ISSN : 0974 - 746X Volume 7 Issue 2

Trade Science Inc.

Inorganic CHEMISTRY

An Indian Journal

Full Paper

ICAIJ, 7(2), 2012 [71-81]

Extraction of uranium and rare earth elements from sulfate solutions by using D_2EHPA impregnated rice straw

E.M.El-Sheikh[1], T.E.Amer[1], E.A.Khaled[1]*, A.I.Hashem[2]

[1]Nuclear Materials Authority, P. O. Box 530, El-Maadi, Cairo, (EGYPT)

[2]Faculty of Science, Ain Shams University, Cairo, (EGYPT)

E-mail: lolla_5210@yahoo.com

Received: 28th February, 2012 ; Accepted: 28th March, 2012

ABSTRACT

Rice straw has been used as an adsorbent for impregnation of the cationic organic solvent namely; di-2-ethylhexyl- phosphoric acid (D_2EHPA) for the recovery of both uranium and lanthanum from their synthesized sulfate solutions. The adsorption and desorption behavior of the prepared solvent impregnated rice straw (SIRS) toward uranium and lanthanum was investigated by batch technique at different experimental conditions. Kinetic characteristics of the adsorptions process have been investigated. Also, the work has been shifted to investigate the potentiality of the prepared SIRS for the recovery of uranium and rare earth elements from an actual sulfate leach liquor of El-Sella ore material (South Eastern Desert of Egypt).

KEYWORDS

Rice straw;
D_2EHPA;
Impregnated resin;
Uranium;
Lanthanum;
Adsorption;
Desorption.

INTRODUCTION

Solvent extraction and ion exchange techniques have been mostly applied to the recovery and separation of metal ions from their solutions. However, recovery and separation by solvent extraction requires multiuse extraction and back-extraction in order to get successful separation. Also, ion exchange resins have lower extraction selectivity for transition metals with respect to alkali metals. As an alternative approach, solvent impregnated resins have been proposed by Warshawsky[25] for selective separation of metal ions by direct adsorption of the extractant into macroporous polymeric supports.

Impregnated resins bridge the gap between solvent extraction and ion exchange[26]. They combine not only the advantages of resin ion exchange for processing dilute solutions with specific properties of the extractants, but also a high distribution ratio and selectivity characteristic of the extractants dissolved in a liquid organic phase with the simplicity of equipment and operation characteristics of solid ion-exchange technology

Recently, extractant impregnated resins have been used in the extraction of metals from a multi-component mixture in various analytical applications. The impregnated extractants include acidic organo-phosphorus compounds such as di (2-ethyl hexyl)phosphoric acid[3] and bi-functional organo-phosphorus compound[16]. Some other extractants such 4-(2-thiazolylazo)resorcinol[13], bicine[4], quinoline-8-ol[7], 2-oxo-propyl phosphonic acid dibenzyl ester[21], succinic acid[18] 8-hydroxy quinoline[23] tiron[10], p-tert-butylcalix

arene[11,20], o-vanilinsemicarbazone[8] and humic acid[5] have also been used.

On the other hand, it would be greatly advantageous to use agricultural wastes in a manner to benefit from their ligno- cellulosic structure; a matter which would be greatly friendly for the environment. Among the former, rice straw represents an important waste due to two main reasons. Firstly, the structure of rice straw is greatly attractive where it is mainly composed of cellulose and hemicellulose[22] which are quite suitable to be solvent impregnated resin. In this manner, it would be possible to convert such a waste material, which might result in heavy black clouds if burned in open air, to a useful material. Secondly, it is also quite important and greatly attractive to indicate that rice straw is actually a low cost renewable lignocellulosic biomass resource. This is due to the fact that, rice is routinely cultivated in large quantities.

For proper preparation of rice straw to be solvent impregnated resin, its alkali pre-treatment (mercerization) would lead to silica separation thereof and which would thus represent an added value[19]. In addition, this treatment would in the meantime modify the cellulosic structure though removal of lignin.

In the light of the above mentioned givings, this work is designed to investigate the potentiality of rice straw as an adsorbent for impregnation of the cationic organic solvent applied in the present work namely D_2EHPA (di-2-ethyl hexyl- phosphoric acid)for the recovery of both U and the La elements from their solutions.

EXPERIMENTAL

Characterization of the working raw rice straw

(A) Chemical analysis

The working sample of the Egyptian rice straw has been collected from the country sides of Cairo City. This sample was first carefully washed with distilled water, dried and was kept in polyethylene bags for 24 h till proper cooling. The dried sample was then ground to a mesh size below 0.85 mm. The ground sample was then subjected to different analyses to estimate its moisture content as well as the contents of the resin and wax, the lignin, the pentosane, the cellulose besides the contents of the ash and the silicates and the silica amounts in the ash according to TAPPI (1972).

(B) Infra-red analysis

Infra-red spectral analyses were studied upon the raw rice straw, the prepared rice straw treated with sodium hydroxide as well as the impregnated one with D_2EHPA. The infrared spectrometric analysis (Bruker vector spectrophotometer model FT-IR-22Germany) was performed in the wavelength between 1000 and 4000cm^{1-} using KBr binding material sample pellets. The samples prepared as pellets. The IR analysis was conducted in the Micro Analytical Center, Cairo University. Infra Red absorption spectra in the mentioned region were recorded.

Preparation of solvent impregnated rice straw (SIRS)

Before impregnation, the rice straw was firstly purified with 50% methanol–water solution containing 4M HCl in order to remove inorganic impurities and monomeric materials. After that, it was washed thoroughly with distilled water to eliminate chloride ions

(A) Mercerization of the raw rice straw

The dry ground rice straw was first treated by sodium hydroxide (alkali treatment) to eliminate silica and to modify the cellulose structure through removal of lignin. This process is known as mercerization.

