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Treatment by agricultural by-products of Industrial effluents polluted with heavy metals

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Due to the increasing concern about the environmental pollution problems, it is so important to perform a number of methods for removing hazardous heavy metals from industrial liquid wastes. Adsorption technique is the most effective and economical one. In the present study, two agricultural by-products namely; cottonseed and soybean hulls, resulting from the oil industry, have been used in the adsorption of thorium element from a wastewater effluent coming from different industries. The results obtained indicate that maximum removal of thorium from a prepared solution takes place at *p*H 5 where equilibrium was attained after 100 min; using an adsorbent dose of 3 and 3.5 g/L for cottonseed and soybean hulls, respectively. On the other hand, the obtained mathematical data together with the obtained adsorption kinetic parameters indicate that both of cottonseed and soybean hulls could be useful adsorbents for thorium removal from industrial liquid wastes, especially when the low cost, environmental issues and high availability of these materials are considered.

Keywords: Adsorption, Cottonseed, Heavy metals, Removal of thorium, Soybean hulls

In the recent years, there has been a great concern for caring about the environment from industrial wastes and its hazardous effects on water and plants pollution and its consequent health impacts on the public. Water pollution is generally due to the presence of dissolved inorganic and organic minerals found in domestic and industrial waters. Water pollution might be also due to some physical factors such as turbidity, color, temperature, associated radioactivity, etc.[1-3].

On the other hand, many industrial activities that are seldom considered as contributing to stream pollution may nonetheless, alone or in combination with others, create pollution problems of considerable magnitude. These include nuclear industries, phosphoric acid production industries, and zirconium oxide industries, etc. It is worthy to mention herein that, among the most frequent sources of radioactive wastes is the research-laboratories waste which contains all the materials prevalent in chemical, metallurgical and biological research operations. One of the problems in this respect is the presence of heavy metal ions such as U, Th, Hg, Co, etc., which exist in wastewater effluents coming from different industries. The recovery of these strategic metals from waste streams is necessary due to their hazardous effect and their inherent value[4].

In fact, many methods have been proposed to remove toxic metals from water. The most important of these include chemical precipitation, ion-exchange, reverse osmosis and adsorption. The latter technique is the most effective and economical one. Besides, this technique is convenient in separating and isolating elements from solutions. The greatest advantage of the adsorption technique is the possibility to separate small amounts of substances from a very large volume of solution[5].

Activated carbon is the most active material for adsorption of pollutants, but it is expensive. So, there is a growing interest in using low cost and easily available materials. The two materials which were used in the present work for the adsorption of thorium element, from a prepared solution, are cottonseed and soybean hulls, which are produced as by- products of the oil industry and are of low cost and are greatly available.

In this work, the sorption of thorium on cottonseed and soybean hulls is investigated. The effects of various operating variables, viz., initial metal concentration, solution *p*H, adsorbent mass and its particle size, contact time, agitation rate, and temperature have been studied. On the other hand, the adsorption data obtained were mathematically analyzed using both Langmuir and Freundlich adsorption models to determine the relevant adsorption parameters. In addition, the thermodynamic parameters, viz., free energy change (ΔG), enthalpy (ΔH) and entropy (ΔS) have been also determined.

Experimental Section

Materials

These include adsorbents, adsorbate, and chemicals.

Adsorbents

The adsorbents used in the present work are agricultural by-products namely; cottonseed and soybean hulls which were obtained from oil industry (Detergents and Oil Nile Company in Bani- Kora, Assuit, Egypt).

These by-products were washed thoroughly with distilled water to remove dirts and other particulate matter. The washed material was dried at 40°C and milled to particle sizes in the range of 25 - 70 mesh size. The adsorbents were characterized in terms of compositional analysis which is given in Table 1. From this table it is clearly evident that both of the cottonseed and soybean hulls by-products are having several components namely; protein, lignin, cellulose and hemicellulose which have the potential to adsorb metals. Protein content is low in the two by-products. These materials are polymers built of amino acid units, which contain nitrogen in the form of ($-NH_2$) groups. The polymer chain of protein vary from 100 to 1000 amino acids in length and are called polypeptide chains because the linkage between each amino acid unit and its neighbor is known as a peptide bond. About twenty different amino acids are linked together in various combinations to form polypeptide chains. Two of these amino acids contain sulpher. So, most proteins contain small amounts of sulphur that is essential to their structure and function, Fig. 1.

