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Sorption behaviors of uranium (VI) ions on α-FeOOH

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ABSTRACT

The objective of this study was the examination of the ability of a synthetic goethite nanocrystal to remove hexavalent uranium from aqueous solutions under various conditions. Goethite (α-FeOOH), which has a strong affinity for adsorption of the uranyl (UO_2^{2+}) ion, was synthesized in the laboratory and used as adsorbent. Batch studies have been carried by observing the effects of pH, temperature, concentration of the adsorbate, contact time, etc. Various sorption isotherm models like, Langmuir, Freundlich and Dubinin–Radushkevich have been carried out for the adsorbent. The sorption on the goethite has been found endothermic and feasible in nature. Various thermodynamic parameters, such as Gibb's free energy, entropy and enthalpy of sorption process, have been calculated. Furthermore, the Lagergren first-order, pseudo-second-order and the intraparticle diffusion models were used to describe the kinetic data. The experimental data fitted well the pseudo-second-order kinetics. The product material was characterized by powder X-ray diffraction for crystalline phase identification, scanning electron microscope (SEM) and multi point Brunauer, Emmett and Teller (BET).

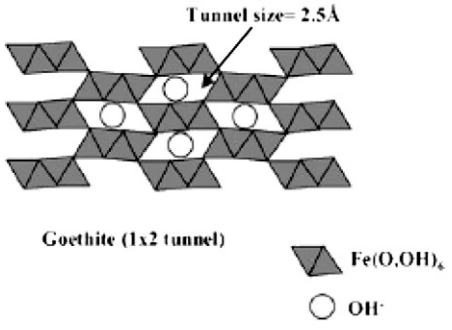
1. Introduction

Uranium is a toxic heavy metal arising from the nuclear industry as well as from anthropogenic activities. It is usually found in the environment in the hexavalent form, as the mobile, aqueous uranyl ion, UO_2^{+2}. This ion has been shown to be strongly sorbed onto clay minerals and metal oxides under appropriate chemical conditions and therefore such materials can be used for the U (VI) remediation of aqueous solutions [1–6]. Under toxic conditions, uranium is highly soluble due to the formation of a numerous U (VI) complexes in aqueous solutions. The aqueous concentration of U (VI) is limited by its tendency to strongly sorbs to Fe oxides and oxide hydroxides [7].

Iron oxy-hydroxides such as goethite, akaganeite, ferrihydrite, magnetite and hematite show high specific surface area and their surface is positively charged at low and circum neutral pH values. These minerals play a main role in the retardation of the transport of different contaminants because they are present in many natural media in contact with water and they have well known high sorption capacities for a number of trace elements such as arsenic, selenium, selenite, zinc and phosphate [8–13].

Goethite (α-FeOOH) is a major constituent of many soils, sediments and iron ores and it is thermodynamically stable iron oxide in most soils. It also appears as the weathering product of various rocks which are containing iron. The color of goethite can vary from dark brown to lemon yellow, as observed with the naked eye. Under natural pH values (pH between 7.3 and 7.8) it is highly insoluble and has a net positive surface charge making it an effective sorbent of metal anion complexes from aqueous solutions. In colloid and surface chemistry, the synthetic α-FeOOH particles are often used as a model adsorbent in fundamental studies of the adsorption/desorption phenomena [8,9,11,14–22].

Furthermore goethite mineral has a (1×2) tunnel structure and the structure can be described as polyhedral clusters of $Fe^{3+}O_3(OH)_3$ octahedral, which are OH-bridged by edges and form double chains along [001] with hydroxide ions in the tunnel [11].



Polyhedral frameworks of goethite with tunnel structures.

This paper deals with the investigation of the best separation and recovery conditions of uranium on goethite adsorbent as a function of the initial uranium concentration, pH, shaking time and temperature. The thermodynamic parameters such as free energy (ΔG°), enthalpy of adsorption (Δ*H*°) and entropy (Δ*S*°) were calculated. The applications of the isotherm models and kinetics have been studied to explain the sorption characteristics of the goethite.

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2. Material and methods

2.1. Method

180 mL of 5 M KOH (Merck, Analar) was added rapidly with stirring to 100 mL of 1 M $Fe(NO_3)_3$ (Merck, Analar) solution in a 2-L polyethylene (HDPE) vessel. The resulting solution was then brought to a 2-L total volume with deionized water (18 MΩ cm^{-1}) and heated at 70 °C for 68 h. The precipitated product was recovered by centrifugation (60 min, 2500 rpm) using (HDPE) bottles of 250 mL. Supernatant solutions were decanted and subsequently vacuum filtered through 0.45 μm Millipore® HA-type filters to recover suspended goethite crystallites. Total goethite was later resuspended in deionized water and centrifuged as above until the conductivity and pH of the supernatant solution remained constant after three consecutive wash cycles. The precipitated product was freeze-dried [15].

2.2. Material

All chemicals and reagents used for experiments and analyses were of analytical grades. A stock solution of 1000 mg L^{-1} U (VI) was prepared by dissolving an appropriate amount of $UO_2(NO_3)_2{\cdot}6H_2O$ in deionized water. The initial pH of the working solutions was adjusted by addition of HNO_3 or Na_2CO_3. Dibenzoyl methane-tri-*n*-octylphosphine oxide (DBM-TOPO) and salicylic acid were obtained from Merck Co. The buffer solutions (pH 4, 7 and 9) to calibrate the pH-meter Model 8521 from Hanna Instruments were also purchased from Merck.

