

# Sorption of Technetium-99 from Low-Level Radioactive Waste Using Different Adsorbent Materials

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This work aims to investigate the empathy and adsorption capacity of <sup>99</sup>Tc in pertechnetate form (TcO<sub>4</sub><sup>-</sup>) using three prepared activated carbons. The carbon samples were activated with phosphoric acid using 50 % saw dust + 50 % rice husk (C-1), 100 % saw dust (C-2) and 100 % rice husk (C-3). Adsorption of <sup>99</sup>Tc is pH dependent, where the adsorbed value of <sup>99</sup>Tc decreases as the pH increases. Around 3 h mixing time is enough for TcO<sub>4</sub><sup>-</sup> sorption by C-1 and C-3, while 100 min are sufficient for adsorption by C-2. The distribution coefficients evaluated from this study reveal that the adsorption empathy towards TcO<sub>4</sub><sup>-</sup> follows the sequence: C-2 > C-3 > C-1 with K<sub>f</sub> values 16121, 6328 and 5431, respectively. The maximum adsorption capacities (q<sub>max</sub>) calculated from Langmuir equation follow sequence of: 316, 264 and 250 mg Kg<sup>-1</sup> for C-2, C-3 and C-1 sample, respectively. The results showed that the locally prepared low-cost activated carbon is a promising candidate for a sustainable solution for <sup>99</sup>Tc removal and immobilization.

Keywords: Pertechnetate, Adsorption, Activated carbon, Low-level radioactive waste.

## INTRODUCTION

Low level liquid radioactive waste (LLLRW) can be produced from various nuclear industries, civil activities, research laboratories and medical wastes. Obtaining suitable waste forms of these liquid wastes for final disposal<sup>1</sup> is required to minimize the release or widespread dispersion of radionuclides into aquatic ecosystems. This can be achieved by volume reduction and/or hardening of these LLLRW. <sup>99</sup>Tc radioisotope, an artificial radioactive element, is of interest due to the environmental concerns in respect of the following; (a) it is a long-lived (t<sup>1</sup>/<sub>2</sub> =  $2.13 \times 10^5$  years), β-emitting radionuclide and high environmental mobility. Tc(VII) in the form of pertechnetate (TcO<sub>4</sub>) is itinerant due to its minimum interactions with the surfaces different mineral with a wide range of pH values. Therefore, <sup>99</sup>Tc is an important dose, subscriber in the evaluated health hazardness for many nuclear facilities worldwide<sup>2,3</sup>.

Immobilization of long-lived radionuclides, such as <sup>99</sup>Tc, into a relatively small volume waste form is vital for longterm permanent disposal. This target has been accomplished *via* conversion of Tc(VII) to Tc(IV) and co-deposition as  $TcO_2^4$  or by sorption of TcO\_4<sup>-</sup> using organic resins as an ion exchanger<sup>5,6</sup>. However, these remediation methods are potentially problematic because Tc(IV) can be oxidized to the more mobile Tc(VII) O<sub>4</sub><sup>-</sup> species and the anion exchange resins are expensive and subject to degradation at high temperature and long-term storage periods. Cost-effective adsorbents include natural and synthetic materials have been used successfully to remove <sup>99</sup>Tc from liquid waste and especially contaminated groundwater. Activated carbon is a promising candidate for <sup>99</sup>Tc treatment and immobilization because it is a non-hazardous, stable sorbent with a high surface area (600-1600 m<sup>2</sup> g<sup>-1</sup>) due to the porous structure<sup>7</sup>. Also, activated carbon is inexpensive and its sorption capability could be further enhanced by treatment with specific chemicals to increase the surface selectivity and capacity.