Table 1 — Compositional analysis of by-products cottonseed cottonseed and soybean hulls

Component	mg/g dry weight	
	Soybean hulls	Cottonseed hulls
Lignin	50.3	201
Cellulose	652	516
Hemicellulose	139	183
Protein	112	32.4
Lipid	9.5	4.9
Ash	20.4	9.8
Phatic acid	0.5	6.0
Silica	8.0	0.7

The net charge on the organic amino acid molecule is a function of the acidity of the solution. In acid solution, the molecules bear a positive charge (on the nitrogen atom). So, the very low values of uptake by protein are due to electrostatic repulsion between amino acid molecule and metal ions and due to that most protein molecules are relatively compact and globular. Each kind having a unique three-dimensional shape, essential to the protein specific function[6]. The other components such as lignin have been shown to be effective in removing metals from aqueous solution, e.g., it can remove 95% copper with a suspension of lignin in buffer[7]. However, among these by-products, lignin content is the lowest in soybean hulls. Cellulose (Fig. 2) and hemicellulose were the most important in the adsorption capacities because these components in acidic medium bear negative charge as a result of coordination through the lone pairs of electrons of its oxygen. The high uptake of metals by these components can be explained by a physical adsorption mechanism where positive charge cations are bound by negatively charged cellulose material of by-products (Sand op. cited).

Lignin, cellulose and hemicellulose together (the lignocellulosic fraction), as horticultural peat, which contains about 82% lignocellulosic material[8] was shown to remove Zn (II), Cu (II), and Ni (II) from

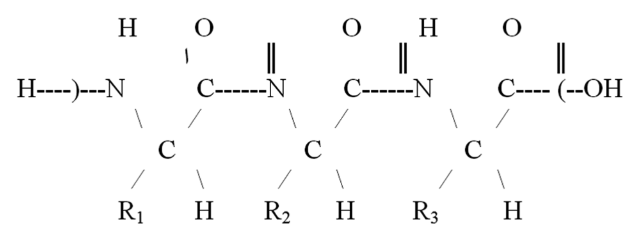

Fig. 1 — Protein molecule (where R_1, R_2 and R_3 stand for the side chains that distinguish different amino acids from one to another)

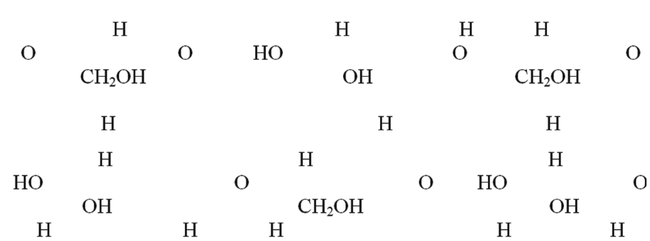

Fig. 2 — Cellulose molecule

municipal wastewater[9]. Lignocellulosic material constitute (90%) and (84.1%) of cottonseed and soybean hulls, respectively.

The lignocellulosic fraction undoubtedly contributes substantially to metal ion adsorption for these by-products. The observed differences in adsorption capacities are probably related to the complex manner in which lignin, cellulose and hemicelluloses are spatially distributed within a cell wall matrix to create adsorption sites.

Adsorbate

The standard thorium solution was prepared by dissolving analytical grade of thorium nitrate (Th $(NO_3)_2$) salt, then adding some drops of concentrated HNO_3 acid.

Chemicals

All chemicals used in this work are of analytical reagent grade.

Methods

These include adsorption experiments and spectrophotometer determination of thorium.

Adsorption experiments

The adsorption of thorium ions on cottonseed and soybean hulls by-products was studied using batch technique. Thus, a known weight of the adsorbents (i.e. 5g) were equilibrated with 100 mL of metal solution of known concentration (100 ppm Th) in stopper glass flask at a fixed temperature in a thermostatic shaker water bath for a known period of time.

The parameters studied in this work are agitation time, agitation rate, temperature, *p*H value, adsorbent mass, initial metal concentration and particle size. In each experiment one parameter was changed while other parameters were fixed during adsorption. The adsorbent was separated by centrifuge and then by filter paper to remove any suspended particles. Then the residual thorium in the filtrate was determined by the spectrophotometer using Aresenazo - III[10].

Spectrophotometric determination of thorium

Place a sample solution in a 50 mL volumetric flask. Add 12 mL of Conc. HCl and 5 mL of oxalic acid solution (8%), and mix well. Add 4 mL of the aresenazo - III (0.05%) solution, dilute to the mark with distilled water, and measure the absorbance at 650 nm against a reagent blank solution. The adsorption yield (%) was calculated according to the following equation:

Adsorption yield (%) = [(Co - Ce/ Co)] × 100

where Co = initial concentration of solute (mg/L)

Ce = equilibrium concentration of solute (mg/L)

Results and Discussion

Operating variables

In the present work, it is managed to study the operating variables of the adsorption process by applying batch technique in order to determine the optimum conditions of adsorption.

In batch-type contact operations, a quantity of the adsorbent is mixed continuously with a specific volume of wastewater until the pollutant in that solution is decreased to the desired level. The adsorbent is then removed and either discarded or regenerated for use with another volume of solution.

