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Selective removal of uranium from wastewater using sludge collected from refinery wastewater treatment: Equilibrium, thermodynamic and kinetics studies

Ahmed M. Soliman[a,d,*], Ahmed A. Murad[b], Ehab S. El Sheikh[d], Ali M. Massad[c], Ismail M. Ali[d]

[a] Chemistry Department, College of Science, United Arab Emirate University, United Arab Emirates
[b] Geology Department, College of Science, United Arab Emirate University, United Arab Emirates
[c] Chemistry Department, Faculty of Science and Technology, Umdorman Islamic University, Sudan
[d] Nuclear Fuel Technology Department, Hot Laboratory Center, Atomic Energy Authority, Egypt

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ABSTRACT

Adsorption of uranium as uranyl ion UO_2^{2+} was investigated on the surface of pretreated refinery wastewater sludge. The sludge was chemically activated using different acids (HCl, HNO_3, H_2SO_4, H_3PO_4), and its uranium uptake capacity from aqueous solution was checked after each activation process. The highest uptake capacity was obtained for sludge treated by phosphoric acid followed by washing with Na_3PO_4 (0.2 M). The effect of pH, point of zero charge pH pzc, uranyl ion concentration and adsorbent dose on adsorption processes were studied. The adsorption is high in the pH range of 3.5–7.2 with optimum value at pH 5.3. The point of zero charge was found to be at pH 3.95. The adsorption capacity increases with increasing uranyl ion concentration but decreases with increasing sludge dose. The equilibrium studies showed that the adsorption fits Langmuir adsorption isotherm. Also, the kinetic studies showed that the adsorption is pseudo-second order with activation energy 31.15 kJ/mol, indicating that the process is chemical in nature. The activated sludge showed high selectivity for UO_2^{2+} among Zr(IV), Fe(III), Cr(III), Gd(II), Sr(II), Co(II), Ca(II), Cs(I) and Na(I) ions.

1. Introduction

Recognition of the faith of emitted radioactive waste from a variety of industries such as nuclear and medical practices remains a highly challenging task globally [1]. Uranium represents a vital component of the nuclear fuel cycle and because of its increasing demand in the nuclear industry, the efforts are being made to recover of uranium from expected high-level effluents [2]. Moreover, uranium-bearing effluents may contaminate surface and groundwater and thus become a source of health hazard. The toxic nature of uranium causes many health problems as liver and kidney damage [3].

Several techniques are available for removal of U(VI) from aqueous solution: including solvent extraction, chemical precipitation [4], membrane filtration processes [5], reverse osmosis [6] and ion exchange and adsorption, which are effective and economic methods. Adsorption technology is one of the effective methods to remove heavy metals from aqueous solutions. Low-cost adsorbents from industrial waste by-products and agricultural wastes are the most potential water treatment methods [7,8]. Industrial waste: waste slurry, iron (III) hydroxide, blast – furnace slag and red mud from aluminum industry were used for removal of heavy metals from wastewater [9–12]. Electrocoagulation processes for waste water treatment generate large quantity of sludge. This sludge is mainly composed from alumina when aluminum metal is used as anode.

In the present investigation, inexpensive and accessible sludge composed of mainly aluminum oxide with minor metals was used in the experimental design with details of the material composition reported by Ahmed et al. [13]. The major objective is to explore the adsorption and selectivity of the activated refinery wastewater sludge for removal of uranium from aqueous solutions. The activation of the collected and treated sludge was accomplished through treatment with different acids (HCl, HNO_3, H_2SO_4 and H_3PO_4).

The selectivity of the activated sludge for UO_2^{2+} was explored in the presence of different competing ions (Zr^{4+}, Cr^{3+}, Gd^{2+}, Sr^{2+}, Co^{2+}, Cs^{+} and Na^{+}) which expected to be in the nuclear effluent especially from nuclear power plants or polluted groundwater sites. The effects of different factors as uranyl ion concentrations, adsorption doses, pH, point of zero charge and temperature on the adsorption process were studied. Additionally, the equilibrium isotherm, kinetics and thermodynamics of adsorption processes are further evaluated by

* Corresponding author.
E-mail address: a.soliman@uaeu.ac.ae (A.M. Soliman).

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batch experiments.

2. Experimental studies

2.1. Sludge collection and activation

The aluminum sludge generated from refinery of wastewater by electrochemical coagulation was used for purification of wastewater polluted with organic pollutants [13]. Previous study showed that this sludge is chemically stable and insoluble in moderate acidic and basic media as well as high thermal stability [13]. The sludge used in this investigation was collected and treated according to the earlier reported procedure [13]. The chemical composition of the sludge contains 92% alumina (Al_2O_3) with traces of iron, chromium, silicon and sulfur and its chemical formula is: Al_{15} $(Cu_{0.4}Ca_{0.3}Fe_{1.4})(SiO_4)_{0.3}Cl$ $(SO_4)_{0.3}(OH)_{45}.xH_2O$. In this work, the sludge was activated by soaking 5 g sludge in 250 ml solution of 0.2 M HNO_3, H_2SO_4, HCl and H_3PO_4 separately for 24 h, followed by washing with deionized water. The modified sludge was oven dried at 80 °C for 4 h before using for adsorption tests. Further treatment of the sludge was made with 0.2 M Na_3PO_4 solution for adsorption experiments. Samples from each activation method were collected and tested for uranium adsorption. Scanning electron microscope (SEM) supplied with Electron Dispersive X-ray spectroscopy (EDXS) model (Joel, JSM 840-A, Japan) was used for elemental analysis of sludge before and after the uranium adsorption experiments.

