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Solid Phase Extractive Pre-Concentration of Uranium(VI) from Liquid Waste onto Peach Stone Steam Pyrolysis Activated Carbon

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Drinking water contaminants, especially heavy metals and uranium, have been recognized as a worldwide problem pose a serious threat to human health. Among several treatment technologies applied for contaminant removal, adsorption methods have been studied extensively and proven to offer satisfactory results with high selectivity. In this study, steam pyrolysis activated carbons from biomass were synthesized with characterizations giving a higher capacity for uranium and other heavy metal contaminants. In this study, a batch equilibration pre-concentration of uranium(VI) was carried out in the pH range (2-10), adsorbent dosage (0.166-0.833 g L^{-1}), sorption time (5 min to 24 h), temperatures (25, 50 and 70 °C), different types of activated carbon precursor, uranium initial concentration (50-500 mg L^{-1}) and different interfering ions (cations: Cr, Pb, Fe, K and anions: NO_3^-, Cl^-, SO_4^{2-}, HPO_4^{2-}). The equilibrium data fitted well to the Freundlich and Langmuir equilibrium models in the studied concentration range and temperatures. The kinetics of the adsorption process followed a second-order adsorption and intra-particle diffusion is not the only rate determining step. 0.25 M H_2SO_4 was effective in uranium recovery. The results indicated that the conversion of naturally abundant peach stone of the nuisance value to valuable material exhibited considerable potential for application in pre-concentration and separation of uranium from aqueous solution.

Keywords: Pre-concentration, Uranium(VI), Liquid waste, Peach stone, Steam pyrolysis activated carbon.

INTRODUCTION

Contamination of the aquatic environment by metal has become an important issue with respect to the environment and human health. In recent years, studies directed to quantify the adsorption of toxic and heavy metals from subsurface environment, industrial and research wastes through sorption [1]. In the nuclear fuel, processing steps cycle generates wastewater streams containing a variety of dissolved metals, including lanthanide and actinide elements. The origin of this problem is the continuous production of huge volume, low activity and waste requiring permanent and efficient treatment. Environmental protection by remediation of toxic metals and radionuclides from aqueous solutions, has been studied extensively, because of their hazardous even at low concentration [2]. When dealing with uranium contamination of the environment, special interests are raised. High mobility is the major concern with uranium as it is highly soluble and occurs in the hexavalent form as a mobile hydrated uranyl ion in the pH ranges of acid rain. If it is present at a concentration above 0.1 mg/kg of body weight, uranium can cause transient chemical damage to the kidney [3].

Physical, physico-chemical and chemical principles are different techniques adopted by various researchers for pre-concentration of uranium [4-6]. Preconcentration techniques have come to the forefront compared to other solid phase extraction (SPE) or solid-liquid extraction (SLE) due to the following advantages. Higher pre-concentration factors are included, the emulsion is absent, with respect to hazardous samples it is safe, due to low consumption of reagents it has a minimal cost, flexibility and easier incorporation into automated analysis techniques [7,8]. Neutral polymer-Amberlite XAD series [9-11], octadecyl silica membrane discs, silica [12,13], activated silica gel [4], polyurethane foam [14], controlled pore glass and cationic or anionic exchange resins [15-19] as a number of solid. Sorbents have been reported for the pre-concentration of uranium(VI) from dilute solutions prior to determination by a variety of analytical techniques. Bearing in mind high retention capacity, ready availability, the ease of elution and regeneration and efficient applicability to pre-concentration of trace amounts of inorganic, activated carbon were chosen as a solid phase extraction sorbent in the present study. Tailored activated carbons were reported for the sorption of Cu, Mn, Co, Cd, Pb, Ni, Cr and lanthanides. To our best of

knowledge, there is no solid phase extraction procedure reported for uranyl ion using steam pyrolyzed activated carbon. The fruit stone is available free of cost from fruit processing industries. Therefore, only the cost of transport is involved in the wastewater treatment. Hence, recycling of this solid waste and converting it to valuable materials (activated carbon) for wastewater treatment would not only be economical but also help to solve solid waste disposal problems. The objectives of this study were to: (i) preparation of steam pyrolysis activated carbon, (ii) selection of the sample of activated carbon with the highest uptake of uranium, (iii) characterization of the peach stone prepared activated carbon, (iv) Study the influence of various parameters on adsorption of uranium, (v) applications of above solid phase extraction for pre-concentration of uranium from laboratory wastewater using a batch technique.

EXPERIMENTAL

Activated carbon based on steam pyrolysis of biomass: The raw materials used, are agricultural by-products. They give low yields of activated carbon because they have high volatile content. They are relatively economical starting materials. In Egypt, large amounts of agricultural by-products (mango stone, peanut shell, cotton stalk, charcoal, date pits, rice husk, apricot stone, corn cobs, peach stone, sawdust, olive stone and bagasse pith) are available. The production of activated carbon from these sources is one of the most important phases of this study. Steam pyrolysis activated carbon from agriculture by-product was obtained by heating 30 g of the clean, dry natural raw material to the specified temperature in a tube furnace. Different precursors were placed in the reactor to be situated in the hot zone of tube furnace. Activation temperature was raised by the rate of (50 °C/10 min.), to permit free evolution of volatiles, up to around 350 °C. Then, pure steam was introduced through the heated mass and heating was continued up to 750 °C. In the presence of steam, the material was soaked 2 h at this temperature, then the product was cooled to room temperature and weight determined. The produced samples take the following abbreviation; MS-S75, PSh-S75, CSt-S75, C-S75, DP-S75, RH-S75, AS-S75, CC-S75, PSt-S75, SD-S75, OS-S75, BP-S75.

Phosphoric acid and steam pyrolysis activated carbons (one step): In this experiment a known weight of rice husk (RH) was soaked in pre-diluted phosphoric acid solutions of different concentrations. By dilution of 85 wt % H_3PO_4 (BDH), the following concentrations were obtained: 50, 60,70 and 80 wt %. The rice husks mass was slightly agitated to ensure penetration of the acid throughout, then the mixture heated to 80 °C for 1 h and left overnight at room temperature to help appropriate wetting of the precursor. Next day, the impregnated samples were treated as mentioned above. The cooled product was washed with distilled water to the pH of 6-7, then dried at 110 °C and weighted. In this category we obtained 4 samples of activated carbons with the following notations: RH-P5S5, RH-P6S5, RH-P7S5, RH-P8S5.

Silica extracted from rice husk: Raw rice husk was stirred with the concentration of 4 % KOH at a weight ratio 1:10 of rice husk to solution, respectively. And heated to boiling for 0.5 h, then the mixture was left overnight, filtered and washed twice with hot distilled water. The filtrate was collected and subsequently used, as it is predicted to contain leached silica. To the filtrate, 20 % HCl was added so as to precipitate dissolved silica, until the pH reached (6-7), a white precipitate was formed, which was filtered, dried and weighed. The residual desilicated rice husk was steam pyrolyzed at the 750 °C for 2 h. Samples Si and DRH-S75 were obtained.

