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POTENTIALITY OF URANIUM ADSORPTION AND ITS ASSOCIATED ELEMENTS FROM WASTE LABORATORY LIQUIDS USING BLACK TEA WASTE

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ABSTRACT

The black tea waste, representing an efficient natural ,bio-adsorbent has been applied for adsorption of some hazardous elements. Several batch wise experiments are conducted to determine the relevant factors affecting its adsorption characteristics especially for uranium. The studied factors are the effects of stirring, agitation time, pH, solid/ liquid ratio and initial metal concentration.

The equilibrium data are found to be satisfactorily fitting to Langmuir isotherms. A maximum-metal uptake of 60.56 mg/g was observed for uranium at a solution pH range of 4.5-5.5. The studied elements include U, Th and REEs in the presences of some possible interfering elements. Elution of the studied interesting elements has been achieved and from their eluates proper concentrates have been prepared.

INTRODUCTION

Contamination of the environment by toxic metals from several types of both natural and industrial operations is a world wide phenomenon. Their removal by various physical, chemical or biological methods has been repeatedly attempted to overcome this problem. In the same time, the utilization of agricultural waste materials has become of vital concern as these wastes represent serious disposal problems. Numerous waste biomass sources are available and upon which several experimental adsorption studies were performed e.g. rice husk (Zulkali et al., 2006), peanut shells (Wafwoyo et al., 1999) ,corn cobs (Vaughan et al., 2001) saw dust (Sciban et al., 2006),etc.

Bio-sorption of heavy metals occur upon such biomass sources as a result of physiochemical interaction-mainly ion exchange or complex formation -between metal ions and the functional groups present on the cell surface of these sources like carboxyl, amine , amide, etc. There is a considerable potential for adopting such systems in the form of used black tea waste resulting in large quantities as a waste byproduct in cafeterias as an adsorbent for the removal of hazardous metal values from aqueous solutions.

Amarasinghe and Williams (2007) reported that non treated black tea waste is a good adsorbent for the removal of Cu and Pb from waste water. Highest metal uptake attaining 48 and 65 mg/g are reported for Cu and Pb, respectively. Tan (1985) has also reported that the consumed coffee powder and black tea waste were found to be able to remove substantial amounts of Cu (II) ions from aqueous solutions. The obtained results were found to be consistent with the fact that the Cu (II) uptake mechanism was due to specific ion adsorption via chelating and to a lesser degree of ion-exchange reaction.

The present work is designed to investigate the potentiality of black tea waste to adsorb some metal values from aqueous lab waste solutions as means for their recovery e.g. Cu, U, Th, REEs, etc. For this purpose several series of adsorption experiments have first been performed using proper synthetic solutions to optimize the different factors.

EXPERIMENTAL

Materials

Preparation of black tea waste

The black tea is indeed prepared from the green tea being mainly produced from its vast plantations in Ceylon, India and Kenya. For this purpose, the green tea is subjected to poly phenyl oxidation through its fermentation. The black tea waste used for adsorption experiments in the present work has first been thoroughly washed with boiling water for the removal of soluble and colored components. The washed waste black tea is then washed with distilled water followed by washing with 5% HCl. Then it is dried overnight at 70 °C before storing in polyethylene bags. Acid washing is intended to keep the black tea waste away from its decomposition by various bacteria and fungi.

Preparation of synthetic solutions

Synthetic solution of uranium and other working elements have been prepared from their proper salts. Different metal solutions were thus prepared by dissolving analytical grade metal salts in distilled water or mineral acids to obtain accurate concentration as ppm (mg/l). From the latter, the working solutions were prepared by dilution to realize the required concentration. The pH of these solutions was measured and adjusted at 4.5 ± 0.5 and all the adsorption experiments run at room temperature 25 ± 2 °C. The metal salts used include the nitrate salts of U, Cu ,Ca, Pb and Th ,the chloride salts of Fe and Cd and the hydroxide salts of Ni and REEs (Y and Ce).

