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Adsorption of Th (IV) by peat moss

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ABSTRACT

The peat moss has been characterized and used for the removal of Th (IV) from aqueous solutions using batch adsorption experiments. Effects of factors such as pH, ionic strength, contact time, peat moss dosage and initial thorium concentration on thorium adsorption were studied. The results demonstrated that adsorption of Th (IV) on peat moss increase with increasing pH from 1 to 12 and with decreasing ionic strength. The kinetic process of adsorption can be described by the pseudo-second-order kinetics equation satisfactory. The adsorption isotherm was fitted reasonably well by Langmuir adsorption model.

Keywords: Adsorption; Peat moss; Thorium

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1. Introduction

Thorium (Th) is only stable at its valence +IV in solution, and is usually selected as a chemical analogue for other tetravalent actinides, besides the fact that is has 4f electron [1]. Over the last fifty years there has been interest in utilizing thorium as a nuclear fuel since it is much more abundant in nature than uranium. The use of thorium fuel in the Candu reactors at Qinshan country in China was developed and demonstrated in mid-2009. Thorium currently occurs with rare earth element, with China producing 97 percent of the world's thorium. All twelve known isotopes of thorium are radioactive and find their way to the natural surface water bodies and environment. Environmental contamination caused by Th (IV), even at trace levels, is a serious problem worldwide. For this reason, removal of thorium from wastewater is of great importance [2].

The commonly used procedures for removing thorium from effluents include chemical precipitation, ion exchange, oxidation/reduction, reverse osmosis, membrane filtration and solvent extraction [3]. These techniques have disadvantages like ineffective thorium removal at lower concentration, high reagent and energy requirements, and generation of toxic sludge or other waste products that require further disposal. The use of adsorption systems for the heavy metal ions elimination from diluted solutions has emerged as a potential alternative method from techno-economic considerations. A search for a low-cost and easily available adsorbent has led to the investigation of materials of biological and agricultural origin as potential metal ion adsorbents, such as peat moss [4,5], rice hulls [6], fibers [7], apple residues [8], plant leaves [9], saw dust [6] and tree leaves [10–13].

Peat moss is a rather complex porous material mainly containing lignin and cellulose [14]. Functional groups in lignin that include alcohols, aldehydes, ketones, acids, phenolic hydroxides, and ethers allow it to bind with various metals ions [15–17]. Peat moss is abundant in China and available at a low cost. In this work, peat moss has been characterized in terms of its surface area, porosity, and pore volume and it has been

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used as thorium adsorbent from aqueous solutions. The solution pH, contact time, peat moss dosage, initial thorium concentration and ionic strength are important parameters for the elimination of Th (IV) present in aqueous matrices through adsorption. The application of the kinetic models and the isotherm models has been studied to explain the adsorption characteristics of peat moss and understand the process of removal of Th (IV) in a better way.

2. Materials and methods

Peat moss was obtained from Xinyuan city of Liaoning Province, China, dried under 100°C for 24 h and used through 80 mesh sieve to maintain a uniform particle size. Surface area of the particles was analyzed by volumetric BET method and was found to be 166.68 m^2/g. The average pore diameter was 2.0230 nm, which was determined by porosimetric method. A stock solutions of $Th(NO_3)_4$ was prepared by dissolving ThO_2 in HNO_3. All chemicals were analytical grade. Each experiment was performed twice at least under identical conditions.

Fourier transform infrared spectroscopy (NICOLET 380) was done to identify the chemical functional groups present on native peat moss. IR spectrograms of peat moss embedded in KBr pellets were recorded for wavenumbers in the range of 400–4000 cm^{-1} CHNS Elemental Analyzer (Vario EL) was used for the elements analyses, and visual spectrophotometer (721E) was used to determine the concentration of Th (IV) at wavelength of 650 nm by using Th (IV)-arsenazo III complex [18].

