Sindh Univ. Res. Jour. (Sci. Ser.) Vol.43 (1) 91-96 (2011)

SINDH UNIVERSITY RESEARCH JOURNAL (SCIENCE SERIES)

A Green and Economical Method for Uranium Removal

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Received 20th May 2011 and Revised 01st June 2011

Abstract: Banana Peel a largely produced fruit waste has been utilized to remove/preconcentrate Uranium from aqueous solution. Removal was characterized by Fourier Transform Infra Red spectroscopy and SEM techniques. Effect of pH on removal of Uranium showed the gradual increase in removal up to pH 3 then was nearly constant up to pH 10. A 1710±10 µg of Uranium was removed per 100 mg of banana peel within the exposure time of 30 min. Maximum removal of 1800±10 µg per 100 mg of banana peel was achieved after exposure time of 24 hr. Energy dispersive X-ray analysis of Uranium adsorbed banana peel showed a peak of Uranium at 3.2 keV which confirmed the adsorption of Uranium onto banana peel. FT-IR spectroscopy confirmed the involvement of –COOH group in adsorption of Uranium on banana peel. Data followed the kinetic models in the order: Pseudo-First order Model> Elovich Model >Intra-particle diffusion Model. Adsorbed Uranium was recovered with 5 ml of 0.1M HNO_3.

Keywords: **Uranium remediation; Removal mechanism; Banana Peel; Adsorption; Kinetic modeling.**

INTRODUCTION

Groundwater contamination with radionuclide and heavy metals wastes is great threat for government agencies, industry and communities (Jaeyoung *et. al.*, 2009). Industrial activities and the processing of ore mining are the major sources through which these metals and radionuclide have been introduced into the environment (Fullur *et. al.*, 2002). Naturally occurring uranium possess mainly toxicological health risk than radiological risks (Klaassen, 2001). Most commonly used methods for treatment are chemical precipitation, reverse osmosis, ion-exchange, filtration, and evaporative recovery but all these methods are only effective for treatment of liquid effluents containing high concentration of metal ions and are expensive. Also these become inefficient for treatment of effluents containing metal ions in the range of 100 mg/l (Suman, 2008). Among all these techniques adsorption has become known as a cost effective and environmental friendly alternative. Various adsorbents have been used for the removal of uranium such as zero-valent iron nanoparticles (Kilimkova *et.al.*, 2011), collagen–tannin resin (Sun, 2010), grafted copolymer of densified cellulose (Anirudhan *et .al.*, 2010), alginate coated $CaSO_4 \cdot 2H_2O$ sepiolite and calcined diatomite earth (Donat *et. al.*, 2009), algae immobilized in calcium alginate (Singhal, 2004), humic acid-immobilized zirconium-pillared clay (Aniruthan *et. al.*, 2010) manganese oxide coated zeolite (Han, 2007). Most of the adsorbents reported need some kind of modification/ treatment. In current study an effort has been made to develop an efficient and cheap method using banana peel without prior treatment to remove radioactive uranium. Removal Mechanism is also discussed.

MATERIALS AND METHODS

All chemicals used were supplied by Merck (Darmstadt, Germany) and of analytical or equivalent grade. An appropriate amount of nitrate salt of uranium was dissolved in deionized water (conductivity <0.5_Scm−1) to make standard stock solution of 1000 ppm, the stock solution was acidified with a small amount of nitric acid. Buffer solutions of pH 1–3, 4–6 and 7–9 were prepared freshly by mixing appropriate ratios of acids/bases and their conjugate base/acid.

2.2. Chemical analysis

A HORIBA Jobin Yvon (Stanmore, UK) model Ultima ICP-OES was used to quantify uranium in sample solutions. ICP-OES analysis was performed for uranium at 385.958 nm. The instrument was allowed for 30 min to warm up with the continuous aspirating of deionized water. Barloworld Scientific (Staffordshire, UK) Stuart rotator model SB3was used for the batch experiments, pH measurements were made with a WTW (Weilheim, Germany) digital pH meter equipped with a calibrated combined pH glass electrode. Banana Peel was characterized by Perkin Elmer FT-IR equipped with diamond accessory.