The stock solutions of uranium(VI) were prepared (NMA laboratories) by dissolving $UO_2(NO_3)_2{\cdot}6H_2O$ (Merck) in distilled water. The activated carbon samples were thoroughly pre-wetted with agitation in 50 mL of distilled water for 3 h to remove trapped air from the pores. All other reagents used were analytical reagent grade.

Batch adsorption studies: Adsorption experiments were performed at 298 ± 2 K by mixing 0.02 g of adsorbent with a 20 mL uranium solution of desired concentrations in 50 mL stoppered plastic bottles in shaking thermostat machine at a speed of 150 rpm. The equilibrium isotherms were determined by varying initial uranium concentrations in the range of 50-500 mg L^{-1} and using equilibrium time of 3 h. The effect of solution pH on the uptake of uranium was investigated between pH 1 and 10. The pH was adjusted using 0.1 M HNO_3 or 0.1 NaOH solutions. Also, the effect of adsorbent dosage was evaluated in the range 0.005-0.025 g/30 mL of uranium solution under the similar experimental conditions at desired pH. For the kinetic and thermodynamic studies, the sorption time varied between 0 and 24 h and the adsorption was evaluated at temperatures: 298, 323 and 343 K. At predetermined times, the samples were withdrawn and centrifuged at 15,000 rpm for 10 min and the supernatant solutions were analyzed for the residual uranium concentration in the solution using a sensitive and simple spectrophotometric method based on coloured complexes with ArIII in aqueous medium [20]. The absorbance of the solution was measured at 655 nm wavelength using a UV-visible spectrophotometer. All the experiments were carried out in duplicate. Kinetic desorption experiments were also performed after 24 h with sorption experiments by replacing the uranium solution with different eluting solution without a uranium (*i.e.*, uranium-free solution). The remaining procedures are the same as the sorption experiment.

RESULTS AND DISCUSSION

The parameters which affect the uranium pre-concentration, such as types of activated carbon precursor and method of activation (thermal or chemical method), contact time, pH, initial concentration, adsorbent weight, temperature and the presence of interfering ions in aqueous solution have been investigated**.** Also, the elution (or recovery) of adsorbed uranium was checked using different acids and base to determine the reusability of activated carbon and/or recovery of uranium.

Effect of precursor's type on sorption of uranium: From Fig. 1, it is suggested that (i) the same treatment (steam pyrolysis) of different precursors leads to activated carbon with different affinity of uranium (sample 1 to sample 12). (ii) Same precursor (sample 6 and samples from 13-18) give different sorption affinity of uranium with different methods of activation (steam pyrolysis and/or treatment with different concentration of acid

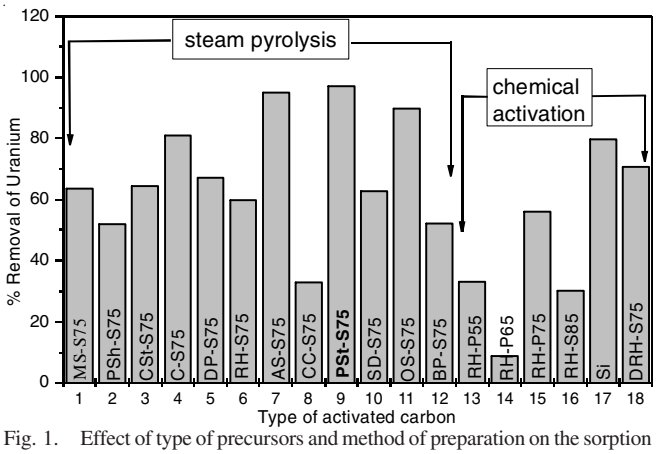

Fig. 1. Effect of type of precursors and method of preparation on the sorption of uranium

or base). (iii) From all prepared samples, the highest sorption value is for the peach stone (PSt) thermally activated with steam at temperature of 750 °C (S75). So, this sample (PSt-S75) was selected to complete the investigation of other parameters influence the pre-concentration of uranium from liquid waste.

Characterization of PSt-S75 activated carbon

Surface area and pore size distribution: The surface area of the selected sample was measured by BET method (using Quanta chrome NOVA 1000e, USA) and the presence of micropores, mesopores and macropores in the PSt-S75 was illustrated by the pore size distribution as depicted in Fig. 2. The pore characteristics, a proximate analysis and the physico-chemical characterization of PSt-S75 activated carbon are summarized in Table-1.

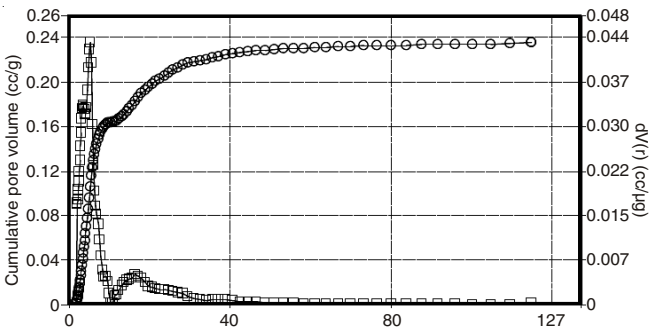

Fig. 2. Pore size distribution of PSt-S75 activated carbon

FTIR spectral studies: In general, the biomass consists of cellulose, hemicelluloses, lignin and some protein, offering many functional groups which can bind ions such as carboxyl, hydroxyl, carbonyl and amino groups. The IR spectrum of the uranium loaded PSt-S75 was compared with the IR spectrum of PSt-S75 alone (Fig. 3). The shift of some bands observed in the IR spectra to higher and/or lower wave numbers in addition to the appearance of new bands in the region of low frequency (1650-600 cm^{-1}) are most likely corresponding to the participation of the oxygen and/or nitrogen of the amino acids of the PSt-S75 in the complex formation with the uranium ions [21]. The observed band at 940-935 cm^{-1} and bands at 830-750 cm^{-1} may be assigned to ν_{as}(O=U=O) and ν_s(O=U=O) [22], respectively.