2.3. Batch sorption experiment

Batch sorption experiments were carried in a thermostated shaker bath, GFL-1083 model. Goethite (0.01 g), which has 75 μm particle sizes, was added to 10 mL solution containing various uranium concentrations at different temperatures for various contact time. The pH was adjusted by adding HNO_3 and Na_2CO_3 to the solutions at the each experiment. The suspension was filtered by using Whatman filter paper No:44. A simple and sensitive spectrophotometric method was used in the experiments to determine uranium in solution. The uranium remained in solution was analyzed with the DBM-TOPO as complexing agent at 405 nm against reagent blank employing spectrophotometric method on Shimadzu UV-1601 UV-VIS spectrophotometer [23,24]. The amount of sorbed uranium was estimated from the difference of the uranium concentrations in the aqueous phase before and after the removal. The influence of specific process parameters such as initial uranium concentration, pH of the solution, contact time and temperature was determined by calculating uranium (VI) sorption by goethite and changing a parameter and keeping other parameters constant. Each experiment was repeated at least three times and the results were given at the average values. The percentage sorption of uranium from aqueous solution was computed as follows:

$$\text{Sorption}\% = C_{\text{int}} - C_{\text{fin}} / C_{\text{int}} \times 100 \quad (1)$$

Where, C_{int} and C_{fin} are the initial and final uranium concentration, respectively.

The uranium sorption capacity of goethite was determined after obtaining the optimum conditions. The 0.01 g of the adsorbent contacted with 10 mL of 2380 mg L^{-1} of standard uranium solution at 30 °C for 24 h. The sorption capacity for UO_2^{2+} was determined spectrophotometrically using salicylic acid method as complexing agent at 468 nm against reagent blank [25]. The amount of sorbed uranium was estimated from the difference of the uranium concentrations in the aqueous solution before and after sorption. Each experimental result was obtained by averaging the data from three parallel experiments.

2.4. Desorption experiments

Goethite which is loaded with uranium at optimum adsorption conditions was used for desorption studies. For desorption experiments, loaded and dried sorbent (0.01 g) was contacted with 0.1 M HCl , HNO_3 , H_2SO_4 , NaCl, $NaNO_3$, NaOH, CH_3COONa and stirred at 750 rpm for 120 min at 25 °C. After obtained the appropriate desorption reagent, different concentrations of this reagent were tested to recovery of uranium from the sorbent at the same experimental. After that, loaded sorbent was contacted with appropriate desorption reagent using different contact time at the same experimental conditions. The final uranium concentration in the aqueous phase was determined with a Shimadzu UV-1601 UV-VIS spectrophotometer by measuring absorbance at λ_{max} of 405 nm. The desorption ratio was calculated from the amount of uranium sorbed on the sorbent and the final uranium concentration in the desorption medium, using the following equation,

$$\text{Desorption ratio (\%)} = (\text{amount of metal ion desorbed / amount of metal ion adsorbed}) \times 100 \quad (2)$$

2.5. Applications of goethite

The goethite can take up a quite high quantity of uranium from the aqueous solution containing only uranium. However, the uranium uptake decreases when the goethite is treated with solution containing matrix (competing ions) elements. To determine the competing ions effect on the uranium uptake, the uranium solution from matrix medium on the goethite was studied by batch technique. Acidic mine wastewater including uranium was used as matrix medium. The ore sample is taken from the Koprubasi-Manisa district in Western Aegean Region in Turkey. It is well known that there are uranium anomalies in these districts and uranium exploration of this ore sample was accomplished by radiometric and chemical analysis at Ege University, Institute of Nuclear Sciences [26,27]. The leaching conditions were given in Table 1 [28].

A known weight, i.e., 0.01 g of the goethite was equilibrated with 10 mL of leaching solutions containing uranium at a fixed temperature (25 °C) in a thermostated shaker for 2 h. After equilibration, the suspension was filtered with Whatman 44 paper. The amounts of uranium and other elements in the solutions were determined by Perkin Elmer Optima 2000 DV Inductively Coupled Plasma–Optical Emission Spectrometer (ICP-OES) on the basis of initial concentration.

Also a synthetic matrix solution including some heavy metals was prepared as 20 mg L^{-1} for Al^{3+}, Cd^{2+},Pb^{2+}, Ni^{2+}, Cu^{2+}, Fe^{2+} and 40 mg L^{-1} for UO_2, respectively, and equilibrated with 10 mL of matrix solutions at a fixed temperature (25 °C) in a thermostated shaker for 2 h for goethite. After equilibration, the suspension was filtered with Whatman 44 paper. The amounts of uranium and other

Table 1
Conditions of the leaching processes.

Parameter	Uranium-acidic leachate solution
Amounts of ore	500 g
Solid/aqua ratio	2/3 g/ml
Concentration of reagent	175 kg H_2SO_4/ton
Leaching time	3 h
Temperature	24 °C