Two grams of dry ground rice straw of -0.85 mm mesh size were refluxed with 15ml of sodium hydroxide 6% (w/v) for 3h. The residue was filtered and washed by distilled water until no color with phenol phthalein (ph.ph.), The residue was then washed with diluted HCl (5%) and then washed with distilled water until no color with methyl orange (M.O). Finally, it was dried giving the natural ion exchanger treated with sodium hydroxide. The latter alone disorder the Skelton of liginocellulosic and the crystallinty index[19].

$$\text{Cell—OH}^{+} \quad \text{NaOH} \longrightarrow \text{Cell—O Na}$$

(B) D_2EHPA impregnation upon mercerized rice straw

For the impregnation process, the dry method was used. One gram of mercerized rice straw (MRS) was placed in kerosene mixture containing extractant D_2EHPA at different concentrations for different time intervals under the fixed conditions of S/L ratio 1/10,

shaking rate (180 rpm/min), the MRS mesh size of -0.85mm at room temp. After that, the rice straw beads were separated through a porous filter using a vacuum pump, washed with water and dried at room temperature.

Preparation of the working solutions

(A) Preparation of U and La synthetic solutions

Synthetic solutions of uranium and Lanthanum have been prepared from their proper salts. Different metal solutions were thus prepared by dissolving analytical grade metal salts in distilled water to obtain accurate concentration ppm (mg/L) solution. From the latter, the synthetic solutions were prepared by dilution to realize the required concentration. The pH of these solutions was measured and adjusted at 4.5(controlled pH) and all the adsorption experiments were run at room temperature 25±20 ?C. The metal salts used includes, the acetate salts of U and the chloride salts of La.

(B) Preparation of El-Sella sulfate leach liquor (case study)

Gabal (G.) El-Sella area is located at Halaib environ (Eastern Desert, Egypt) at about 20Km west of Abu Ramad City covering an area of about 128Km2.

For the present study, the mineralized younger granite has been used as a case study for the recovery of its uranium and REEs contents. For this purpose the optimum leaching conditions that have been determined by Abu Khoziem[1] were applied. These include sulfuric acid agitation leaching using 300 g/L H_2SO_4 concentration, S/L ratio of ½, 4h as leaching time at 100oC as leaching temperature upon an ore size sample ground to -200 mesh.

In the present work, 500 g of G. El-Sella technological sample assaying 2480 ppm U besides 2800 ppm REEs was leached by applying the above mentioned optimum leaching conditions.

Extraction procedures

(A) Adsorption process

Batch adsorption tests under controlled pH of 4.5 (to avoid U & REEs precipitation) with mechanical shaking (180rpm/min) were carried out by mixing of one g of the MRS with 100 ml of the two different working synthetic solutions of known uranium and lanthanum concentrations in proper glass beakers. 2ml sample solution was 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 was used as the contact time for almost batch tests except in the experiment of the effect of the initial uranium concentration.

On the other hand, for the determination of uranium equilibrium isotherm, the corresponding experiments were conducted by mixing 1 g of the SIMRS with 100 ml of uranium solution using an initial metal concentrations ranging from 100 to 5000 mg/l. In these experiments, the mixture was shaken for a contact time up to 3h to reach equilibrium.

For each adsorption experiment the adsorptive capacity (qe) was determined according to the following equation;

$$qe = V (C0-Ce)/M$$

where V is the total volume of the solute solution (L), M is the weight of adsorbent used (gm), C0 is the initial concentration of the solute (mg/L) and Ce is the residual equilibrium concentration of the solute (mg/L).

(B) Desorption process

The loaded rice straw obtained from the previously mentioned synthetic solutions of the two studied elements was thus subjected to desorption process. In this process one eluant has been used namely; 150 g/L of 3/1 Na_2CO_3/ $NaHCO_3$ solution for the uranium and lanthanum.

Control analyses

Uranium in the different processing streams was analyzed by an oxidimetric titration method using ammonium metavanadate[14]

Concerning the total REE, a visible- ultra violet spectrometer (Shimadzu UV- 160) was used for its quantitative analysis using 0.015 % arsenazo III at 654 nm using Ce as reference[15].

RESULTS AND DISCUSSION

Chemical composition of the raw rice straw

According to procedures adopted by Tappi (1972), a proper sample of the working rice straw

was chemically analyzed to determinate its relative amounts of cellulose, lignin and resin wax. The obtained results TABLE 1 was greatly similar to that given by published data.

On the other hand, according to Bishay (2010), the elemental organic composition C–H–O of the Egyptian rice straw is about 47.8% carbon, 6.0 % hydrogen and 45.3% oxygen in addition to 0.5% nitrogen and 0.2% sulfur.

TABLE 1 : Composition of the working rice straw.