TABLE-1
PHYSICO-CHEMICAL PARAMETERS OF PSt-S75 ACTIVATED CARBON

Parameters	Values
Carbon yield (%)	35
Ash content (%)	4.8
Methylene blue number (mg g^{-1})	190
Packed density (g mL^{-1})	0.484
Apparent density (g mL^{-1})	0.27
BET surface area (m^2 g^{-1})	478.42
Langmuir surface area (m^2 g^{-1})	496.71
Average pore radius (Å)	10.82
Micropore surface area (m^2 g^{-1})	518.31
Total pore volume (cm^3 g^{-1})	0.2583
Micropore volume (cm^3 g^{-1})	0.1840
Mesopores volume (cm^3 g^{-1})	0. 074
Phenol number (mg)	180
Iodine number (mg g^{-1})	530
Particle size (mm)	1.0 - 0.25
Matter soluble in water (%)	1.50
Matter soluble in acid (%)	1.92
Matter soluble in base (%)	1.81
Moisture content (%)	8.9
C %	79.37
H %	2.52
N %	0.154
S %	–
O % (by difference)	10.056
pH	8.1

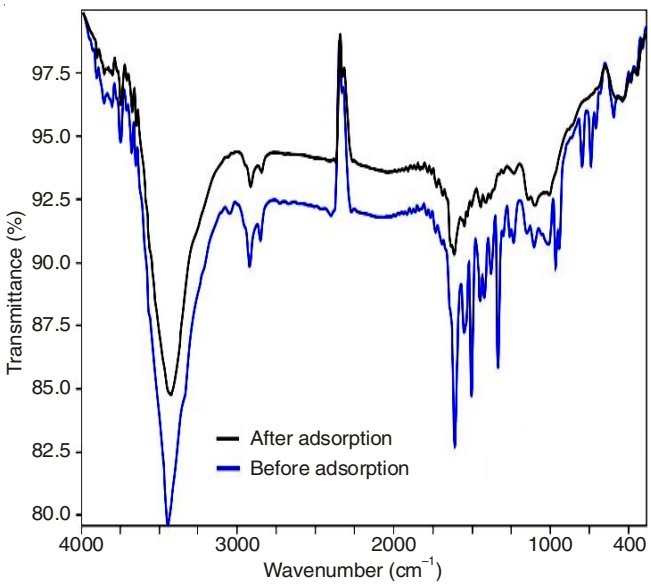

Fig. 3. FTIR spectroscopy of the PSt-S75 before and after adsorption of uranium

Scanning electron microscope (SEM): Scanning electronic microscope with an energy dispersive X-ray spectrometer (SEM/EDX) was used for analysis of the PSt-S75 before and after adsorption of uranium. Elemental micropre and distribution mapping techniques were used to analyze the uranium distribution on the surface of the PSt-S75 activated carbon.

Fig. 4(a) and 4(b) shows the SEM photograph and the uranium distribution on the PSt-S75 activated carbon surface at a plateau. Furthermore, the EDX analysis indicated that the uranium was evenly adsorbed and distributed on the surface of PSt-S75 activated carbon as illustrated in Fig. 5.

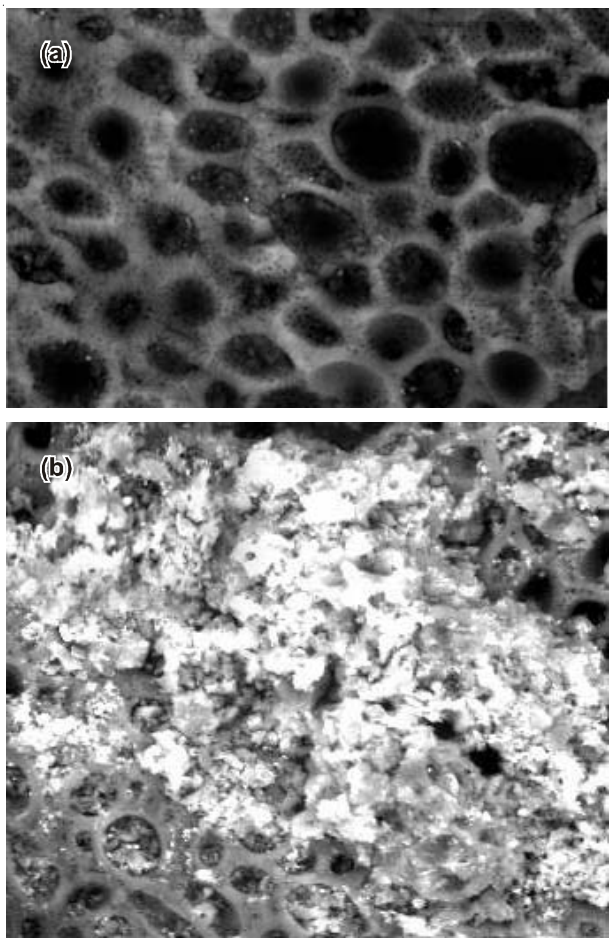

Fig. 4. SEM of PSt-S75 (a) before adsorption and (b) after adsorption of uranium

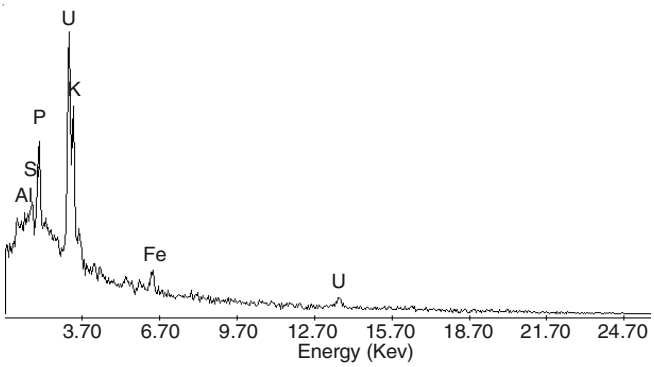

Fig. 5. EDX of PSt-S75 loaded with uranium

Thermo gravimetric analysis (TGA): Carbon samples were heated in an oven prior to the TGA tests to remove moisture. The sample was first heated from room temperature to 800 °C at a heating rate of 20 °C/min to drive off volatile materials, *i.e.*, water, carbon dioxide and low molecular-weight hydrocarbons. The concentrations of these volatile materials varied from one precursor to another. Once 800 °C was reached, the temperature was held constant until the TGA curve became flat, so that the volatile materials were completely released. The entire TGA test was completed when the height of the weight loss curve stopped changing. A TGA analysis on oxygenated PSt-S75 shows that desorption of surface oxides as CO_2 reaches its peak rate at around 500 °C and as CO at around 700 °C. Further increase in temperature will shorten the pre- and post-treatment time, but may take a risk of having carbon annealed at above 800 °C (Fig. 6). This confirms our results that a temperature of 750 °C is best for treatment of peach stones.

