Applied Clay Science 47 (2010) 448–451

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Note

Adsorption of uranium (VI) from aqueous solution on calcined and acid-activated kaolin

Guanghui Wang [a,*], Xuegang Wang [a], Xinjun Chai [a], Jinsheng Liu [a], Nansheng Deng [b]

[a] *Department of Civil and Environmental Engineering, East China Institute of Technology, 56 Xuefu Road, Fuzhou, 344000, PR China*
[b] *School of Resources and Environmental Science, Wuhan University, 129 Luoyu Road, Wuhan, 430079, PR China*

ARTICLE INFO

Article history:
Received 29 July 2009
Received in revised form 5 November 2009
Accepted 10 November 2009
Available online 24 November 2009

Keywords:
Uranium (VI)
Kaolin
Acid-activation
Calcination
Adsorption

ABSTRACT

Kaolin was modified by calcination followed by acid-activation. This type of modification strongly increased the adsorption of uranium (VI) on kaolin. The equilibrium data agreed very well with the Langmuir model. Kinetic studies showed that the adsorption followed the pseudo-second-order model. Thermodynamic parameters showed the endothermic heat of adsorption and the feasibility of the process.

1. Introduction

Uranium is one of the most dangerous heavy metals in the environment because of its chemical toxicity and radioactivity (Yusan and Akyil, 2008). It is usually found in the environment in the hexavalent form. Uranium is likely to occur as a contaminant in the environment as a result of emissions from the nuclear industry, release in mill tailings, and the combustion of coal and other fuels (Krestou et al., 2004). The World Health Organization has determined that uranium (VI) is a human carcinogen and its concentration in water should not exceed 50 mg L^{-1}. The U.S. Environmental Protection Agency has recommended a drinking water standard of 20 mg L^{-1} for ^{238}U. Therefore, this has prompted the development of various technologies for its removal from wastes produced from nuclear power programs and nuclear fuel reprocessing activities. Many processes have been proposed for uranium (VI) removal from industrial wastewaters and radioactive wastes. Chemical precipitation, membrane processes, ion exchange, solvent extraction and adsorption are the most commonly used methods (Ganesh et al., 1999; Kryvoruchko et al., 2004; Mellah et al., 2006; Sodayea et al., 2009; Donia et al., 2009). Adsorption has been found to be an effective and economic method with high potential for the removal, recovery and recycling of metal ions from wastewater. A number of materials, such as activated carbon, zeolite, olivine rock, coir pith, smectites, kaolinite, bentonite, montmorillonite, biomass, goethite, and polymeric materials have been used for adsorption of uranium (VI) (Mellah et al., 2006). Among them, natural clays as low-cost adsorbent, have received much attention in heavy metals adsorption from contaminated water. Kaolin is abundant in China (Sari and Isıldak, 2006). A number of studies concerning kaolin and kaolinite used to adsorb metals such as Fe(III), Co(II) and Ni(II) from aqueous solution have been reported (Adebowale et al., 2006; Bouchenafa-Saib et al., 2007; Turan et al., 2007; Bhattacharyya and Gupta, 2008a,b). Typically, kaolinite has a low cation exchange capacity (CEC) (0.03–0.15 meq/g) (Grim, 1968; Bhattacharyya and Gupta, 2006; Jiang et al., 2009), while the specific surface area (SSA) of kaolinite ranges between 10 and 20 m^2/g (Yong et al., 1992). However, clay minerals could be modified to improve the adsorption capacity (Adebowale et al., 2005; Caballero et al., 2007; Unuabonah et al., 2007a,b). Recent research suggested that chemically modified clay minerals represent a new and promising class of adsorbents for water purification and industrial wastewater treatment (Malakul et al., 1998). In this present study, kaolin was modified by calcination followed by acid-activation.

2. Materials and methods

2.1. Materials

Kaolin was purchased from Damao Chemical Reagent Factory (Tianjin, China) and its properties are shown in Table 1. A Stock solution of 1000 mg/L uranium (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 NaOH solution. 0.1% Arsenazo III solution was prepared by

---

* Corresponding author.
E-mail address: wgh68611@163.com (G. Wang).

0169-1317/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.clay.2009.11.003

Table 1
Properties of kaolin.

Main characteristics	
Particle size distribution (%)	
0.05–1 mm	0
<0.05 mm	100
0.01–0.05 mm	0
0.005–0.01 mm	39.6
0.001–0.005 mm	25.4
<0.001 mm	35.0
Organic content (g/kg)	0
Cation exchange capacity (mmol/100 g)	3.85

dissolving 1 g of the reagent in 1000 mL of deionized water. All other reagents and solvents used were of analytical reagent grade unless otherwise stated. The water used throughout the work was deionized by a Milli-Q Water Purification system.

2.2. Preparation of modified kaolin

Modified kaolin was prepared as described by Suraj et al. (1998). The kaolin sample was calcined at 600 °C for 2 h. Samples of 2 g of calcined kaolin were reacted with 50 mL of 2.5 M HCl in a 70 °C water bath for 8 h, filtered, washed with water and dried at room temperature in air.