Component	Present work Wt, %	Published data.* Wt,%
Hemicellulose	26.3	19-28
Silica	23.8	---
Cellulose	22.6	32-47
Lignin	15	5-24
Ash content	9.45	---
Resin and wax	2.95	---

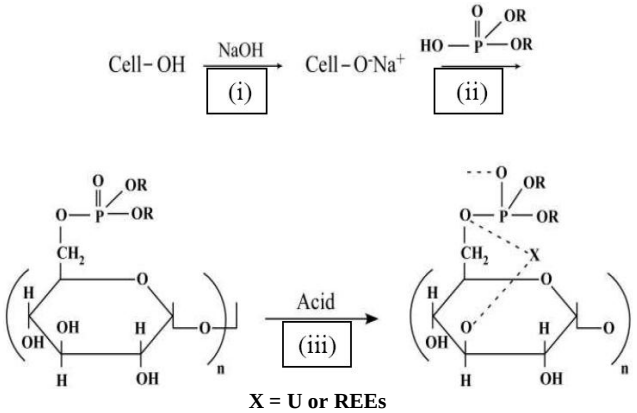
***= (Karimi et al (2006) & Yao et al (2008).**

Mechanism of rice straw as solvent impregnated resin

Due to the fact that repeated adsorption and desorption of U and/ or REEs successfully achieved, it can thus be proposed that the applied impregnated D_2EHPA should have been chemically interacted with the mercerized rice straw. The proposed mechanism involves the following sequence of reactions:

1) Mercerization
2) Impregnation
3) Metal- solvent interaction

These interactions start by the breakdown of the hydrogen bond between C_3 and C_6 followed by bonding with the working metal species.



Optimization of the impregnation process

The adsorption efficiency of the mentioned different types of rice straws to adsorb uranium and lanthanum from different acid media have been studied, for this purpose, two series of adsorption experiments have been performed using batch technique with mechanical shaking (180rpm/min). The first one for the adsorption of U while the other one was used for the adsorption of lanthanum. In each series 1g of the different mentioned types of rice straw was used in a S/L ratio of 1/100 using two samples of synthetic solution one of them assaying 500 ppm U and the other one assaying 500ppm lanthanum. The pH was controlled at 4.5. After stirring for 2h, different rice straw samples were filtered and the obtained filtrates were analyzed for uranium and lanthanum.

From the obtained results, TABLE 2 it was clear that, treated the rice straw with NaOH followed by D_2EHPA (1mole) i.e. SIMRS is quite important for attaining a high uranium and lanthanum adsorption efficiencies. Thus the former has reached 83 %, while under the same experimental conditions, adsorption efficiency of lanthanum reached 90%. It is important to mention herein that, the modification of rice straw with D_2EHPA as solvent impregnated resin increases the adsorption capacity of D_2EHPA to about more than 20% TABLE 2. On other hand, adsorption capacity of the MRS, also increased to the extent of 37% for U & 30% for lanthanum after a modification with D_2EHPA.

TABLE 2 : The effect of different treatment types of rice straw upon U and La adsorption efficiency.

Types of rice straw	Adsorption efficiency,%	
	U Sample	La Sample
Raw rice straw	30	47
MRS	46	60
D_2EHPA	60	70
SIMRS	83	90

(A) Results of D_2EHPA impregnation upon the MRS

The relevant factors affecting the preparation of the solvent impregnated mercerized rice straw (SIMRS) have been studied. These factors have actually included the D_2EHPA concentration of the loading phase, the soaking time and medium composition as well as its

required concentration. For studying the effects of these factors upon proper preparation of workable SIMRS, the loading capacities of uranium and lanthanum from their separate synthetic solutions upon the prepared rice straw have been determined. In this testing, the other experimental conditions are fixed at MRS/ D_2EHPA phase ratio of 1/10 (g / L) at room temperature and -0.85 mm mesh size of MRS.

(i) Effect of loaded D_2EHPA concentration

To study this effect, a number of loading experiments have been performed in which the D_2EHPA concentration (in kerosene) has been varied between 0.5 to 2 M. On the other hand, the uranium and lanthanum concentration in their solutions used for testing the effect of D_2EHPA loading was fixed at 500 ppm for each. For this testing 1g of the D_2EHPA loaded MRS was stirred in 100 ml of both uranium and lanthanum solutions for 2h at room temperatures under the above mentioned fixed conditions of SIMRS.

The obtained data figure 1 have evidently indicated that uranium adsorption efficiency is sharply increased from 35.26% to 88.0% when using 0.5M to 1.5M D_2EHPA. When the concentration of D_2EHPA increased to 2M, a slight increase in U adsorption efficiency was observed. On the other hand, for lanthanum the adsorption efficiency is almost complete when the D_2EHPA concentration increased to 1.5 mole.

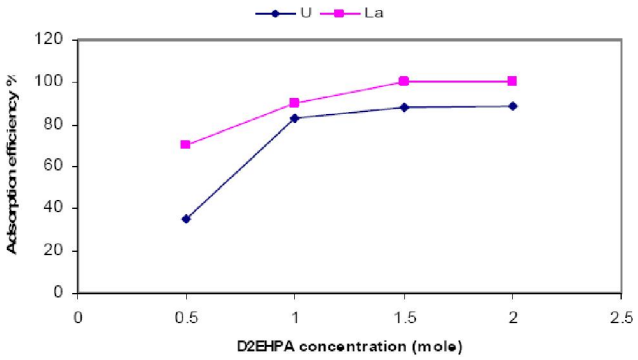


Figure 1 : The effect of D_2EHPA concentration upon U and La adsorption efficiencies.

(ii) Effect of soaking time

The effect of soaking time for loading D_2EPHA upon the MRS was studied, where a series of impregnation experiments was performed under the fixed conditions D_2EPHA concentration of 1.5 mole, mesh size of one gram rice straw, -0.85 mm at room temperature using S/L ratio 1:10 and the applied soaking time ranged from 2 up to 12h. The adsorption process was performed at S/L ratio 1:100 for 2h while the uranium or lanthanum concentration was fixed at 500 ppm. The obtained results (Figure 2) revealed that the maximum adsorption capacity of the SIMRS for uranium and lanthanum ions occurred after 12h as soaking time where about 88% of uranium was adsorbed on the rice straw while most of lanthanum was removed from the solution.

