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Adsorption of uranium by low-cost adsorbent derived from agricultural wastes in multi-component system

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ABSTRACT

The impact of common cations and anions on the adsorption of uranium on rice straw activated carbon has been examined. The presence of these ions in solution was found to inhibit the uptake of cadmium by chitin to different degrees. Presence of Fe ions depressed the uranium removal to 77 and 20% at 20 and 100 mg/l, respectively. Coexistence of some anions induced small positive effect on uranium adsorption percent like Cl^-; 91.0%, CO_3^{2-}; 89.3%, HCO_3^-; 88.8%, $S_2O_3^{2-}$; 93.8%, and OH^-; 91.6% compared to 84.2% uranium removal. Simultaneous presence of both uranium and thorium reduced uranium sorption from 100 to 35.9 mg/g. Data were good fitted by the Langmuir isotherm with correlation coefficient higher than 0.998. This means, the adsorption is monolayer chemical in nature on homogenous surface.

Keywords: Multi component adsorption; Uranium; Wastewater treatment

1. Introduction

The environmental pollution is the most serious problem that should be taken into consideration due to increasing population and growth of technology. Like many other heavy metals, uranium is toxic to humans and animals, the most sensitive toxicological endpoint is damage to the kidney through chemical interactions [1]. Carcinogenic and genotoxic effects of uranium appear to be associated with higher exposure levels than the chemical toxicity [2].

The adsorption process has long been used in the water and industrial wastewater treatment for removal of color, odor, and organic and inorganic pollutants. In order to concentrate aqueous nuclear waste solutions, many processes are being used, such as precipitation, ion-exchange, solvent extraction, and adsorption. Adsorption of uranium onto various solids is important from purification, environmental, and radioactive waste disposal point of view [3–5]. The preconcentration and separation procedures on adsorption phenomena are important in nuclear and radiation chemistry, industry, medicine, and daily life [5]. Interest in the adsorption of metal ions for recovery purposes has increased manifold in recent years, because of its simplicity, selectivity, and efficiency [4].

The presence of a single heavy metal in natural water and wastewater is a rare situation. Industrial application of sorption process must deal with the fact

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that metal bearing waste effluents often contain other innocuous ions that may interfere in the uptake of the ions of interest. This paper presents data and discussion regarding the influence of the different cations such as Na^+, K^+, Li^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, and anions such as Cl^-, CO_3^{2-}, HCO_3^-, $S_2O_4^{2-}$, $S_2O_3^{2-}$, OH^-, NO_3^-, S_2^-, and PO_4^{3-} on uranium sorption by activate carbon prepared from low-cost materials, in batch conditions. The choice of these ions has been made because of their permanent presence in industrial waste waters. This work will constitute a contribution in the comprehension and application of radionuclides sorption phenomenon by activated carbon especially and by materials in general.

2. Materials and methods

Activated carbon was prepared by steam pyrolysis elsewhere [6]. The obtained rice straw carbon was oxidized using HNO_3 and KOH to produce modified carbons according to the procedures described earlier by [7, 8] and denoted as RSN and RSK, respectively.

Stock solution (1,000 mg/l) of uranium U and thorium Th were prepared by dissolving 2.10 of uranyl nitrate and 2.46 g thorium nitrate in 1L distilled deionized water acidified by 2 ml nitric acid to prevent the hydrolysis. Various fresh standard solutions were obtained daily as required.

Batch sorption studies were performed to obtain both rate and equilibrium data due to their simplicity. A known amount of RSK and RSN was added to ten milliliter of U or Th solution followed by agitation for 3 h. 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 multicomponent system were obtained at pH 5. Sorption capacity of adsorbent was calculated by: $q_e = V(C_o - C_e)/m$ and sorption efficiency based on the percentage of metal removal: $R\% = (C_o - C_e/C_o) \times 100$, where C_o and C_e are the initial and equilibrium concentration (mg/l), respectively, M is the mass of dry carbon sample used (g), and V volume of solution (ml).

