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

Mohamed Ahmed Mahmoud

1Reactors Material Treatment Department, Nuclear Material Authority, Kattamiya Road, Maddi, Cairo, Egypt
2Chemical 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.

Keywords: Uranium; Orange peel; Adsorption; Aqueous solution; Langmuir

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 was 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 (UO₂(NO₃)₂.6H₂O, 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 Na₂CO₃ 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 (%)=[(C₀ – Cₑ) /C₀] x 100 (1)

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

\[ q_e = \frac{(C_0 - C_e)}{M} \times V \]  

Where  
\[ C_0 = \text{initial concentration of solute (mg/L)} \]  
\[ C_e = \text{concentration of solute at equilibrium (mg/L)} \]  
\[ V = \text{volume of solution (L)} \]  
\[ M = \text{adsorbent dose (g)} \]

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 m²/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...
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$_2$CO$_3$, [UO$_2$CO$_3$]$^2-$ [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 0.1 to 0.5 g, is shown in Table 1. Increasing the adsorbent dose to 0.3 g 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: 

$q_e = \frac{Q_0bC_e}{1 + bC_e}$  \hspace{1cm} (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): 

$Ce/q_e = 1/Q_0b + C_e/Q_0$  \hspace{1cm} (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].
\[
R_L = \frac{1}{1 + b \cdot C_0} \quad (5)
\]
When \(0 < R_L < 1\) indicate that the adsorption process is favorable.

**Freundlich model** represented as: \(q_e = K_F C_e^{1/n}\) \quad (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): \(\log q_e = \log K_F + \frac{1}{n} \log C_e\) \quad (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:
\[
\frac{t}{q_t} = \frac{1}{q_e} + \frac{1}{k_1 q_e} t
\]

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 \(q_e\) and \(k_1\) were determined from the intercept and slope of Figure 4, respectively.

**Mechanism of adsorption**

The orange peel can adsorb uranium ions through electrostatic interaction and/or ion exchange, complexion, 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
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**