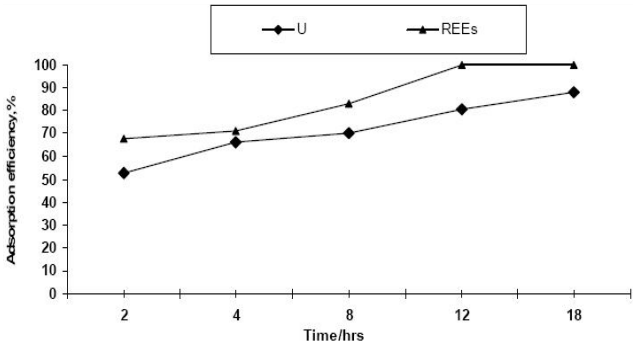


Figure 2 : The effect of soaking time for loading D_2EPHA upon the MRS on U and La adsorption efficiencies.

(iii) Effect of medium

Three loading experiments were performed to determine the best working acidic medium with the prepared SIMRS. Two solutions of the three different acid media namely; HCl, H_2SO_4 and HNO_3 of fixed conc. 20 g/L for each one of them contains 500 ppm uranium and the other containing 500 ppm lanthanum. The other fixed conditions include soaking the D_2EHPA of 1.5 mol concentration upon 1g of MRS of -0.85 mm mesh size for 12h. The other fixed adsorption conditions include S/L ratio of 1/100 and 2h as soaking time at room temp. The results shown in TABLE 3 indicate that, the maximum adsorption efficiency has been achieved when using both of nitric and sulfuric acids. The latter was preferred due to its low cost and availability.

TABLE 3 : The effect of D_2EPHA medium with MRS upon U and La adsorption efficiencies.

Acid (Conc. 20 g/l)	Adsorption Efficiency,%	
	U Sample	La Sample
HCl	85.98	63
H_2SO_4	88.00	100
HNO_3	88.00	98

Full Paper

(iv) Effect of sulfate medium concentration

The effect of H_2SO_4 acid concentration upon the adsorption efficiency of uranium and lanthanum was studied between 10 to 40 g/L H_2SO_4 acid, while fixing the other factors (12h soaking time, -0.85mm mesh size, 1.5M D_2EHPA concentration with S/L ratio1:10) at S/L ratio 1/ 100 for 2h as shaking time at room temperature. The adsorption efficiencies of uranium and lanthanum are plotted in figure 3. The obtained results indicate that lanthanum is relatively more efficient when adsorbed upon 1 g of MRS than uranium at the medium of low acid concentration (i.e. 10-20 g/L). Increasing the acid medium concentration to 30 and 40 g/L, uranium adsorption efficiency slightly proportionally increased.

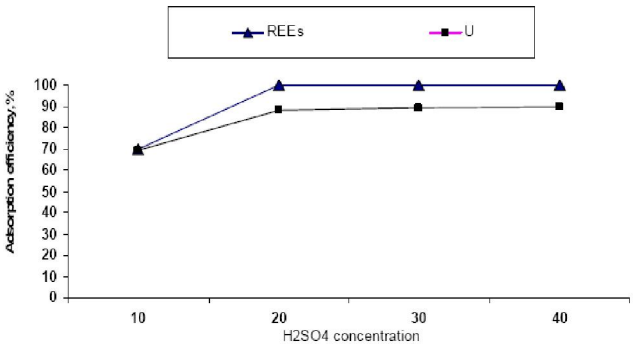


Figure 3 : The effect of H_2SO_4 acid medium Conc. upon U and La adsorption efficiencies.

From the foregoing study of optimizing impregnation process it can be concluded that the optimum impregnation conditions can be summarized as follows:

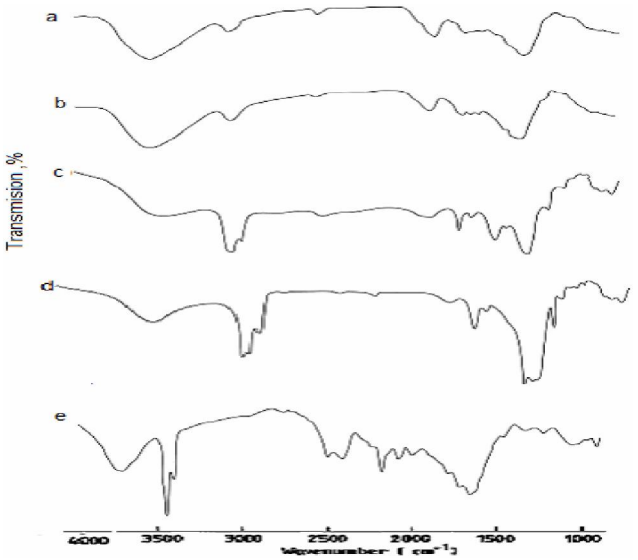
Grain size of MRS	:	– 0.85 mm.
D_2EHPA concentration	:	1.5 mole.
S/L ratio (MRS/ D_2EHPA)	:	1/10
Soaking time of D_2EHPA	:	12h.
Impregnation temperature	:	25 °C (room temp.)
Impregnation medium	:	Sulfate medium
Impregnation medium conc.	:	20g/L H_2SO_4

(B) IR spectral characteristics of the raw and optimized loaded SIMRS

IR spectral analysis of the raw rice straw, treated with sodium hydroxide and impregnated with D_2EHPA was recorded in the wavelength between 1000 and 4000cm^{1-} (Figure 4, a-e).

The infrared spectrum of rice straw (a) shows an absorption broad band at 3399-3431 characteristics of the chelated OH groups. In the MRS (b) the above band became sharper due to the conversion of most OH groups into O-Na.

