The Removal of Uranium and Thorium from Aqueous Solutions Onto by-pass Cement Dust (BCD)

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Abstract

The adsorption behavior of uranium and thorium from aqueous solutions by By-pass cement dust (BCD) has been investigated by a batch technique. The uranium and thorium adsorption on BCD was studied as a function of initial concentration, weight of BCD, pH, shaking time and temperature. The uptake of uranium and thorium at the determined optimum conditions follows Freundlich isotherm. The adsorption control of both thorium and uranium are first order and uptake energy of activation E_a =10 and 15 kJ/mol for thorium and uranium respectively. Thermodynamic parameters such as ΔH^o, ΔS^o and ΔG^o were also investigated.

Introduction

Pollution with radioactive elements has been a matter of great concern for the last decades for human health and animals. Uranium and thorium are the most important natural radioactive elements affecting the environment. Therefore the removal of uranium and thorium from water is very important [1-3].

Various techniques are employed for the removal of uranium ions from wastewaters and radioactive wastes. Chemical precipitation, membrane processes, ion exchange, solvent extraction, photo catalysis and adsorption are the most commonly used methods [4-9]. Adsorption of uranium (VI) onto various solids is important from purification, environmental and radioactive waste disposal points of view [10,11]. In recent years, attention has been focused on various adsorbents with metal-binding capacities and low-cost, such as chitosan, zeolites, clay or certain waste products [12].

24 different materials have been studied for the remediation of U-and Mo-containing groundwater. It was found that the best results were achieved with hydroxyapatite (HAP), fly ash, TiO_2, $BaCl_2$, hydrated lime, peat and lignite [13].

HAP is readily available from natural resources as well as a synthetic product from chemical industry [14]. In general removal of U from ground-water in contact with HAP can occur by sorption onto HAP surfaces or by precipitation of uranyl phosphates [15].

The adsorption of uranium (VI) from aqueous solutions onto activated carbon using a batch technique indicated that the optimum parameters that affect the uranium (VI) adsorption are (contact time 240 min; pH 3.0 ± 0.1; initial uranium concentration 100 mg/L; temperature 293.15 K), also the Freundlich model can be applied and the activation energy = 7.91 kJ/mol [16].

The adsorption behavior of thorium from aqueous solutions by Polyacrylonitrile PAN/zeolite composite has been investigated. It was found that the most important parameters on the sorption system, which can influence the sorption behavior of thorium are: initial thorium concentration, pH value of the solution is important factor and the optimum value of pH is 4, the sorption of thorium slightly increases with increasing shaking time and the thorium sorption yield was increased with increasing temperature [17].

It was found that the using of By-pass cement dust (BCD) enhances significantly the percentage removal of the heavy metals and it has a great potential to be used as low cost raw material for removal of metal pollutants from industrial wastewaters discharged by industries [18-19].

The aim of this work is to investigate the adsorption and the mechanism of by-pass cement dust (BCD) to remove uranium and thorium from aqueous solutions.

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Experimental

Materials

By-pass cement dust (BCD)

BCD was brought from National Cement Co. Egypt. The chemical composition were determent by XRF and is illustrated in table 1.and the X-Ray diffraction pattern is shown in Fig.1 where it is clear that BCD mainly consists of calcite, calcium sulphate, mono calcium silicates, calcium carbonate, quartz, sodium chloride.

The received BCD was put in a glass container which is in turn was kept in a desiccator all the time of the experiments.

Reagents

Standard individual metal ion solutions (1000 ppm) for U(VI) and Th(IV) were prepared from $UO_2(NO_3)_2 \cdot 6H_2O$ and $Th(NO_3)_4 \cdot 5H_2O$ by dissolving 2.10 and 2.46 g in 1 L of double distilled water. Arsenazo III was obtained from Aldrich Chem. Co. All other reagents used were analytical reagent grade.

