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Modeling of mass transfer of uranium on different nanoadsorbents for the remediation of contaminated aquatic system

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ABSTRACT

Iron oxides, as a group, have important applications as pigments, catalysts, gas sensors, magnetic recording media, etc. Among these iron oxides, akaganeite (β-FeOOH) and goethite (α-FeOOH) have attracted much investigation because of its unique sorption, ion exchange, and catalytic properties. The present study on uranium transport through akaganeite and goethite has been performed using batch experiments. The transport mechanism of uranium which comprises a diffusion process from aqueous phase on akaganeite and goethite was described by two kinetic models consisting of derived equations: the homogenous particle diffusion model (HPDM) and the shell progressive model (SPM). It was confirmed that the process was controlled by diffusion rate of uranium that penetrated the reacted layer at uranium concentrations in range of 75–150 mg/L. The effective particle diffusion coefficient D_{eff} values were calculated from both the HPDM and SPM equations. The theory–experiment comparison has revealed that predicted values are in excellent agreement with the experimental values.

Keywords: Uranium; Nano iron oxides; Adsorption; Kinetic models; Diffusion coefficient

1. Introduction

Environmental pollution due to the accumulation of the toxic contaminants, such as heavy metals, synthetic pollutants, nuclear waste liquids, etc., is one of the greatest problem that the world is facing today. Among these toxic pollutants, uranium (U) has high radioactivity and chemical toxicity. Excessive amounts of wastewater containing uranium are produced by nuclear industry, ore mining, and industrial applications. Accumulated uranium in the environment can reach the food chain and then excessive intake of uranium may cause liver and kidney damages and even death [1]. Therefore, removal of the contaminants by choosing an effective and economic method is quite important. Traditional methods have been employed for the elimination of radionuclides and toxic heavy metal ions such as electrodeposition, solvent extraction, coagulation, electrochemical treatment, sorption,

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membrane processing, ion exchange, and reverse osmosis [2,3]. Among these approaches, sorption has been widely employed to remove radionuclides and heavy metal ions in industrial wastewater because it is cost-effective, simple operation, and high efficiency.

The iron oxides are common and important materials in the environment and they exist mostly in atmosphere, soil, water, sedimentary rock, and mine drainage. They can exist as oxides, hydroxides, or oxyhydroxides forms. Iron oxyhydroxides such as akaganeite, goethite, magnetite, and hematite might represent a main role in the retardation of the transport of different contaminants due to their high sorption capacities for anionic and cationic pollutants. For this reason, iron particles, iron oxides, and iron oxyhydroxides have been used as adsorbents by many researchers for the removal of uranium from aqueous solutions [4–11].

Akaganeite, β-type FeOOH, has a large tunnel-type structure where iron atoms are strongly bonded to framework, and this tunnel structure makes it especially an interesting material in the areas of catalysis and ion exchange [4]. Goethite, α-FeOOH, is a major constituent of many soils, sediments, and iron ores. α-FeOOH particles are often used as adsorbent in the adsorption/desorption phenomena because at natural pH values, it is highly insoluble and has a net positive surface charge that makes it an effective sorbent of metal anion complexes from aqueous solutions [12–15].

In this study, removal of uranium from aqueous solutions by akaganeite and goethite was studied using adsorption technique. Synthetic adsorbents were synthesized in the laboratory and then characterized by several techniques that were given in the previous studies [4,5]. Yet, evaluation of the sorption data with the kinetic models such as HPDM and SPM models has not been considered. Therefore, the purpose underlying this present work is to evaluate the sorption kinetic process from the microscopic point of view and to investigate the applicability of the homogeneous particle diffusion model (HPDM) and shell progressive model (SPM) kinetic models in the analysis of the experimental data.

2. Materials and methods

2.1. Materials

Synthesis of akaganeite and goethite was first reported in our previous studies [4,6]. In the previous paper, akaganeite samples were prepared by two different methods, but in this study, akaganeite sample which was prepared by precipitation from aqueous solution of iron(III) chloride by adding of aqueous solution of ammonium carbonate was used. Characterization and U(VI) sorption properties of the akaganeite and goethite were presented in previous papers [4–6].

All chemicals and reagents used for experiments and analyses were of analytical grades. A stock solution of 1,000 mg/L U(VI) was prepared by dissolving an appropriate amount of $UO_2(NO_3)_2 \cdot 6H_2O$ provided by Merck, A. R, in deionized water. The pH of the working solutions was adjusted by the addition of HNO_3 or Na_2CO_3. Dibenzoyl methane-tri n-octyl phosphine oxide (DBM-TOPO) was 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.