The appearance the new absorption bands at 2930cm^{-1} characteristics of γ_{-CH2} and 1230 cm^{-1} due to the $\gamma_{p=O}$ in curve (c) reveals the incorporation of D_2EHPA in the MRS. The curve (d) and (e) the appearance of absorption bands at 1132cm^{-1} and 1447cm^{-1} revealed the incorporation of U and REEs in the treated rice straw.



a) Rice straw; b) Mercerized rice straw; c) Mercerized rice straw with D2EHPA (SIR); d) SIR treated with U; e) SIR treated with REEs

Figure 4 : Infrared spectra of different modified cellulose

Results of separate recovery of uranium and lanthanum from their synthetic sulfate solutions

(A) Adsorption results of uranium and lanthanum

In order to determine the optimum conditions of the adsorption process, it was found necessary to study the controlling factors of the process. These include, stirring time, pH of the two samples of synthetic solutions of uranium and lanthanum, as well as S/L ratio.

(i) Effect of stirring time

For studying the effect of stirring time upon uranium and lanthanum adsorption efficiencies, two series of experiments have been performed in which the stirring time was varied between 15 and 120 minutes and the initial uranium concentration fixed at 500ppm and at 500 ppm as initial concentration of lanthanum in the other sample. In these experiments, one gram of the

optimized SIMRS was allowed for stirring within the uranium and lanthanum solutions at the fixed pH of 4.5 and S/ L ratio 1/100 at room temperature. The obtained results are plotted in figure 5. From these results it is noticed that by increasing the stirring time, the adsorption efficiency of uranium increases and reaches its maximum value after 120 min. On other hand, lanthanum adsorption efficiency reached its maximum value after only 30 min.

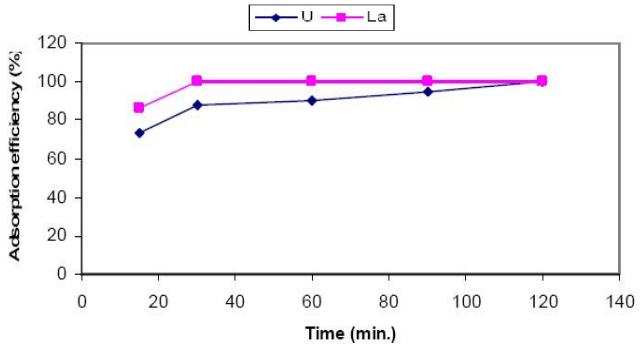


Figure 5 : Effect of stirring time upon uranium and lanthanum adsorption efficiencies.

(ii) Effect of pH

As a matter of fact, the most important parameter that affects the adsorption uptake is actually pH value of the synthetic solutions. For this purpose, two series of adsorption experiments have been performed at room temperature, for uranium and lanthanum adsorption at different pH. The pH of the two initial solutions have been studied in the range of 2 to 9 using 100 ml solutions of uranium (500 ppm) and lanthanum (500 ppm), and one g sample (i.e. S/L 1/100) of the optimized SIMRS was stirring for 15 minutes. From the obtained results shown in figure 6, it was found that, the adsorption efficiencies of the studied metal values increase till the pH 5. After this pH, hydrolysis takes place.

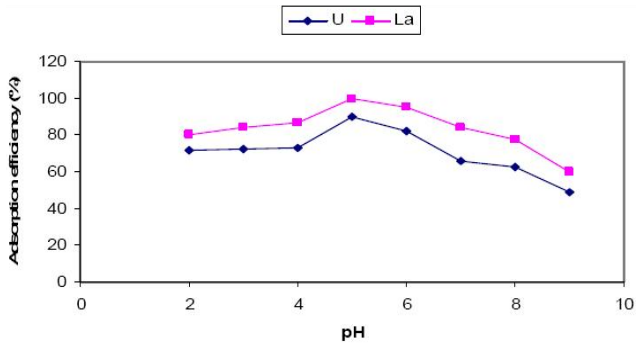


Figure 6 : Effect of pH upon uranium and lanthanum adsorption efficiencies.

(iii) Effect of solid/ liquid ratio

The effect of S/L ratio upon uranium and lanthanum adsorption efficiencies was studies using working synthetic solutions of uranium and lanthanum at room temperature by stirring one g of the optimized SIMRS with the metal solutions assaying 500 ppm uranium and lanthanum at different S/L ratios ranging from 1:100 to 1:250 for 15 min. The pH of uranium and lanthanum solutions was adjusted at 4.5 (to avoid the precipitation of uranium at pH 5). The obtained results indicated that by decreasing the S/ L ratio, the uranium adsorption efficiency was decreased. The latter was found to decrease from 90.23 to 56.00% when the S/ L ratio decreased from 1/100 to 1/250, figure 7. On the other hand, with respect to lanthanum, the adsorption efficiency decreased with decreasing the S/L ratio figure 7.

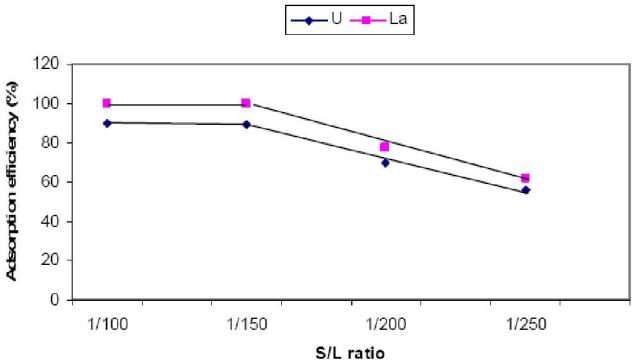


Figure 7 : Effect of S/L ratio upon uranium and lanthanum adsorption efficiencies.