The multi-component systems involve the presence of both radionuclides in mixture and also involve the adsorption of radionuclide in presence of common cations and anions different species. Uranium sorption in the presence of other cations was tested in ionic combinations; 10 ml of 100 mg U/l with 10 mg/l or 100 mg/l concentration of these cations which were added to 10 mg of RSK. The tested cations were Na^+, K^+, Li^+, Ca^{2+}, Mg^{2+}, and Fe^{3+} (all in chloride forms). For the anionic interference experiments, adsorbent was placed in solutions containing equal quantities of uranium and the particular anions as their sodium salts (100 mg/l). The anions tested were Cl–, CO_3^{2-}, HCO_3^-, SO_4^{2-}, $S_2O_3^{2-}$, OH^-, NO_3^-, S_2^-, and PO_4^{3-}. 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 reagents [9]. The concentration of uranium and thorium in mixture was determined by arsenazo I method [10]. This method depends on that thorium form a complex with arsenazo I with maximum at 565 nm when pH of the solution is within the range 1.0–2.3, while uranium will 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.

3. Results and discussion

Modification of the surface chemistry of porous carbons might be a viable attractive route toward novel applications of these materials. Surface area of our prepared carbon was lower for the commercial carbons. Therefore, we conduct a surface modification for these carbons to obtain the highest adsorption capacity. The main physicochemical characteristics of RSK carbon were given in Table 1. It is clear that RSK carbon has more mespores than micrpores. Mesopores volume is three times greater than micropores volume. This is good for our carbon as it was reported that the carbon mesopores enhanced its adsorption capacity for metals. The high ash contents of RSK carbon (50%)

Table 1
Characterization of RSK carbon

S_{BET} m^2/g[a]	143.3
Surface area fraction[b]	
Micro-	0.7
Meso-	0.3
Total pore volume (cc/g)	0.175
Pore volume fraction[b]	
Micro-	0.25
Meso-	0.75
Pore radius, nm	2.45
Basicity meq/g	10.1
Acidity meq/g	5.95
pH_{pzc}	10.25
Ash content %	50.5

[a] The specific surface area calculated with the Brunauer–Emmett–Teller (BET) model.

[b] The surface area or pore volume fraction in each pore size range obtained from the density functional theory (DFT) analysis.

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 coexistence of acidic and basic surface sites in RSK carbon that indicate its amphoteric behavior. Potassium hydroxide treatment results in the appearance of surface oxygen groups like hydroxyl, carboxyl as indicated from IR analysis in Fig. 1. Bands around 2,300 cm^{-1}, perhaps due to ketene or ketone. The band in the region of 1,800–1,540 cm^{-1} (1,580 cm^{-1}) was assigned to the presence of highly conjugated carbonyl groups. The 1,420 cm^{-1} band attributed to lactone structure. The 1,100 cm^{-1} peak corresponds to C–O stretching vibration and O–H bending modes of alcoholic, phenolic, and carboxylic groups.

RSK showed high affinity for the removal of uranium while RSN was superior for thorium than non-oxidized carbon. Uranium removal by RSK carbon was maximum at PH 5.5 and equilibrium time of 40 min with equilibrium adsorption capacity 100 mg/g. The values of adsorption capacity for the removal of U(VI) were reported to be 58.43, 18.72, 28.49, and 28.30 mg g^{-1} onto mesoporous silica [11], diarylazobisphenol modified carbon [12], modified carbon [13], and activated carbon [14], respectively. Therefore, it was clear that RSK carbon is more effective for this purpose. As a continuation of our work, the present study describes the results of the experimental investigation of the influence of the different ions presence such as the adsorption of uranium by RSK carbon.

Industrial application of sorption process must deal with the fact that heavy metal bearing waste effluents often contain other innocuous ions that may interfere in the uptake of the metal ions of interest. Multi-component competitive interactions in solution with the sorbent material are one of the basic factors affecting the degree of metal removal by sorption. Thus, the effect of various cations such as Na$^+$, K$^+$, Li$^+$, Ca^{2+}, Mg^{2+}, and Fe^{3+} on the adsorption of uranium onto RSK has been examined. The results of coexisting cations upon the removal percentage of uranium (C_o = 100 mg/l) are presented in Table 2.

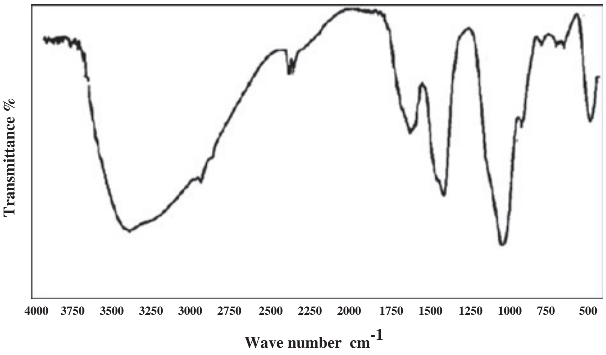

Fig. 1. FTIR spectra of RSK carbon.