The working conditions of the adsorption process are summarized in Table 2. The variables studied as affecting the adsorption process were as follows:

Effect of agitation time

The effect of agitation time on the removal of thorium ions from the prepared aqueous solution is represented in Fig. 3(a). Measurements of the remaining

Table 2 — Working conditions of the operating variables

Factors	Range	Fixed condations
Agitation time (min.)	10,20,30,40,60,80,100,120,140,160,180	Adsorbent mass-m_g cottonseed & 3.5_g soybean hulls, Particle size=60-70 mesh, Th Conc. 100 ppm *p*H 5,25°C, 200 rpm
Adsorbent mass (g)	0.5,1,1.5,2,2.5,3,3.5,4,4.5,5,5.5,6	60-70 mesh, 100 ppm Th *p*H 5,25°C, 200 rpm, 100 min.
Initial metal Conc. (ppm)	50,100,150,200,250	3 g cottonseed & 3.5 g soybean hulls, 60-70 mesh, *p*H 5,25°C, 200 rpm, 100 min
Agitation rate (rpm)	40,80,120,180,200	3 g cottonseed & 3.5 g soybean hulls, 60-70 mesh, 100 ppm, Th, *p*H 5, 25°C, 100 min
Particle size (mesh)	25-30, 30-35, 45-60, 60-70	3 g cottonseed & 3.5 g soybean hulls, 100 ppm Th, *p*H 5,25°C, 200 rpm, 100 min
*p*H	1,2,3,4,5,6,7,8,9	3 g cottonseed & 3.5 g soybean hulls, 60-70 mesh 100 ppm, Th, 25°C, 200 rpm, 100 min

thorium are made at time intervals in the range 10 - 180 min; keeping other experimental conditions unchanged Table 2.

From the obtained results, it is clearly evident that the removal of thorium ions increases as the agitation time increases until reaching to a certain time (100 min.) where further increase in the agitation time is not associated with an increase in Thorium ions removal. This is because agitation is intended to make the adsorbate available for the adsorbent's sites, but after a certain time the adsorption sites are almost occupied by the adsorbate ions; a condition which does not offer a chance for the adsorption process to continue[11].

Effect of adsorbent mass

Varying amounts of cottonseed and soybean hulls by-products (in the range 0.5- 6 g) were used under the fixed experimental conditions mentioned in Table 2.

Figure 3(b) shows the results of the effect of the adsorbent mass on the percentage removal of Th ions. It is clear that, the rate of Th removal increases with increasing the amount of the adsorbent; there is a significant increase in Th uptake when the amount of the adsorbents is increased from 0.5 to 3.0 g for cottonseed and from 0.5 to 3.5 g for soybean hulls when treating an effluent of 100 ppm Thorium concentration. Any additional amount of adsorbents does not cause significant change in the value of Th uptake. Percentage removal of Thorium of 98.4 is attained at these values for the mass of adsorbent.

Effect of adsorbate initial concentration

The effect of adsorbate initial concentration on the adsorption process was studied using different concentrations of 50, 100, 150, 200 and 250 ppm Th solution and the recommended mass of adsorbent as

