



Adsorption of Uranyl Ion onto Peat with Pseudo-Second-Order Kinetic Models

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Kinetic experiments were carried out to investigate the effects of pH and initial uranyl ions concentration on the adsorption capability of peat by batch tests. Both the regression coefficient and the deviation of adsorption capacity at equilibrium were employed as error analysis methods to determine the best-fitting kinetic model. The results indicate that the adsorption process can be described by type 1 of the pseudo-second-order kinetic model excellently by linear regression method when compared to other type of the pseudo-second-order kinetic model.

Key Words: Peat, Uranyl ions, Adsorption, Pseudo-second-order kinetic model, Linear regression.

INTRODUCTION

Uranium is toxic and radioactive for both the environment and the people even at trace levels. Normal functioning of the kidney, brain, liver, heart and other systems can be affected by uranium exposure. The increasing nuclear wastewater containing uranium being released into the environment is a serious problem worldwide¹.

Uranium in wastewater is a widespread issue and is usually found as an anion complex. The techniques developed for the removal of uranium from residual waters include chemical precipitation, ion exchange, oxidation/reduction, reverse osmosis, membrane processes, adsorption and solvent extraction. Among the various treatment technologies, the use of adsorption systems for the uranium removal from large volumes of solution are economically viable and environment friendly methods from techno-economic considerations. However, the high production and regeneration costs of effective commercial synthetic adsorbents have prompted the search for natural materials that are available and accessible in large quantities^{2,3}. Peat is the partially decomposed remains of plants and the first material formed in the process that transforms plant matter into coal. Peat is an example of such an adsorbent. As known, peat is a rather complex material containing lignin and cellulose as major constituents. Because of the fairly polar character of this material, the specific adsorption for dissolved transition metals and polar organic molecules is quite high^{4,5}.

Adsorption processes include equilibrium and kinetic aspects. Although the time dependence of adsorption process

is at least as important as the features of the adsorption system in equilibrium, the kinetics of adsorption is one of the fundamental studies necessary for better understanding the mechanisms of adsorption and optimizing its operational conditions. The faster adsorption kinetics has significant practical importance as it facilitates smaller adsorption equipment volumes ensuring higher efficiency and economy^{6,7}. Few researchers have predicted the rate at which uranium is removed from different pH aqueous solution containing different initial uranyl ions concentration.

In this work, peat has been used as uranium adsorbent from aqueous solutions. The solution pH, contact time and initial uranyl ions concentration are important parameters for the removal of uranyl ions present in aqueous media through adsorption. Although several kinetic models in literature such as first-order kinetic model and second-order kinetic model are available, except Ho's pseudo-second-order kinetic model no other kinetic model was fitted well to the experimental kinetic data for most of the adsorption systems⁷. Ho⁸ described adsorption, which included chemisorption and provided a different idea to the second-order equation called a pseudo-second-order rate expression. Moreover, the pseudo-second-order equation does not have the problem of assigning effective adsorption parameters, *i.e.*, the adsorption capacity, the rate constant of pseudo-second-order, without knowing any parameter beforehand. Even though non-linear method provides a better result, the linear least-square method is still often preferred in favour of its simplicity and convenience⁸. However Ho^{7,8} did not show the reason why the linear regression was used. The applications of the kinetic models have been studied

to explain the adsorption characteristics of peat and understand the rate of removal of different initial uranyl ions concentration at different pH value in a better way.

EXPERIMENTAL

The peat sample from Xinyuan city of Liaoning Province of China was dried in an oven at 100 °C for 24 h and then was sieved using a British Standard 80 mesh sieve to maintain a uniform particle size. The sample was stored in a sealed, dry container for subsequent use. The synthetic solution of U(VI) were prepared from $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (AR grade) by dissolving in slightly acidified double distilled water. All chemicals were analytical grade.

Fourier transform infrared spectroscopy (NICOLET 380) was done to identify the chemical functional groups present on native peat for wavenumbers in the range of 4000-400 cm^{-1} . CHNS Elemental analyzer (Vario EL) was used for the elements analyses and UV-Visible spectrophotometer (721E) was used to determine the concentration of uranyl ions using arsenazo III as chromogenic reagent at a wavelength of 665 nm.

Batch static method was performed to optimize the basic experimental conditions such as contact time, pH and initial uranyl ions concentration. Adsorption capacity of peat was carried out by agitating pre-weighed amount of peat with 8 mL aqueous solution of uranium of desired initial concentration, temperature and pH in different polyethylene plastic centrifuge tubes on shaking thermostat at 100 rpm for predetermined time intervals, followed by centrifugation to separate peat from uranyl ions solutions. Residual concentration in the supernatant uranium solutions was determined by spectrophotometry. The initial pH values of the solution were adjusted by adding negligible volumes of either 0.1 mol/L HNO_3 or NaOH solutions. Uranyl ions adsorption on peat was calculated by eqn. (1).

$$Q_t = \frac{(C_0 - C_t)V}{W} \quad (1)$$

where, Q_t is the adsorption at any time t (mol/g), C_0 is the initial concentration of uranium solution (mol/L), C_t is the concentration of uranium solution at any time t (mol/L), V is the volume of the solution (L), W is the mass of dry peat used (g).