The optimum adsorption conditions:

Stirring time : 15 min.
pH : 4.5
S/L ratio : 1/100
Temp. : Room temp.

(B) Desorption results of uranium and lanthanum

The loaded SIMRS was thus subjected to desorption process of the mentioned elements. For this purpose, one adsorbent was used; namely 150 g/L of (3:1) Na_2CO3 /$NaHCO_3$ solution to remove uranium and lanthanum, under the fixed conditions of S/L ratio of 1/ 75, stirring time of 15 min. at room temperature.

The obtained results indicated that, after passing only 15 min., about 99.6 % of the loaded lanthanum has been desorbed, while under these conditions, desorption efficiency of uranium attended only 0.9%. It is

interesting to mention herein that about 90% of the uranium content was desorbed after 2h under the above mentioned desorption conditions.

(C) Combined recovery of uranium and lanthanum from their synthetic solutions

(a) Adsorption of uranium and lanthanum from mixture solution

To detect the effect of the adsorption process upon mixture solution containing both of uranium and lanthanum, it was found necessary to apply the obtained optimum adsorption conditions of the two different basic solutions (one for uranium and the other for lanthanum) upon this mixture solution.

For this purpose, a synthetic admixture solution (100ml) containing 500ppm uranium and 500ppm lanthanum was contacted with 2g of the working SIMRS (to ensure the adsorption of both the interested metal values) under the following optimum adsorption conditions:

Stirring time : 15 min.
pH : 4.5
S/L ratio : 1/50
Temp. : Room temp.

This resulted in an adsorption efficiency of about 80% for uranium and 75% for lanthanum.

(b) Desorption of uranium and lanthanum from loaded SIMRS

With respect to the above mentioned admixture solution, the loaded SIMRS was subjected to the desorption process under the above mentioned fixed conditions of 150 g/L of (3:1) Na_2CO3 /$NaHCO_3$ solution, S/L ratio of 1/ 75, stirring time of 15 min. at room temperature using batch technique. This resulted in a desorption efficiency of about 90% for uranium and 99% for lanthanum.

Kinetics of adsorption process

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

(A) Langmuir adsorption isotherm

Langmuir isotherm (L-shaped) model was developed by Irving Langmuir 1918[12], and called the ideal localized monolayer model. Langmuir 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:

$$q = \frac{q\,max.\ b.\ Ce}{1 + b.\ Ce}$$

Where q is 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[2]. The Langmuir isotherm is based on these assumptions[12]:

- 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.

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

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 Co is the initial concentration of metal ions in the solution. The RL value indicates the shape of isotherm. According to[17], RL values if between (0 – 1) indicate favorable adsorption, if equal to (1) indicate linear adsorption and if above (1) indicate unfavorable adsorption.

In the present work, the obtained results have thus been linearized using the mentioned Langmuir equation and plotting the Ce/qe vs. Ce was constructed The Langmuir constant "q max" (measures the monolayer adsorption capacity of solvent impregnated mercerized rice straw was obtained as 243mg/g for uranium and

250mg/g for lanthanum.

The Langmuir constant "b" (denotes adsorption energy) which was obtained as 0.002 and 0.0012 l/mg for U and Lanthanum respectively. The determined high coefficient value (r^2 = 0.955 and 0.990 for uranium and lanthanum respectively.) thus indicates a good agreement between the experimental values and the isotherm parameters and also confirms the monolayer adsorption up take of the working adsorbance surface. (Figure 8, a & b). The dimensionless parameter of "RL" (measures the adsorption favorability) was found to attain 0.0873 for uranium and 0.0734 for lanthanum (i.e. 0 < RL < 1); a matter which confirms the favorability of the adsorption process for the uranium removal using the modified rice straw waste. It was also, found that when the RL value approaches to zero the irreversible adsorption was favored.

(B) Freundlich isotherm

The Freundlich isotherm[6] is the earliest known relationship describing the sorption equilibrium. This fairly satisfactory empirical isotherm can be used for non-ideal sorption and is expressed by the following equation[17]:

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

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 was used to evaluate the sorption data and is represented as:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e$$

According to[9], 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 (Figure 9, a & b). It was thus found that the determined coefficient of Freundlich isotherm model for working SIMRS was

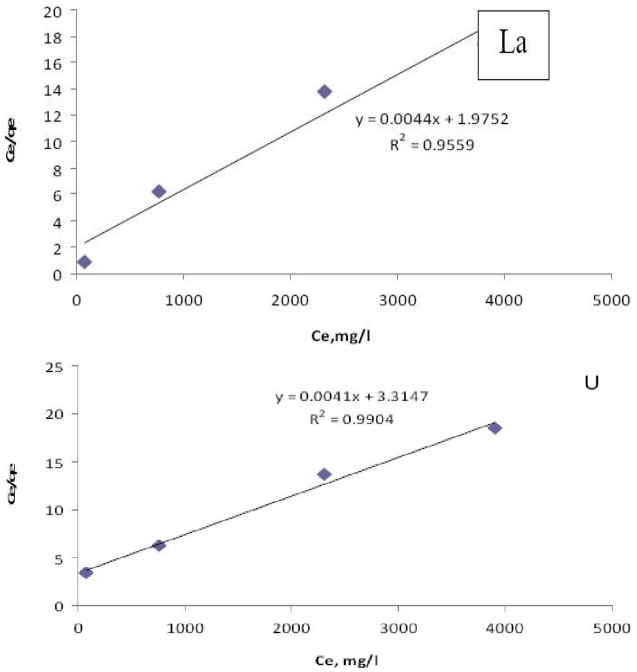


Figure 8a-b : Langmuir isotherm constants for lanthanum and uranium uptake upon the working SIMRS at room temperature.