Adsorption Experimental Procedure

Batch adsorption tests are conducted by mixing of 2 g of the working black tea waste with 100 ml of the different working solutions of known metal ion concentration in proper glass beakers. The prepared mixture is shaken in a mechanical shaker and a 2ml sample solution is periodically withdrawn from the beaker at known time intervals. Preliminary experiments have shown that adsorption is adequately fast and the removal rate was actually found to be negligible after 60 min. Therefore, 60 min is used as the contact time for almost batch tests except in the experiments of the effect of the initial uranium concentration. At the end of each experiment, the black tea waste sample is filtered and washed to remove any fine particles before being analyzed for the adsorbed metal ions. Several series of experiments are thus conducted to determine the optimum values of the relevant factors controlling the adsorption process. As previously mentioned, The solution pH all the time is fixed at 4.5±0.5 and all the experiments are conducted at room temperature (25 ± 2 °C).

On the other hand, for the determination of uranium equilibrium isotherm, the corresponding experiments are conducted by mixing 1 g of the working black tea waste with 50 ml of uranium of initial concentrations ranging from 10 to 2000 mg/l. In these experiments, each batch mixture is shaken for a contact time of up to 3 h to reach equilibrium. For each adsorption experiment the adsorptive capacity (qe) is determined according to the following equation;

$qe = V (C_0 - Ce)/M$

where V is the total volume of the solute solution (in L), M is the weight of adsorbent used (gm), C_0 is the initial concentration of the solute (mg/l), and Ce is the residual equilibrium concentration of the solute (mg/l).

After studying the adsorption character of agitation solution containing U and possible interferers an application experiment is conducted upon the actual working lab waste solution . For the latter, both a loading test is achieved followed by elution and precipitation of REEs ,U and Th . Concerning the application studies upon a working laboratories waste solution , a recovery test of U, Th and REEs have been performed by proper elution and precipitation.

Analytical Procedures

The various metal ions are determined using atomic absorption spectrometer (A AS) (Unicam 969, England). Meanwhile, thorium and REEs are spectrophotometerically determined by the chromogenic reagent Arsenazo-III (Merczenko, 1986), while uranium analysis in different processing stream solutions is performed by an oxidimetric titration method using ammonium metavanadate. On the other hand, the obtained REEs ,U and Th final products have been subjected to proper analysis using both the ESEM-EDX and XRD techniques.

RESULTS AND DISCUSSION

Structure of the Working Black Tea Waste

According to Harler (1963), the ethanol insoluble black tea waste is mainly composed of cellulose, lignin and some structural proteins in different ratios. To assess the working black tea waste, a proper sample is subjected to a chemical analyses of these major components for the determination of their relative amounts. For this purpose, the procedures adopted by Tappi(1957) for cellulose lignin and carbohydrate and by Bradford, (1976) for protein have been applied. The obtained results (Table1) have indicated an almost complete similarity to that given by Harler (1963).

Table1: Chemical composition of ethanol insoluble material extract of the working insoluble black tea waste (dry weight basis) in comparison with that of Harler (1963)

Constituent	Working black tea waste (wt%)	Tea waste (Harler, 1963), (wt%)
Cell wall material	-	38.2
Hot water-soluble polysaccharide and proteins	9.05	8.10
Hot water insoluble proteins	11.22	10.08
Lignin and structural proteins	13.17	12.25
Cellulose	30.81	31.00

As a matter of fact, the fresh green tea leaves contain indeed nine main compounds, namely: polyphenols (sometimes called tannins), alkaloids, protids, organic acids, glucids, lipids, cholorphylls, mineral salts and volatile substances. Each of these can be further divided into subcategories. Yang and Wang(1996) have reported that the manufacture of the black tea from the green tea would cause changes in the chemical formulae of these components (Fig. 1).