RESULTS AND DISCUSSION

Elemental analyses show that the carbon content was 30.41 %, whereas the contents of hydrogen, nitrogen and oxygen in peat were 3.76, 1.83 and 64.00 %, respectively. Peaks observing in the infrared spectra of peat are assigned to various groups and bonds in accordance with their respective wavenumbers as reported in literature⁹.

Generally speaking, the adsorption of heavy metals ions has often been observed to occur in two stages; an initial rapid uptake due to surface adsorption and a subsequent slow adsorption due to intra-particle diffusion of the metals ions. Fig. 1 shows the effect of contact time on adsorption of uranyl ions with peat. The percentage of removed uranium increases quickly at the beginning as the contact time increases. That is

probably due to much free peat active site being available for uranyl ions at the beginning. It does not seem to be much benefit from contact time longer than 2 h.

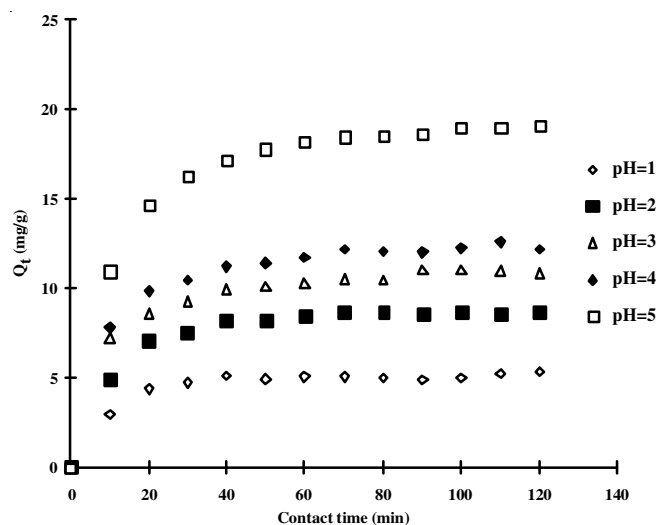


Fig. 1. Effect of pH and contact time on adsorption of uranyl ions onto peat; experimental conditions: initial uranyl ions concentration = 1 mg/L; solid/liquid ratio = 5 g/L; temperature = 25 °C

In aqueous solution and acidic pH conditions, uranium normally exists in its hexavalent form as the uranyl cation UO_2^{2+} ¹⁰. The effect in the pH region between 1 and 5 on the amount of uranyl ions adsorbed on peat is also investigated in Fig. 1. In all cases, the uranyl ions uptake increases as the pH increases. This result is consistent with previous studies¹¹. The increase of the amount of uranyl ions adsorbed at equilibrium with an increase in pH may be due to the decrease of the competitive effect of the protons with uranyl ions.

An expression of the pseudo-second-order rate based on the solid capacity has been presented for the kinetics of adsorption of divalent metal ions onto peat. The pseudo-second-order kinetic model is considered more appropriate to represent the kinetic data in bio-sorption systems. However, the pseudo-second-order kinetic model can be linearized as four different following types. Four different linear regressions will produce very different outcomes and result in different parameter estimates⁸.

$$\text{Non-linear form: } Q_t = \frac{kQ_c^2 t}{1 + kQ_c t} \quad (2)$$

$$\text{Linear form of type 1: } \frac{t}{Q_t} = \frac{1}{kQ_c^2} + \frac{1}{Q_c} t$$

Plot form: $\frac{t}{Q_t}$ vs. t (3)

$$\text{Linear form of type 2: } \frac{1}{Q_t} = \frac{1}{kQ_c^2} \times \frac{1}{t} + \frac{1}{Q_c}$$

Plot form: $\frac{1}{Q_t}$ vs. $\frac{1}{t}$ (4)

$$\text{Linear form of type 3: } \frac{Q_t}{t} = kQ_c^2 - kQ_c Q_t$$

Plot form: $\frac{Q_t}{t}$ vs. Q_t (5)