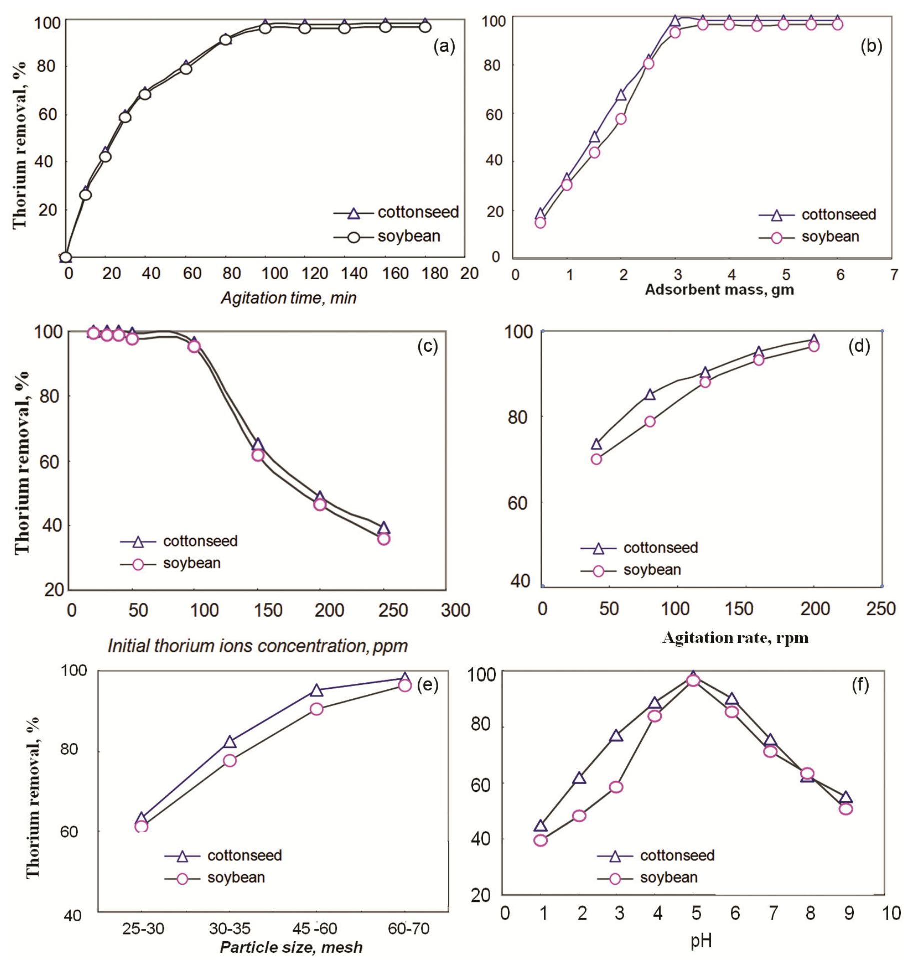

Fig. 3 — (a) Effect of agitation time on the adsorption of thorium ions onto cottonseed and soybean hulls; (b) Effect of adsorbent mass on the adsorptionof thorium onto cottonseed and soybean hulls; (c) Effect of initial concentration on the adsorption of Thorium onto cottonseed and soybean hulls; (d) Effect of agitation rate on the adsorption of thorium onto cottonseed and soybean hulls; (e) Effect of particle size on the adsorption of thorium onto cottonseed and soybean hulls and (f) Effect of *p*H value on the adsorption of thorium ion onto cottonseed and soybean hulls.

given in section III.1.2. before; under the above mentioned experimental conditions Table 2 and the results are presented in Fig. 3(c).

Figure 3(c) clarifies that the percentage of thorium ions removal reaches its maximum values (94.8%) at low initial ion concentrations; up to 100 ppm. Beyond this value for initial concentration the percentage removal decreases drastically and continues decreasing till the end of experiment; at 200 ppm initial concentration. This is because after 100 ppm Thorium concentration there will be a lack in the adsorption sites and it will not be enough to adsorb the extra amount of Thorium ions present in the highly concentrated effluent. A percentage removal of 99.2 was accomplished when using cottonseed hulls and the corresponding value was 98.8% when soybean hulls is used.

Effect of agitation rate

The effect of agitation rate on the adsorption process was studied at different agitation rates of 40, 80, 120, 180 and 200 rpm; while other factors were kept constant as in Table 2.

The results shown in Fig. 3 (d), indicate that the percentage recovery of Thorium increases with increasing agitation rate. This is due to the dispersion of the adsorbent particles in the aqueous solution which leads to reducing the thickness of the boundary layer; thus reducing its resistance to mass transfer and even it may increase the velocity of particles which, in turns, increases the adsorption efficiency. A percentage Thorium recovery of 98 and 96.6% was obtained for cottonseed hulls and soybean hulls, respectively at rate of agitation of 200 rpm.

Effect of adsorbent particle size

The effect of adsorbent particle size upon the adsorption of thorium ions is shown in Fig. 3(e). Different ranges of adsorbent particle size were used as 25 - 30, 30-35, 45- 60, and 60 -70 mesh size under the above mentioned experimental conditions of Table 2.

The results obtained show that, percentage thorium ions removal increases with decreasing the adsorbent particle size. This is due to the fact that the adsorption process is a surface phenomenon. Thus, the extent of adsorption is proportional to the specific surface area. The smaller particle size offered relatively larger surface area and hence higher adsorption at equilibrium[12].

Effect of effluent *p*H

The effect of effluent *p*H upon the adsorption process was studied using different values of *p*H in the range 1 to 9; while keeping other operating conditions constant as given in Table 2. The adsorbate *p*H was adjusted by using dilute HNO_3 (1M) or NaOH solution.

The obtained results are presented in Fig. 3(f). Examination of this figure clarifies that percentage thorium removal increases with increasing the adsorbate *p*H up to *p*H 5. Beyond *p*H 5, thorium removal efficiency begins to decrease. The variation in the ions removal efficiency with *p*H can be explained by considering the surface charge of the adsorbent. In acidic medium, the charge of the adsorbent surface becomes -ve while in the alkaline medium it becomes +ve[11]. So, in the low *p*H range the lower values for adsorption of metal ions is due to the competition on the active sites between metal ions and hydrogen ions (H^+) in the solution[12]. With increasing *p*H values, the -ve charge of the adsorbent surface would increase. This leads to an increase in the removal efficiency of Th ions due to the electrostatic attraction between the -ve charges of the adsorbent surface and the +ve charges of the adsorbate ions. On the other hand, when the *p*H values increases beyond *p*H 5, thorium removal efficiency decreases. This is due to the electrostatic repulsion between + ve charges of the adsorbent surface and charged metal ions. From these results it is evident that the *p*H value which satisfies maximum uptake of Th ions is *p*H 5.