Results of Uranium Adsorption Upon Black Tea Waste

Effect of stirring state

In order to study the effect of stirring state upon uranium adsorption efficiency, two adsorption experiments have been performed using mechanical shaking in one of them. In these experiments, 2g weight of black tea waste sample is used in a S/l ratio of 1/50 using a uranium solution assaying 100 ppm and its pH was fixed at 4-5. After 1 hour, the black tea waste sample is filtered and the obtained filtrate is analyzed for uranium. From the obtained results, it is clear that stirring is quite important for attaining a high uranium adsorption efficiency. Thus, the latter has reached up to 95.67 %. while under the same conditions, the mere soaking has attained a much lower efficiency reaching only 51.13% (Fig. 2).

Effect of agitation time

For studying the effect of agitation time upon uranium adsorption efficiency, three series of experiments have been performed in which the uranium concentration was varied between 25 and 100 ppm . In these experiments, about 2g of black tea waste were allowed for stirring within the uranium solution having different concentrations at a fixed pH of 4-5. The applied agitation time periods involved 15, 30, 60, 90, 120 and 180 min. The obtained results are shown in Table (2) and plotted on Fig (3). From the latter results, it is noticed that by increasing the agitation time, the adsorption efficiency increases during the





Major components of black tea

Fig. 1: The major functional groups of the green tea leaves and black tea (Yang and Wang 1996).



Fig. 2: Effect of stirring state on uranium adsorption efficiency by working black tea waste Table 2: Effect of agitation time on uranium adsorption efficiency by the working black tea waste

Time, min U conc.(ppm)	15	30	60	90	120	180
25	90.3 %	94.57 %	97.3 %	97.44 %	99.6 %	99.999 %
50	82.9 %	93.96 %	96.83 %	96.63 %	98.99 %	99.999 %
100	74.37 %	91.91 %	95.73 %	96.137 %	98.12 %	99.999 %

first one hour after which the increase in uranium adsorption is quite low. On the other hand, the adsorption efficiency decreases with increasing the uranium concentration. It is thus interesting to calculate the adsorption capacity when using contact time periods of 15 and 60 minutes and a uranium concentration of 25 and 100 ppm. The calculated adsorption capacity when using 25 ppm uranium concentration is found to attain 1.13 and 1.21 mg/g for 15 and 60 minutes respectively. While when using 100ppm uranium concentration, the adsorption capacity is found to reach up to 3.72 and 4.79 mg/g respectively.



Fig. 3: Effect of agitation time upon uranium adsorption efficiency by the working black tea waste

Effect of pH

As a matter of fact, the most important parameter affecting the adsorption uptake is actually the pH value. Therefore, the effect of pH has been studied in the range of 4 to 9 using 100 ml sample of uranium solutions assaying 100 ppm, 2g weight of black tea waste sample for a contact time 60 minutes. From the obtained result shown on Fig.(4), it is found that the adsorption was rapidly increased between the pH 4 and 5. This phenomenon can be attributed to interaction between the surface charge of the adsorbent and the H⁺ ions concentrations in the solution. At high pH values the surface of the adsorbent would have much higher negative charges; resulting higher attraction of the solution cations. The obtained data are actually in agreement with comparable results obtained for other biomass materials such as the orange waste (Dhaka et al., 2005), the sago waste(Quek et al., 1998)

and the saw dust (Sciban et al., 2006)etc. Obviously, the uranium adsorption onto the black tea waste would thus be optimum in the pH range 4.5-5.5. On the other hand, at very high pH values, decrease in adsorption would occur due to other effects viz hydrolysis and precipitation (Gaikwad, 2004 and Sciban et al., 2006).



Fig. 4: Effect of pH upon uranium adsorption efficiency by the working black tea waste

Effect of solid/ liquid ratio

The effect of the solid liquid ratio upon the uranium adsorption efficiency is studied by agitating 2 g of the black tea waste in a uranium solution assaying 100 ppm at different solid /liquid ratios; namely 1:50, 1:75, 1:100 and 1:150 for one hour. The pH of the uranium solution was adjusted at 4.5-5.5. The obtained results indicated that by increasing the liquid /solid ratio, the uranium adsorption efficiency would decrease. The latter is found to decrease from 95.7 to 86.75% when using a solid liquid ratio of 1/50 to 1/150 respectively (Fig. 5).



