Research Article   **Open Access**

Removal of Uranium (VI) from Aqueous Solution using Low Cost and Eco-Friendly Adsorbents

Mohamed Ahmed Mahmoud[12]*

[1]*Reactors Material Treatment Department, Nuclear Material Authority, Kattamiya Road, Maddi, Cairo, Egypt*
[2]*Chemical Engineering Department, Faculty of Engineering, Jazan University, Jazan, Saudi Arabia*

Abstract

Adsorption process is an important technique in separation processes, which is used in heavy metals removal from aqueous solution. Orange peel has been investigated for the adsorption of uranium ions from aqueous solution. The parameters of pH, contact time, initial uranium ion concentration, temperature and adsorbent dose have been investigated in batch experiments. The adsorption kinetics were described using pseudo-second order model and the adsorption isotherms were described by Langmuir and Freundlich isotherms which indicate that the uranium adsorption onto orange peel fitted well with Langmuir isotherm.

Introduction

Several methods are used to remove uranium from liquid wastes. These include volume reduction followed by chemical, physical and biological treatment. However, these processes are both costly and ineffective, particularly when the concentration of uranium in liquid waste is a very low [1,2]. Adsorption process using agricultural material is the important technique in the wastewater treatment processes. Numerous researches have been carried out for using of low cost and eco-friendly adsorbents, such as peat [3,4], agricultural byproducts [5-7], and microbial biomass [8]. In the present work, the sorption of U (VI) onto orange peel carried out by studying the effect of various parameters such as pH, contact time, initial uranium concentration and adsorbent dosage in batch experiments. The kinetics and equilibrium of adsorption process are studied.

Experimental

Adsorbate

1000 mg /l of uranium solutions (Synthetic wastewater solutions) were prepared by dissolving a certain amounts of uranyl nitrate ($UO_2(NO_3)_2 \cdot 6H_2O$, Aldrich), in distilled water. The required concentrations were prepared by dilution solution. The concentrations of U (VI) in solution were determined spectrophotometrically using Shimadzu UV-VIS-1601 spectrophotometer using arsenazo (III) as complexing reagent at 510 NM against reagent blank [9,10].

Adsorbent

Orange peels, were collected from by-products of fruit industries. Orange peels were used without any treatment for the preparation of adsorbent, which were cut into small pieces, washed multiple times with distilled water and dried at 105°C. Then, milled and sieved by a size of 150-mesh size.

Methods

To study the influence of different parameters such as pH, contact time, initial metal ion concentration, temperature and dose of adsorbent for the removal of uranium, batch experiments were carried out by mixing 0.3 g of orange peels with 50 ml of adsorbate solution in 100 ml stoppered conical flask using a thermostatic water bath shaker of type (Julabo, Model SW -20°C, Germany), at 200 rpm. The influence

of pH on the adsorption process was studied from pH 2.0 to 8.0. 0.1 M HCl or 0.1 M Na_2CO_3 solutions were used to adjust pH. Different concentrations of uranium ion solution from 25 to 200 ppm,, were used to study the influence of initial uranium ion concentration. The samples were taken and centrifuged at 5000 rpm for 5 min and were analyzed. Adsorption percent (%) was determined by the following equation: Adsorption percent (%)=$[(C_0 - C_e)/C_e]$ x 100 (1)

In addition, the adsorption capacity (qe) is determined according to the following equation:

$$q_e = (C_0 - C_e) V/M \tag{2}$$

Where

C_0=initial concentration of solute (mg/L)

C_e=concentration of solute at equilibrium (mg/L)

V=volume of solution (L)

M=adsorbent dose (g)

Results and Discussion

Characterizations of adsorbent

Orange peel was studied using scanning electron microscopy (SEM) (Figure 1), showed that the orange peel has an irregular and porous surface, which have surface area of 0.98 m^2/g by BET method.

Effect of pH

The influence of pH on the removal of uranium ions onto orange peels was presented in Table 1. The percent of removal increases with

Figure 1a, 1b: Scanning electron micrographs (SEM) of orange peel.

Table 1: Adsorption data of adsorption of U (VI) onto orange peel.