From the foregoing results, it can be concluded that the optimum conditions for removing thorium ions from the prepared wastewater by using the two agricultural by- products cottonseed and soybean hulls are as follows:

Agitation time : 100 min.
Adsorbent mass : 3 g for cottonseed & 3.5 g for soybean hulls
Concentration : 100 ppm
Agitation rate : 200 rpm
Adsorbent particle size : 60-70 mesh size
Effluent *p*H : 5

When using the above-mentioned conditions, the adsorption efficiencies of cottonseed and soybean hulls were found to be 98.1 and 96.5%, respectively.

Adsorption studies

Transfer of species within the adsorbent particles controls the rate of adsorption because diffusion through solid is naturally slower than through fluids. Therefore, the process continues until a characteristic equilibrium is attained.

At equilibrium, there is a definite distribution of solute between the liquid and solid phases. The distribution ratio is a measure of the position of equilibrium in the adsorption process and is presented in the form of adsorption capacity of the solid phase, i.e., the amount of adsorbent needed to remove a given amount of pollutant. This is important to determine the applicability and usefulness of the adsorption process.

Adsorption isotherm

The adsorption isotherm was determined for the adsorption of thorium ions onto cottonseed and soybean hulls by -products. The results are shown in Figs. 4 (a) and (b) as a plot of adsorption capacity (q_e) against equilibrium concentration of solute (Ce); where the adsorption capacity is calculated according to the following equation:

$$q_e = (C_o - C_e)\, V/M$$

where, C^o is the initial concentration of solute (mg/ L)
V is the volume of solution (L)
M is the mass of adsorbent (g)

From these Figures, it is clear that the isotherms rise in the initial stages of the adsorption process where low C_e and q_e values occur. This is due to the presence of a plenty of readily accessible adsorption sites. On the other hand, as the Ce values increased considerably, a small increase in q_e takes place. This is possibly due to less active sites being available at the end of the adsorption process[13].

Accordingly, the obtained results indicate that the adsorption capacity of thorium ions onto cottonseed and soybean hulls by-products were 3.27 and 2.75 mg/g, respectively.

Isotherm analysis

Isotherm analysis is important to indicate the favorability of the adsorption by using both cottonseed and soybean hulls, and to develop an equation that accurately represents the results which could be used for design purposes. For the present work, two from several isotherm equations were selected; namely Langmuir and Freundlich isotherms. The Langmuir type isotherm corresponds to surface homogeneity of the adsorbent while the Freundlich one is an indication of surface heterogeneity of the adsorbent.

Langmuir isotherm

The Langmuir isotherm[14] is valid for monolayer adsorption on a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption on the surface, and the adsorption sequentially fills surface sites until monolayer coverage is achieved at constant temperature. The Langmuir expression is represented by the following equation:

$$q_e = a\, b\, C_e / (1+a\, C_e)$$

Where: q_e is the mass of the adsorbate per gram of adsorbent at equilibrium (mg/g)
C_e is the concentration of the adsorbate at equilibrium (mg/L)
a is the Langmuir constant
b is the monolayer coverage (mg of solute adsorbed /g of adsorbent)

The linear form of Langmuir equation, which can be used for the linearization of the experimental data, is expressed by the following equation:

$$C_e/ q_e = 1/ab + C_e/b$$

From this equation, the constants (a) and (b) can be determined. The linear plots of C_e/ q_e against C_e for thorium in Fig. 5(a) suggest the applicability of the Langmuir isotherm for the present system, showing the formation of monolayer coverage of the adsorbate

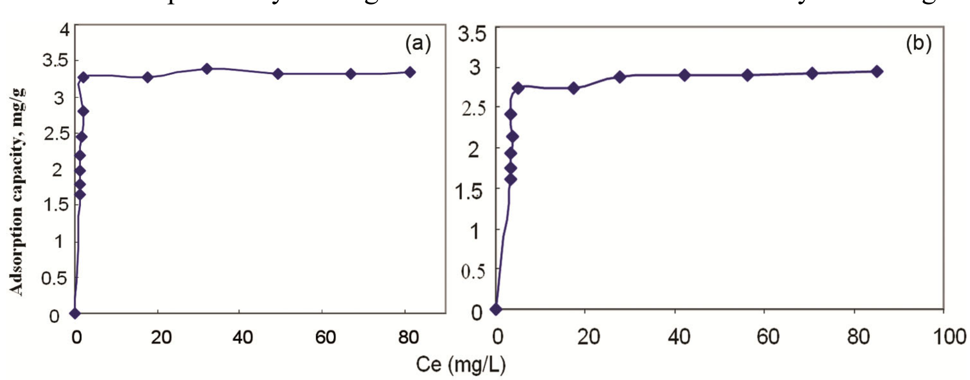

Fig. 4 — (a) Equilibrium adsorption of thorium onto cottonseed and (b) Equilibrium adsorption of thorium onto Soybean hulls.