2.2. Batch adsorption experiments

Batch adsorption experiments were carried in a thermostated shaker bath, GFL-1083 model. Akaganeite and Goethite (0.01 g), which have 75 μm particle sizes, were added to 10 mL solution containing various uranium concentrations at different temperatures for various contact times. The effect of pH on the adsorption capacity of akaganeite and goethite was investigated using solution of 50 mg/L uranium(VI) for a pH range of 2.0–8.0 at 25°C for 120 min and maximum uranium attenuation was obtained at pH 6.0 for both of the adsorbents. The suspension was filtered 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 (detection limit: 20 mg/L) [16]. The amount of adsorbed uranium was estimated from the difference of the uranium concentrations in the aqueous phase before and after the adsorption. Each experiment was repeated at least three times and the results given are the average values.

For adsorption kinetics, concentrations of 150 and 75 mg/L U(VI) solutions were agitated with known amounts of adsorbents akaganeite and goethite, respectively at different time intervals until the equilibrium was achieved.

3. Results and discussion

3.1. Kinetic studies

Kinetic studies are important to understand the dynamic of the reaction such as solute uptake rate that evidently controls the residence time of adsorbate uptake at the solid–solution interface. Analyses of the rate data give information about the mechanism of the sorption process such as mass transfer and chemical reaction. Moreover, in order to understand the ion-exchange/sorption kinetic process from the microscopic point of view and to define which mechanism controls the adsorbate uptake, the kinetic models selected to describe the ion-exchange/sorption data are two models widely used for fitting: HPDM and SPM [17].

Sorption kinetics is generally controlled by various factors including:

(1) Transport of molecules or ions from the bulk of the solution to the exterior surface of adsorbent particles through a boundary layer (liquid film or external diffusion);
(2) Diffusion of the molecules or ions through the interior pores of the adsorbent (intra particle or internal diffusion); and
(3) Adsorption of adsorbate ions or molecules onto the adsorbent active sites by the mechanisms of ion exchange, precipitation, complexation, or chelation.

One of the steps which offers much greater resistance than the others can be considered as the rate-limiting step of the process.

3.1.1. Homogeneous particle diffusion model

In this model, the rate-determining step of sorption is normally described by either diffusion of ions through the liquid film surrounding the particle, called film diffusion, or diffusion of ions into the sorbent beads, called particle diffusion mechanism. The Nernst Plank equation [18] was used to establish the HPDM equations. If the diffusion of ions, from the solution to the sorbent beads, is the slowest step i.e. the rate-determining step, the liquid film diffusion model controls the rate of sorption. The film diffusion mass transfer rate equation presented as:

$$-\ln(1 - X(t)) = K_{li}t \quad \text{with} \quad K_{li} = \frac{3DC}{rC_r}, \tag{1}$$

where C (mol/L) and Cr (mol/L) are the equilibrium concentrations of the ion in solution, and solid phases, respectively, D (cm/s) is the diffusion coefficient in the liquid phase, $X(t)$ is the fractional attainment of equilibrium at time t, r (cm) is the radius of the adsorbent particle, and t (min) is the time.

$X(t)$ values could be calculated using the equation:

$$X(t) = \frac{q_t}{q_e} \tag{2}$$

where q_t is the concentration of the sorbed ion (mg/g) at time t and q_e is the concentration of the sorbed ion (mg/g) at the equilibrium.

If the diffusion of ions through the adsorbent beads is the slowest step, the particle diffusion will be the rate-determining step, and the particle diffusion model can be applied to calculate the diffusion coefficient. Then, the rate equation is expressed by:

$$-\ln(1 - X^2(t)) = 2Bt \quad \text{with} \quad B = \frac{\Pi^2 D_r}{r^2} \tag{3}$$

where D_r (cm^2/s) is the particle diffusion coefficient.

3.1.2. SPM or the Shrinking core model

This model is based on the fluid-particle chemical reactions [19] and the reaction is considered to take place first at the outer surface of the particle. Then the region of the reaction goes into the solid and the reacting particle shrinks during the reaction. The SPM assumptions can be mentioned as (1) Pore diffusivity is independent of concentration, (2) Adsorption isotherm is irreversible, (3) Pseudo steady-state approximation is valid, (4) The driving force in both film and particle mass transfer is linear, (5) Adsorbent particles are spherical [20].