Adsorption experiments

The adsorption experiments have been studied by a batch technique in a thermostat>s shaker bath Stuart model SBS,U.K. The shaking rate was constant for all the experiments. The adsorbent material (BCD) (0.01 g) and standard aqueous solution of uranium and thorium (50 ml) were shaken at different temperatures for various mixing time. The pH of the aqueous solutions was maintained by Thiel buffer solution in the pH range (2 - 6) [20] since the adsorbent is affected by strong acidic or basic solutions. Filtration/separation of solid phase from liquid was followed by centrifuging at 4000 rpm for 15 min. The uranium and thorium were determined spectrophotometrically using Arsenazo III method

Table1.
Major Chemical constituents of BCD

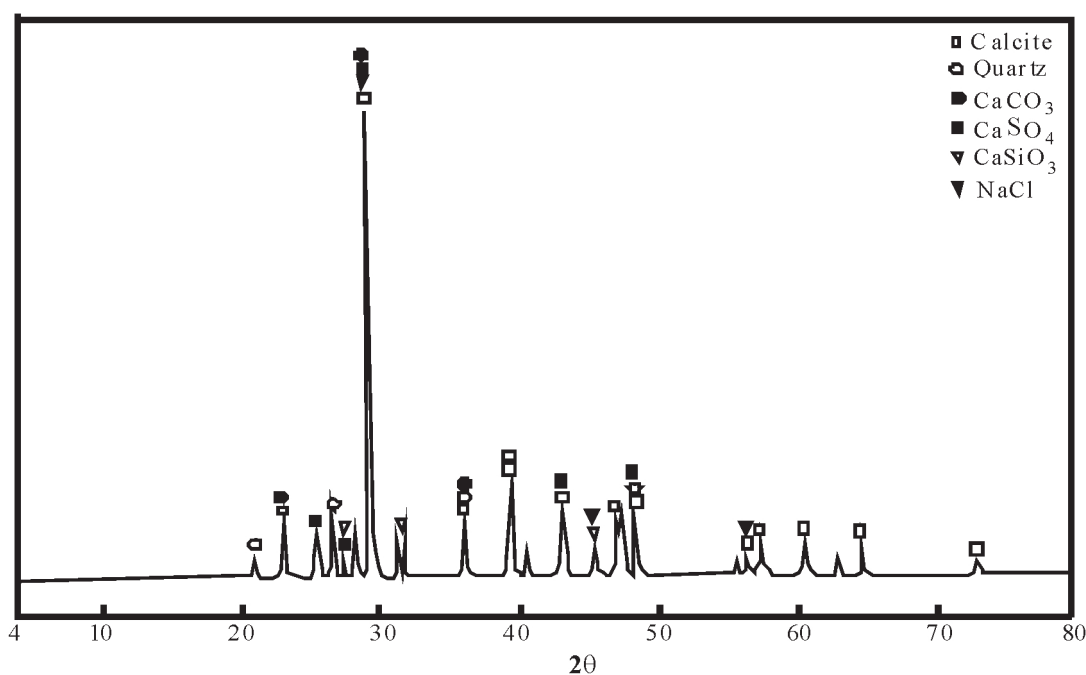| Chemical constituent	CaO	SiO$_2$	MgO	Fe$_2$O$_3$	Na$_2$O	K$_2$O	P$_2$O$_5$	Al$_2$O$_3$
Percentage %	44.24	10.54	1.45	1.92	2.00	3.5	6.35	4.7

Fig.1. X-ray diffraction of by-pass cement dust

as complexing agent at 655 nm and 659 nm, respectively against reagent blank [21] employing Shimadzu UV–Vis160A Spectrophotometer. For calculating the uranium or thorium concentration, the absorbance of complex solution was compared with a calibration curve plotted of absorbance versus standard concentration of uranium or thorium at fixed λmax for the colored complexes of the metal ions the amount of adsorbed uranium or thorium was estimated from the difference of the concentrations in the aqueous solution before and after the adsorption process.

Calculation

The Uptake percentage (%) and distribution constant KD (ml/g) was calculated from the equations

$$Uptake\ percentage\ (\%) = 100 \times [C_0 - C_f / C_0] \quad (1)$$

$$K_D = M_{ads}\ V / M_{sol}\ W \quad (2)$$

where C_0 and C_f are the concentration of the metal ion in the initial and final solutions (mg/l), Mads and Msol are the amount of metal ion on adsorbent and in solution (mg), V is the volume of the solution (ml), and W is the weight of the adsorbent (g).