Activated carbon used recently to remove pertechnetate ions efficiently for treatment and environmental immobilization. Li *et al.*<sup>8</sup> evaluated 13 effective and inexpensive sorbent materials including activated carbon for pertechnetate (TcO<sub>4</sub><sup>-</sup>), iodide (I<sup>-</sup>) and cesium (Cs<sup>+</sup>) uptake from polluted wells water and sediments. An effective approach for separation and recovery of <sup>99</sup>Tc was reported<sup>9</sup>. Batch adsorption and column investigation assured a high selectivity and % removal of activated carbon for TcO<sub>4</sub><sup>-</sup> through a broad range of pH and ionic strength < 0.01 M with a K<sub>d</sub> of 12000 mL/g. Holm *et al.*<sup>10</sup> investigated the sorption of Tc in TcO<sub>4</sub><sup>-</sup> form on a commercial active carbon powder. Reduction of technetium by the carbon is proposed as an important mechanism of adsorption process. The sorption behaviours of TcO<sub>4</sub><sup>-</sup> onto activated carbon from mineral acid and salt concentrations were also investigated<sup>11,12</sup>.

Almost, all previous research used commercially available activated carbons which, in most cases, are expensive for low income and developing countries. The current study aims to prepare three activated carbon samples at different conditions from local resources as cost-effective materials and apply them to adsorb and remove pertechnetate  $(TcO_4)$  from a synthetic LLLRW as relation to pH, shaking time and concentration of pertechnetate.

#### **EXPERIMENTAL**

1 M sodium nitrate and sodium perchlorate were used as carrier in adsorption studies. The radioactive tracer ( $^{99}\text{TcO}_4$ ) was generated by extraction from old  $^{99\text{m}}\text{Tc}$  columns collected from hospitals using a dilute nitric acid solution.

Preparation of activated carbons: The agro-residue precursor, rice husks (RH) and saw dust (SD), were supplied from El-Dakahlyia Governorate in Egypt. They were collected, rinsed with deionized water, dried at 110 °C for 48 h, to facilitate subsequent crushing and grinding. The dried rice husk and saw dust were crushed and used for preparation of activated carbon by impregnation in phosphoric acid. The concentration of 70 % (w/v) H<sub>3</sub>PO<sub>4</sub> (BDH) was obtained by dilution of 85 wt. %. Three equal weights of the crushed agro-residues were prepared; mixture of 50 % rice husk and 50 % saw dust, 100 % saw dust and 100 % rice husk (C-1, C-2 and C-3, respectively). All the three samples were impregnated in sufficient  $H_3PO_4$ solution, mixed and heated to 80 °C for 1 h and then left overnight. The treated masses were dried at 80 °C overnight, admitted into the carbonization tube, then well-placed in electric furnace. The temperature was increased with the rate of 5 °C/min to attain 350 °C which allowed free evolution of volatiles and draining of tarry matter. After that, pure steam is introduced from the top of the tube using a steam generator to hold the internal temperature at 500 °C for 2 h. The obtained materials were washed with hot distilled water. The final products were desiccated at 110 °C for 48 h and finally kept in tightly closed bottles.

**Characterization of prepared activated carbon:** The syllable structure of synthetic adsorbents was examined using a JEOL scanning electron microscope (SEM) (JSM-6510LA model, Japan). The adsorbent elemental analyses were performed using Energy-Dispersive X-ray spectroscopy (EDX) connected to the same JOEL SEM instrument. The surface area of the three prepared activated carbon was determined by NOVA 1000e Quantochrome using the BET equation. The kind and intensity of the functional groups on the surface of prepared sample (FTIR) were recorded on Pomen, Hartman Spectrophotometer.

**Batch adsorption studies:** The adsorption experiments were performed by mixing 0.015 g of prepared activated carbons with 10 mL of <sup>99</sup>TcO<sub>4</sub> solution at  $25 \pm 1$  °C and NaNO<sub>3</sub> 0.01 M ionic strength. After shaking, the adsorbents were separated from solution by centrifugation at 4000 rpm for 20 min using a Hettich Centrifuge, model ROTOFIX 32 A. Liquid scintillation counting system (type 2770 TR/SL) supplied from Canberra-Packard, USA (model Tri-Carb) was used to analyze the initial and final concentration of <sup>99</sup>TcO<sub>4</sub>.

The effect of pH on the adsorption of  ${}^{99}\text{TcO}_4^-$  of initial concentrations 6.96 µg L<sup>-1</sup> (4365 Bq L<sup>-1</sup>) was studied in the range from 2 to 10 and the pH values were measured with an Orion 3-star plus pH meter. The effect of shaking time, from 5

to 1000 min and initial concentrations, varied from 6.96 to 38.73  $\mu$ g L<sup>-1</sup> (4365 to 24300 Bq L<sup>-1</sup>), of <sup>99</sup>TcO<sub>4</sub><sup>-</sup> at constant temperature and pH (5.5) were investigated. The data were represented by Frendluich and Langmuir isotherm models.

