competition with humic acids, Appl. Surf. Sci. 280 (2013) 745–750.

[19] K. Štamberg, K.A. Venkatesan, P.R. Vasudeva Rao, Surface complexation modeling of uranyl ion sorption on mesoporous silica, Colloids Surf. A: Physicochem. Eng. Aspects 221 (2003) 149–162.

[20] A.M. Starvin, T.P. Rao, Solid phase extractive preconcentration of uranium(VI) onto diarylazobisphenol modified activated carbon, Talanta 63 (2004) 225–232.

[21] C. Kütahyalı, M. Eral, Selective adsorption of uranium from aqueous solutions using activated carbon prepared from charcoal by chemical activation, Sep. Purif. Technol. 40 (2004) 109–114.

[22] A. Mellah, S. Chegrouche, M. Barkat, The removal of uranium(VI) from aqueous solutions onto activated carbon: Kinetic and thermodynamic investigations, J. Colloid Interface Sci. 296 (2006) 434–441.

[23] J. Wang, P. Liu, Z. Li, W. Qi, Y. Lu, W. Wu, Th(IV) adsorption onto oxidized multi-walled carbon nanotubes in the presence of hydroxylated fullerene and carboxylated fullerene, Materials 6 (2013) 4168–4185.

[24] M. Metaxas, V. Kasselouri-Rigopoulou, P. Galiatsatou, C. Konstantopoulou, D. Oikonomou, Thorium removal by different adsorbents, J. Hazard. Mater. 97 (2003) 71–82.

[25] S.K. Yang, N. Tan, X.M. Yan, F. Chen, Y.C. Lin, Adsorption of thorium(IV) from aqueous solution by non-living biomass of mangrove endophytic fungus *Fusarium* sp. #ZZF51, J. Radioanal. Nucl. Chem. 298 (2013) 827–833.

[26] M. Tsezos, B. Volesky, Biosorption of uranium and thorium, Biotechnol. Bioeng. 23 (1981) 583–604.

[27] R.A.A. Muzzarelli, O. Ubertini, Chitin and chitosan as chromatographic supports and adsorbents for collection of metal ions from organic and aqueous solutions and sea-water, Talanta 16 (1969) 1571–1577.

[28] C.-k.D. Hsi, Adsorption of uranyl onto ferric oxyhydroxides: Application of the surface complexation sitebinding model, Geochim. Cosmochim. Acta 49 (1985) 1931–1941.

[29] A. Saeed, M. Iqbal, Bioremoval of cadmium from aqueous solution by black gram husk (*Cicer arientinum*), Water Res. 37 (2003) 3472–3480.

[30] M.Z.C. Hu, J.M. Norman, B.D. Faison, M. Reeves, Biosorption of uranium by *Pseudomonas aeruginosa* strain CSU: Characterization and comparison studies, Biotechnol. Bioeng. 51 (1996) 237–247.

[31] P. Sar, S. Kazy, S. D'Souza, Radionuclide remediation using a bacterial biosorbent, Int. Biodeterior. Biodegrad. 54 (2004) 193–202.

[32] S.A. Dastgheib, D.A. Rockstraw, A systematic study and proposed model of the adsorption of binary metal ion solutes in aqueous solution onto activated carbon produced from pecan shells, Carbon 40 (2002) 1853–1861.

[33] C.H. Giles, T.H. Mcewan, S.N. Nakhwa, D. Smith, Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids, Am. Chem. Soc. 82 (1960) 3973–3993.

[34] H.M.F. Freundlich, Uber die adsorption in lösungen (Over the adsorption in solution), Phys. Chem. 57 (1906) 385–470.

[35] I. Langmuir, The constitution and fundamental properties of solids and liquids. Part I. Solids, J. Am. Chem. Soc. 38 (1916) 2221–2295.

[36] A. Gücek, S. Şener, S. Bilgen, M.A. Mazmancı, Adsorption and kinetic studies of cationic and anionic dyes on pyrophyllite from aqueous solutions, J. Colloid Interface Sci. 286 (2005) 53–60.

[37] S.V. Mohan, N.C. Rao, J. Karthikeyan, Adsorptive removal of direct azo dye from aqueous phase onto coal based sorbents: A kinetic and mechanistic study, J. Hazard. Mater. 90 (2002) 189–204.

[38] P.R. Puranik, K.M. Paknikar, Influence of co-cations on biosorption of lead and zinc—A comparative evaluation in binary and multimetal systems, Bioresour. Technol. 70 (1999) 269–276.

[39] S. Serrano, F. Garrido, C.G. Campbell, M.T. García-González, Competitive sorption of cadmium and lead in acid soils of Central Spain, Geoderma 124 (2005) 91–104.

[40] D. Mohan, S. Chander, Single component and multicomponent adsorption of metal ions by activated carbons, Colloids Surf. A: Physicochem. Eng. Aspects 177 (2001) 183–196.

[41] D. Mohan, K.P. Singh, Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse—An agricultural waste, Water Res. 36 (2002) 2304–2318.

[42] C. Uyguner, M. Bekbolet, Evaluation of humic acid, chromium (VI) and TiO2 ternary system in relation to adsorptive interactions, Appl. Catal. B: Environ. 49 (2004) 267–275.

[43] G. Newcombe, Activated carbon and soluble humic substances: Adsorption, desorption and surface charge effects, J. Colloid Interface Sci. 164 (1994) 452–462.

[44] E.M. Murphy, J.M. Zachara, S.C. Smith, Influence of mineral-bound humic substances on the sorption of hydrophobic organic compounds, Environ. Sci. Technol. 24 (1990) 1507–1516.

[45] M. Ochs, B. Ćosović, W. Stumm, Coordinative and hydrophobic interaction of humic substances with hydrophilic Al_2O_3 and hydrophobic mercury surfaces, Geochim. Cosmochim. Acta 58 (1994) 639.

[46] F.H. Chi, G.L. Amy, Kinetic study on the sorption of dissolved natural organic matter onto different aquifer materials: The effects of hydrophobicity and functional groups, J. Colloid Interface Sci. 274 (2004) 380–391.

[47] A.P. Davis, V. Bhatnagar, Adsorption of cadmium and humic acid onto hematite, Chemosphere 30 (1995) 243–256.

[48] W.L. Yan, R. Bai, Adsorption of lead and humic acid on chitosan hydrogel beads, Water Res. 39 (2005) 688–698.

[49] J.P. Chen, S. Wu, Simultaneous adsorption of copper ions and humic acid onto an activated carbon, J. Colloid Interface Sci. 280 (2004) 334–342.

[50] N. Miekeley, I.L. Küchler, Interactions between thorium and humic compounds in surface waters, Inorg. Chim. Acta 140 (1987) 315–319.

[51] K. Schmeide, S. Sachs, M. Bubner, T. Reich, K.H. Heise, G. Bernhard, Interaction of uranium(VI) with various modified and unmodified natural and synthetic humic substances studied by EXAFS and FTIR spectroscopy, Inorg. Chim. Acta 351 (2003) 133–140.

[52] A. Szalay, Cation exchange properties of humic acids and their importance in the geochemical enrichment of UO_2^{2+} and other cations, Geochim. Cosmochim. Acta 28 (1964) 1605–1614.

[53] C.-H. Lai, C.-Y. Chen, B.-L. Wei, S.-H. Yeh, Cadmium adsorption on goethite-coated sand in the presence of humic acid, Water Res. 36 (2002) 4943–4950.