The amount of metal ion uptake qt at time t, was calculated from the mass balance equation

$$q_t = (C_0 - C_t)V / W \quad (3)$$

Where t is the equilibrium contact time, $C_t = C_e$, $q_t = q_e$, and the amount of metal ion sorbed at equilibrium, q_e, is calculated using Eq. (3).

Adsorption kinetics

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 Lagergren pseudo first-order equation in the following form [22]

$$dq_t /dt = k_1\ (q_e - q_t) \quad (4)$$

Where k_1 is the rate constant of first-order adsorption and qe denotes the amount of adsorption at equilibrium. After definite integration by applying the initial conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Eq. (4) becomes

$$Log\ (q_e - q_t) = log\ (q_e) - k_1\ t/2.303. \quad (5)$$

The slopes of the plots of *log* $(q_e - q_t)$ versus *t* were used to determine the first order rate constant k_1 that it can be used to determine the activation energy of the adsorption process using Arrhenius equation.

Desorption experiments

Desorption of uranium and thorium from BCD was performed also by batch technique. Some acids *e.g.* HNO$_3$, HCl and H$_2$SO$_4$ were treated with loaded adsorbent to recover the metals from the adsorbent as a function of desorptive reagents concentration, time and temperature.

Adsorption isotherm

The adsorption isotherms were obtained by analyzing solutions in contact with adsorbent before and after equilibrium and plotted in terms of the equivalent fraction of metal ion on the adsorbent solid phase against the equivalent fraction in the aqueous phase.

Thermodynamic parameters

0.01 g of adsorbent was treated with metal ion solution of 100 mg/l at constant pH 4 and 3 for uranium and thorium, respectively for constant shaking time 7 min for both elements in different temperatures. The thermodynamic parameters (ΔHº, ΔGº and ΔSº) were calculated from the adsorption results.

Results and discussion

Adsorption experiments

The parameters which affect the uranium and thorium uptake on by pass cement dust, such as initial concentration of metal ion, contact time, adsorbent weight, pH and temperature were investigated.

Effect of initial concentration of metal ion

The effect of the initial concentration of uranium and thorium on the adsorption rate was studied by contacting a fixed weight of BCD (0.01g) at a fixed temperature (293.15 K) and initial pH (3.0±0.1) for thorium and pH (4.0±0.1) for uranium with varied initial concentrations (50 – 600 mg/l) in volume 50 ml of UO$_2^{2+}$ or Th^{4+} ions aqueous solutions. The results are given in Fig.2 which reveals that the

adsorption percentage of uranium is increased with decreasing the initial uranium concentration, but in case of thorium the percentage is decreased with increasing initial thorium concentration up to 400 mg/l. This may be due to the geometrical shape and size of UO_2^{2+} which is greater than that of Th^{4+}, thus as the concentration of UO_2^{2+} increases the adsorption percentage decreases.
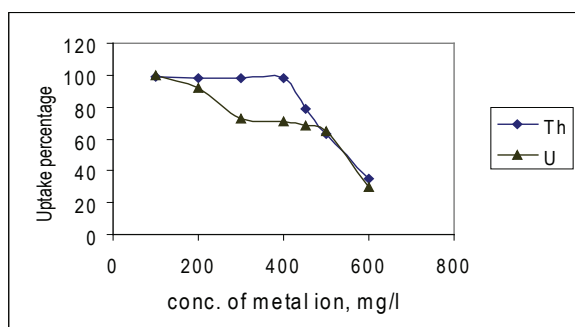

Fig.2. Variation of the uptake percentage with the metal ions initial concentration