The slowest of these steps is considered the rate-determining step. If the process is the fluid film diffusion control, the model is represented by:

$$X = \frac{3C_A K_F}{zrC_s}t \tag{4}$$

If the process is the product layer diffusion control, the model is represented by:

$$[3 - 3[1 - X]^{2/3}\ 2X] = \frac{6D_e C_A}{zr^2 C_s}t \tag{5}$$

If the process is the chemical reactions control, the model is represented by:

$$[1 - (1 - X)^{1/3}] = \frac{k_s C_A}{r}t \tag{6}$$

where C_A (mol/L) is the concentration of metal in solution, C_s (mol/L) is the concentration of metal ions

Table 1
The calculated values of diffusion coefficients for akaganeite and goethite

	HDPM				SPM					
	$-\ln(1-X^2)$		$-\ln(1-X)$		X		$[3-3(1-X^{2/3})-2X]$		$[1-(1-X^{1/3}]$	
Adsorbent	R^2	D_r (m^2/s)	R^2	D (m/s)	R^2	K_F (cm^2/s)	R^2	D_e (cm^2/s)	R^2	K_S (cm/s)
Akaganeite	0.21	3.37×10^{-9}	0.23	3.00×10^{-6}	0.42	3.43×10^{-8}	0.32	1.70×10^{-10}	0.30	3.38×10^{-3}
Goethite	0.85	4.87×10^{-9}	0.85	7.68×10^{-6}	0.70	3.25×10^{-8}	0.81	2.77×10^{-10}	0.83	7.57×10^{-3}

remained in solution after the sorption process, K_F (cm/s) is the mass transfer coefficient of species through the liquid film, D_e (cm^2/s) is the diffusion coefficient through the reacted layer in the solid phase, k_s (cm/s) is the reaction constant based on surface, and r (cm) and z are the average radius of adsorbent particles and the stoichiometric coefficient, respectively. All experimental data were treated graphically with all the fractional attainment of equilibrium functions $G(X) = f(t)$ defined above for both the HPDM and SPM models.

Experimental data obtained from kinetic studies for the two materials were processed by applying the HPDM and SPM for establishing the rate-decisive step of the adsorption process.

The results of the linear regression analysis for the two models are summarized in Table 1. The linear correlations coefficients indicate that particle diffusion can be considered as the rate-limiting step of the process for goethite since the fit gives a relatively straight line. Figs. 1 and 2 show the results of the different U(VI) sorption kinetics in the form of Eqs. (1) and (3) for the HPDM model and Eqs. (4–6) for the SPM model. It can be observed from Figs. 1 and 2 that film diffusion and chemical reaction control can be discarded as the controlling step since the fit did not give a linear dependence for U(VI) sorption onto akaganeite but external diffusion can be a rate-limiting step for akaganeite hence it gives a straight line. On the other hand, film diffusion and chemical reaction control can be a controlling step since fit gave a linear dependence with little derivations for goethite adsorbent.

The slope values were used to calculate diffusion coefficients using the equation for all diffusion equations. The calculated values of diffusion coefficients are presented in Table 1.

A comparison of the diffusion coefficients proposed for both kinetic models shows that the diffusion coefficient values for akaganeite are greater than for goethite, so in the first case, mass transfer resistance is lower and the adsorption process arises more easily. These results also support the rate-limiting steps for both the adsorbents for U(VI) ions that is fixed for mass transfer.

These results are expected to be different when these materials are tested in real waters. Because, the presence of dissolved carbonates which act as the natural buffer for most surface waters and groundwater is the major problem, and effect the removal of uranium by iron oxides. At neutral pH, carbonate species of uranium such as $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$