TABLE-1
PSEUDO-SECOND-ORDER KINETIC PARAMETERS OBTAINED BY DIFFERENT LINEAR METHODS AT DIFFERENT pH VALUE

Type	Parameters	pH = 1	pH = 2	pH = 3	pH = 4	pH = 5	Mean
Type 1	$Q_{e,exp}$ (mg/g)	5.3793	8.7153	11.0632	12.5791	19.0632	-
	$Q_{e,cal}$ (mg/g)	5.3819	9.0498	11.3766	12.7877	19.8807	-
	Deviation (%)	0.0483	3.838	2.8328	1.6583	4.2884	2.5332
	k (g/mg min)	0.0461	0.0249	0.0179	0.0164	0.0092	-
	R	0.9950	0.9976	0.9974	0.9975	0.9976	0.9970
Type 2	$Q_{e,cal}$ (mg/g)	5.5705	9.7087	11.4548	13.0719	20.7469	-
	Deviation (%)	3.5544	11.3983	3.5397	3.9176	8.8322	6.2484
	k (g/mg min)	0.0207	0.0112	0.0144	0.0114	0.0055	-
	R	0.9260	0.9716	0.9846	0.9942	0.9946	0.9742
Type 3	$Q_{e,cal}$ (mg/g)	5.7891	9.6699	11.5396	13.0958	20.6730	-
	Deviation (%)	7.6181	10.9532	4.3062	4.1076	8.4445	7.0859
	k (g/mg min)	0.0196	0.0115	0.0136	0.0112	0.0056	-
	R	0.8188	0.9336	0.9716	0.9862	0.9920	0.9404
Type 4	$Q_{e,cal}$ (mg/g)	5.6146	9.5614	11.4900	13.0711	20.6471	-
	Deviation (%)	4.3742	9.7082	3.8578	3.9112	8.3087	6.0320
	k (g/mg min)	0.0248	0.0125	0.0140	0.0113	0.0056	-
	R	0.8188	0.9336	0.9716	0.9862	0.9920	0.9404

$$\text{Linear form of type 4: } Q_t = Q_e - \frac{1}{kQ_e} \times \frac{Q_t}{t}$$

$$\text{Plot form: } Q_t \text{ vs. } \frac{Q_t}{t} \quad (6)$$

where: k is the rate constant of adsorption, g/mg min; Q_e is the amount of uranyl ions adsorbed onto peat at equilibrium, mg/g; Q_t is the amount of uranyl ions adsorbed onto peat at any time t , mg/g.

The parameters in the four types of linearized pseudo-second-order kinetic equation were determined from the slopes and intercepts of the plots and presented in Table-1. The deviation of Q_e is provided in Table-1 to infer the validity of kinetic models, defined as:

$$\text{Deviation (\%)} = \frac{Q_{e,cal} - Q_{e,exp}}{Q_{e,exp}} \times 100 \quad (7)$$

where $Q_{e,exp}$ and $Q_{e,cal}$ are the experimental and calculated Q_e values respectively.

Parameters Q_e and k as well as the regression coefficient (R) of determination of Type 1 to Type 4 expressions differed. The excellent regression coefficients indicate that pseudo-second-order kinetics is applicable to the adsorption system studied. It is found that Type 1 is superior to other three ones for the description of kinetic data. The first fitness is justified based on the fact that the mean regression coefficients are 0.9970, 0.9742, 0.9404 and 0.9404, respectively. The second fitness is done based on the fact that the mean deviations of Q_e are 2.5332, 6.2484, 7.0859 and 6.0320 %, respectively. Type (1) will be adopted in order to produce accurate outcomes. In addition, the mean deviation of Q_e method for error analysis may be better to determine the best-fitting model than the mean regression coefficient method.

As evidenced by the values of the rate constant of adsorption (k) shown in Table-1, the rate constant of adsorption decreases with the increase of pH from 1 to 5. It takes longer contact time to reach the equilibrium for pH from 1 to 5. Portioning of the hydrolyzed uranium species depends on the solution pH and on the total uranium concentration in the solution. Variation in pH affects uranium speciation and

stability of soluble species as well as the peat surface properties. In the range of acidic to near neutral pH values, more hydrolyzed uranium species (*i.e.*, $[\text{UO}_2(\text{OH})]^+$, $[(\text{UO}_2)_2(\text{OH})_2]^{2+}$, $[(\text{UO}_2)_3(\text{OH})_5]^+$ and $[(\text{UO}_2)(\text{OH})_2]^0$) would compete the active adsorption sites with the free uranyl ions (UO_2^{2+}). It possibly suppresses the enhancement of the rate of uranium adsorption on the peat¹². On the other hand, as more uranyl ions are adsorbed onto the peat with increase of pH from 1 to 5, more hydrogen ions are released from the peat into the solution. More hydrogen ions of the solution might prolong the contact time to the equilibrium between uranyl ions and the peat.