Adsorbent weight

Effect of adsorbent weight on the adsorption process of the investigated metal ions is shown in Fig.3. The adsorption experiments were carried out for study this effect with different amounts of adsorbent (BCD) ranging from 0.01 g to 0.05 g at fixed temperature 293.15 K using metal ion concentration of 100 mg/l at pH (3±0.1) for thorium and pH (4.0±0.1) for uranium in volume 50 ml and 7 min shaking time. It was found that the uptake percentage of both metal ions increased with increasing the amount of adsorbent up to 0.02 g and stays nearly constant with no significant increase in its value. The reason that the uptake reaches 100% at 0.02 g .so no more uptakes and there is no uptake >100%.
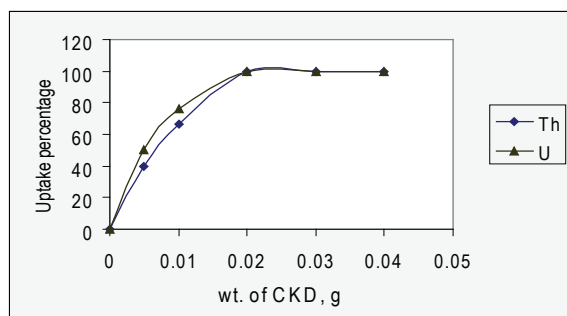

Fig.3. Variation of the uptake percentage with the adsorbent weight

Effect of pH

The adsorption experiments are carried out for study this effect with fixed amounts of adsorbent (BCD) (0.02 *gm*) at fixed temperature 293.15 K using metal ion concentration of 100 mg/l and 7 min shaking time. Fig.4 shows the influence of pH on the adsorption of uranium and thorium on BCD. The percentage of adsorption increases with increasing pH to a maximum value at pH (4±0.1) and then becomes constant. The influence of pH on uranium adsorption can be explained in the following way: hydrolysis of uranyl ion takes place as the pH varies from 2 to 6, Uranium exists in hydrolyzed form and the following ionic species have been exist UO_2^{+2}, $[(UO_2)_2(OH)_2]^{2+}$ dimer, $[(UO_2)_3(OH)_5]^+$ trimer that are adsorbed on the surface of BCD. The optimum removal took place at pH (4±0.1).

In case of thorium below pH 3, the predominant thorium ion would be the positively charged Th^{4+} [17].Thorium uptake on the adsorbent reached a maximum of 100% at pH (3±0.1). Above pH 3, the uptake percentage decreases with increasing pH.
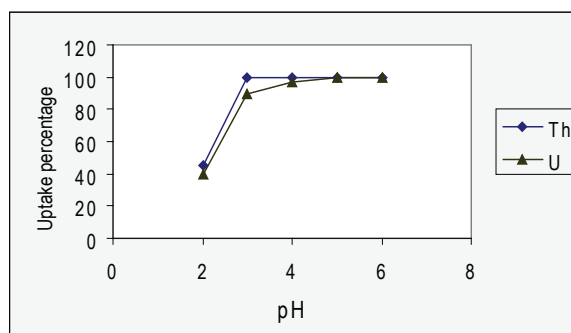

Fig.4. Variation of the uptake percentage with pH

Effect of temperature and Adsorption dynamics

The relation between the uptake percentage of uranium and thorium by BCD and time for different temperature are illustrated in Figs.5-6 using concentration of metal ion 200 mg/l, pH (3±0.1) and 0.02 gm BCD. it is clear that the adsorption rate very high at the initial time then the rate decreased. The analyses of the curves relating the uptake percentage and time show that each curve has 3 different slopes indicating 3 different values of adsorption rates. The first value is high, while the second is somewhat slower and the third is the slowest one. Also it can be observed that both elements uptake was increased with increasing temperature.

The increase of adsorption percentage with rise of temperature may be due to the increase of number of reacting moles having excess of energy which leads to the increase of adsorption rate, also the raise of temperature leads to an increase of the rate of mass transfer of the diffusion and rat of adsorption [23-24].
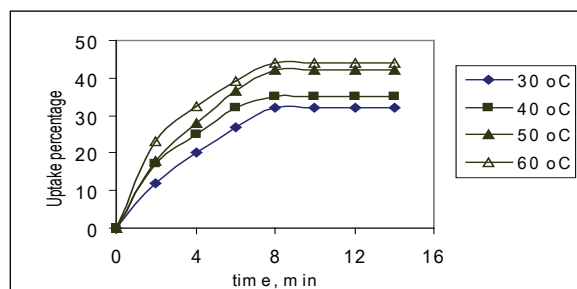

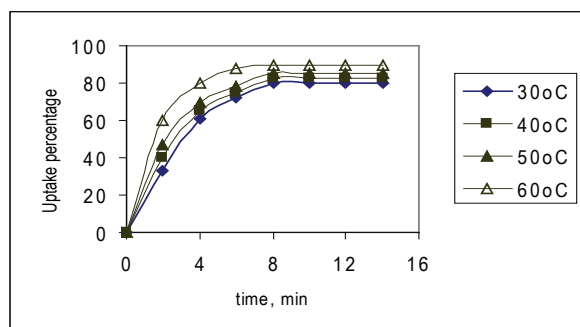Fig.5. adsorption of uranium on BCD at different temperatures.