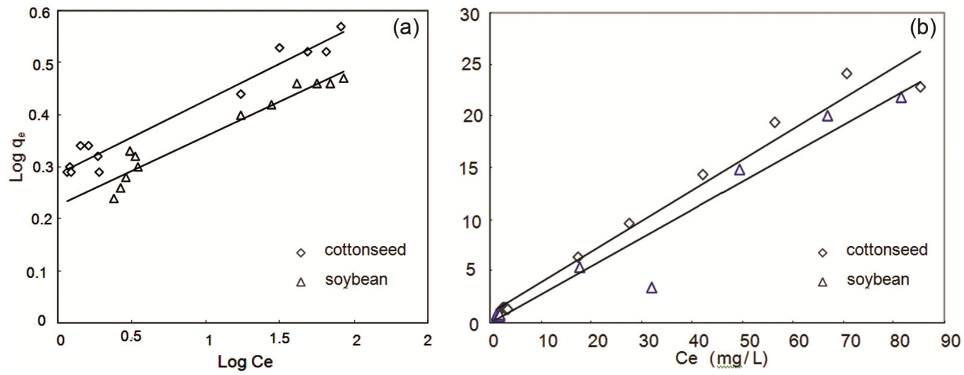

Fig. 5 — (a) Langmuir isotherm of adsorption of thorium onto cottonseed and soybean hulls and (b) Freundlich isotherm of adsorption of thorium onto cottonseed and soybean hulls.

at the outer surface of adsorbent. The values of constants (a) and (b) of the metal ions are listed in Table 3. The value of (b) represents the maximum adsorption capacity (q max) of cottonseed and soybean hulls by- products.

On the other hand, the essential characteristics of Langmuir isotherm may be expressed in terms of dimensionless equilibrium parameter R_L (Ref.15) which is defined by the following equation:

$$R_L = 1/(1+a\ C_e)$$

This parameter indicates the shape of the isotherm, accordingly:

R_L + value	type of isotherm
$R_{L>}1$	unfavourable
$R_L = 1$	linear
$0<R_L < 1$	favourable
$R_{L=}0$	irreversible

R_L is calculated from Langmuir isotherm and listed in Table 3. It was found to be in the range of $0< R_L < 1$. This indicates a highly favourable sorption process.

Freundlich isotherm

The Freundlich isotherm[16] is an exponential model. It empirically relates the isotherm data and it has been found to fit much adsorption systems in dilute solutions. Also, it is suitable for heterogeneous surfaces that are more often seen in natural systems. The Freundlich expression is in the form:

$$q_e = K_f\ C_e^{\ 1/n}$$

where (K_f) and (n) are constants and (n) is greater than one. Taking the logarithmic of both sides, the equation will be in the linear form as follow:

Table 3 — Langmuir constants of adsorption system

Adsorbent materials	Thorium ion					
	r^2	R_L	q_{max}	K_L	B	a
Cottonseed hulls	0.951	0.027	3.66	1.28	3.66	0.35
Soybean hulls	0.975	0.029	3.35	1.127	3.35	0.33

Table 4 — Freundlich constant of adsorption system

Adsorbent materials	Thorium ion		
	r^2	n	K_f
Cottonseed hulls	0.6130	7.67	2.09
Soybean hulls	0.6714	8.07	1.78

$$\text{Log } q_e = \log K_f + 1/n \log C_e$$

A plot of log Ce against log q_e yields a straight line which indicates the confirmation of the Freundlich isotherm for adsorption. On the other hand, the magnitude of the exponent (n) gives an indication of the favorability of the adsorption process.

Figure 5(b) represents the Freundlich isotherm of thorium ions. The parameters (n) and (K_f) have been determined and tabulated in Table 4.

From the obtained results, it is clearly evident that the values of Freundlich exponent (n) are greater than one. This indicates favorable adsorption for thorium by both cottonseed and soybean hulls by-products.

Adsorption kinetics

Effect of temperature

The effect of temperature on the adsorption of thorium ions onto cottonseed and soybean hulls by-products is shown in Figs. 6 (a) and (b).

From these figures, it is evident that the adsorption of Th ions decreased with increasing the temperature; indicating that the process is exothermic in nature.