Batch static method was performed to optimize the basic experimental conditions for quantitative analyte adsorption such as pH dependence, ionic strength, adsorption isotherm and kinetic studies. Adsorption capacity of peat moss was carried out by agitating 40 mg peat moss with 8 ml aqueous solution of thorium of desired concentration, temperature, pH, and ionic strength in different polyethylene plastic centrifuge tubes on shaking thermostat at 100 rmp for predetermined time intervals, followed by centrifugation to separate peat moss from thorium solutions. Residual concentrations in the supernatant thorium solutions were determined by spectrophotometry UV-Vis [19]. The initial pH values of the solution were adjusted by adding negligible volumes of 0.01 mol/l HNO_3 or NaOH. The total volume of the solution in each polyethylene plastic centrifuge tube was made exactly to 8 ml by adding the KNO_3 of the certain ionic strength. The adsorptive percent of Th (IV) (%) was calculated as

$$\text{Adsorptive percent} = \frac{C_o - C_t}{C_o} \times 100 \tag{1}$$

where C_o is the initial concentration of Th (IV) solution (mol/l), C_t the solution concentration after at any time t (mol/l).

Th (IV) adsorption on peat moss was calculated by Eq. (2):

$$Q_t = \frac{(C_o - C_t)V}{W} \tag{2}$$

where Q_t is the adsorption at any time t (mol/g), C_o is the initial concentration of Th (IV) solution (mol/l), C_t is the concentration of Th (IV) solution at any time t (mol/l), V is the volume of the solution (l), W is the mass of dry peat moss used (g).

3. Results and discussion

3.1 Physiochemical characteristics of peat moss

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. In Fig. 1, infrared spectra show that there are many deprotonated carboxyl groups in peat moss, which act vital role in coordination with Th (IV) [20].

3.2. Effect of contact time

The effect of contact time on adsorption of Th (IV) onto peat moss showed in Fig. 2 may be explained as following. During the initial stage much free peat moss active site being available for Th (IV) lead to a high adsorption rate. In addition, during the same stage the higher concentration gradient between the bulk solution and the solid-liquid interface lead to higher adsorption rate.

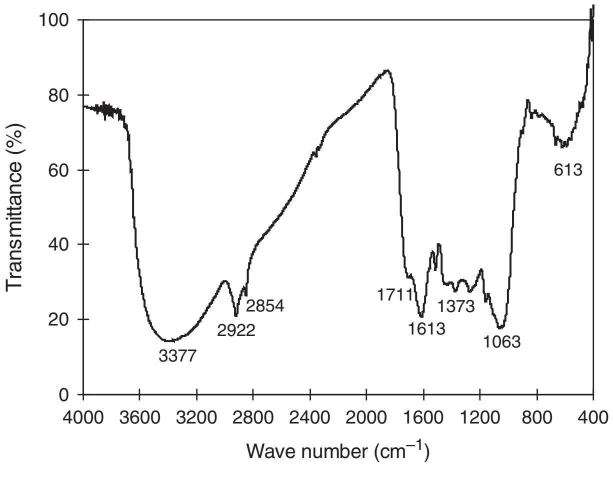

Fig. 1. FTIR spectra of peat moss.

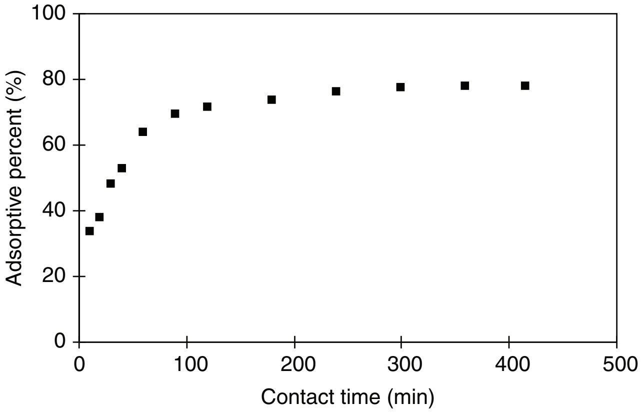

Fig. 2. Adsorption of thorium ion onto peat moss as a function of contact time I (KNO$_3$)(Ionic strength)= 0.10 mol/l, m/V (Adsorbent dosage) = 5 g/l, C_o = 4.310 × 10^{-4} mol/l, pH=5.5, T (Temperature) = 25°C.