Parameter		Ce (mg/L)	Adsorption percent (%)	q (mg/g)
pH:	2	61.10	38.90	6.483
(Condition: [U(VI)] = 100 mg L-1, V = 50 mL, mass = 0.3 g, 3 h, 28 ˚C)	3	34.30	65.70	10.95
	4	4.50	95.50	15.91
	5	9.55	90.45	15.07
	6	14.59	85.41	14.23
	7	16.77	83.23	13.87
	8	24.55	75.45	12.57
Time (min):	10	69.90	30.20	5.016
(Condition: [U(VI)] = 100 mg L-1, V = 50 mL, mass = 0.3 g, pH= 4 , 28 ˚C)	20	49.79	50.21	8.368
	40	18.67	81.33	13.55
	60	4.50	95.50	15.91
	80	4.50	95.50	15.91
	100	4.49	95.51	15.91
	120	4.50	95.50	15.91
Initial concentration (mg/l):	25	0.45	98.16	4.091
Condition: pH= 4, V = 50 mL, mass = 0.3 g, 60 min, 28 ˚C	50	1.05	97.72	8.158
	75	2.40	96.68	12.10
	100	4.50	95.50	15.916
	125	29.54	76.36	15.91
	150	54.54	63.64	15.91
	175	79.60	54.51	15.90
	200	104.60	47.70	15.90
Temperature (ºC):	28	4.50	95.50	15.91
Condition: [U(VI)] = 100 mg L-1, V = 50 mL, 60 min, pH= 4, mass = 0.3 g	40	4.51	95.49	15.91
	55	4.49	95.51	15.91
Adsorbent dose (g):	0.1	79.10	41.80	10.45
Condition: [U(VI)] = 100 mg L-1, V = 50 mL, 60 min, pH= 4, 28 ˚C	0.2	41.32	96.04	14.67
	0.3	4.50	95.50	15.91
	0.4	4.52	95.45	11.93
	0.5	4.49	95.44	9.551

increasing pH until reaches maximum at pH 4, then decreases with increasing pH. This is due to the competing of H+ with uranium ions for the adsorption sites of orange peel, lead to decreasing the removal percent of uranium ions. However, after pH 4 the percent of removal decreases. This is due to the formation of stable complexes with carbonates such as UO_2CO_3, $[UO_2CO_3]^{2-}$ [11,12].

Effect of contact time

The influence of time on the adsorption of uranium ions was investigated from 10 to 120 min. Table 1 noted that the percent of removal increase with increasing time until reaching to a certain time

60 minutes. After 60 minutes, there is no significant change in the removal percent of uranium ions.

Effect of initial concentration of metal ions

Table 1, shows that the adsorption capacity (q_e) increases with increasing in equilibrium uranium ion concentration (C_e) until reaches the maximum q_e (15.91 mg/g), and then decreases with increasing C_e. This is due to saturation of adsorption sites of the adsorbent material.

Effect of adsorbent dosage

The adsorption percent at various doses of orange peel from 0.1to 0.5 g, is shown in Table 1. Increasing the adsorbent dose to 0.3g increase the adsorption percent of metal ions, which is due to the increasing in adsorption sites of adsorbent material resulting from increasing of surface area of adsorbent. However, further increase of adsorbent dosage does not afford exhaustive adsorption of U (VI). This may be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles. In addition, the amount of ions bound to the adsorbent and the amount of free ions remains constant even with further addition of the dose of adsorbent.

Effect of temperature

The effect of different temperature on uranium removal is carried out at different temperature (30, 40 and 55 ºC), is shown in Table 1. The results show that the adsorption percent of uranium ions remain almost the same in the studied temperature range.

Equilibrium adsorption isotherm

Experimental results were studied using Langmuir and Freundlich isotherms [13-16], and these isotherms were analyzed by determination of correlation coefficients (r^2). The Langmuir isotherm supposes that the adsorbate molecules adsorbed as a monolayer on the surface of adsorbent material [15].

Langmuir model is represented as: $q_e = Q_0 b C_e / (1 + bC_e)$ (3)

Where q_e is the adsorption capacity of orange peel (mg/g), C_e is the equilibrium concentration of adsorbate (mg/L), b is the constant of Langmuir (L/mg) and Q_0 is the maximum monolayer coverage (mg/g).