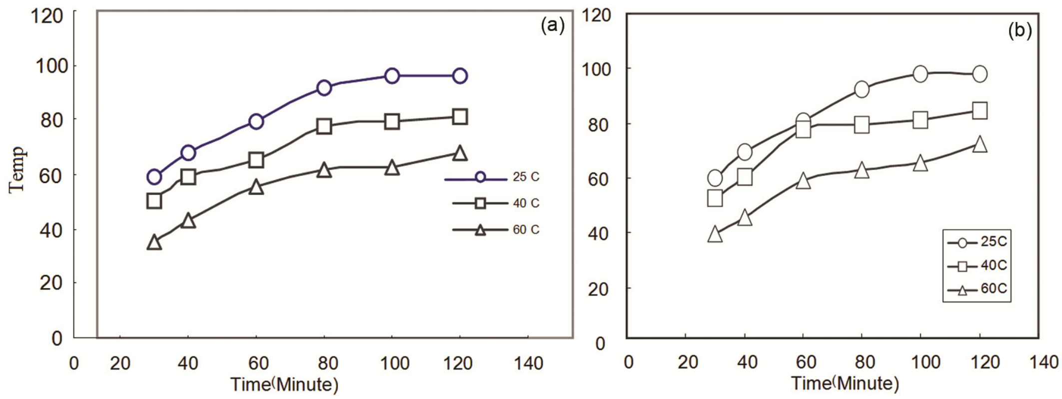

Fig. 6 — (a) Effect of temperature on the adsorption of thorium onto cottonseed hulls and (b) Effect of temperature on the adsorption of thorium onto soybean hulls.

Thermodynamic parameters

The thermodynamic parameters such as free energy (AG^0), enthalpy (AH^0) and entropy change (ΔS^0) were determined using the following equations[17,18]

$$\Delta G^0 = - RTlnK_c \quad \text{…(1)}$$

$$\Delta G^0 = AH^0 - AS^0 \quad \text{…(2)}$$

Where,
ΔG^0 : change in free energy, KJ $mole^{-1}$
ΔH^0 : change in enthalpy, KJ mol^{-1}
ΔS^0 : change in entropy $(mol\ K^{-1})^{-1}$
T : absolute temperature, K
R : gas constant= 8.314 $X10^{-3}$
K_c : equilibrium constant
K_c may be defined as:
$K_c = C_{Ae}/ C_e$

Where, C_{Ae} and C_e are the equilibrium concentrations (mg/L) of the metal ion on the adsorbent and in the solution, respectively. Equations (1) and (2) can be rewritten as:

$$LogK_c = \Delta S^0/2.303R - \Delta H^0 /2.303RT$$

When Log K_c is plotted against 1/T Fig. 7 straight line with slope $\Delta H^o/2.303R$ and intercept $\Delta S^o/2.303R$ is obtained. The values of ΔH^o and ΔS^o are obtained from the slope and intercept of the Vant't Hoff plots of log K_c vs 1/T. The thermodynamic parameters for the adsorption process are given in Table (5). Negative values of ΔH^o suggest the exothermic nature of the adsorption process. The negative values of ΔG^o indicate spontaneous nature and feasibility of the adsorption process and the negative values of ΔS^o indicate the probability of favourable adsorption and the low values of ΔS^o indicate that the process is more arranged.

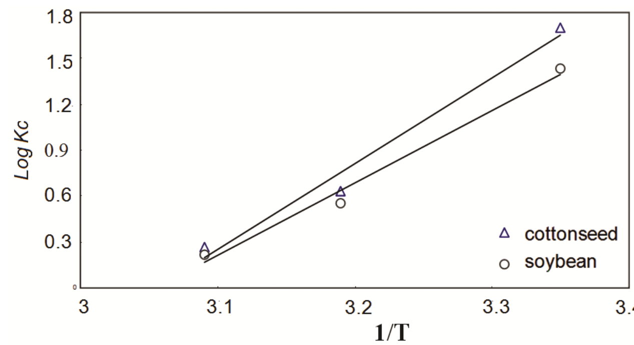

Fig. 7 — Van't Hoff plot of adsorption of thorium onto cottonseed and soybean hulls

Case study

An effluent sample of radioactive wastewater coming from different research laboratories was collected for use in a case study. The concentration of Th ions in this sample was found to be 29.3 ppm. The sample is brought to contact with the cottonseed and soybean hulls by- products at the obtained optimum equilibrium conditions of the present work.

After treatment, the concentration of Th ions in the tested sample was found to be 2.9 and 3.1 ppm when using cottonseed and soybean hulls, respectively. The corresponding adsorption efficiencies were 90.1 and 89.2 %, respectively.