Fig. 5 :Effect of solid/ liquid ratio on uranium adsorption efficiency by the working black tea waste

Effect of initial uranium concentration

The effect of the initial uranium concentration upon the adsorption capacity of the working black tea waste is studied by contacting a 2g fixed mass of black tea waste with uranium solution having different concentrations ranging from 10 to 2000 ppm. In these experiments a fixed temperature of ≈ 25 °C is used beside an initial pH range of 4.5 to 5.5 and solid/liquid ratio of 1/50, while using a contact time of 3 h to ensure the attainment of the equilibrium state. Plotting the obtained relationship between the uranium concentration and its adsorption capacity was found to be non-linear (Fig 6). In other words, a maximum adsorption capacity of about 60 mg/g has been attained when using a uranium solution assaying ≥ 1500 ppm.



Fig. 6: Effect of initial uranium concentration upon the adsorption capacity of the working black tea waste

On other hand ,it is found greatly beneficial in the present work to determine the adsorption isotherm according to langmuir and Freundlich equations. The purpose is describing the adsorption mechanism for the interaction of uranium ion on the working adsorbent surface and to express its surface properties and its affinity towards the uranium ions.

Applicability of equilibrium isotherm

Langmuir adsorption isotherm

Langmuir isotherm (L-shaped) model is developed by Irving Langmuir in 1918 described as the ideal localized monolayer model. This isotherm represents the equilibrium distribution of metal ions between the solid and liquid phases. The following equation can be used to model the adsorption isotherm:

$$= \frac{qmax \cdot b \cdot ce}{1 + b \cdot Ce}$$

q

where q is the milligrams of metal accumulated per gram of the sorbent, Ce is the metal residual concentration in solution; qmax is the maximum specific uptake corresponding to the site saturation and b is the ratio of adsorption and desorption rates (Chong and Volesky, 1995).

The Langmuir isotherm is based on these assumptions (Langmuir, 1918):

• Metal ions are chemically adsorbed at a fixed number of well defined sites.

• Each site can hold only one ion.

• All sites are energetically equivalent.

• There is no interaction between the metal ions.

When the initial metal concentration rises, adsorption increases while the binding sites are not saturated. The linearized Langmuir isotherm allows the calculation of adsorption capacities and the Langmuir constants and is equated by the following equation.

$$Ce/q = 1/(qmax \cdot b) + Ce/qmax$$

The linear plots of Ce/q vs Ce show that adsorption follows the Langmuir adsorption model.

The essential characteristics of the Langmuir isotherms can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, RL, which is defined as:

RL = 1 / (1 + b.q max)

where b is the Langmuir constant and C_o is the initial concentration of metal ions in the solution. The RL value indicates the shape of isotherm. According to Metcalf and Eddy, (2003), RL values if between (0 – 1) indicate favourable adsorption, if equal to (1) indicate linear adsorption and if above (1) indicate unfavourable adsorption.

From plotting the obtained data Using Langmuir equation ,it is found that the relation Ce/qe vs is clearly linearized (Fig. 7). The Langmuir constant "q max" measures the monolayer adsorption capacity of the black tea waste and is found to attain 60.56 mg/g .The Langmuir constant "b" (denotes adsorption energy) which was obtained as 0.173 l/mg. The determined high coefficient value ($r^2 = 0.999$) thus indicates a good agreement between the experimental values and the isotherm parameters and also confirms the monolayer adsorption uptake of the black tea waste surface (Table 3). The dimensionless parameter of "RL" (measures the adsorption favorability) is found to attain 0.0871 (i.e. 0 < RL < 1) confirming the favorability of the adsorption process for the uranium removal using the black tea waste. It is also found that when the RL value approaches to zero the irreversible adsorption was favored.