However, during the later stage, the lower adsorption may be attributed to active site diminished and the lower diffusion rate of the solute into the interior of peat moss. It does not seem to be much benefit from contact time longer than 4 h.

A study of adsorption kinetics is desirable as it provides information about the process of adsorption. The kinetic parameters for the adsorption of thorium onto peat moss were obtained by application of classic absorption kinetic equations given as

Elovich equation: $Q_t = a + b\ln t$

Two-constant rate equation: $\ln Q_t = a + b\ln t$

Parabolic diffusion equation: $Q_t = a + bt^{\frac{1}{2}}$

Pseudo-second-order kinetics equation: $\frac{t}{Q_t} = a + bt$

where Q_t is the amount of adsorbent at any time t (mg/g adsorbent), a and b are empirical parameters.

The parameters in the four kinds of kinetic equation were determined from the slopes and intercepts of the plots and listed in Table 1. As evidenced by the values of the regression coefficient and F -test shown in Table 1, the pseudo-second-order kinetic equation fit the data best. This equation has been widely used in adsorption kinetics, and it describes adsorption mechanism in nature. It indicates that pseudo-second-order kinetics is applicable to the adsorption system studied.

3.3 Effects of adsorbent dosage

As shown in Fig. 3, the percentage of removed Th (IV) increased as adsorbent dosage increased from 2.5 g/l to 17.5 g/l. It may be explained that at lower peat dosage, Th (IV) were competing for limiting adsorption sites. However, as per unit mass of peat moss was increased, the more available vacant adsorption sites eased resulting in greater percentage removal of Th (IV).

3.4. Effects of pH and ionic strength

The ionic strength can influence the double layer thickness and interface potential, thereby can affect the

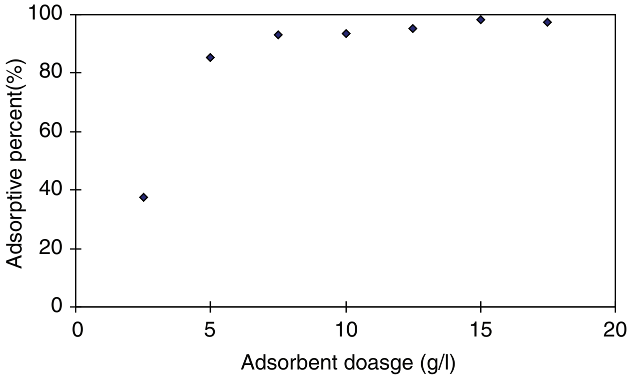

Fig. 3. Adsorption of thorium ions onto peat moss as a function of adsorbent dosage I(KNO$_3$) = 0.10 mol/l, m/V = 5 g/l, C_o = 4.310 × 10^{-4} mol/l, T = 25°C, pH = 5.5.

Table 1
Parameters of kinetic equation for adsorption of thorium ions onto peat moss

Parameters	Elovich equation	Two-constant rate equation	Parabolic diffusion equation	Pseudo-second-order kinetics equation
R	0.9944	0.9485	0.9062	0.9996
F^a	885.3642	89.6535	45.9279	12492.5005
a	−0.0299	−7.154	0.7965	1.1497
b	0.3442	0.2453	0.0691	0.0611

[a] $F_{0.05}$ (1,12–2) = 4.9.

binding of the adsorbed species [21]. As shown in Fig. 4, removal of Th (IV) decreases with increasing ionic strength in the range 0.05–0.25 mol/l. This effect has been attributed to the presence of KNO_3 in the solution which screens the electrostatic interaction of opposite charges of the peat moss surface and Th (IV) [22]. It is well known that ion exchange or outer-sphere surface complexation is influenced by ionic strength [23–24].