Examination of the results of experimental work on the prepared effluent shows that the adsorption efficiency of cottonseed and soybean hulls was 98.1 and 96.5%, respectively. While the results for the industrial liquid waste was 90.1 and 89.2% for cottonseed and soybean hulls, respectively. This may be due to the presence of other elements (when using industrial liquid waste) which are also adsorbed on the adsorbent materials.

In both cases; experimentation on a prepared solution or on an industrial liquid waste, the two used

Table 5 — Thermodynamic parameters for the adsorption of thorium ions onto cottonseed and soybean hulls

Adsorbent	ΔS° (JmolK^{-1})$^{-1}$	ΔH° (Kjmol^{-1})	ΔG° (Kjmol^{-1})	K_c	Temperature, °C
Cottonseed hulls			-7.45	50.8	25
	-230.63	-76.21	-5.52	4.3	40
			-3.29	1.9	50
Soybean hulls					
	-200.5	-65.35	-5.60	27.30	25
			-4.30	3.85	40
			-2.57	1.69	50

agricultural by-products after being used in metal adsorption become contaminated by metals, i.e. it becomes radioactive solid waste. These solid wastes could be discarded by one of these methods:

a) Burned at high temperature (incineration) and the leachate or ash used to recover metal ions by a suitable process.
b) Reduction of adsorbent volume by compaction or incineration and encapsulation in cement mass and burying in earth depth.

Conclusion

From the foregoing study, the following conclusion could be made:

Cottonseed and soybean hulls by-products, which are plentiful and low cost materials, are capable of being used as adsorbing materials for removing thorium ions from aqueous solutions.

Increasing the agitation time does not have a positive effect on the removal of Thorium ions beyond a time limit of 100 min; both for cottonseed and soybean hulls.

The maximum adsorption capacity of thorium was 3.27 and 2.75 mg/g when using cottonseed and soybean hulls by-products, respectively.

The *p*H value which satisfies maximum uptake of Th ions is *p*H 5.

Cottonseed and soybean hulls by-products can adsorb thorium ions at or below metal ion concentration of 100 ppm. In this regard, it may be used as polishing adsorbents.

The percentage recovery of Thorium increases with increasing agitation rate. A percentage Thorium recovery of 98 and 96.6% was obtained for cottonseed hulls and soybean hulls, respectively at rate of agitation of 200 rpm.

The most suitable conditions for achieving the highest percentage Thorium recovery are: using 3g of cottonseed hulls or 3.5 g of soybeans hulls of 60-70 mesh particle size at 25°C and 200 rpm for 100 min. of treatment. These conditions are true for 100 ppm Thorium solution at *p*H value 5.

References

1 Zhou W, Ren L & Zhu L, *Environ Pollut*, 223 (2017) 247.
2 Kashfi H, Mousavian S, Seyedsalehi M, Sharifi P, Hodaifa G, Salehi A S & Takdastan A, *Int J Environ Sci Technol*, 16 (2019) 2905.
3 Uosif M A M, Issa S, Zakaly H M, Hashim M & Tamam M, J Nucl Phys, Mat Sci, Rad Appl, 3 (2016).
4 Ionita D, Nicoara A & Stoian A B, *Revista de Chimie*, 70 (2019) 1911.
5 Pawar P R & Bhosale S M, *Int J Curr Eng Technol*, 8 (2018) Please tell me pages number.
6 Sanad W A, Flex H & Alan K F, *Arab J Nucl Sci Appl*, 31 (1998) 91.
7 Vitas S, Keplinger T, Reichholf N, Figi R & Cabane E, *J Hazard Mater*, 355 (2018) 119.
8 Adeeyo O A, Oresegun O M & Oladimeji T E, *Am J Eng Res*, 4 (2015) 14.
9 Acharya J, Kumar U & Rafi P M, *Int J Curr Eng Technol*, 8 (2018) 526.
10 Mahmoud M R, Soliman M A & Allan K F, *J Radioanal Nucl Chem*, 300 (2014) 1195.
11 Rahimi M, *J Chem*, (2013)1.
12 Kumar P S, Korving L, Keesman K J, van Loosdrecht M C & Witkamp G J, *Chem Eng J*, 358 (2019) 160.
13 Abdelghany E A, *J Mater Environ Sci*, 9 (2018) 570.
14 Roy A & Bhattacharya J, *Nanotechnol Indust Wastewater Treat*. IWA Publishing (2015).
15 Legrouri K, Khouya E, Hannache H, El Hartti M, Ezzine M & Naslain R, *Chem Int*, 3 (2017) 301.
16 Das L, *Synthesis of Low Cost Adsorbents for Mitigation of p-cresol*, MS thesis, North Carolina University (2012).
17 Babarinde A & Onyiaocha G O, *Chem Int*, 2 (2016) 37.
18 Jain C K Sharma M K, *Water Air Soil Pollut*, 137 (2002) 1.