Fig. 7:Linear form of Langmuir model for uranium adsorption on the working tea waste

Table 3: Langmuir and Freundlich isotherm constants for uranium uptake by the working black tea waste at room temperature

Metal	Adsorbent	Langmuir model parameters		Freundlich	ameters		
		qmax (mg/g)	b (mg/ L)	R ²	1/n	K _f (mg/g)	R ²
Uranium	Black tea waste	60.65	0.173	0.999	1/0.20684	17.14	0.9

Freundlich adsorption isotherm

The Freundlich isotherm is the earliest known relationship describing the sorption equilibrium. This fairly satisfactory empirical isotherm which can be used for non-ideal sorption and is expressed by the following equation (Metcalf and Eddy, 2003):

$$q = Kf Ce^{1/n}$$

where Ce is the equilibrium concentration (mg/l), q is the amount adsorbed (mg/g) and Kf and n are constants incorporating all parameters affecting the adsorption process, such as adsorption capacity and intensity respectively. The linearized forms of Freundlich adsorption isotherm and which used in the present work to evaluate the obtained sorption data is as follows:

$$\log q_{\rm e} = \log K_{\rm f} + \frac{1}{n} \log C_{\rm e}$$

Where according to Kadirvelu and Namasivayam (2000) n values between 1 and 10 represent beneficial adsorption.

Both the Freundlich constants Kf and n are obtained by plotting log qe versus log Ce (Fig. 8). It is thus found that the determined coefficient of Freundlich isotherm model for working black tea waste attain 0.9 which is lower than that of Langmuir isotherm model. Accordingly, it can be concluded that the obtained experimental data has actually been fitted to Langmuir isotherm and not to that of Freundlich (Table 3).



Fig. 8: Freundlich isotherm model for the uranium adsorption on the working black tea waste

Loading and Elution Characteristics of a Synthetic Solution

A proper solution of some elements that might be associated with uranium e.g. Cd, Pb, Ni, Fe, Th, Cu, Ca besides Ce and Y is prepared from their respective solutions, thus assaying a total of 100 ppm . In other words, the prepared solution of ten studied elements would assay 10 ppm of each of its components.

Loading characteristics of the synthetic solution

An adsorption experiment upon the working black tea waste was then performed by stirring in the prepared synthetic solution for one hour at a solid liquid ratio of 1:50. The pH of the solution is first adjusted at pH 4.5 -5.5. The obtained adsorption results are calculated and shown in Table (4) using the following equation:

Adsorption capacity as $mg/g = V (C_0-Ce) /M$,

where V is the total volume of the solute solution (L),M is the weight of the adsorbent used (gm), C_0 is the initial concentration of the solute (mg/l) and Ce is the residual concentration of the solute (mg/l).

Table 4: Adsorption levels of U and its associated elements mg/g from the synthetic solution on the working black tea waste

Elements	Adsorption level mg/g	Elements	Adsorption level mg/g
Pb	0.48	Cd	0.41
Cu	0.39	Ni	0.39
Fe	0.40	Th	0.34
Ca	0.50	Ce	0.39
U	0.39	Y	0.31

From these results it is indicated that the working black tea waste has the ability to adsorb the studied elements according to the following order of preference $Ca > Pb > Cd > Fe > Ni \ge Cu \ge U \ge Ce \ge Th and Y$. The adsorption level of these elements ranges from 0.31 mg/g for Y to 0.5 mg/g for Ca. This order might be interpreted as due to the size of ionic species of these elements and/or the charge assumed by these species.

Elution characteristics of the loaded REEs, Th and U

To study the elution characteristics, interest has been limited to the REEs, uranium, and thorium representing hazardous' materials. The loaded black tea waste obtained from the previously mentioned synthetic solution of the 10 studied elements is thus subjected to elution studies of the three mentioned elements. For this purpose, two eluants have been used; namely an alkali solution for the REEs and an acidified NaCl solution for both uranium and thorium.

Alkali elution of the REEs

Three alkali elution experiments have been batchwise performed at a S/l ratio of 1/100 using Na₂CO₃ /NaHCO₃ solution of 150 g/l total concentration at different ratios of either. In these experiments a stirring time of 15 minute has been used at room temperature. From the obtained results shown in Table (5) and plotted on Fig. (9), it is indicated that the sodium carbonate/sodium bicarbonate solution ratio of 2/1 has yielded up to 99.2 % elution efficiency of the loaded REEs. Analysis of both uranium and thorium has shown that under these condition , their elution efficiencies have only been 0.52 and 0.64 % respectively.