By linearized Eq. (3): $C_e/q_e = 1/ Q_0 b + C_e/ Q_0$ (4)

Q_0 and b can be determined from the intercept and slope of the straight line resulting from Figure 2, respectively. The basic attributes of the Langmuir model can be expressed by dimensionless constant term (R_L) [17].
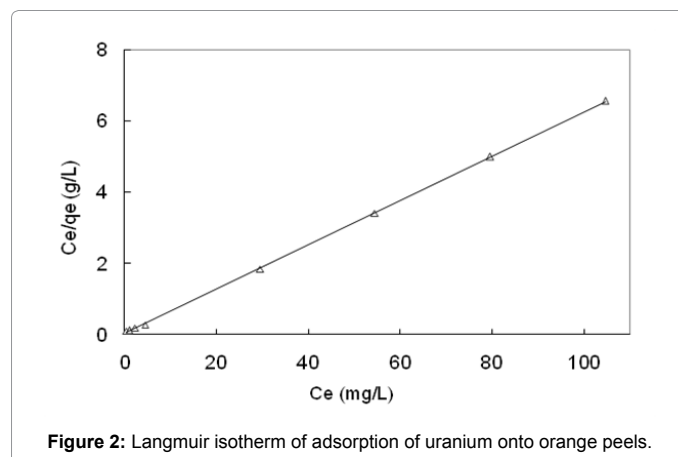

Figure 2: Langmuir isotherm of adsorption of uranium onto orange peels.

$R_L = 1/(1 + b C_0)$ (5)

When $0 < R_L < 1$ indicate that the adsorption process is favorable

Freundlich model is represented as: $q_e = K_F C_e^{(1/n)}$ (6)

Where K_F is the constant of Freundlich model [(mg/g)/(mg/l)] and n is a parameter refers to adsorption tendency.

By linearized Eq. (6): $Log q_e = \log K_f + 1/n \log C_e$ (7)

K_F and n can be determined from the intercept and slope of the straight line resulting from Figure 3, respectively. From Figures 2 and 3, and the result data in Table 2, show that the Langmuir isotherm model is the best fitting model because it gives a higher correlation coefficient (r^2=0.999) value than Freundlich isotherm model (r^2=0.682).

Adsorption kinetics

To study the adsorption kinetics of U (VI) ions onto the orange peel were tested using Pseudo-first-order and pseudo-second order model [18,19].

Pseudo- first -order model: The equation represents this model is:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t$$ (8)

Where q_e and q_t (mg/g) are the adsorption capacity of U (VI) ions at equilibrium and at time t, respectively, k_1 is the pseudo first order constant (min^{-1}). The values of qe and k_1 were determined from the intercept and slope of Figure 4, respectively.
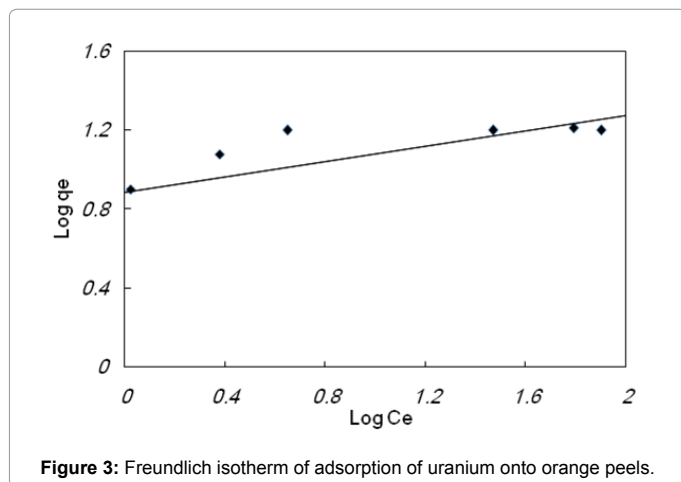

Figure 3: Freundlich isotherm of adsorption of uranium onto orange peels.
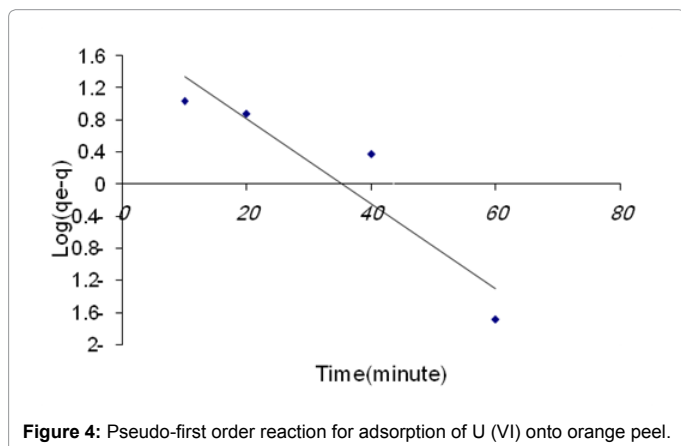

Figure 4: Pseudo-first order reaction for adsorption of U (VI) onto orange peel.