Fig.6. adsorption of thorium on BCD at different temperatures.

Fig.7. illustrates the relation between log (qe-qt) against time for adsorption of uranium at different temperatures, from which it is clear that the relationship is represented by straight line of slope equal to the value of the rate constant, K_1.
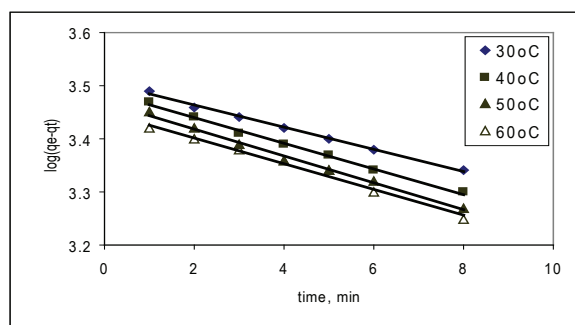

Fig.7. Determination of the rate constant of pseudo-first-order adsorption for uranium, K_1.

The natural logarithms of K_1 were used according to the Arrhenius equation to calculate the activation energy of adsorption reaction. A plot of $log\ K_1$ and $1/T$ gives a straight line as shown in Fig. 8, from which it is clear that the activation energy for first order E_{a1} = 15 kJ/ mole.
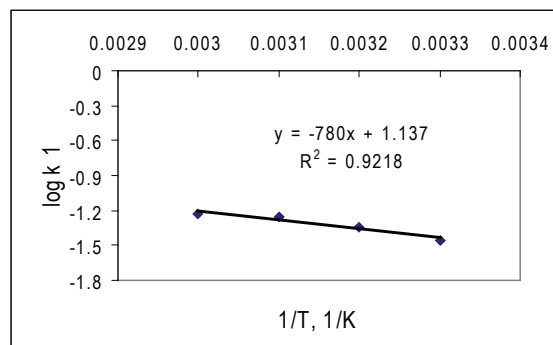

Fig. 8. The relation between log K_1 and $1/T$ for first order odsorption for uranium (Arrhenius plot)

Fig.9 illustrates the relation between $log\ (q_e\text{-}q_t)$ against time for adsorption of thorium at different temperatures at different times from which it is clear that the relationship is represented by straight line of slope equal to the value of the rate constant, K_1.
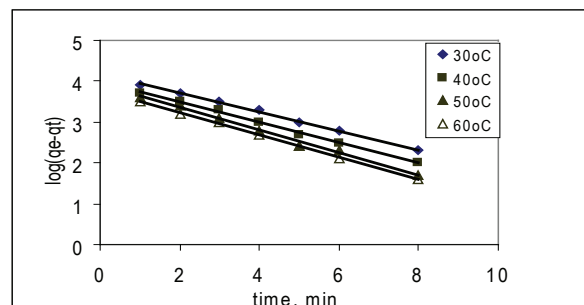

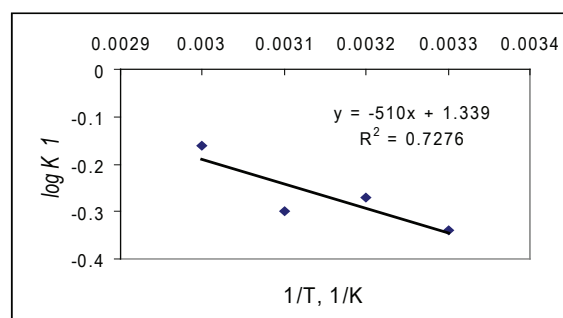Fig. 9. Determination of the rate constant of pseudo-first-order adsorption for thorium, K_1

Fig.10 the relation between log K_1 and $1/T$ for first order (Arrhenius plot)

The natural logarithms were used according to the Arrhenius equation to calculate the activation energies of adsorption reaction. A plot of Log K_1 and $1/T$ gives a straight line as shown in Fig. 10 from which it is clear that the activation energy of first order for thorium E_{a1} = 9.8 kJ/ mole.