## **RESULTS AND DISCUSSION**

Scanning electron microscopy (SEM-EDX): The analysis of the prepared activated carbons using SEM and EDX are represented in Fig. 1. SEM shows that the precursor has strong effect on the texture and porosity of obtained activated carbons. C-2 prepared from saw dust has clear large pores with hexagonal and square shape compared to other samples where the pores take the shape of repeated tunnels in C-1 and burrows caves in C-3. Porosity in activated carbons are classified into three groups based on pore size (ps) according to Galiatsatou et al.<sup>13</sup>: microspores (pore size < 20 Å), mesopores (20 Å < pore size < 500 Å) and macro pores (pore size > 500 Å). During adsorption, macro and mesopores allows rapid transportation of solute into the internal of carbon for next diffusion into micropore volume. Thus, a developed porous network leads to amended adsorption capacity of the carbon. The SEM-EDX analysis revealed that the C-1 sample contains P, Si, Al, Na, O and C while, C-2 and C-3 samples also contain C, O and P. The presence of P comes from the H<sub>3</sub>PO<sub>4</sub> used in the activation process, while the O and C come from the cellulosic materials of the two precursors. The presence of Si, Na and Al in C-1 comes mainly from rice husk precursor.



Fig. 1. Scanning electron microscopy (SEM) and EDX of prepared activated carbons; 50 % saw dust + 50 % rice husk (C-1), 100 % saw dust (C-2) and 100 % rice husk (C-3)

**Fourier transforms infrared (FT-IR) spectra:** The spectra in Fig. 2 show the FT-IR of three prepared activated carbon



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samples. Complex nature of the surface functional groups of C-1 sample is indicated by number of absorption peaks as it contain peaks present, also, in the other two samples as it prepared from 50 % rice husk and 50 % saw dust. The broad peak at 3419 cm<sup>-1</sup> may be due to bonded OH group<sup>14</sup>. This peak modified to a sharp one at 3428 cm<sup>-1</sup> in the C-2 which was prepared from saw dust only and it shifted to 3391.8 cm<sup>-1</sup> in the C-3 prepared from rice husk only. Also, these bands can arise from the N-H stretching vibration in primary amines. The band at 2918 cm<sup>-1</sup> in C-2, arises from the -CH stretch of methylene<sup>15</sup>. Furthermore, the peak at 1189 cm<sup>-1</sup> in C-1 (prepared from rice husk + saw dust) is related to C-O stretching vacillation in carboxylic groups<sup>16</sup>. This peak moved to 1162 cm<sup>-1</sup> in C-2 (prepared from saw dust) and shifted to 1181 cm<sup>-1</sup> in C-3 (prepared from rice husk only). Hydroxyl, carboxylic and amino groups are available as an important exchange sites as indicated by great shifts in the absorption bands. The >C=C<skeletal stretch in condensed aromatic system is represented by the band at 1597 cm<sup>-1</sup>. Moreover, the band at 754 cm<sup>-1</sup> can be related to C-H bending out-of-plane modes of an organic compound<sup>17</sup>. Lignin, cellulose, hemicelluloses and some proteins; are the main constituents of biomass makes them high effective adsorbents for dissolved solutes.

Surface area and elemental analysis: Performance in the adsorption processes can greatly influenced by the differences in the surface area and porosity of adsorbent material which may have the same physical dimensions. The average pore radius, total pore volume and total surface area obtained for our prepared samples by applying the BET equation for  $N_2$  adsorption are summarized in Table-1.