The Brnauer-Emmett-Teller surface area and micropore volume of sludge were determined under nitrogen gas at −196 °C by using a physisorption analyzer Micrometrics Tri-Star II plus (Tri-Star II 3020).

2.2. Adsorption parameters

The effect of adsorbent dose on adsorption capacity was carried out using different quantities (0.1-0.5 g) of adsorbent which were equilibrated with a fixed quantity (50 ml) and concentration of uranyl ion at pH 4.0 (UO_2^{2+}) and room temperature. The concentration of residual uranium species at equilibrium was calculated. The effect of different uranyl ion concentrations (20–260 ppm) on the adsorption capacity was studied by equilibration with fixed quantity of sludge at pH 4.0 and room temperature.

The point of zero charge, (the net charge on the surface of sludge at specific pH values), was determined by the method of shift in pH [14]. 0.2 g of sludge was equilibrated with 50 ml of 0.1 M KNO_3 solution in the pH range of pH (2.0–10.0) for 24 h. Initial pH values were adjusted by adding appropriate amounts of 0.1 M KOH or HNO_3 solution, keeping the ionic strength constant. The final pH was measured after 24 h under agitation at room temperature. The initial and final pH values were measured using pH meter Orion model 150A+ pH meter. The point of zero charge was determined as the pH value at which a plateau is obtained on the graph $pH_{final} = f(pH_{initial})$. Finally, the effect of pH on uranyl ion adsorption was achieved using of 50 mg sludge that containing 50 ml uranyl solution (40 mg/L) under shaking condition at 25 °C. The experiments were carried out in the pH range of 2.0–10.0 for 280 min contact time shaking at 120 rev/min. The pH was adjusted by adding few drops of dilute 0.1 M HNO_3 or 0.1 M NaOH.

2.3. Batch experiments

Uranium stock solution (1000 mg/L) was prepared by dissolving 2.013 g of uranyl nitrate hexahydrate $UO_2(NO_3)_2{\cdot}6H_2O$ (FLUKA) in 1L deionized H_2O.

The adsorption equilibrium experiments were carried out by adding a fixed amount of sludge 50 mg to 50 ml of uranyl ion of different initial concentration in plastic vials. All adsorption experiments were carried out twice and the mean value was taken.

The sample was agitated for 180 min at 25 °C in water bath shaker model (HACK SWB 20) at 120 rev/min and the adsorbent is separated by using centrifuge BECKMAN model, TJ-6 at 5000 rpm. The concentration of uranyl ion at equilibrium and at t = 0 was measured by using Cary 50 Conc. VARIAN spectrophotometer at λ_{max} 384 nm after complexation with 8-hydroxy quinolone.

The uranyl samples were mixed with 1.5% 8- hydroxy quinolone in ethanol at pH 5 then the adsorption spectra were measured to determine the amount of uranyl ion [15]. Calibration curve was constructed and used for determination of the concentration of the uranyl ion of samples after equilibrium. The quantity adsorbed at equilibrium Q_e (mg/g) was calculated as:

$$Q_e = \frac{Co - Ce}{m} V \quad (1)$$

where C_o and C_e in mg/l are the initial and equilibrium uranyl ion concentration respectively.

V (liter) is the volume of uranyl ion solution and *m* is the mass of the dried sludge in gram. The percentage removal was also calculated as:

$$\%Removal = \frac{C_0 - C_f}{C_0} \times 100 \quad (2)$$

where C_o and C_f in mg/l are the initial and final uranyl ion concentration respectively.

For kinetic studies, 50 mg of sludge was contacted with 50 ml of uranyl solution at concentration ranged from 10 to 260 mg/L, then shaking (120rev/min) at 25 °C. Periodically, solution was analysed for uranium content. These experiments were carried out at different temperatures using thermostatic shaker (HAAK SW20). The amount of adsorbed uranyl ion at different times was calculated by Eq. (1).

Batch adsorption experiments were carried out to explore selectivity of the prepared sludge for uranyl ion. A specific quantity of sludge was equilibrated with multi-ions. The selectivity of the activated sludge was tested by competition adsorption experiments of uranyl ion in a mixture of Zr^{4+}, Cr^{3+}, Gd^{2+}, Sr^{2+}, Co^{2+}, Cs^{+} and Na^{+} which were expected to be present in wastewater and groundwater. The concentration was 0.5 mmol for each metal ion and the mixture solution pH was 4. The metal ions concentration was measured before and after adsorption experiments using ICP-OES (Varian model 710).

Uranium selectivity *(Su)* was used to describe the efficiency and degree of selectivity of the prepared activated sludge for sorption of uranium. The selectivity was calculated by the equation given as [16].

$$Su = \frac{Qeu}{Qet} * 100 \quad (3)$$

Where Q_{eu} is the amount of uranium sorbed, and Q_{et} is the amount of all sorbed metals in (mmol g^{-1}).

Batch and column reusability tests were carried out in triplicate for reproducibility of the data. The obtained experimental data were within the average error limit of 3%.

2.4. Column adsorption study of UO_2^{++}

Sorption and desorption study were carried out to check the reusability of the spent sludge. A steal cylindrical tube of 0.5 cm inner diameter and a height of 25 cm was used as an adsorbent column. The column was packed with the adsorbent between cotton wool and supported by inert glass beads (Anti-bumping granules BDH). The UO_2^{++} solution at 80 mg/L was passed through the column with help of peristaltic pump at an optimum flow rate of 0.25 ml/min. The solutions coming out from the column were taken out periodically and analysed for UO_2^{++}. Till its concentration was found to be equal to the inlet feed so the breakthrough and the exhaustion points can be determined. Desorption study of UO_2^{++} was carried out with 1 M HNO_3. Then the column was washed with deionised water and used for another adsorption desorption cycle.