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 of Fe ion (%R was 20%). Muzzarelli and Tubertini (1969) showed that K$^+$, Na$^+$, and Mg^{2+} ions did not interfere with the removal of many metal ions from their solutions by chitin [15]. Hsi (1985) found that Ca^{2+} and Mg^{2+} at 10^{-3} M did not significantly affect uranyl adsorption onto ferric oxyhydroxides [16].

These results show that RSK have much higher relative affinities for uranium metal ions than for the light metal ions studied. These could be explained by the low value of acidic groups in RSK carboxyl, hydroxl, and carbonyl [17] to which alkali ions can attach [18]. Therefore, alkali metal ion was not adsorbed and did not affect uranium adsorption.

It is therefore suggested that RSK could be used in the preconcentration, purification, and separation of uranium from other elements over a wide range of concentration. Also, these observations point to a significant advantage in favor of RSK compared with other ion-exchange resins systems in industrial wastewater treatment plant. It is well known that the binding of Ca^{2+} and Mg^{2+} with these resins limits their application for the sorption of other metals, since particularly both these divalent cations are present in high concentrations in wastewaters [19].

Dissolved iron is a natural component of most ground water and significantly affects the uranium adsorption. Coexistence of iron ions at high levels

Table 2
Effect of different cation and anions on Uranium adsorption by RSK

Cation	% adsorption at			% adsorption at 100 mg/l
	10 mg/l	100 mg/l	Anion	
Nil	84.2	84.2	Nil	84.2
Na$^+$	78.0	63.7	Cl$^-$	91.0
K$^+$	83.0	84.2	CO$_3^{2-}$	89.3
Li$^+$	77.8	85.7	HCO$_3^-$	88.8
Ca^{2+}	80.5	82.1	S$_2$O$_4^{2-}$	80.3
Mg^{2+}	82.2	79.8	S$_2$O$_3^{2-}$	93.8
Fe^{3+}	77.1	20.0	OH$^-$	91.6
			NO$_3^-$	85.9
			S$_2^-$	81.5
			PO$_4^{3-}$	77.3

may compete strongly for the adsorption sites with uranium ions resulting in a substantial reduction of uranium removal. It is clear that iron had a much stronger effect on the uptake of uranium (Fig. 2), especially at concentration higher than 20 mg/l then as the iron concentration increased, U-removal decreased. Fe^{3+} cation is considered as the most potent competitor of uranium for binding sorptive sites [20]. Such inhibition of U sorption by Fe^{3+} is a common phenomenon, and has been demonstrated in [20,21]. It could be concluded that, Ferric ion was a strong inhibitor of uranium binding, thus limits the wastewater treatment by this sorbent. Therefore, iron should be removed from waste solution before treatment to remove uranium.

The adsorption behavior of uranium ions in the presence of various anions such as Cl^-, CO_3^{2-}, HCO_3^-, SO_4^{2-}, $S_2O_3^{2-}$, OH^-, NO_3^-, S_2^-, and PO_4^{3-} were examined in another experiments. The concentrations of added anions were fixed at 100 mg/l and the pH of the solution was kept constant at 5.5 during these studies. For all tested anions, sodium ion was used as the cationic component. The results of the experiments are shown in Table 2. 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. Sometimes, the presence of added anions induced small positive effect on uranium adsorption. 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 [22]. 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 anions instead of as cations. Since RSK is H-type, which 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).

Carbonates are the most known anions which interfere with the sorption of U(V1) due to the formation of stable tricarbonato complex, $UO_2(CO_3)_3^{4-}$. However, we find that carbonate anions did not interfere with the uranium adsorption at pH 5.5. 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 [22].