TABLE-1 PHYSICAL AND CHEMICAL PROPERTIES OF SYNTHETIC ACTIVATED CARBONS							
Parameter	C-1	C-2	C-3				
Elemen	Elemental analysis (%)						
Nitrogen	0.44	0.31	0.39				
Carbon	11.20	60.70	21.60				
Hydrogen	3.10	2.20	0.70				
Sulfur	0.00	0.00	3.50				
Physical properties							
BET surface area (m <sup>2</sup> /g)	18	1110	324				
Langumir surface area	30	1598	487				
Total pore volume (cc/g)	0.02	0.73	0.24				
Average pore radius (Å)	20.4	35.7	14.7				

The data reveal that the BET surface area obtained from  $N_2$  adsorption isotherm ranges from 18 to 1110 m<sup>2</sup>/g and follows the order C-2 > C-3 > C-1. The total pore volume ranges from 0.02 to 0.73 cm<sup>3</sup> g<sup>-1</sup>; the highest value was reported also for C-2 which has the highest value of surface area and an average pore radius of 35.7 Å. The adsorption isotherms were classified into six types. Prepared adsorbents showed type IV according to IUPAC<sup>18</sup> which indicates the presence of micro-mesoporous structure of the adsorbents. Type (IV) isotherms with H<sub>1</sub>-type Hysteresis loops, describe the presence of tubular capillaries pores in the particles which is coincident with the result obtained from the SEM investigations. The results of surface area indicate that C-2 is prospective to have the highest adsorption efficiency.

Effect of pH on adsorption of  $TcO_4$ : The effect of pH on the adsorption of  $TcO_4$  onto the three prepared adsorbents was investigated in the range pH = 2 to 10 in 0.01 M NaNO<sub>3</sub> background solution (Fig. 3).



Fig. 3. Uptake of  $TcO_4$  on activated carbons as a function of initial pH in 0.01 M NaNO<sub>3</sub>

This pH range generally represents the LLLRW and groundwater. The results indicate that percentage removal of TcO<sub>4</sub><sup>-</sup> slightly decreases as pH increases from 2 to 10. The highest percentage removal of TcO<sub>4</sub><sup>-</sup> was reported at pH = 3 for investigated activated carbons following the order: C-2 > C-3 > C-1. The obtained results illustrate that TcO<sub>4</sub><sup>-</sup> can be separated from radioactive solution over a wide range of pH using active carbons in the presence of 0.01 M NO<sub>3</sub>. A high percentage removal of TcO<sub>4</sub><sup>-</sup> onto C-2 was recorded; where about 70 % of TcO<sub>4</sub><sup>-</sup> was treated<sup>5</sup> at pH ≈ 9.5 and > 92.0 % at pH ≈ 3. The other C-1 and C-3 samples revealed a similar behaviour, but with a lower adsorption percentage compared to C-2 samples, especially at low pH range. However, C-3 revealed a higher uptake and K<sub>d</sub> value at pH 9.8 giving 1550 mL g<sup>-1</sup> relative to 762 and 1190 mL g<sup>-1</sup> for C-1 and C-2 at the same pH value.

Aqueous speciation of Tc as a function of pH was calculated using PHREEQC software. The data show that the dominant species of Tc is  $TcO_4$ . This suggests that the adsorption of <sup>99</sup>Tc be based on the activated carbons surface in addition to the speciation of the studied radionuclide and the mechanism of adsorption is governed by anion exchange reactions. The low economically cost of locally prepared active carbon and the easy remedy process make this technology costeffective compared to anion exchange resins or liquid-liquid extraction techniques<sup>19,20</sup>. The process of anion exchange resins usually generates a large volume of spent sorbent that needs storage and disposal<sup>9,21</sup>. Generally, comparatively considerable amounts of resins and longer times (ranging between 24 h to 6 weeks) were recorded as necessary for these resins to reach equilibrium. Only 90 % of TcO<sub>4</sub><sup>-</sup> was removed from the Paducah groundwater (1 L) with 1 g Dowex SRB-OH resin after 4 days of equilibration as reported by Del-Cul *et al.*<sup>22</sup>. In contrast, TcO<sub>4</sub><sup>-</sup>, adsorption onto prepared activated carbon is relatively fast and much more effective.

Adsorption kinetic and modeling: Kinetic experiments were done and their results are shown in Fig. 4 which represent the corresponding model fitting of the adsorption reaction of  $5.1 \,\mu g \, L^{-1} \, (3200 \, Bq \, L^{-1}) \, TcO_4^{-}$  onto the locally prepared active carbons as a function of shaking time.