2.3 Esterification of banana peel

Modification of the carboxylic groups on the surface of the banana peel using acidic methanol was performed as follows: 9 g of dry-washed banana peel was suspended in 633 mL of 99.9% methanol to which 5.4 mL of concentrated HCl was added (0.1 M HCl final concentration). The solution was continuously stirred and heated at 60 °C for 48 h. The banana peel was then washed three times with cold deionized water in order to quench the esterification reaction (Memon *et.al.* 2008).

2.4 Batch sorption study of Uranium

A weighed amount of banana peel was equilibrated with 20 ml solution of U(VI) maintained at pH 3 and ionic strength (0.001 mol l^{-1}) at 25±1°C. The sorbent was filtered and the equilibrium concentration was determined by ICP-OES.

2.5 Data-Aanalysis

The distribution ratio, R_d, and percentage sorption of μ(VI) ions are determined using following equations.

$$\% \text{ Sorption} = \frac{A_i - A_f}{A_i} \times 100 \qquad (1)$$

where
A_i = Absorbance of solution before sorption
A_f = Absorbance of solution after sorption

RESULTS AND DISCUSSION

3.1 Effect of pH and retention mechanism

The pH of the metal ion solution is the most important parameter to identify the type of species being adsorbed on the surface. The effect of pH of uranium ion solution was optimized with respect to the amount of metal ion loaded onto the surface. **(Fig.1)** shows the initial increase in uptake of metal ions with increasing pH up to pH 3. After pH 3 a decrease of ~ 30% was recorded and the uptake was found to be nearly constant up to pH 10. The main hydrolyzed species of uranium (VI) is UO_2^{2+} up to pH 3. At pH 5 uranium exists as 5% $UO_2(OH)^+$, 1% $(UO_2)_3(OH)_5^+$ and 7% of $(UO_2)_2(OH)_2$ a neutral species it become ~22% at pH 5.5. From the results of variation of metal ions uptake as a function of pH it could be concluded that the charged species of uranium adsorbed onto the surface. The decrease of ~30% can be explained on the basis of formation of neutral $(UO_2)_2(OH)_2$species (Charles *et. al.,*).

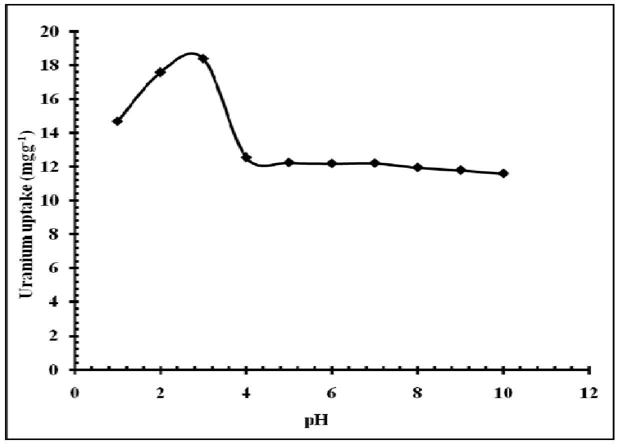

Fig.1. Uptake of uranium on baana peel as a function of pH

In order to explore the surface group responsible for the binding of uranium, FT-IR spectra of plain banana peel and uranium loaded banana peel at different exposure times were recorded and shown in **(Fig 2)** Plain banana peel exhibits peaks at 3324.5 cm^{-1}, 2919.32 cm^{-1}, 1607.19 cm^{-1}, 1735 cm^{-1}, and 1021 cm^{-1} corresponds to –OH stretching, -CH aliphatic stretching, aromatic ring structure, -COOH and –CO stretching respectively (Socrates, 1976). IR spectra of metal loaded banana peel shows the reduction in the intensities of functional group peaks showing the interaction of these groups with metal ions. The major impact of metal uptake on the functional group can be seen on the peak at 1734 cm^{-1} the peak has been nearly diminishes while loaded with uranium shows that the –COOH can be the major contributor towards the uptake of uranium on banana peel.