2.3. Determination of uranium (VI)

The concentration of uranium (VI) was determined by the Arsenazo III spectrophotometric method (Wei et al., 2007) on a Shimadzu UV-1601 spectrophotometer (Tokyo, Japan). 1 mL of uranium (VI) solution, 5 mL of chloroacetic acid sodium acetate buffer solution (pH 2.5) and 1.0 mL of 0.1% Arsenazo III aqueous solution were added to a 25 mL standard flask and made up to the volume with deionized water. After 10 min, the absorbance was measured at 650 nm. Measurements were made in duplicates for each experiment with errors less than 5%.

2.4. Adsorption experiments

The modified kaolin samples were dispersed in the uranium (VI) solution of a given concentration and pH value for 1 h at 25 °C, then centrifuged at 4000 rpm for 10 min. The amount of adsorption at time t, q_e (mg/g), was calculated from the concentration changes.

2.5. Equilibration calculation

All speciations in this study were performed with MEDUSA, a chemical equilibrium calculation program (Chen et al., 2007).

3. Result and discussion

3.1. Influence of contact time on the adsorption

At the conditions of 50 mg adsorbent, pH 5.0, 25 °C and 20 mg L^{-1} uranium (VI), the time dependence of uranium (VI) adsorption experiments is shown in Fig. 1. Equilibrium was reached within 60 min. Under the conditions in Fig. 1, removal of uranium (VI) was increased from 15% to 81% after modification.

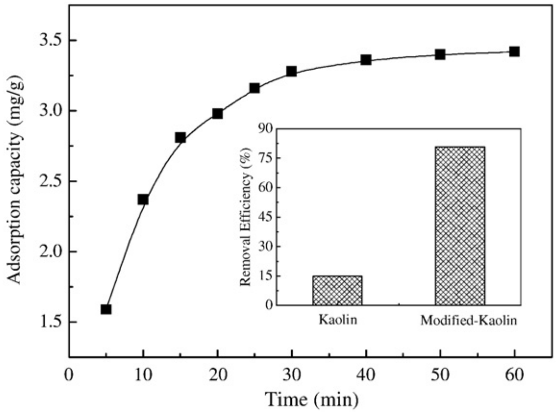

Fig. 1. Influence of contact time on the adsorption of uranium (VI) ($[UO_2^{2+}] = 20$ mg/L, Adsorbent mass = 50 mg, pH = 5.0, $T = 25$ °C).

3.2. Influence of initial pH values

The influence of pH on the adsorption of uranium (VI) on modified kaolin was investigated using 100 mL of uranium (VI) 20 mg/L at pH 2.0–7.0 at 25 °C for 60 min (Fig. 2). Uranium (VI) adsorption strongly depended on the solution pH and increased with increasing pH. At low pH, the number of H_3O^+ ions exceeds that of the UO_2^{2+} several times and the surface is most likely covered with H_3O^+ ions, reducing the number of binding sites for the adsorption of UO_2^{2+}. When pH increases, more and more H_3O^+ ions leave the clay mineral surface making the sites available to the cation exchange with the UO_2^{2+} ions. When pH value increased beyond 3, hydrolysis precipitation starts due to the formation of complexes in aqueous solution. Hydrolysis products are shown in Fig. 3, including $UO_2(OH)^+$, $(UO_2)_2(OH)_2^{2+}$, $(UO_2)_3(OH)_5^{3+}$, $(UO_2)_2(OH)_2$, which increase uranium (VI) removal (Parab et al., 2005).

3.3. Influence of initial uranium (VI) concentration

The influence of the initial uranium (VI) concentration on the adsorption removal efficiency was studied by contacting a fixed mass of modified kaolin (50 mg) at 25 °C and initial pH = 5.0 using a range of initial uranium (VI) concentrations (20, 30, 40, 50, 60, 70 and 80 mg/L) (Fig. 4). Removal of uranium (VI) decreased with increasing initial uranium (VI) concentration. However, the adsorption capacity of modified kaolin for uranium (VI) increased with increasing initial uranium concentration. This result is similar to that reported by Kütahyalı and Eral (2004) in their study on selective adsorption of uranium from aqueous solutions using activated carbon prepared from charcoal by chemical activation.

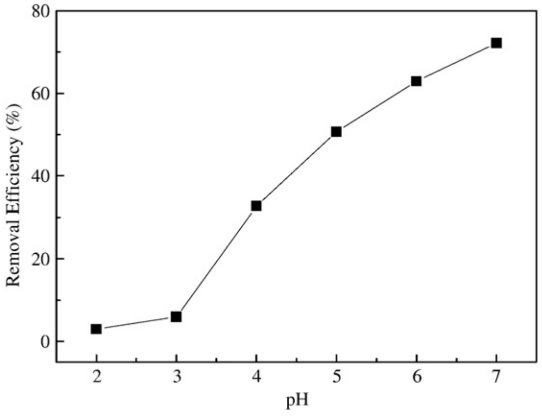

Fig. 2. Influence of pH on the adsorption of uranium (VI) ($[UO_2^{2+}] = 20$ mg/L, Adsorbent mass = 50 mg, $T = 25$ °C).