The results also indicate that the uptake of thorium increase with increasing pH from 1 to 4 under the same ionic strength. But there is a little difference in removed thorium at pH 5–12. At low pH values, H^+ ions and Th (IV) compete by the adsorption site of the peat moss. The more availability of H^+ ions in more acidic solutions thereby leads to the decrease in the retention of Th (IV). Another aspect that must be considered is thorium species in aqueous media, which is also pH-dependent. Indeed thorium solubility decreases, with pH increase, $Th(OH)^{3+}$, $Th(OH)_2^{2+}$, $Th_2(OH)_2^{6+}$, $Th(OH)_3^{+}$, $Th(OH)_{15}^{9+}$ appear as more significant ionic species, that Th^{4+} [25]. The hydrolyzed Th (IV) species probably favor the adsorption of thorium by being adsorbed more efficiently than the simple Th^{4+} ion. On the other hand, the concentrations of surface species (peat-OH uncharged surface group, peat-OH_2^+ positive charged surface group, peat-O^- negative charged surface group) of peat change under different pH values. With increasing pH, the negative charged group of peat increases and the adsorption of Th (IV) also increases.

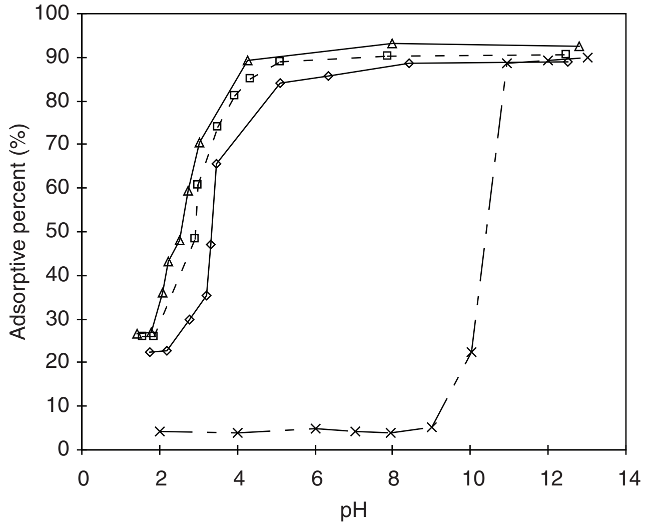

Fig. 4. Adsorption of thorium ions onto peat moss as a function of pH and ionic strength $I(KNO_3)$, mol/l: Δ0.05 □0.10 ◇0.25 × Surface precipitation of thorium onto peat moss $C_o = 4.310 \times 10^{-4}$ mol/l, T = 25°C, m/V = 5g/l.

3.5. Adsorption isotherm

The adsorption isotherms of thorium on peat moss at different ionic strengths are shown in Fig. 5. The adsorption capacity is the highest at 0.05 mol/l KNO_3 and is the lowest at 0.25 mol/l KNO_3. This result indicates that low ionic strength is advantageous for thorium adsorption on peat moss. The adsorption capacity of thorium onto peat moss, as expected, increases with the increase of equilibrium concentration of Th (IV) in aqueous solution.

Peat moss has a limited adsorption capacity, thus the adsorption could be better described by Langmuir isotherm equation rather than by Freundlich isotherm equation, since an exponentially increasing adsorption was assumed in the Freundlich isotherm equation [4]. The Langmuir isotherm equation assumes that there is no interaction between the adsorbate solutes and the adsorption is localized in a monolayer. The Langmuir isotherm equation can be rearranged to a linear form as below:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max}} C_e + \frac{1}{Q_{max} K_L} \qquad (3)$$

where Q_e is the amount of Th (IV) adsorbed per unit mass of peat moss (mol/g) at equilibrium, C_e is the equilibrium concentration of Th (IV) (mol/l), Q_{max} is the maximum adsorption capacity of peat moss (mol/g), K_L is the affinity constant (l/mol). The values of Q_{max} and K_L can be determined from the intercept and slope of the plot of C_e/Q_e versus C_e.