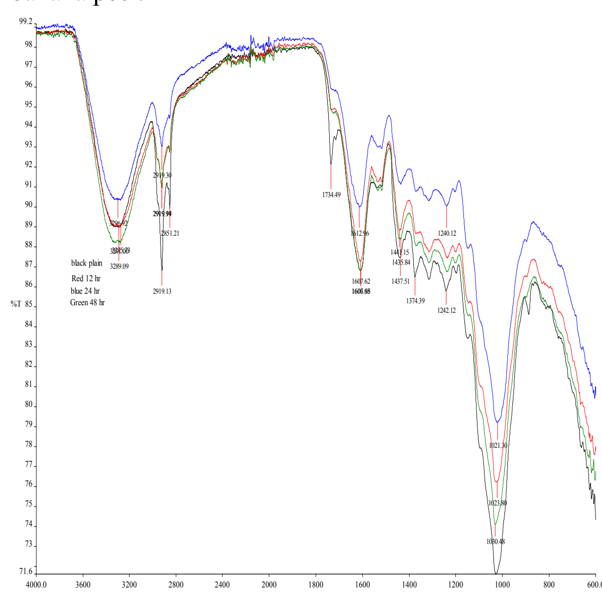

Fig.2 a IR-Spectra of plain and uranium loaded banana peel at different exposure time.

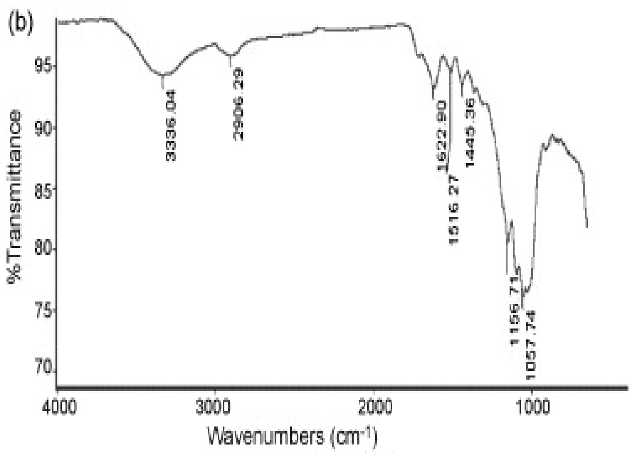

Fig 2b-Spectra of estrified banana peel

3.2 Sorption of Uranium on esterified banana peel

In an attempt to further clarify the involvement of the -COOH group for uranium removal, experiments were carried out on esterified banana peel. Results from the removal experiments showed that the amount of uranium bound was reduced from 1710±10 μg to ~21±2μg. Reduction in uptake of uranium on esterified banana peel confirms the involvement of –COOH groups for the selective removal of uranium.

3.3 Energy dispersive X-ray (EDS) Analysis of banana peel

In order to confirm the presence of uranium onto the surface plain and uranium loaded banana peel was examined Energy dispersive X-ray analysis. The results are shown in **(Fig 3 a-b).**It is clear from the Fig 3(a) that the plain banana peel do not contain any uranium peak whereas the uranium loaded banana peel showed a peak at 3.2keV and a v small peak at 13.8keV confirms the presence of uranium at the surface of banana peel.