When the adsorption starts, numerous functional groups as an active sites are presents and pertechnetate ions reacted simply with the functional groups and consequently a higher rate of uptake is recorded. During the first 20 min about 83, 92 and 89 % of TcO<sub>4</sub><sup>-</sup> were adsorbed by C-1, C-2 and C-3, respectively. The remaining radionuclide concentrations were adsorbed during 3 h. Based on the obtained results, 3 h shaking time is enough for TcO<sub>4</sub><sup>-</sup> treatment by C-1 and C-3, whereas 100 min are sufficient for adsorption by C-2. Holm *et al.*<sup>10</sup> recorded a different kinetic action for TcO<sub>4</sub><sup>-</sup> treatment using an activated carbon, where, 5 h of contact were required for the adsorption to reach equilibrium<sup>10</sup>.

Three different models were used to calculate the kinetic of  $TcO_4^-$  adsorption by the prepared adsorbents. The pseudo first order (eqn. 1) and intra particle diffusion (eqn. 2) were applied using non-linear regression analysis<sup>23 24</sup>, while the pseudo second order (eqn. 3) was fitted using linear regression analysis<sup>25</sup>. These models are given as the following:

$$\mathbf{q}_{t} = \mathbf{q}_{e} [1 - \exp(-\mathbf{k}_{1} \mathbf{t})] \tag{1}$$

$$\mathbf{q}_{t} = \mathbf{K}_{\mathrm{D}} \cdot \mathbf{t}^{\mathrm{m}} \tag{2}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$
(3)

where:  $q_i$  is the value of TcO<sub>4</sub><sup>-</sup> removed using different prepared activated carbons at time (t);  $q_e$  is the uptake of TcO<sub>4</sub><sup>-</sup> at equilibrium (mg g<sup>-1</sup>);  $k_1$  (min<sup>-1</sup>) and  $k_2$  (Kg mg<sup>-1</sup> min<sup>-1</sup>) are the Lagergren and pseudo second order rate constants, respectively;  $K_D$  is the diffusion rate factor and m is a non-dimensional coefficient that indicates the sorption mechanism.

In the intra-particle diffusion model, A value of m = 0.5 denotes intra-particle diffusion as the rate controlling step. The fitting of the three kinetic equations to the obtained results is shown in Fig. 4 and summarized in Table-2.

Fitting of the first order and intra-particle diffusion models by non-linear regression is represented in Fig. 4(A). They provide close fits to sorption kinetic results with an average regression coefficient ( $r^2$ ) value of 0.996 ± 0.01 for all activated carbon samples. The amounts of metal species calculated at equilibrium  $(q_e)$  are 0.55, 0.60 and 0.58 mg Kg<sup>-1</sup> for C-1, C-2 and C-3, in the same order. The first order rate constants of <sup>99</sup>TcO<sub>4</sub> adsorption were found to be the same for the investigated carbon samples, with a k<sub>1</sub> value of 10 Kg mg<sup>-1</sup> min<sup>-1</sup>. The correlation coefficient supporting that sorption of <sup>99</sup>TcO<sub>4</sub> onto activated carbons follows the pseudo-second-order rate model. According to the correlation coefficient of pseudo second order was found to give exact fitting to three investigated activated carbons of r<sup>2</sup> values varied from 0.999 to 1.0, Fig. 4(B). Although, C-2 gives the highest qe with amount 0.62 mg kg<sup>-1</sup>, the second order rate constants of  $TcO_4^{-1}$ adsorption were found to obey the order: C-3 > C-2 > C-1 with  $k_2$  values 4.17, 1.33 and 0.81 kg mg<sup>-1</sup> min<sup>-1</sup>, respectively.