Table 5: Elution efficiency of the loaded REEs from the black tea waste using sodium carbonate /sodium bicarbonate eluent

Na ₂ CO ₃ /NaHCO	O ₃ Elutio	Elution efficiency %				
ratio	REEs		Th			
1:1	78.98	-	-			
2:1	99.20	0.52	0.64			
3:1	95.34	8.00	6.30			
REE 90 80 80 80 80 80 80 80 80 90 90 90 90 90 90 90 90 90 9	U U U U U U U U U U U U U U U U U U U	e	Th			

Fig. 9: Elution efficiency of the loaded REEs from the black tea waste using sodium carbonate and sodium bicarbonate eluent

Salt elution of uranium and thorium

After elution of the REEs ,the elution of still loaded uranium and thorium has also been actually batchwise achieved (S/l ratio 1/100) using NaCl acidified solution by sulfuric acid to the extent of 0.15,0.25 and 0.35 M. (EL-Sheikh, 2006) at room temperature for 15

minutes. From the obtained results shown Table(6) and plotted on Fig.(10), it is clearly evident that the adopted acidified salt solutions are quite efficient for elution of both uranium and thorium. Thus using 1/0.15 salt /acid molar ratio, the elution efficiencies of both uranium and thorium have attained up to 95.2 and 94.1 % respectively. Increasing the acid molarity to 0.35 result in almost complete elution namely; 98.9 and 97.14 for uranium and thorium respectively.

Table	e 6: E	lution e	effici	ency of	of the	loaded	l uranium	and	tho-
rium	using	, acidif	ied s	sodiun	n chlo	oride so	olution		

NaCl /H2SO4 molar ratio	Elution efficiencyc%			
	U	Th		
1:0.15	95.24	94.11		
1:0.25	96.57	96.87		
1:0.35.	98.9	97.14		



Fig. 10: Elution efficiency of the loaded uranium and thorium from black tea waste using sodium chloride and sulfuric acid in different molar ratios

Loading and Elution Characteristics of Lab Waste Solution

Loading characteristics of the lab waste solution

As a matter of fact, the specification of the black tea waste is actually considered as an important factor in determining its capacity in removing elements from different media. For practically testing the working black tea waste ,it is applied upon an actual lab waste solution whose chemical composition is summarized in Table (7) .Accordingly, about 500 ml of this lab waste is stirred with 10 g of the working black tea waste for one hour, after adjusting its pH at 4.5-5.5. At the end of the experiment the solution is analyzed for the remaining amounts of the study elements. Their adsorption efficiencies have been calculated as shown in the mentioned table.

Table 7:Chemical composition of the tested lab waste solution and adsorption efficiency of its element

Elements	Conc. g/l	Adsorption efficiency %
Р	11.4	99.12
Na	3.36	89.40
S	6.31	95.76
Ca	0.12	91.66
U	0.033	93.03
REEs	0.393	91.85
Th	0.040	75.00

To interpret the adsorption mechanism it has been indicated that the cellulose materials (black tea waste) has indeed been modified to act as a natural adsorbent for treating different waste media. For this purpose and as previously mentioned, the working black tea waste has only been modified via a mineral acid treatment at room temperature $(25\pm1 \ ^{\circ}C)$ creating certain suitable characteristics. The latter could be summarized as follows:

-Pores in the cellulose fibers are indeed naturally present and can also be generated during chemical and mechanical treatments (Park et al., 2006). An EDAX photograph obtained using the Scanning Electron Microscope (SEM) clearly indicates the mentioned pores (Fig. 11a). These pores have actually been filled after the treatment of the black tea waste with the actual lab waste (Fig. 11b). The EDAX analytical data of the native black tea waste i.e before treatment and shown in (Fig.12a) demonstrate the absence of any radioactive elements (U and /or Th) or REEs in its pores . On the other hand, the EDAX analytical data of the black tea waste treated by actual lab waste clearly indicate the presences of theses elements, Fig. (12b).