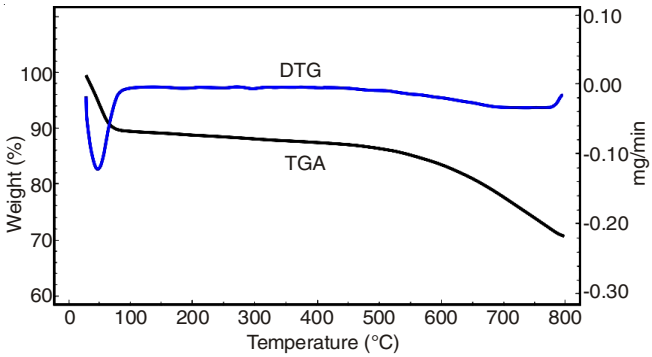

Fig. 6. TGA and DTG of PSt-S75obtained by steam activation at 800 °C

Uranium sorption *versus* pH: To investigate the kinetics of uranium sorption and the sorption capacity of PSt-S75 activated carbon towards this ion, it is convenient to study the influence of pH on the uranium adsorption in order to establish the pH range where the sorption is maximal. In fact, it is known that uranium has sorbed in a narrow range of pH ($4.5 < pH < 5.5$) [23,24]. The change of the uranyl ions state in solution explains this fact, which depends on the uranium concentration and on the solution pH.

The percentage of adsorption of uranium using PSt-S75 sample increases with increasing pH to a maximum value (pH 4.33) and then declines rather rapidly with further increase in pH as shown in Fig. 7 [25]. Further then pH of 4.33, precipitation may be started due to the formation of complexes in aqueous solution and consequently, the adsorption decreases [26]. Thus, the optimum adsorption take place at pH 4.33. At lower pH the % removal of uranium is low, which may be explained by H^+ competition with uranium binding sites and the formation of extractable uranium species at higher pH. The hydrolysis of uranyl ion plays an important role in determining the equilibrium between uranium on adsorbent and in solution. Speciation of uranium in solution may be explaining the pH profiles.

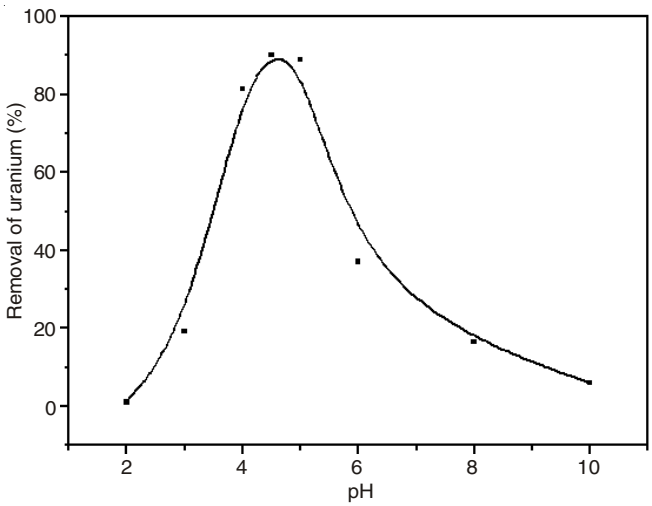

Fig. 7. Effect of pH on uranium(VI) sorption onto PSt-S75 activated carbon

When the pH increases from an acidic to a neutral value, different hydroxo complexes may be form as reported by Parab *et al.* [27]. Hydroxo complexes repartition was determined by equilibrium as the following:

$$UO_2^{2+} + 2H_2O \rightleftharpoons UO_2(OH)^+ + H_3O^+ \text{ (pk = 5.80)} \quad (1)$$

$$2UO_2^{2+} + 4H_2O \rightleftharpoons (UO_2)_2(OH)_2^{2+} + 2H_3O^+ \text{ (pk = 5.62)} \quad (2)$$

$$3UO_2^{2+} + 10H_2O \rightleftharpoons (UO_2)_3(OH)_5^{2+} + 5H_3O^+ \text{ (pk = 15.63)} \quad (3)$$

Below the pH value of 2.5, the predominant species are UO_2^{2+}; but at higher pH values, hydrolysis products include $UO_2(OH)^+$, $[(UO_2)_2(OH)_2^{2+}]$ dimer and $[(UO_2)_3(OH)_5^{2+}]$ trimer.

Several mechanisms such as ion exchange, electrostatic interaction and complexation can explain the effect of pH on the sorption of uranium. The influence of pH on removal of uranium can be explained on the basis of an electrostatic interaction model [28]. As the pH decreases, the surface of carbon exhibits increasing positive characteristics. Since the species to be adsorbed are also positive, the adsorption is not favoured. Besides this H^+ ions present at higher concentrations in the reaction mixture competes with positive ions for the adsorption sites resulting in the reduced uptake of uranium. On the contrary, as the pH increases the adsorbent surface becomes more and more negatively charged and therefore the adsorption of positively charged species is more favourable. The reduction in H^+ ions also facilitates preferential uptake of the metal. The mechanism of adsorption of uranium may also be explained based on ion-exchange model. A pure carbon surface is considered to be non-polar, but in actual practice some carbon-oxygen complexes (C_XO, CO_X and C_XO_2) are usually present, which render the surface slightly polar. Since there is no satisfactory method for determining the polar character of the surface quantitatively, the statement is relative [29]. The surface oxygen complexes hydrolyze water molecules as shown below, this makes the adsorbent weakly acidic cations exchanger. PSt-S75 can bind these hydroxo complexes very well.

$$C_XO + 2H_2O \rightarrow C_XOH_2^{2+} + 2OH^- \quad (4)$$

$$CO_X + XH_2O \rightarrow CO(OH)^+_X + X(OH)^- \quad (5)$$

$$C_XO_2 + H_2O \rightarrow C_XO^{2+} + 2OH^- \quad (6)$$

Fig. 8 presents typical data for uranium adsorption at various pH values plotted as the log distribution coefficient, K_d (cm^3/g), *versus* pH. As shown, the slope of log K_d is divided into four parts: (1) pH range 2-4.33 in which the slope = 1.26 indicating that the adsorption is ion-exchanging mechanism (cations exchange). It is likely that carboxylic groups with a pK value of 4-5 are largely responsible for the ion exchange of uranium from near-neutral aqueous solutions. The mechanism of uranium sorption is predominantly by cations exchange at the weakly acidic functional groups and this can be described by the following equilibrium reaction for divalent uranyl ions:

$$2(R\text{-}COO^-H^+) + UO_2^{2+} \underset{pH<4}{\overset{pH=4}{\rightleftharpoons}} (R\text{---}COO^-)_2UO_2^{2+} + 2H^+ \quad (7)$$

Similar ion-exchange reactions can be postulated for the other hydrolyzed ionic species of uranium. Other oxygenated weak acid groups. *e.g.*, phenolic and lactone-type groups are capable of ion exchange provided that the pH of the solution exceeds the dissociation pK value of the functional group.