TABLE-2
XINETIC PARAMETERS OF TCO." ADSORPTION USING PREPARED ACTIVATED CARBONS

Adsorbant -	1 <sup>st</sup> order			2 <sup>nd</sup> order			Intraparticles diffusion		
Ausorbent -	$q_e^*$	k1**	$r^2$	q <sub>e</sub>	k <sub>2</sub>	$\mathbf{r}^2$	K <sub>D</sub> ***	m	$r^2$
C-1	0.55	10	0.956	0.59	0.81	0.999	0.48	0.03	0.992
C-2	0.60	10	0.991	0.62	1.33	1.000	0.56	0.02	0.999
C-3	0.58	10	0.971	0.60	4.17	0.999	0.52	0.023	0.990

Transport of  $TcO_4^-$  from to the interior of the adsorbent materials is influenced by its characterization and behaviour with  $TcO_4^-$ . Impact of concentration gradients can be the factor affecting on the solute movement by diffusion from one fluid body to the other in case of the adsorbent in the form of porous barriers<sup>26</sup>. The non-linear intraparticle diffusion equation was applied for prediction the rate controlling step of pertechnetate uptake using prepared activated carbons. The m value equals 0.02-0.03 which is less than 0.5. These results indicate that intraparticle diffusion has a very limited effect in controlling the rate of treatment of <sup>99</sup>TcO<sub>4</sub><sup>-</sup> onto prepared adsorbents. The diffusion rate factor (K<sub>D</sub>) was found to be 0.56 for C-2, with values of 0.48 and 0.52 for C-1 and C-3, respectively.

Adsorption isotherms: The adsorption of <sup>99</sup>TcO<sub>4</sub><sup>-</sup> onto prepared activated carbons was fitted by Freundlich and Langmuir isotherm equations (Fig. 5) and reported in Table-3.



Fig. 5. Adsorption isotherms of TcO<sub>4</sub><sup>-</sup> onto prepared activated carbons using non-linear Frundlich and Langmuir equations

	TABLE-3
	FREUNDLICH AND LANGMUIR PARAMETERS OF TcO <sub>4</sub> -
	ADSORPTION ONTO SYNTHETIC ACTIVATED CARBONS
_	

Adapthant	]	Freundlic	h		Langmuir	•
Ausorbeni	K <sub>f</sub>	1/n	$r^2$	b	$q_{\rm m}$	$r^2$
C-1	5431	1.06	0.999	14.70	250.3	0.997
C-2	16121	1.08	0.998	30.50	316.0	0.995
C-3	6328	1.05	0.998	18.40	264.4	0.996

With three samples the adsorption of  ${}^{99}\text{TcO}_4$  increases as the concentrations increase. The Freundlich isotherm gives a closer fit with  $r^2 = 0.998 \pm 0.0005$  whereas the Langmuir model gives  $r^2 = 0.996 \pm 0.001$ . The Freundlich parameter was calculated from the equation:

$$\mathbf{q}_{e} = \mathbf{K}_{f} \mathbf{C}_{e}^{1/n} \tag{4}$$

1/n and K<sub>f</sub> are Freundlish constants. The value 1/n indicates the favourability of adsorption process. When n > 1 the adsorption is favourable.

Although, the better fit of the obtained results with studded models proposes that the three activated carbons characterized by heterogeneous surface with active sites of different affinity<sup>27</sup>, this cannot be applied in the current case due to the low  $TcO_4$  concentration range used. In accordance with the distribution coefficients deduced from the Freundlich isotherm, the sorption affinities towards  $TcO_4$  take the concatenation : C-2 > C-3 >

C-1 with  $K_f$  values of 16,121, 6,328 and 5,431, respectively. This affinity sequence follows the same order of surface areas and porosities reported in Table-1 for the activated carbons.

In present study, the Langmuir isotherm model was also used to estimate the adsorption capacity  $(q_m)$  of the concerned radionuclide from the following equation:

$$q_e = q_m \frac{bC_e}{1 + bC_e}$$
(5)

 $C_e$  is the solute concentration at equilibrium (mg L<sup>-1</sup>), q<sub>e</sub> is the uptake of TcO<sub>4</sub><sup>-</sup> ions at equilibrium (mg Kg<sup>-1</sup>), while q<sub>m</sub> and b are Langmuir parameters refer to the adsorption capacity and energy, respectively. The maximum uptake (q<sub>m</sub>) calculated from the Langmuir equation take the sequence of C-2 > C-3 > C-1, with sorption capacities of 316, 264 and 250 mg Kg<sup>-1</sup>, respectively. The variation in adsorption capacities of the prepared activated carbons for TcO<sub>4</sub><sup>-</sup> may be mainly consequent to the surface area, porosity and the corresponding pore size where SEM images (Fig. 1) show a clear large hexagonal pore structure for C-2 in comparison to the other activated carbons.