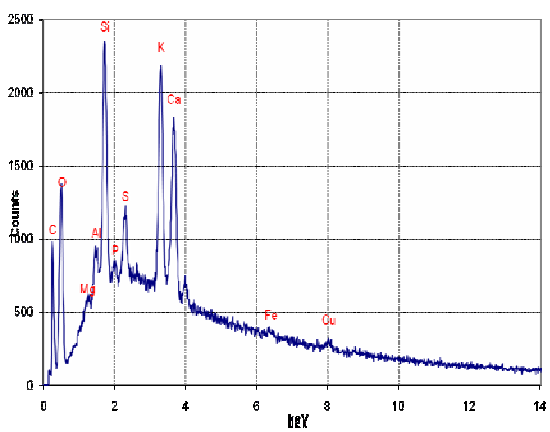

Fig.3 a EDS spectrum of banana peel

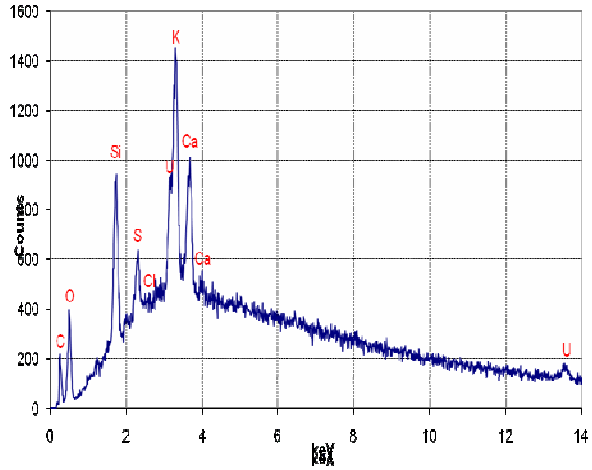

Fig.3 b EDS spectrum of uranium loaded banana peel

3.4 Effect of contact time and the kinetics of adsorption

Uptake of uranium as a function of equilibration time is shown in **(Fig 4).** Initially a small decrease in uptake was recorded but after some time uptake increases and remains nearly constant up to 48 hr. Uptake of 18mgg^{-1} was achieved within the exposure time of 24 hr. Kinetic data were tested by Pseudo-first order, Elovich and Intra-particle diffusion models.

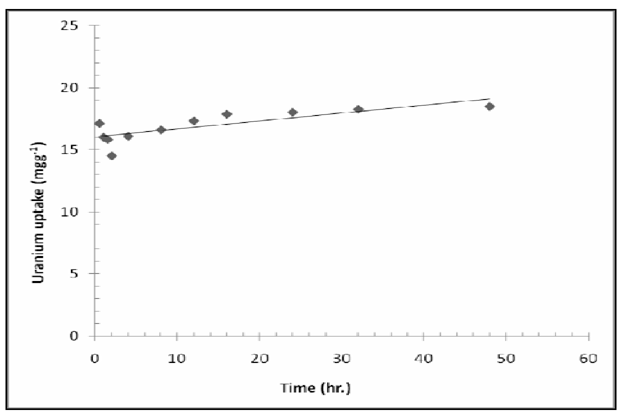

Fig.4. Effect of exposure time on uranium ion uptake on banana peel

Kinetic parameters calculated from all these equations are given in **(Table1)**.

Table 1. Kinetic parameters for the adsorption of uranium onto banana peel

Pseudo-First order Model	Elovich Model	Intra-particle diffusion Model
k (min^{-1}) = 0.0882 r = 0.982	α = (1.1±0.001)×10^{6} g.mg^{-1} β = 0.815±0.0002 mg.g^{-1}.min^{-1} r = 0.977	R_d= 0.50±0.003 mg.g^{-1}.min$^{-1/2}$ r = 0.964

Morris Weber equation is tested in following form

$$q_t = R_d\sqrt{t} \qquad (2)$$

Morris-Weber plot **(Fig.5)** indicates that the mechanism of uranium adsorption on banana peel was complex and could be both surface adsorption as well as intraparticle diffusion, as the linear portion of the curve did not pass through the origin. Similar phenomenon has been observed for the adsorption of arsenic on bone char by Y.N. Chen *et. al.*, 2008.