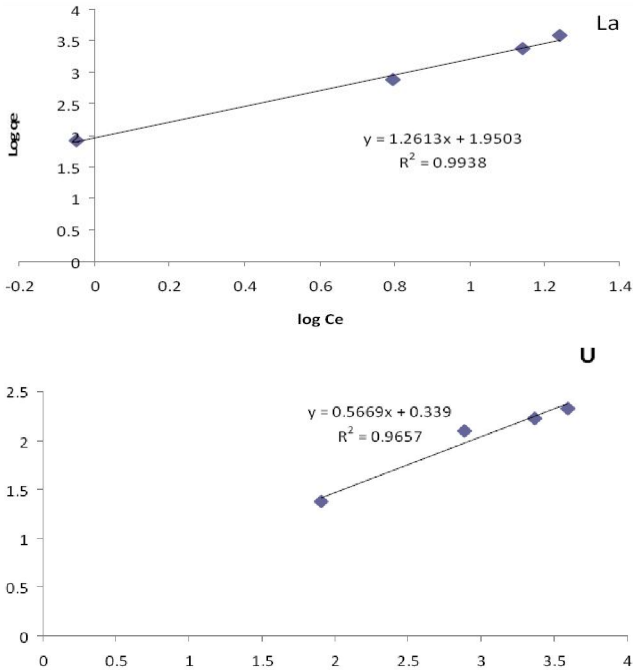


Figure 9a-b : Freundlich isotherm constants for lanthanum and uranium uptake upon the working SIMRS at room temperature.

TABLE 4 : Langmuir and Freundlich isotherm constants for uranium uptake upon the working SIMRS at room temperature.

Metal	Adsorbent	Langmuir model parameters			Freundlich model parameters		
		Qmax (mg/g)	*B (mg/ L)*	R^2	*1/n*	K_f *(mg/g)*	R^2
Lanthanum	SIMRS	250	.0020	0.9559	.261	.198	0.9938
Uranium	SIMRS	243	0.0012	0.9904	.3390	2.13	0.9657

found to attain 0.95 and 0.99 for U and Lanthanum respectively, Accordingly, it can be concluded that the obtained experimental data was fitted to Langmuir isotherm and Freundlich TABLE 4.

Case study

For applying the working SIMRS for the recovery of both uranium and REEs from their mineralization in El- Sella granite ore material (2480 ppm uranium and 2800 ppm REEs), an actual sulfate leach liquor of both metal values was prepared. For this purpose, the optimum sulfuric acid leaching factors determined by Abu Khoziem[1] were performed.

(A) Preparation of El-Sella pregnant solution

According to Abu Khoziem (op.cited), the optimum leaching conditions of both uranium and REEs from their mineralization at G.El- Sella (300 g/L H_2SO_4 acid, agitation time 4h, S/L ratio 1/2, ore grain size –200 mesh, and 100°C as leaching temperature) were applied. Under these conditions, the obtained leaching efficiencies were 35 and 75% for uranium and REEs respectively. Analysis of the prepared leach liquor is given in TABLE 5.

TABLE 5 : Chemical composition of the prepared pregnant solution from G. El-Sella ore material.

Component	Concentration (g /L)
U	0. 14
REEs	1.05
Fe_2O_3	3.12
SO_4^{--}	174.00
pH	1.2

The studied SIMRS was used to recover uranium and REEs by batch technique from this real sample solution (prepared pregnant solution).

(B) Recovery of U and REEs from El-Sella sulfate leach liquor

Both uranium and REEs have then been recovered from their prepared sulfate leach liquor of El-Sella mineralization using the prepared SIMRS. For this purpose, El-Sella leach liquor was treated by the working SIMRS through batch equilibrium technique using the previously studied optimum conditions.

(a) Adsorption process

The adsorption process was carried out upon the prepared SIMRS under the optimum adsorption conditions of:

Stirring time : 15 min.
pH : 4.5
S/L ratio : 1/50
Temp. : Room temp.

However, before performing adsorption of both metal values, it has been found necessary to eliminate iron from the working leach liquor in order not to compete both metal values besides their contamination.

The obtained results indicate that the adsorption efficiency attained 71.5% for uranium and 69% for REEs. This realized about 89.4 and 92% from the calculated theoretical adsorption efficiency for uranium and REEs respectively.

(b) Desorption process

Desorption of the loaded SIMRS was carried out by using the previously mentioned conditions. The working sample of SIMRS loaded with uranium and REEs was then desorbed in a batch wise procedure using 150 g/L of 3:1 Na_2CO_3 and $NaHCO_3$ at S/ L ratio of 1/75.

After 15min. of stirring time, the working slurry was filtered and the filtrate was analyzed for uranium and REEs. However it was found that up to 76% of the adsorbed REEs have been desorbed from the loaded SIMRS with a negligible % of uranium.

The filtered SIMRS which still loaded with uranium was then stirred in a second elution step using a fresh batch of the working eluant, and sample fractions from the filtrate was analyzed every 30min. However, desorption was quite negligible before 2h, after that about 78% of the loaded uranium was desorbed.

(c) Precipitation of uranium and REEs

To prepare a proper concentrate of REEs from rich fraction of desorbed solution, it was found convenient to precipitate REEs as their oxalate with 20% oxalic acid at pH 1.

On the other hand, the second eluate solution containing U value was subjected to precipitation step by adding NH_4OH solution till pH range of 12-13 where uranium was precipitated as ammonium di- urinate.

Finally, from the obtained results, it can be concluded that the prepared solvent impregnated resin of the present work is promising in the field of uranium and REEs recoveries from their real ores.