Thermodynamic parameters

The thermodynamic parameters obtained for the adsorption process for both uranium and thorium were calculated using the equations

$$ln\ K_D = \Delta S_0/R - \Delta H_0/RT$$

Where K_D is the distribution coefficient (ml/g), ΔS_0 is standard entropy (J/mol.K), ΔH_0 is standard enthalpy (kJ/mol), T is the absolute temperature (K), and R is the gas constant (8.314 J/mol.K). The experiments were carried out at 303.15, 313.15, 323.15, and 333.15 K for uranium (VI) and thorium (IV) using concentration 200 mg/l. The standard Gibbs free energy ΔG_0 values (kJ/mol) was calculated from the equation
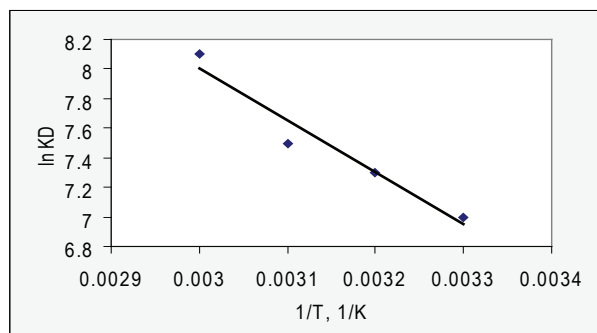
$$\Delta G_0 = \Delta H_0 - T\Delta S_0$$

The values of ΔH_0, ΔS_0 and ΔG_0 were calculated from the slopes and intercepts of linear regression of ln K_D versus $1/T$ as shown in Figs.11-12. The values are tabulated in table 3. In fact, the positive value of enthalpy change ΔH_0 for the processes further confirms the endothermic nature of the process, the positive entropy of adsorption ΔS_0 reflects the affinity of the adsorbent material toward both elements.

It is clear that the free energy for both element adsorptions are negative and the negative free energy values ΔG_0 indicate the feasibility of the process and its spontaneous nature without an induction period.

Sorption isotherms

The sorption data have been subjected to different sorption isotherms namely Langmuir and Freundlich. The simple Freundlich isotherm was able to describe the adsorption over all the concentration range used according to the equation:

$$Log\ q_e = log\ K + 1/n\ log\ C_e$$

Where qe is the amount of solute adsorbed per unit weight of BCD at equilibrium (mg/g) and C_e is the equilibrium concentration of metal ion in solu-
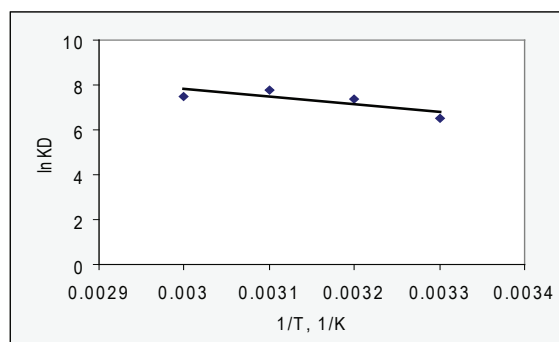

Fig.11. Relationship between ln K_D and $1/T$ for uranium.

Fig.12. Relationship between ln K_D and $1/T$ for thorium.

Table 2.

Thermodynamic parameters for adsorption of thorium(IV) and uranium(VI) on BCD

Element	ΔH_0 (kJ/mol)	ΔS_0 (J/mol.K)	ΔG_0 (kJ/mol)			
			303 K	313 K	323 K	333 K
Thorium	28	0.15	-16.7	-18.2	-19.7	-21.2
Uranium	29	0.14	-16.75	-17.95	-19.45	-20.95

tion (mg/l). *K* and 1/*n* are the Freundlich constants related to sorption capacity and sorption intensity of the sorbent, respectively. A plot of *log q_e* vs. *log C_e* as seen in Fig.13 would result in a straight line with a slope of (1/*n*) and intercept of *log K* as in table 2. It was found that the slope value ranges between 0 and 1. It can be concluded that the sorption of the investigated elements takes place through the formation of a single monolayer of the sorbed species. The Freundlich equation was found to fit the data in the whole range of Th^{4+} and U^{6+} concentrations tested.