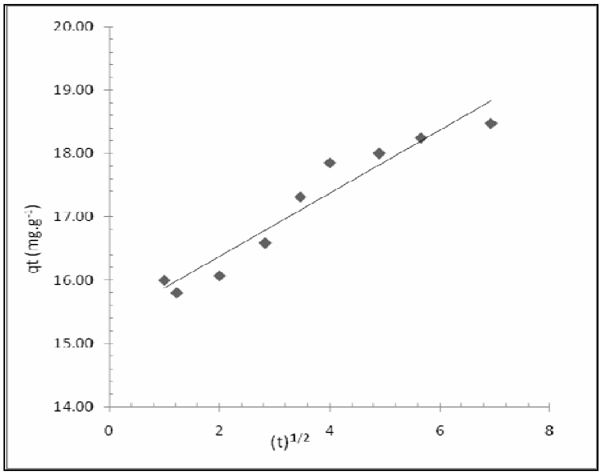

Fig.5. Morris-Weber plot for the adsorption of uranimu on banana peel

In order to further understand the kinetics of uranium removal through banana peel, pseudo-first order eq. 3 and Elovisch eq. 4 were used to testify the observed data. It was found that data did not follow second order rate equation. Therefore, pseudo first order rate equation was tested in the following linear form:

$$\log(q_e - q_t) = \log q_e - \frac{kt}{2.303} \qquad (3)$$

$$\frac{1}{qt} = \ln\frac{\alpha\beta}{\beta} + \frac{lnt}{\beta}q \qquad (4)$$

Where k is the pseudo second order rate constant (g $mg^{-1}min^{-1}$), qe is the amount of uranium adsorbed at equilibrium (mg g^{-1}), and qt is amount of uranium ion on the banana peel at specified time (mg g^{-1}), α is the initial adsorption rate ($mg.g^{-1}.min^{-1}$) and, β is desorption constant ($mg.g^{-1}.min^{-1}$) during any one experiment.

Plot of qt versus ln t is linearly correlated with coefficient of correlation 0.982, this supports that the sorption system belongs to pseudo-first order kinetic. The constants α and β computed from the slope and intercept of Elovich model graph are 1.1×10^6 $g.mg^{-1}$and 0.815 $mg.g^{-1}.min^{-1}$ respectively.

3.5 Desorption characteristics

Regeneration process is important while describing the cost effectiveness of removal process. It describes the recycling of the adsorbent for its reuse in multiple cycles. Desorption process was carried out as a function some parameters such as the kind of eluent, concentration of eluent, contact time and number of desorption stage. After adsorption of uranium onto banana peel, banana peel was treated with different desorptive solutions to recover the adsorbed uranium from banana peel. Desorption yields are shown in **(Table 2)** banana peel showed the lower desorption yield using Acetic acid and H_2O compared to the other desorptive solutions. HNO_3 represents relatively high desorption yield for uranium. The effect of concentration of HNO_3 solution on desorption of uranium from banana peel showed that both 0.1 M HNO_3 and 1.0 M HNO_3 solutions have nearly similar yield (98.7%). Desorption tests showed that uranium could be quantitatively desorbed with 1 M HNO_3 in one stage.

Table 2. Desorption yields of some desorptive solutions

Elution solution	Desorption (%)	Elution solution	Desorption (%)
0.1M CH_3COOH	14.5±0.5	0.1 M HNO_3	98.7±3.1
1 M CH_3COOH	25.0±1	1 M HNO_3	99.0±2.7
0.1M HCl	51.8±1.4	0.1M NaOH	47.6±2.5
1 M HCl	69.3±2.0	1 M NaOH	63.9±1.1
0.1 M H_2SO_4	55.8±2.0	H_2O	1.9±0.1
1 M H_2SO_4	78.3±2.3		

CONCLUSIONS

Present work explores removal efficiency of banana waste material to enrich/removal uranium from aqueous solutions. It has been found that the banana peel can efficiently be used to remove uranium ions without any modification/treatment and –COOH group of surface is responsible for the removal. EDS analysis confirms the presence of uranium at the surface of banana peel. It can be concluded that the banana peel can be used as a replacement to existing expensive methods.

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