Fig. 11a,b: ESEM photos showing the working black tea waste before (a) and after (b) mixing with studied lab waste solution



Fig 12a: ESEM - EDAX analysis of the working black tea waste before its treatment with the studied lab waste solution



Fig.12b: ESEM- EDAX analysis of adsorbed uranium, thorium and REEs element on the black tea waste

-Cellulose is considered as a high uniform polyacetal containing three reactive hydroxyl groups being called a hydro glucose unit. Based on this molecular structure, the ordered hydrogen bond system forms various types of super molecular semi crystalline structure, which are essential for natural functions and commercial applications e.g. cellulosic fibers. Elements are known to interact with the cellulose surface through one or both faces of the cellulose-binding domain and the cellulose proximal surface of the catalytic domain (Mc-Carter et al., 2002; Linder and Teeri, 1997).

-Acids and especially the mineral acids have an important effect on the cellulosic material where they exert an effect upon its physical properties .The latter are represented by their swelling besides acquiring higher hygroscopic as well as greater reactivity towards adsorption reactions (Mobarak et al., 1985).

-Improvement in both pyrolysis properties as well as dimension stability(Rowell, 1984).

-Finally it is interesting to refer to the fact that preparation of the black tea waste from the green tea is greatly advantageous where it becomes highly enriched in the theaflavins and the arubigens having sevseral COOH⁻, COORand OH moieties which would play both as anion and cation exchange compounds.

Elution characteristics of the loaded REEs, U and Th

As mentioned above, the elution of REEs, U and Th from the black tea waste loaded from the prepared synthetic solution is proceeded through two steps; the REEs were first eluted followed by the simultaneous elution of both U and Th. Similary elution of the black tea waste loaded from the actual lab waste is undertaken using the previously mentioned conditions. Thus the working loaded black tea waste is firstly conducted with 15 % Na₂CO₃ /NaHCO₃ (2:1) to elute the loaded REEs with an elution efficiency of 95%. In the next elution step a mixture of sodium chloride solution and sulfuric acid in the molar ratio 1:0.35

has led to almost complete elution of U and Th with an efficiency of 98.7 and 97.1 % respectively.

Prepartion of the REEs, U and Th Concentrates

To prepare a proper concentraties of the three intersting elements eluted from actual lab waste solution namely; REEs,U and Th,it is found convenient to apply two precipitation techeniques. The REEs have been first precipitate as their hydroxides with few drops of conc. HCl till pH 6-7. The obtained precipitate is checked by an EDAX analysis and is shown on Fig.(13) which clearly indicates that it assays about 90 % REEs including about 65 % La,Ce and Nd while Gd, Dy, Er and Yb about 15% beside Lu content of 1.86. %



Fig. 13: ESEM-EDAX analysis of the prepared REEs concentrate

In the next elution step, uranium and thorium being simultaneously eluted, have been seperated by selective precipitation where Th was recovered as its oxalate adding an excess amount of 10% oxalic acid at pH 1-2. The obtained thorium oxalate concentrate is filtered, dried and subjected to XRD analysis and is found to conform with the Card No. 11-903 (Fig. 14).

 $Th^{+4}+(COOH)_2$ \longrightarrow $Th (C_2O_4)_4$

The oxalate filtrate containing the eluted uranium has first been properly heated to decompose oxalate remaining in the solution whose presence would prevent uranium precipitation. After cooling the pH of the eluate is adjusted to 5.8 using 5% NH₄OH where uranium is precipitated. After drying , the

obtained uranium diuranate concentrate is subjected to EDAX analysis (Fig. 15). From the latter it is found that uranium assay up to about 94%.