The Langmuir isotherm was applied for the sorption equilibrium of BCD:

$$C_e / q_e = 1/b\, Q_0 + C_e / Q_0$$

Where C_e is the equilibrium concentration of metal ion in solution (mg/l), qe is the amount of solute adsorbed per unit weight of BCD at equilibrium (mg/g), and Q_0 and b are the Langmuir constants related to adsorption capacity and energy of adsorption, respectively.

According to the Langmuir model, adsorption occurs uniformly on the active sites of the sorbent, and once a sorbate occupies a site, no further sorption can take place at this site.
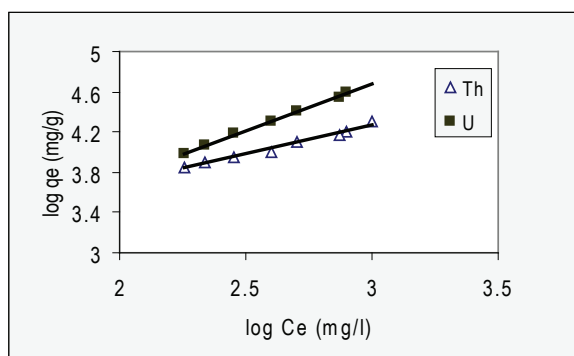
A plot of C_e / q_e vs. C_e would result in a straight line with a slope of (1/Q_0) and intercept of 1/bQ_0 as seen in Fig.14. The values of the slope and intercept of this plot are in table 2.

Desorption experiments

The loaded BCD is treated with different acid solutions *e.g.* HNO_3, HCl and H_2SO_4 of different concentrations. The concentration of the metal ion is determined after the desorption reaction and the stripping percentage is calculated. The factors affecting the desorption process are studied as following.

Effect of desorption time

The desorption from loaded adsorbent has been investigated as a function of equilibrium time in the range of 2-20 min. 50 ml of 0.005 M acid solution were used in the desorption process that is carried out at 30°C. Fig.15 shows that desorption yield increases with increasing shaking time and attains equilibrium within 5 min for uranium, while as the shaking time in case of thorium increases up to 5 min the desorption decreases. Therefore, in further experiments 5 min equilibrium time was used.
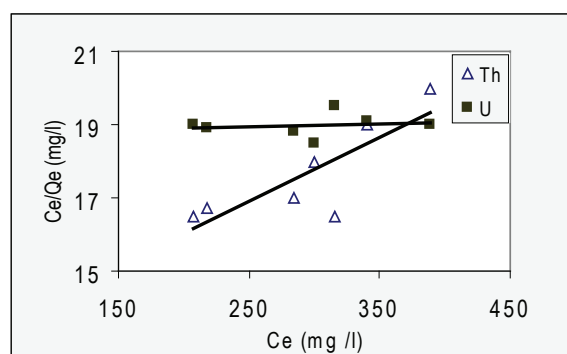
Fig.13 Freundlich isotherm of Th4+ and U6+ sorption by BCD.

Fig.14 Langmuir isotherm of Th4+ and U6+ sorption by BCD.

Table 3.
Isotherms constants and values of R² for BCD

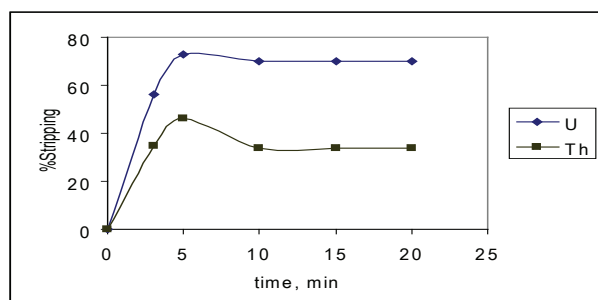| Element	Freundlich isotherm			Langmuir isotherm		
	1/n	*Log K*	R_2	Q_0 *(mg/g)*	*b*	R_2
Thorium	0.5736	2.5444	0.9813	56.8	0.0014	0.6758
Uranium	0.9438	1.854	0.9985	111.1	0.0005	0.0358