**TcO**<sub>4</sub><sup>-</sup> **distribution coefficient (K**<sub>d</sub>) **and sorption thermodynamics:** The distribution coefficient, K<sub>d</sub> (eqn. 6) and Gibbs free energy,  $\Delta G^{\circ}$  (eqn. 8) of TcO<sub>4</sub><sup>-</sup> adsorption on synthetic activated carbons were calculated in water and in 0.01 M NaNO<sub>3</sub> using the following equations:

$$K_{d} = \frac{(C_{o} - C_{e})}{C_{e}} \times \frac{V}{m} \quad mL/g$$
(6)

$$K_{e} = \frac{C_{s}}{C}$$
(7)

$$\Delta G^{\circ} = -RT \ln K_{a} \tag{8}$$

Calculated values of  $K_e$ ,  $\Delta G^o$  and  $K_d$  were reported in Table-4. The average  $K_d$  values for  $TcO_4^-$  adsorption on the prepared activated carbons using 5 different concentrations were found to be 3716 ± 106 g mL<sup>-1</sup> for C-1, 9170 ± 433 g mL<sup>-1</sup> for C-2 and 4391 ± 215 g mL<sup>-1</sup> for C-3. These results indicate that significant energetically favourable sites are still available regardless an increasing pertechnetate concentration. This behaviour may be attributed to the high surface areas and porosity as reported in Table-1. When the solute ions moved through the pores, their diffusion was enhanced but may be retarded when moved through smaller diameter channels<sup>28</sup>.

TABLE-4							
	TcO	<sup>4</sup> DISTRIBUTIO	N COEFFICIENT (I	K <sub>d</sub> ),			
	THERMO	DYNAMIC EQU	ILIBRIUM CONST.	ANT (K <sub>e</sub> )			
	AND SORPTION THERMODYNAMICS						
	Adsorbent	K <sub>e</sub>	$\Delta G^{\circ} (KJ mol^{-1})$	$K_d (mg L^{-1})$			
	C-1	$3.72 \pm 0.11$	$-3.25 \pm 0.07$	$3715 \pm 106$			
	C-2	$9.17 \pm 0.43$	$-5.50 \pm 0.12$	$9170 \pm 433$			
	C-3	$4.39 \pm 0.22$	$-3.70 \pm 0.12$	$4391 \pm 215$			

The grade of spontaneity of the sorption of any solute can be indicated by the Gibbs free energy values, where high negative values of  $\Delta G^{\circ}$  indicate a more energetically favourable sorption process. The  $\Delta G^{\circ}$  indicated that C-2 is a high efficient sorbent with  $\Delta G^{\circ}$  value of -5.50 ± 0.12 KJ mol<sup>-1</sup> followed by C-3 with  $\Delta G^{\circ}$  values -3.70 ± 0.12 and C-1 with  $\Delta G^{\circ}$  values

 $-3.25 \pm 0.07$  KJ mol<sup>-1</sup>. The negative  $\Delta G^{\circ}$  of the three prepared activated carbons revealed that they are good adsorbents for TcO<sub>4</sub><sup>-</sup> removal from low-level liquid radioactive waste.

#### Conclusion

From the results obtained in present study, it is clear that the treatment processes of  $TcO_4$  using three different locally prepared activated carbons are affected by concentration of  $TcO_4$ , contact time and the pH of the solution. The maximum uptake was reported at pH 3 for the three activated carbon adsorbents. From the application of the Freundlich and Langmuir isotherms models on the obtained data, it was found that the C-2 sample prepared from 100 % saw dust and activated with H<sub>3</sub>PO<sub>4</sub> has the highest adsorption affinity and maximum adsorption capacity. From the studied factors that affecting the adsorption process (contact time, pH and adsorption isotherms) it can be concluded that:  $TcO_4$  removal by prepared activated carbons can be a promising efficient and cost effective technique for low-level liquid radioactive waste treatment and remediation of groundwater contaminated with <sup>99</sup>TcO<sub>4</sub>.

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