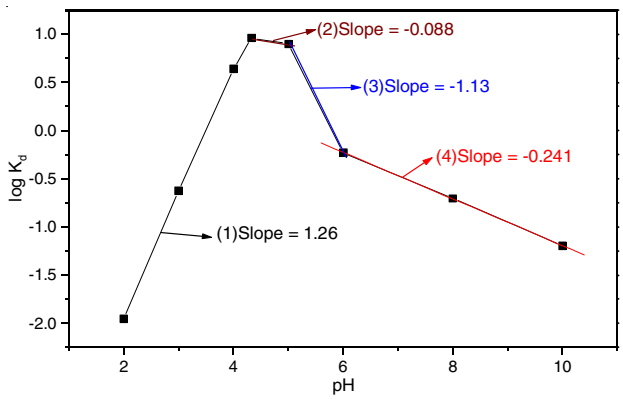

Fig. 8. log K_d *vs*. pH plot at constant uranium concentration

Lowering of the pH value by the addition of acid will tend to protonate the surface groups and lead to desorption of cationic uranium complexes. Acidification with dilute nitric acid will form the neutral $UO_2(NO_3)_2$ species which is not sorbed by an ion-exchange mechanism. According to the electrostatic attraction theory, the increase in the metal removal as the pH increases can be explained on the basis of a decrease in competition between proton and metal species for the surface sites and by the decrease in positive surface charge, which results in a lower coulombic repulsion of the sorbed metal [30]. (2) pH ranges 4.33-5, the slope = -0.088 revealing that after pH 4.33, the desorption start to take place by electrostatic repulsion decreasing the % removal of uranium. (3) pH range 5-6, slope = -1.13 means that the anion exchange desorption is responsible for the high decrease in the % removal of uranium. (4) At pH 6-10, slope = -0.241 indicating that the desorption is not only anion exchange, but also there is another mechanism participate in the desorption of uranium from loaded PSt-S75 [31].

Effect of shaking time: Fig. 9 shows the adsorption of uranium on PSt-S75 as a function of shaking time varying from 5 min to 24 h. The adsorption slightly increases with an increase of shaking time and reaches equilibrium within 3 h indicating some external surface sorption. However, the gradual uptake of uranium is diffusion controlled within the porous structure of micro- and mesopores and therefore the attainment of true equilibrium is slow. The uptake at 19 and 24 h of shaking time was observed to be slightly higher than the shorter shaking times. On the other hand, from the economical point of view 4 h shaking time were selected as optimum parameter [24].

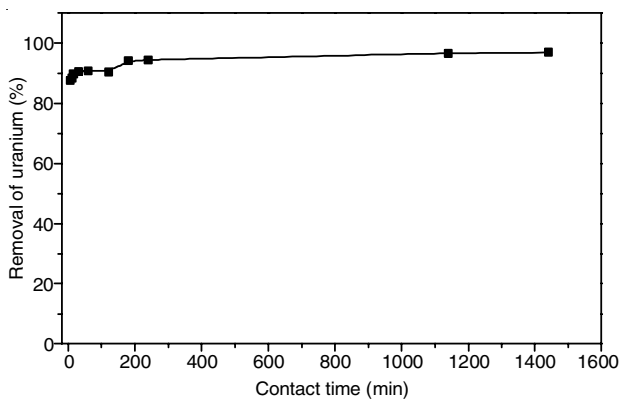

Fig. 9. Effect of shaking time on the adsorption of uranium using PSt-S75 sample

Adsorption dynamics: To examine the controlling mechanism of the adsorption process, several kinetic models are used to test experimental data. A simple kinetic analysis of adsorption is the pseudo-first order equation in the following form [32,33]:

$$\log (q_e - q_t) = \log (q_e) - k_{1ads}t/2.303 \quad (8)$$

where k_{1ads} is the rate constant of pseudo-first-order adsorption and q_e denotes the amount of adsorption at equilibrium. In addition, a pseudo-second-order equation based on adsorption equilibrium capacity may be expressed in the form:

$$1/(q_e - q_t) = 1/q_e + k_{2\,ads}t \quad (9)$$

or equivalently

$$t/q_t = 1/k_{2ads}q_e^2 + t/q_e \quad (10)$$

Eqn. 10 can be rearranged as:

$$t/q_t = 1/k_{2ads}q_e^2 + t/q_e = 1/q_e + 1/h \quad (11)$$

where k_{2ads} is the rate constant of pseudo-second-order adsorption and $h = k_{2ads}q_e^2$ represents the initial sorption rate. The values of q_e, k_{1ads}, $k_{2\,ads}$ and h are calculated from the slopes and intercepts of the straight lines as shown in Fig. 10.

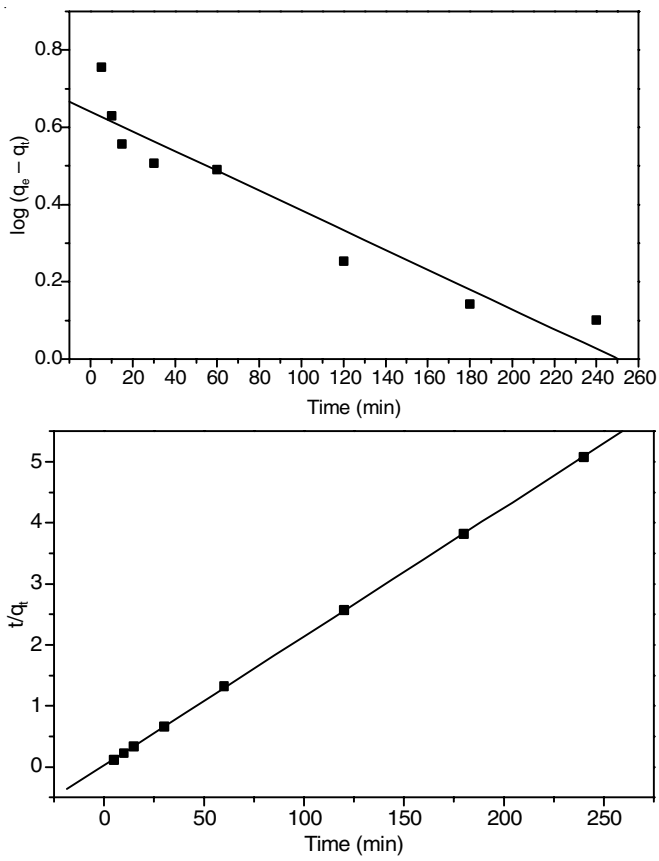

Fig. 10. Determination of the rate constant of pseudo-first-order (k_{1ads}), pseudo-second-order (k_{2ads}) and the amount of uranium ion adsorbed at equilibrium, q_e

The kinetics of uranium adsorption on the PSt-S75 activated carbon followed the second order rate expression. The initial sorption rate h is high (39.52 mg/g min) at the beginning of the contact time as shown from the Table-2 and as the contact time increases, the initial uranium concentrations decrease, leading the low value of second order rate constant (K_{2ads} = 0.0176 mg/g min).