Fig. 2 shows the effect of contact time on adsorption of uranyl ions with peat. The percentage of removed uranium increases at the beginning as the contact time increases. The effect of initial uranyl ions concentration from 1 mg/L to 4 mg/L on the amount of uranyl ions adsorbed on peat is also investigated in Fig. 2. In all cases, the uranyl ions uptake increases and equilibrium time prolongs as the initial uranyl ions concentration increases. This result is consistent with previous studies of Humelnicu *et al.*¹³.

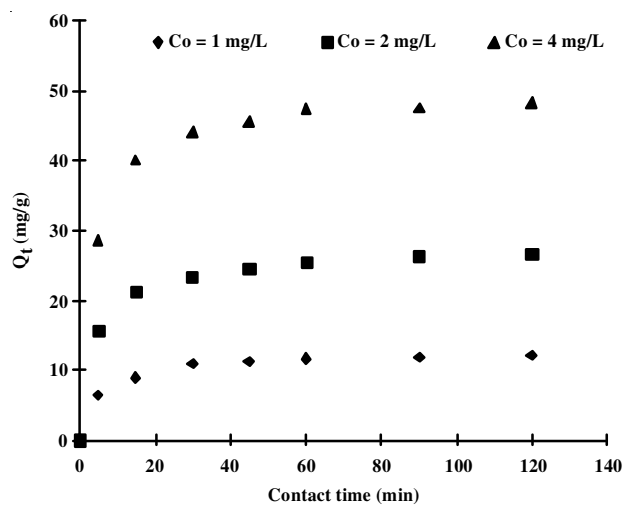


Fig. 2. Effect of initial uranyl ions concentration and contact time on adsorption of uranyl ions onto peat; experimental conditions: pH = 3; solid/liquid ratio = 5 g/L; temperature = 25 °C

TABLE-2
PSEUDO-SECOND-ORDER KINETIC PARAMETERS OBTAINED BY DIFFERENT LINEAR
METHODS AT DIFFERENT INITIAL URANYL IONS CONCENTRATION

Type	Parameters	Co = 1 mg/L	Co = 2 mg/L	Co = 4 mg/L	Mean
Type 1	$Q_{e,exp}$ (mg/g)	12.1793	26.7153	49.0032	-
	$Q_{e,cal}$ (mg/g)	12.2549	27.027	49.0196	-
	Deviation (%)	0.6207	1.1667	0.0335	0.6070
	k (g/mg.min)	0.0384	0.0113	0.0077	-
	R	0.9991	0.9986	0.9991	0.9989
Type 2	$Q_{e,cal}$ (mg/g)	12.3457	26.8097	49.7514	-
	Deviation (%)	1.3663	0.3534	1.5268	1.0821
	k (g/mg.min)	0.0176	0.0103	0.0054	-
	R	0.9870	0.9945	0.9990	0.9935
Type 3	$Q_{e,cal}$ (mg/g)	12.4720	26.9288	49.6771	-
	Deviation (%)	2.4033	0.7992	1.3752	1.5259
	k (g/mg.min)	0.0165	0.0099	0.0054	-
	R	0.9743	0.9866	0.9972	0.9860
Type 4	$Q_{e,cal}$ (mg/g)	12.422	26.8771	49.6543	-
	Deviation (%)	1.9927	0.6056	1.3287	1.3090
	k (g/mg.min)	0.0170	0.0101	0.0055	-
	R	0.9743	0.9866	0.9972	0.9860

It is found that Type 1 is also superior to other three ones for the description of kinetic data. The one fitness is based on the fact that the mean regression coefficients are 0.9989, 0.9935, 0.9860 and 0.9860, respectively. The second fitness is done based on the fact that the mean deviations of Q_e are 0.6070, 1.0821, 1.5259 and 1.3090 %, respectively. Type (1) will be adopted in order to produce accurate outcomes, too.

The values of the rate constant of adsorption (k) shown in Table-2 indicate that the rate constant of adsorption decreases with the increase of initial uranyl ions concentration from 1 mg/L to 4 mg/L. The adsorption of uranyl ions on peat needs longer contact time to reach the equilibrium for initial uranyl ions concentration from 1 mg/L to 4 mg/L.

Conclusion

The pH value and initial uranyl ions concentration of the solution are important factors for the removal of uranyl ions from aqueous solutions. The adsorption of uranyl ions increases with increase of pH from 1 to 5 and increase of initial uranyl ions concentration from 1 mg/L to 4 mg/L. However it takes longer contact time to reach the adsorption equilibrium with increase of pH from 1 to 5 and increase of initial uranyl ions concentration from 1 mg/L to 4 mg/L. Adsorption kinetic data of uranyl ions onto peat are best fit by Type 1 of pseudo-second-order kinetic model. The mean deviation of Q_e method for error analysis may be better to

determine the best-fitting model than the mean regression coefficient method.

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