Pseudo-second-order model: The equation represents this model is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t$$ (9)

Where K_2 is the pseudo second order constant (g/mg min^{-1}). The values of q_e and k_2 were determined from the slope and intercept of Figure 5, respectively. From Figure 4 and 5, and the result data in Table 3, show that the pseudo second order model is the best fitting model because it gives a higher correlation coefficient (r^2= 0.980) than pseudo-first-order (r^2= 0.867).

Mechanism of adsorption

The orange peel can adsorb uranium ions through electrostatic interaction and/or ion exchange, complexation, or by a combination of all the processes Energy-dispersive X-ray spectroscopy (EDX spectra) of the orange peel before and after Adsorption of uranium ions are
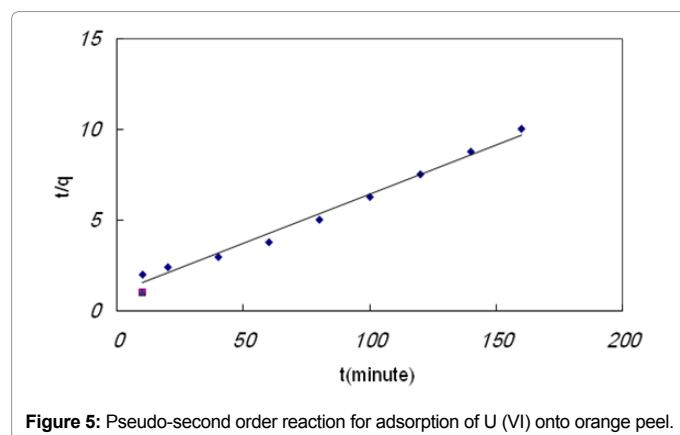

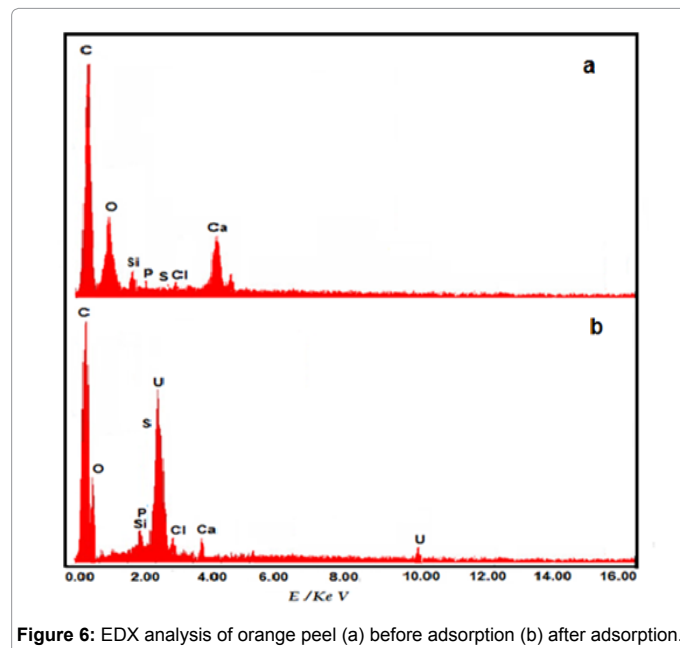**Figure 5:** Pseudo-second order reaction for adsorption of U (VI) onto orange peel.

Figure 6: EDX analysis of orange peel (a) before adsorption (b) after adsorption.

Langmuir constant				Freundlich constant		
b	Q₀	R_L	r²	K_f	n	r²
1.477	16.12	0.0068	0.999	7.655	5.18	0.682

Table 2: Langmuir and Freundlich constant of adsorption system.