TABLE-2
PSEUDO-FIRST AND PSEUDO-SECOND-ORDER AND INTRA-PARTICLE DIFFUSION RATE CONSTANTS AND VALUES OF R^2 FOR ADSORPTION OF URANIUM ONTO PSt-S75 ACTIVATED CARBON

Equation		Values
Pseudo-first order: Log $(q_e - q_t) = \log (q_e) - k_{1ads}t/2.303$.	C_0 (mg/L)	50
	q_e (exp.) (mg/g)	47.24
	q_e (cal.) (mg/g)	4.37
	K_{1ads} (min^{-1})	5.895×10^{-3}
	R^2	0.9547
Pseudo-second order: $t/q_t = 1/k_{2ads}q_e^2 + t/q_e$.	C_0 (mg/L)	50
	q_e (exp.) (mg/g)	47.24
	q_e (cal.) (mg/g)	47.39
	K_{2ads} (mg/g min)	0.0176
	h (mg/g min)	39.52
	R^2	0.9999
Intra-particle diffusion: $q_t = k_{int}t^{0.5} + C$	k_{int1} (mg/g $min^{-0.5}$)	1.284
	k_{int2} (mg/g $min^{-0.5}$)	0.134
	k_{int3} (mg/g $min^{-0.5}$)	1.534
	C_1	40.008
	C_2	44.37
	C_3	39.381
	R^2_1	0.9913
	R^2_2	1
	R^2_3	1

Intra-particle diffusion: The results obtained were used to find the rate limiting step in the adsorption process. The rate of uranium adsorption by the PSt-S75 adsorbent can be interpreted in terms of adherence of uranium on the adsorbent as well as its intra-particle diffusion into the pores of the adsorbent.

$$q_t = k_{int}t^{0.5} + C \quad (12)$$

where q_t is the amount of uranium adsorbed (in mg/g) at time t, k_{int} is the intra-particle diffusion rate constant [in mg/g $min^{-0.5}$] and C is the intercept observed in the plot of q_t *versus* $t^{0.5}$ and known as the boundary layer. In order to show the existence of intra-particle diffusion in the adsorption process, the amount of uranium adsorbed at time t, q_t was plotted *versus* the square root of time, $t^{0.5}$ (Fig. 11) [24].

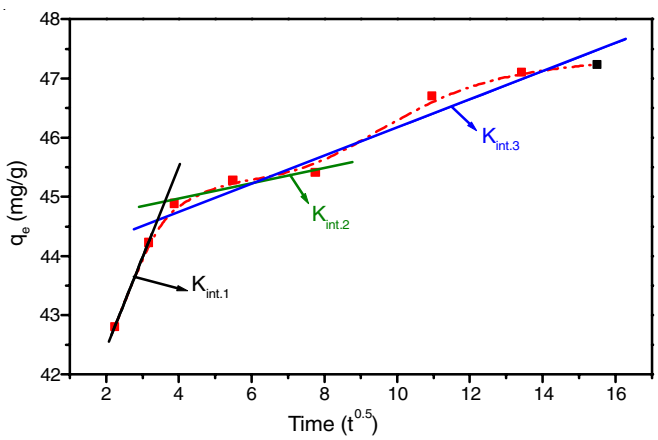

Fig. 11. Intra-particle diffusion of the adsorption of uranium using PSt-S75

The initial curved part of the curves can be attributed to the boundary layer effect while intra-particle diffusion is responsible for the linear sections. The straight lines do not

pass through the origin indicating that intra-particle diffusion is not the only rate controlling step for the concentrations studied. There are three steps in the adsorption when uranium contacted with adsorbent as shown from Fig. 11. These results indicate that intra-particle diffusion was not the rate-determining step in the present process. The value of the intercept, C, provide a measure of the boundary layer thickness; the large value observed, suggesting a considerable boundary layer effect [34]. The values of C from Table-2 indicate that there is a diverse relationship between the boundary layer and the intra-particle rate diffusion. The correlation coefficients, R^2, are close to unity (0.97), this also supports the occurrence of an intra-particle diffusion process. However, divergence in the value of the slope from 0.5 indicates that intra-particle diffusion was only one of a number of rate-limiting steps in the uranium adsorption process [34], since many other processes which control the adsorption rate could have been operating simultaneously.

Effect of PSt-S75 concentration: The effect of PSt-S75 concentration on the adsorption of uranium was studied for the initial concentration of 50 mg/L and is shown in Fig. 12. As seen from the figure, the percent removal of uranium increased with the rise of the concentration of PSt-S75 and attained a maximum value (% 93.12) for adsorbent weight of 25 mg. This is due to enhanced active sites with an increase in the amount of PSt-S75.

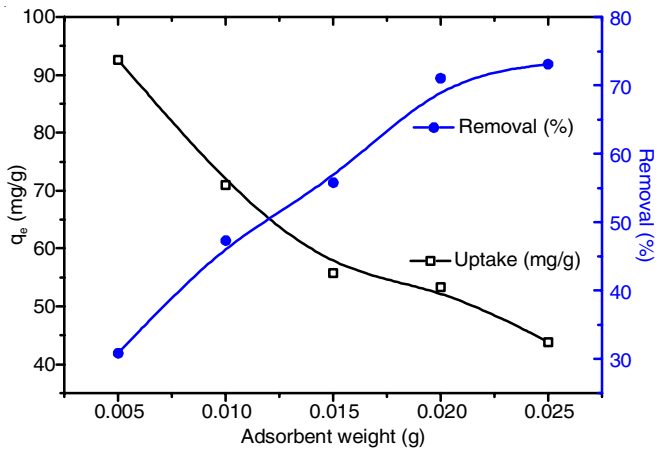

Fig. 12. Effect of PSt-S75 concentration on adsorption of uranium

Effect of temperature and uranium initial concentration: To study the effect of these parameters on the kinetics of uranium sorption by PSt-S75, the following temperatures were selected: at 25, 50 and finally at 70 °C. Equilibrium uptake q_e (mg/g) of uranium adsorbed by PSt-S75 at different temperatures and initial concentrations C_0 (mg/L) are presented in Table-3.

The results of effect of temperature on sorption of different metal-biomaterials systems are disparate [35]. An increase in temperature will be followed by a decrease in sorption capacity if sorption is governed by physical phenomena only. Within the temperature range investigated, it is possible to come to a conclusion that the increase of temperature leads to increase of adsorption capacity and consequently the chemical phenomena participate in the adsorption process and this results

TABLE-3
EFFECT OF TEMPERATURE AND CONCENTRATION ON THE ADSORPTION OF URANIUM USING PSt-S75

25 °C		50 °C		70 °C	
C_o (mg/L)	q_e (mg/g)	C_o (mg/L)	q_e (mg/g)	C_o (mg/L)	q_e (mg/g)
50	45.7	–	–	–	–
100	55.0	100	61.75	100	64.98
200	60.1	–	–	–	–
300	62.9	–	–	–	–
400	63.6	–	–	–	–
500	64.7	–	–	–	–

is confirmed by kinetic study of the uranium adsorption processes previously which indicate that the adsorption follows the second order reaction.