Fig. 14: XRD chart of the prepared thorium oxalate concentrate



Fig.15: ESEM-EDAX analysis of the prapered ammonium diuranate concentrate

Durability (Life Time) of the Black Tea Waste

A solution of about 500 ml sample of the working actual lab waste solution containing U,Th and REEs beside some associated elements is contacted with 10 g of the working dry black tea waste for one hour, after adjusting the pH at 4.5-5.5. The adsorption efficiency of the three working elements is calculated before being properly eluted as previous mentioned. Both the loading and elution processes are then repeated for several times using the same black tea waste sample under the same studied conditions .The purpose was to investigate the durability of the black tea waste. From the obtained result summarized in Table (8), it is clearly evident that by repeated cycling both the loading and elution efficiencies have progressively been decreased .After the 7th cycle, the working tea waste sample has

been completely deteriorated . This relatively short life time of the working black tea waste may be due to its pretreatment procedure .In other words , the HCl treatment might have affected the amount of lignin in its structure, beside its possible hydrolysis during adsorpation and /or elution processes .

Table 8: Durability of the black tea waste via 7 adsorption and elution cycles for the REEs, U and Th

Cycle	Adsorpt	Elutio	Elution efficiency,%			
number	REEs	U	Th	REEs	U	Th
1	75.00	93.03	91.85	95.00	98.70	97.10
2	73.50	91.76	89.18	92.40	96.50	94.44
3	67.39	84.19	81.82	81.96	85.60	83.41
4	55.84	69.77	67.80	74.54	77.86	75.86
5	44.13	55.14	53.58	53.17	54.98	54.18
6	18.53	23.18	22.50	32.78	33.90	33.40
7	9.04	11.34	11.00	20.45	21.15	20.00
8	Complete deterioration			of the	working	sample

CONCLUSION

The efficiency of the black tea waste for adsorption of different hazardous elements

has been properly increased through its pretreatment with a dilute solution of HCl .The relevant adsorption factors have actually been optimized using two synthetic solutions viz a separate U solution and other solution of U,Th,Ce and together with other possible interferents . The obtained results are then applied upon an actual lab waste solution containing U(33 ppm), Th (40 ppm) and REEs (393 ppm) beside some other elements. The former have almost been completely eluted using Na₂CO₃ /NaHCO₃ solution for the REEs, while an acidified NaCl solution is used for elution of both U and Th . The eluted elements have finally been recovered by proper precipitation procedures to obtain suitable concentrate in a manner to represent important added values. The obtained results used to formulate a working flowsheet (Fig.16) for the treatment of hazardous lab waste solutions for removal of their contents of the REEs, U and Th.



Fig. 16: A formulated flow sheet for the recovery of the REEs ,uranium and thorium from hazardous lab waste using black tea waste

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أمكانيه امتصاص اليورانيوم و العناصر المصاحبة من مخلفات المعمل السائلة باستخدام نفايات الشاي الأسود

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تمثّل نفايات الشاي الأسود ممتزات حيوية طبيعيه وتتميز بأنها ذات قدره لادمصاص بعض العناصر التي تتواجد في مخلفات المعامل و قد أجريت عده تجارب(batch wise) لتحديد العوامل الحاكمة التي تؤثّر على فعاليه الامتزاز و خاصة بالنسبة لعنصر اليورانيوم وكانت هذه العوامل المؤثّرة التي تمت دراستها كالتالي : دراسة تأثير التقليب ، ووقت التفاعل ، درجه الأس الهيدروجيني ، نسبه المادة الصلبة إلى السائل وكذلك التركيز المبدئي للعناصر .

وتم تحليل النتائج المعملية طبقا لنموذجى لانجامير و فراوندرليش وقد توافقت النتائج مع نموذج لانجامير اكثر من فراوندرليش واتضح أن أفضل ادمصاص يصل إلى 60.56 ملليجرام لكل جرام من بقايا الشاي عند الأس الهيدروجيني من 4.5 إلى 5.5 هذا و قد شملت عناصر الدراسة أضافه إلى اليورانيوم عناصر الثوريوم و الأرضيات النادرة في وجود بعض العناصر التي يمكن إن تتداخل وقد تمت عمليه الازاحه للعناصر الهامة و تحضير المنتجات على نحو سليم

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