Competitive adsorption of uranium and thorium ions from their binary solutions was investigated. Fig. 3 illustrates 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

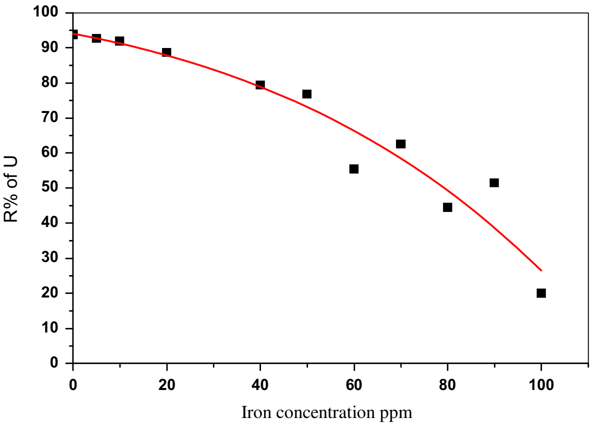

Fig. 2. Effect of iron concentration on Uranium adsorption.

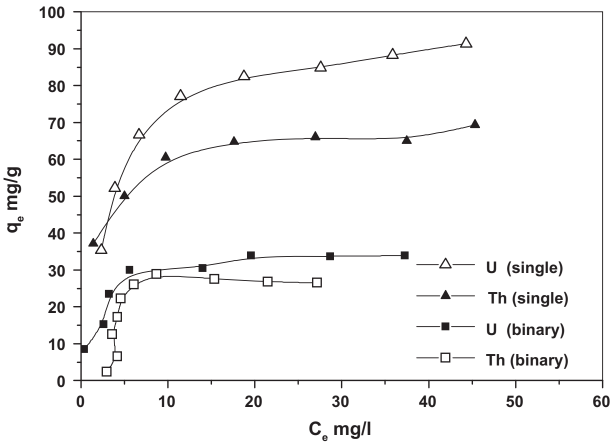

Fig. 3. Uranium and Thorium sorption isotherms from both single and binary systems by RSK.

Table 3
Langmuir parameters for single and multi-component adsorption of Uranium and Thorium by RSK and RSN

Metal	System	q^o	b	R^2	$q^o{}_{\text{mix}}/q^o$
U	U alone-RSK	100	0.277	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 alone-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

q^o is Langmuir maximum adsorption capacity (mg/g) and b is Langmuir constant (L/g).

of uranium and thorium. The result of single metal isotherm is presented in Fig. 3 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 [23]. The initial linear part of the isotherms was shorter and the knee was steeper when compared with monometal sorption. The presence of equal concentrations of uranium and thorium in solution depressed the uptake capacity of the each metal significantly, indicating marked competition between thorium (IV) and uranium (VI) ions for the active sites on the carbon surface.

A detailed analysis of the regression coefficients showed that the data are good fitted by the Langmuir isotherm for all the metal ions in single- as well as in multi-component systems. In single-component system Langmuir isotherm was more appropriate in describing the adsorption over the whole range of concentration more than Freundlich isotherm [17]. Therefore, Langmuir parameters of uranium and thorium adsorption in the presence and absence of other metal ions are calculated and presented in Table 3. The correlation coefficient of Langmuir isotherm was higher than 0.998.

The Langmuir model fitted best 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 [24]. In other words, the Langmuir model is applicable when there is a strong specific interaction between the carbon surface and adsorbate forming single adsorbed layer due to chemical nature of the sorption (chemisorption interaction) [25]. The comparison between single- and multi-element data test, showed that the adsorption parameters were mainly affected by the presence of other metals (Table 3). Uranium and thorium appeared to compete more aggressively for available adsorption sites.

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 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 [26]. The value of b for Th adsorption decreases from 0.56 to 0.41. These indicate that the presence of co-ions decreases 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}/q^o, to the sorption capacity for the same metal when it is present alone in the solution, q^o; such that for: [27]

$$\frac{q^o_{mix}}{q^o} > 1 \quad \text{the sorption is promoted by the presence of other metal ion}$$

$$\frac{q^o_{mix}}{q^o} = 1 \quad \text{no observable net interaction}$$

$$\frac{q^o_{mix}}{q^o} < 1 \quad \text{sorption is suppressed by the presence other metal ion.}$$

As presented in Table 3, the values of q^o_{mix}/q_o are found to be < 1 which are consistent with the sorption isotherms obtained for U(IV) and Th(IV) in the absence and 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_{mix}/q^o for thorium < q^o_{mix}/q^o for uranium, suggesting that thorium sorption was more affected by the simultaneous presence of a competing metal than uranium [26]. The low interference of U with Th binding than vice versa can be that attributed this to a higher oxidation state of Th, along with additional bonding parameters [21].

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