Experimental q_e (mg/g)	Pseudo-first-order kinetics			Pseudo-second-order kinetics		
	K_1 (1/min)	q_e (mg/g)	r^2	K_2(g/ mg.min)	q_e(mg/g)	r^2
15.91	0.119	73.62	0.867	0.0547	18.51	0.980

Table 3: Kinetics data of adsorption of U (VI) onto orange peel.

shown in Figure 6. It is noted that due to uranium ion adsorption by the orange peel, the peaks of Ca weaken with the concomitant appearance of uranium ion peaks, which indicates that there is an ion exchange between calcium and uranium ions, which indicate that ion exchange process is, appears higher than other processes mention above.

Conclusion

The results obtained indicate that orange peels can be used for removal uranium ions from liquid wastes. Performances of adsorption are strongly affected by pH, contact time, initial metal ions and adsorbent dose. The maximum removal of uranium ion was investigated at pH 4 and contact time 60 minutes. Langmuir model was more convenient than the Freundlich model for describing the adsorption conduct of orange peel. The adsorption of U (VI) ions onto orange peels can be described by the pseudo-second order equation.

References

1. Blázquez G, Hernáinz F, Calero M, Ruiz-Núñez LF (2005) Removal of cadmium ions with olive stones: the effect of some parameters. Process Biochem 40: 2649-2654.

2. Konstantinou M, Demetriou A, Pashalidis I (2007) Adsorption of hexavalent uranium on dunite. Global NEST J 9: 229-236.

3. Brown PA, Gill SA, Allen SJ (2000) Metal removal from wastewater using peat. Water Res 34: 3907-3916.

4. Ho YS, Mckay G (2000) The kinetics of sorption of divalent metal ions onto sphagnum moss peat. Water Res 34: 735-742.

5. Jaramillo J, Gomez-Serrano V, Álvareza PM (2009) Enhanced adsorption of metal ions onto functionalized granular activated carbons prepared from cherry stones. J Hazard Mater 161: 670-676.

6. Conrad K, Hansen HCB (2007) Sorption of zinc and lead on coir. Bioresour Technol 98: 89-97.

7. Febrianto J, Kosasih AN, Sunarso J, Ju YH, Indraswati N, et al. (2009) Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: A summary of recent studies. J Hazard Mater 162: 616-645.

8. Ahluwalia SS, Goyal D (2007) Microbial and plant derived biomass for removal of heavy metals from wastewater. Bioresour Technol 98: 2243-2257.

9. Onishi H (1989) Photometric determination of trace metals. Wiley, NY, USA.

10. Korkish J (1974) Modern method for the separation of rare metal ions. Pergamon Press: Oxford, UK.

11. Yusan SA, Mahmoud AA, Turkozu DA, Aycan HA, Aytas S, et al. (2010) Adsorption and thermodynamic behaviour of U(VI) on the Tendurek volcanic tuff. J Radioanal Nucl Chem 283: 231-238.

12. Man JK, Bo EH, Pil SH (2002) Precipitation and adsorption of uranium(VI) under various aqueous conditions. Environ Eng Res 7: 149-157.

13. Sciban M, Radetic B, Kevresan Z, Klasnja M (2007) Adsorption of heavy metals from electroplating wastewater by wood sawdust. Bioresour Tech 98: 402-409.

14. Yusan S, Doyurum AS (2008) Sorption of uranium (VI) from aqueous solutions by akaganeite. J Hazard Mater 160: 388-395.

15. Ahmad R (2004) Sawdust: Cost effective scavenger for the removal of chromium(III) ions from aqueous solutions. Water Air Soil Pollut 83: 163-183.

16. Saeed B, Amir L, Seyed JA, Mohammad FR, Akram H (2010) Uranium removal from aqueous solutions by wood powder and wheat straw. J Radioanal Nucl Chem 283: 289-296.

17. Bhatnagar A, Jain AK (2005) A comparative adsorption study with different industrial wastes as adsorbents for the removal of cationic dyes from water. J Colloid Interf Sci 28: 49-55.

18. Christian TCV, Fauduet H, Porte C, Delacroix A (2003) Removal of Cd(II) and Pb(II) ions, from aqueous solutions, by adsorption onto sawdust of Pinus sylvestris. J Hazard Mater 105: 121-142.

19. Monoj KM (2010) Removal of Pb(II) from aqueous solution by adsorption using activated tea waste. Korean J Chem Eng 27: 144-151.