The Freundlich isotherm model can be expressed in the following linear form:

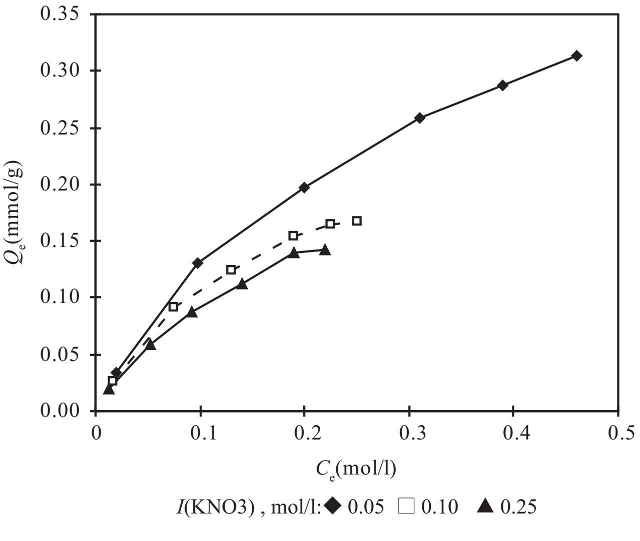

Fig. 5. Adsorption isotherm of thorium ions onto peat moss at different ionic strengths m / V = 5 g/L, T = 25°C, pH = 2.5.

Table 2
Langmuir constants and Freundlich constants of thorium ions adsorption onto peat moss

Ionic Strength (mol/l)	Langmuir constants				Freundlich constants			
	Q_{max}	K_L	R	F^b	n	K_F	R	F^b
0.05	0.2752	0.2765	0.9975	1195.5019	0.7116	0.5879	0.9885	256.3782
0.10	0.2344	0.2720	0.9933	443.2662	0.6923	0.4802	0.9852	198.2139
0.25	0.1249	0.2135	0.9969	963.2443	0.7044	0.4467	0.9900	295.5075

${}^bF_{0.05}$ (1,6-2) = 7.71.

$$\log Q_e = \log K_F + n \log C_e \tag{4}$$

where K_F ($\text{mol}^{1-n}\,\text{l}^n\,\text{g}^{-1}$) represents the adsorption capacity when Th (IV) ion equilibrium concentration equals to 1, and n represents the degree of dependence of adsorption with equilibrium concentration.

It was found that Langmuir isotherm model describe the adsorption processes relatively well, with regression coefficients close to 1and F -values above 7.71, as shown in Table 2.

In adsorption process, adsorption rate and maximum adsorption capacity of peat moss is affected by several factors such as the number of sites in peat moss, the accessibility of the sites, the availability of the sites and the affinity between the sites and the Th (IV) [26–27]. A good adsorbent for metal ions in general should have a low K_L and a high Q_{max}. The values of Q_{max} and K_L obtained from Langmuir isotherm equation for thorium adsorption on peat moss are the highest at 0.05 mol/l KNO_3 and the lowest at 0.25 mol/l KNO_3, which indicates that the maximum adsorption capacity and adsorption rate are hindered with increasing ionic strength. These results are in agreement with observations shown in Fig. 4. Similar results of Cu (II) adsorption on Na-bentonite were also reported [22]. Since, a low value of K_L reflects a high affinity of the biomass for the metal ions [28]. Higher ionic strength will block the availability of adsorption sites and depressed the affinity between the sites and the Th (IV).

4. Conclusions

The results of present investigation show that peat moss can be effectively used for the removal of Th (IV) from aqueous solutions. The pH value of the solution is an important factor. The adsorption of Th (IV) increases with increase of pH from 1 to 4 rapidly. Adsorption kinetic data of Th (IV) onto peat moss were best fit by the pseudo-second-order kinetics equation. The adsorbed amount of Th (IV) decreased with increase in higher ionic strength. The isotherm was fitted reasonably well by Langmuir model.

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