Equilibrium modeling: Developing an equation which can be used to evaluate different biomass in different operating conditions is based on the analysis of the equilibrium data to propose and maximize the working procedure [35]. For water and wastewater treatment applications, the Freundlich and Langmuir equations are generally used for analysis of the adsorption equilibrium data. Sorption on a heterogeneous surface can be expressed by the Freundlish equation in the following form:

$$\ln q_e = \ln K_f + 1/n \ln C_e \quad (13)$$

where q_e is the amount adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration (mg/L). K_f and n are constants indicative of adsorption capacity and adsorption intensity, respectively.

The Langmuir assumes that: (i) the solid surface presents a finite number of identical sites which are energetically uniform; (ii) there is no interactions between adsorbed species, meaning that the amount adsorbed has no influence on the rate of adsorption and (iii) a monolayer is formed when the solid surface reaches saturation. The Langmuir equation has the form:

$$q_e = Q_0 b C_e / 1 + b C_e \quad (14)$$

where q_e is the amount adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration (mg/L), b is a constant related to the energy or net enthalpy of adsorption (L/mg) and Q_0 is the mass of adsorbed solute required to saturate a unit mass of adsorbent (mg/g). Q_0 represents a practical limiting adsorption capacity when the surface is fully covered with metal ions and allows the comparison of adsorption performance, particularly in the cases where the adsorbent did not reach its full saturation in experiments [36]. The Langmuir equation can be described by the linearized form:

$$C_e/q_e = 1/Q_0 b + C_e/Q_0 \quad (15)$$

By plotting (C_e/q_e) *versus* C_e, Q_0 and b can be determined if a straight line is obtained. The linearized form of Langmuir and Freundlich adsorption isotherms obtained at 298 K is given in Fig. 13, whereas the adsorption constants evaluated from the isotherms with the correlation coefficients are given in Table-4.

The higher correlation coefficients showed that both models are suitable for describing the adsorption equilibrium of uranium in the studied concentration ranges. Langmuir and

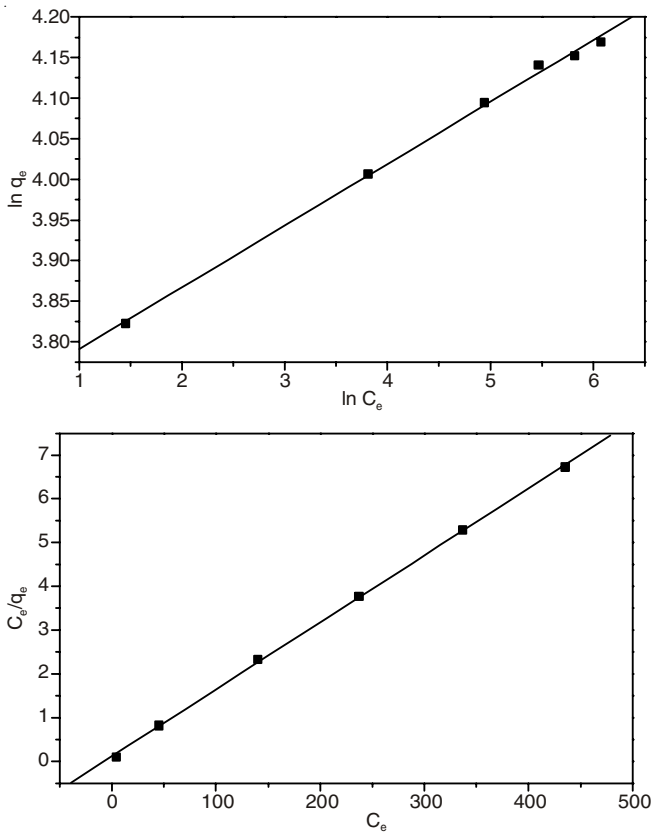

Fig. 13. Linearized Freundlich and Langmuir adsorption isotherms of uranium by PSt-S75

TABLE-4
FREUNDLICH AND LANGMUIR ADSORPTION CONSTANTS ASSOCIATED TO ADSORPTION ISOTHERMS OF URANIUM ON PSt-S75 AT 298 K

Equation	Parameters	Values
Freundlich	K_f	41.6
	n	9.15
	r^2	0.9987
Langmuir	Q_0 (mg/g)	85.43
	b (L/mg)	0.1376
	r^2	0.9997
	R_L	0.0195

Freundlich constants were used to compare the capacity of the PSt-S75 for uranium. The magnitude of K_f and n, the Freundlich constants, showed rapid uptake of the uranium from solutions with high adsorptive capacity of PSt-S75 (Table-4). It is also apparent that value of n obtained for the present system indicates favourable adsorption, as it lies between 1 and 10 [37]. Also, the value of R_L (0.0195), dimensionless separation factor calculated from Langmuir constant indicates that the adsorption of uranium onto PSt-S75 is irreversible. The maximum capacity Q_0 determined from the Langmuir isotherm defines the total capacity of the adsorbent as 85.43 mg/g uranium at 298 K. A high value of b also implied strong bonding of uranium to PSt-S75.

Effect of diverse ions: The effect of diverse ions likely to be present in liquid waste and laboratories effluents on the adsorption of 50 mg of uranium(VI) was studied. The results obtained are compiled in Table-5.

From these results, there is no effect in the presence of anions Cl^-, NO_3^- and SO_4^{2-}. But, there is effect in case of HPO_4^{2-} at 50 mg/L level, which decreases the adsorption of uranium from 92 to 60.66 %. Whereas, in presence of cations; K, increases the pre-concentration of uranium by 2 %. The presence of Cr, Pb and Fe decreases the pre-concentration of uranium from 92 to 43.48, 22.36 and 69.74 %, respectively. Due to the competition between uranium, chromium and lead and the high affinity of Cr and Pb (and slightly Fe) to the surface of PSt-S75 activated carbon, the pre-concentration of uranium decreases as men-tioned above using PSt-S75. From these results it is concluded that (i) PSt-S75 activated carbon can be used in the pre-concentration and separation of chromium, lead and iron from a binary mixture with uranium. (ii) The presence of anions generally (except of HPO_4^{2-}), increases the pre-concentration of uranium from aqueous solution than the presence of cations.