Fig.15 Effect of shaking time on the percentage of stripping of uranium and thorium from BCD.
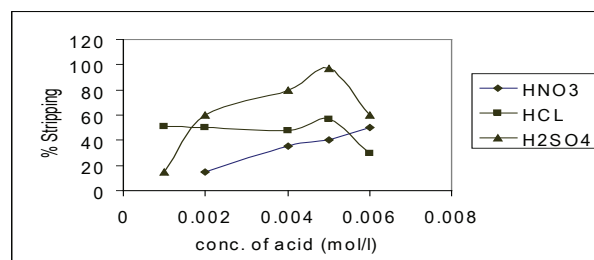

Fig.16. Effect of acid concentration on stripping percentage of uranium from BCD.

Effect of acid concentration

The desorption was studied as a function of 50 ml of HNO3, HCl and H_2SO_4 have concentrations from 0.001 M to 0.006 M employing 5 min shaking time at 30° C. since increasing the concentration of acid may lead to dissolving the adsorbent material. Figs.16-17 show the dependence of desorption on acid concentration. Maximum desorption of thorium and uranium is achieved from 0.005 M to 0.006 M acid solution.

Effect of temperature

Effect of temperature in desorption process was investigated from 30 to 65° C employing 5 min shaking time with 50 ml of 0.005 M acid solution. Fig.18 shows influence of temperature on desorption of metal ion from the adsorbent material. Desorption yield increases with increasing temperature up to 60° C in case of desorption of uranium, while in case of thorium desorption is constant to 60° C and then decreases.
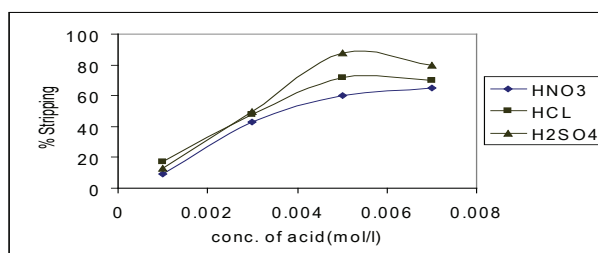
Conclusions

•   The adsorption of uranium and thorium from liquid solutions by BCD has been shown to depend on initial concentration of metal ion, BCD dose, contact time, pH and temperature. The adsorption of these radionuclides can be represented by Freundlich adsorption isotherms. It can be concluded that this BCD can be utilized for removal of radioisotopes from waste solutions.

•   Uranium and thorium recovery is the more important step, owing to its low affinity towards the adsorbent. With acid solutions desorption of U (VI) and Th (IV) is high. Desorption percent for this adsorbent was ranged from (20- 90 %). This may result from creating different physical forms of metal ion with some components of the adsorbent. Some other mechanisms are involved in the observed process.

•   The thermodynamic parameters ΔH_0, ΔS_0, and ΔG_0 values of uranium (VI) and thorium (IV) adsorption onto BCD show endothermic heat of adsorption, favored at high temperatures. The positive entropy value is an indication of the probability of

Fig.17. Effect of acid concentration on stripping percentage of thorium from BCD.
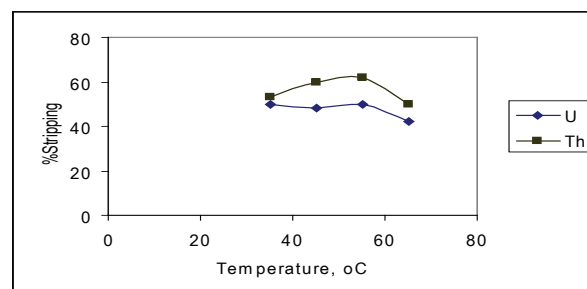
Fig.18 Effect of temperature on the percentage of stripping of uranium and thorium from BCD

favorable nature of adsorption and the process is spontaneous.

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