CONCLUSION

Several methods have been applied for the recovery of metal values from their leach liquors. In this regard solvent impregnated resin (SIR) has been prepared by the modification of the mercerized rice straw with the D_2EHPA as a suitable organic solvent for the impregnation process (SIMRS). Several batch wise experiments were conducted to determine the optimum factors affecting the solvent impregnated mercerized rice straw (SIMRS) as means for the recovery of both uranium and lanthanum elements. The obtained optimum impregnation conditions include 1.5 mole D_2EHPA concentration at MRS/ D_2EHPA ratio: 1/10, soaking time of 12h in 20g/l sulfate solution.

The equilibrium data were found to be satisfactorily fitting to Langmuir and Freundlish isotherms. Maximum- metal uptake of 243 mg U/ g SIMRS and 250 mg La/ g SIMRS was achieved.

For applying the working SIMRS for the recovery of both uranium and REEs from their mineralization in El-Sella granite ore material (case study) as an actual sulfate leach liquor. The adsorption efficiency attained 71.5% for uranium and 69% for REEs. This realized about 89.4 and 92% from the calculated theoretical adsorption efficiency for uranium and REEs respectively. Elution of the studied interesting elements has been achieved and from their elutes proper concentrates have been prepared.

REFERENCES

[1] H.Abu Khoziem; Geochemistry and Processing of Some Valuable Metals from Mineralized Two Mica Granites, SouthEastern Desert, Egypt. Ph.D. Thesis, Faculty of Science, Ain Shams University, Egypt, 136 **(2006)**.

[2] K.H.Chong, B.Volesky; Biotechnology and Bioengineering, **47(4)**, 451 **(1995)**.

[3] J.L.Cortina, A.Warshawsky; 'Developments in Solid-Liquid Extraction by Solvent Impregnated Resins', in: J.A.Marinsky, Y.Marcus, (Eds); Ion Exchange and Solvent Extraction, Dekker, New York, **13**, 195 **(1997)**.

[4] K.Dev, R.Pathak, G.N.Rao; Talanta, **48**, 579 **(1999)**.

[5] S.Erdogan, M.Merdivan, C.Hamamci, O.Akba, A.Baysal; Anal.Lett., **37**, 2575 **(2004)**.

[6] H.Z.Freundlich; Physical Chemistry, **57**, 385 **(1969)**.

[7] J.M.Gladis, T.P.Rao; Anal.Bioanal.Chem., **37**, 867 **(2002)**.

[8] V.K.Jain, A.Handa, S.S.Sait, P.Shrivastav, Y.K.Agrawal; Anal.Chim.Acta, **429**, 237 **(2001)**.

[9] K.Kadirvelu, C.Namasivayam; Environmental Technology, **21(10)**, 1091-1097 **(2000)**,

[10] M.Kumar, D.P.S.Rathore, A.K.Singh; Analyst, **125**, 1221 **(2000)**.

[11] M.Kumar, D.P.S.Rathore, A.K.Singh; Acta, **137**, 127 **(2001)**.

[12] I.Langmuir; Amer.Chemi.Soc., **40(9)**, 1361-1403 **(1918)**.

[13] C.H.Lee, M.Y.Suh, K.S.Joe, T.Y.Eom, W.A.Lee; Anal.Chim.Acta, **351**, 63 **(1997)**.

[14] Mathew, K.J.Bürger, S.Ogt, S.V.Mason, P.M.E.Morales-Arteaga, U.I.Narayanan; 'Uranium Assay Determination using Davies and Gray Titration: an Overview and Implementation of GUM for Uncertainty Evaluation' From the issue entitled Proceedings of the Eighth International Conference on Methods and Applications of Radioanalytical Chemistry (MARC VIII) Kailua-Kona, Hawaii, 5-10 April 2009 - PART II, **(2009)**.

[15] Z.Merczenko; 'Separation and Spectrophotometric Determination of Elements', Harwood, New York, 708 **(1986)**.

[16] Merdivan Melek, M.Zahir Du, Hamamci Candan; Talanta, **55**, 639-645 **(2001)**.

[17] Metcalf, Eddy; 'Wastewater Eengineering-Treatment and Reuse, 4th Edition, McGraw-Hill, New York, USA, ISBN 0-07-041878, **(2003)**.

[18] P.Metilda, K.Sanghamitra, J.M.Gladis, G.R.K.Naidu, T.P.Lao; Talanta, **65**, 192 **(2005)**.

[19] E.O.A.Osman; 'Some Agricultural Waster Raw Material for Metal Ions and Color Removal', Ph.D. Thesis, Faculty of Science, Ain Shams University, 100 **(2004)**.

[20] R.Pathak, G.N.Rao; Anal.Chim.Acta, **335**, 283 **(1996)**.

[21] D.Prabhakaran, M.S.Subramanian; Anal.Bioanal. Chem., **379**, 519 **(2004)**.

[22] H.Salmi; 'Characterization of Film from Rice Straw Hemicellulose', Project Report 2010, Universitiy Teknologi MARA, **(2010)**.

[23] B.N.Singh, B.Maiti; Talanta, **69**, 393 **(2006)**.

[24] Tappi; 'Technical Association of the pulp and paper Industry', www.Tappi.org/Indey.asp; **(1957)**.

[25] A.Warshawsky; Talanta, **21**, 962 **(1974)**.

[26] A.Warshawsky; 'Extraction with Solvent-Impregnated Resins', in: J.A.Marinsky, Y.Marcus, (Eds); Ion Exchange and Solvent Extraction, Marcel-Dekker, New York, **8**, 229 **(1981)**.