Desorption studies: To recover the metal and recycle the PSt-S75, desorption study was carried out. After performing adsorption experiments PSt-S75 loaded with uranium was separated and then it was agitated with 25 mL of different desorbing agents: H_2O, 0.05 M NaOH and 0.05 M of each HCl, HNO_3 and H_2SO_4.

From the preliminary test, the loaded PSt-S75 then agitated with different strengths of H_2SO_4 (0.05-0.50 M) for 1 h and the uranyl ions desorbed into the solution was analyzed as before. It was observed that 95.44 recoveries of the adsorbed uranyl ions were achieved using 0.25 M H_2SO_4 and the increase of H_2SO_4 concentration of 0.40 and 0.50 M has a negligible effect on the desorption therefore it is sufficient to use H_2SO_4 with a concentration of 0.25M (Table-6).

Performance and application of the prepared PSt-S75: The validation of the prepared activated carbon was successfully assessed by comparing the capacity of the used sorbent with some of other sorbents; DCQ-naphthalene, PAN-benzophenone, Q-Amberlite XAD-4, azo-oxime ion exchanger and DAB-AC [38] towards uranium uptake. The results are summarized in

TABLE-5
EFFECT OF INTERFERING IONS ON THE ADSORPTION OF URANIUM USING PSt-S75

No.	C_0 (mg/L)	Interfering ion	U C_F (mg/L)	(q_e) = mg/g		Before	After
1	50	U only	3.63	46.47 (92 %)			
3	50-50	U + Cr	21.74	28.26 (43.48 %)	Cr	50.00	31.26
4	50-50	U + Pb	38.82	11.18 (22.36 %)	Pb	50.00	14.18
5	50-50	U + Fe	15.3	34.70 (69.74 %)	Fe	44.90	34.10
6	50-50	U + K	1.87	48.13 (96.26 %)			
7	50-50	U + KNO_3	2.29	47.71 (95.42 %)			
8	50-50	U + K_2SO_4	3.68	46.62 (90.64 %)			
9	50-50	U + K_2HPO_4	19.67	30.33 (60.66 %)			
10	50-50	U + KCl	3.22	46.78 (93.56 %)			

TABLE-6
ELUTION OF ADSORBED URANIUM USING A DIFFERENT DESORBING AGENT AND DIFFERENT CONCENTRATIONS OF H_2SO_4

No.	Desorbing agents	% Desorption	Different concentration of H_2SO_4 (M)				
1	H_2O	6.42	0.05	0.15	0.25	0.40	0.50
2	0.05 M NaOH	42.52	80.19	89.42	95.44	95.60	95.73
3	0.05 M HCl	33.24					
4	0.05 M HNO_3	65.37					
5	0.05 M H_2SO_4	80.19					

Table-7. The capacity of prepared PSt-S75 (85.43 mg/g) towards uranium is much better than the other solid sorbent. The developed PSt-S75 was successfully used for the removal of uranium from wastewater samples at a concentration of 50 g/L levels and complete retention of uranium was achieved. The retained uranium species were then recovered quantitatively from the PSt-S75 with H_2SO_4 (0.25 M). A satisfactory recovery percentage (95.44) of uranium was achieved confirming the good performance of the developed PSt-S75 in pre-concentration and separation of uranium from liquid waste effluent (laboratories and industrial waste water).

TABLE-7
RETENTION CAPACITIES OF INVESTIGATED PSt-S75 AND OTHER SOLID SORBENTS TOWARDS URANIUM IONS FROM AQUEOUS MEDIA BY BATCH MODE

No.	Solid phase extraction material	Retention/binding capacity (mg/g) of solid phase extraction
1	DCQ-naphthalene	1.88
2	PAN-benzophenone	2.34
3	Q-AmberliteXAD-4	2.74
4	Azo-oxime ion exchanger	7.14
5	DAB-AC	18.35
6	Date pits	10.0 [Ref. 22]
	CTSC 70.448	70.448 [Ref. 38]
7	PSt-S75	85.43 [Present study]

Treatment of laboratories effluent: The aim of the present work is to treatment of liquid waste of laboratories effluents (*e.g.* Nuclear Materials Authority; NMA) and industrial wastewater application using PSt-S75 prepared activated carbon from low cost, locally easy available precursor. The PSt-S75 prepared activated carbon was applied to treat a liquid waste collected from experimental effluent of nuclear materials authority laboratories. The liquid waste sample was analyzed for elements under investigation of our study before and after contact with PSt-S75 at waste pH and adjusted best pH for pre-concentration of uranium and the obtained results was summarized in Table-8.

As seen from the Table-8, the uptake and % R of each metal varies according to meal concentration and affinity to be adsorbed to the surface of PSt-S75 activated carbon. The pH of treated waste plays an important role in the uptake and % R of the metals presents in the solution.

Conclusion

The results obtained confirm that PSt-S75 can remove uranium from aqueous solution and laboratories effluents. The optimum adsorption of uranium took place at pH 4.33. From the economical point of view, 4 h shaking time were selected as an optimum parameter to reach equilibrium. The linearity of the plots t/q *versus* t confirmed that the process followed pseudo second-order kinetics. From the intra-particle diffusion in this study, the straight lines do not pass through the origin indicating that intra-particle diffusion is not the only rate controlling step for sorption of uranium at the concentrations studied. The % removal of uranium increased with the rise of the concentration of PSt-S75 and attained a maximum value (% 93.12) at V/M =1200 mL/g Within the temperature range investigated, it is possible to come to a conclusion that the increase of temperature leads to increase of adsorption capacity and consequently the chemical phenomena participate in the adsorption process. The application of Langmuir and Freundlich models to experimental results showed that the adsorption equilibrium data fitted very well to both the models in the studied concentration range. The rapid adsorption, high capacity and easy desorption of uranium makes PSt-S75 a low-cost, naturally abundant and nuisance biomass with a promising future as an alternative to more costly materials such as commercial activated carbon in the pre-concentration and separation of uranium (and other elements) from aqueous solutions. 0.25 M H_2SO_4 was effective in uranium recovery. More studies are underway to optimize the system from the regeneration point of view and economic considerations.

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TABLE-8
TREATMENT OF LABORATORIES EFFLUENT OF NMA USING PSt-S75

No.	C_O (ppm)	Time (h)	pH	C_F (ppm)	Uptake (q_e, mg g^{-1})	% R
1	32 ppm U	4	4.5	4.1	41.85	87.19
2	32 ppm U	4	Sol. (2.6)	29.69	3.465	7.22
3	13.73 ppm Cr	4	4.4	5.97	11.64	56.52
4	13.73 ppm Cr	4	Sol. (2.6)	10.88	4.275	20.76
5	2.66 ppm Pb	4	4.4	0.15	3.77	94.5
6	2.66 ppm Pb	4	Sol. (2.6)	2.27	0.59	14.66

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