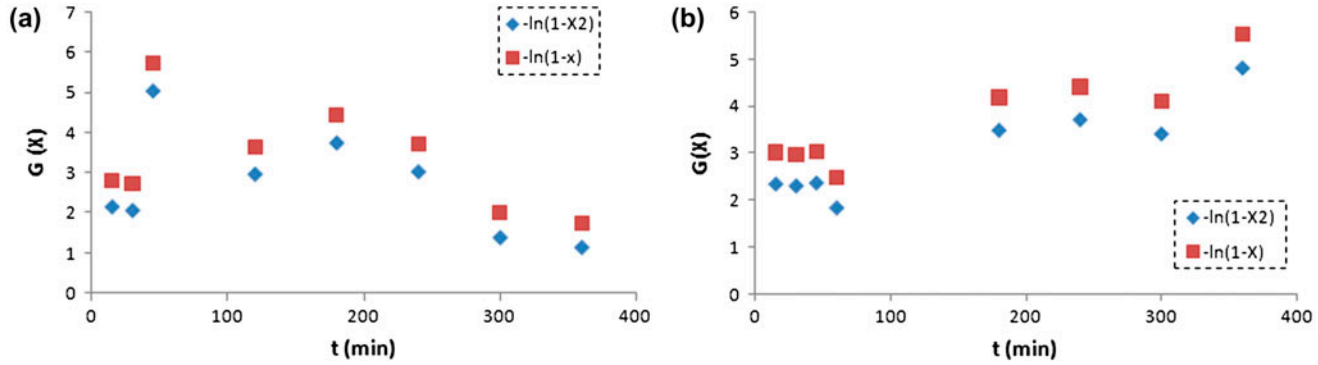

Fig. 1. Test of the kinetic model equations $G(X)$ vs. t defined by the homogenous particle diffusion model for U(VI) sorption on akaganeite (a) and goethite (b) at the concentrations of 150 and 75 mg/L, respectively.

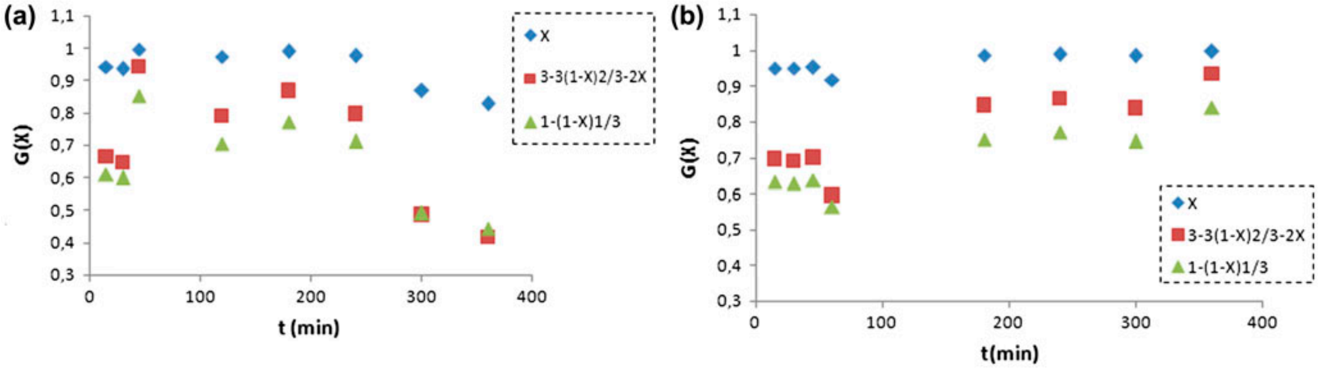

Fig. 2. Test of the kinetic model equations $G(X)$ vs. t defined by the SPM for U(VI) sorption on akaganeite (a) and goethite (b) at the concentrations of 150 and 75 mg/L, respectively.

prevail. Under acidic conditions, uranium is present in the uranyl form (UO_2^{2+}). However at pH > 5, that is the pH range of the most waters (i.e. 6.0–8.0), uranyl carbonate complexes are formed, which become anionic at higher pH values and therefore cannot be efficiently adsorbed onto iron oxyhydroxides. Therefore, if these adsorbents are used for real waters, the effect of carbonate concentration on the uranium sorption should be further examined [11,21].

4. Conclusion

The U(VI) removal was successfully performed by two iron-based adsorbents. Due to the lack of precise information on the uranium sorption reactions onto iron oxyhydroxides, it is unlikely that a rigorous kinetic model can be developed. For this aim, all experimental data were treated graphically and compared with all fractional attainment of equilibrium functions ($G(X) = f(t)$) defined for both models HPDM and SPM as distinct from the similar studies. HPDM and SPM models are used in the study of U(VI) removal by akaganeite and goethite. Fick's law and the shell progressive mechanisms represent good general approaches to the kinetics of the U(VI) sorption on akaganeite and goethite. Results obtained from the kinetics models indicated that the rate-determining step is external diffusion and film diffusion chemical reaction control for akaganeite and goethite, respectively. In addition, calculated diffusion coefficients provided an insight into the diffusion mechanism.

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