Contents lists available at ScienceDirect

Process Safety and Environmental Protection

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

Kinetics and thermodynamics of U(VI) ions from aqueous solution using oxide nanopowder

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ARTICLE INFO

Article history:
Received 21 May 2015
Received in revised form 25 December 2015
Accepted 12 February 2016
Available online 21 February 2016

Keywords:
Adsorption
Recovery
U(VI)
Al_2O_3 nanopowder
Kinetics
Thermodynamics
Isotherms
Design

ABSTRACT

Aluminum oxide nanopowder (AONP) was used for the preconcentration and recovery of uranium ions from an aqueous solution. Adsorption process in batch system was carried out by varying pH, initial U(VI) concentration, adsorbent dose, adsorption time and temperature. The adsorption efficiency could reach 99.85% at pH 5.0, 150 mg dose and 303 K. Desorption of uranium ions can be carried out using 1.5 M HNO_3. Equilibrium adsorption was attained within 40 min at 303 K and within 20 min at 333 K indicating that the rate of U(VI) uptake was found to be faster with increasing temperature. Adsorption data indicates the process following Langmuir isotherm and pseudo-second-order kinetic model. The mean energy, enthalpy, and activation energy confirming that the adsorption of U(VI) onto AONP is physical adsorption. Moreover, the thermodynamic parameters showed the endothermic and spontaneous nature of the adsorption process.

1. Introduction

Uranium is released into the environment through numerous sources, such as nuclear industries, natural deposits, fertilizers and other processing of uranium application (Shin et al., 2002). The presence of U(VI) in wastewater is dangerous to human even in relatively low concentration. The tolerance limit for the discharge of U(VI) into waters is 50 mg/L (Shuibo et al., 2009). The removal of U(VI) from industrial effluents is important before discharging them into aquatic environments or onto land. Several techniques of physical and chemical processes have been used for U(VI) removal from industrial wastewaters and radioactive wastes, such as; chemical precipitation, solvent extraction, membrane processes, cementation, electrochemical, evaporation and adsorption process (Qadeer and Hanif, 1994). Many of these methods are expensive and time consuming and have some limitations. Adsorption technique is a simple and cost-effective technology that has been widely used for removal of heavy metals from aqueous medium. A lot of adsorbent materials are being investigated for the removal of U(VI) ions from aqueous solutions including activated carbon (Abbasi and Streat, 1994), dunite (Konstantin and Demetriou, 2007), akaganeite (Yusan and Doyurum, 2008), graphene oxide (Chen et al., 2013) and orange peels (Mohamoud, 2013). Recently, attention has been focused on the use of nanoparticle minerals as adsorbents. Nanoparticle minerals have better efficiency in removing metal ion pollutants from aqueous solutions, mainly due to their high surface area to volume ratio (Savage and Diallo, 2005; Sharma et al., 2009). The use of alumina nanoparticles for the removal of heavy metals has been investigated due to its low cost, high surface area, surface reactivity, porosity, mechanical strength, and thermal stability (Stietiya and Jim, 2014). The objective of the present work was to study the feasibility of using aluminum oxide nanoparticles for preconcentration and recovery of U(VI) from aqueous solutions. The adsorption kinetics, isotherms and thermodynamics of

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http://dx.doi.org/10.1016/j.psep.2016.02.008
0957-5820/

Table 1 – Characteristics of aluminum oxide nanopowder (AONP).

Parameters	Value
Purity	99.9%
Particle size	<20 nm
Appearance	White powder
Nanoparticles (Al_2O_3) morphology	Nearly spherical
Density	3.97 g cm^{-3}
BET surface area	>138 m^2 g^{-1}

U(VI) ions were studied in batch experiments. Desorption and recovery of uranium ions are also studied.

2. Materials and methods

2.1. Preparation of adsorbent material

Aluminum oxide nanopowder (γ-nano-Al_2O_3) (AONP) used in this study was obtained from Beijing, China, Mainland (Model Number: DK420). The characteristics of Al_2O_3 nanopowder provided by the supplier are presented in Table 1.

The X-ray diffraction analysis (XRD) and environmental scanning electron microscope (ESEM) of AONP is also performed before and after adsorption.

2.2. Preparation of uranium(VI) stock solution

Stock solution (1000 mg/L) of uranium(VI) was prepared from $UO_2(NO_3)_2{\cdot}6H_2O$, Sigma Aldrich, USA. For experiments, the required concentrations were prepared by dilution. The pH of solutions was adjusted by 0.1 M Na_2CO_3 or 0.1 N HCl. All chemicals and reagents used in this work, including HCl, HNO_3, H_2SO_4 and Na_2CO_3 were analytical reagent grade. Distilled water was used throughout the experiments. The other stock solutions of various metals (Pb(II), Cd(II), Zn(II), Ni(II)) used as interfering ions were prepared as chloride salts.

2.3. Adsorption and desorption

Batch experiments were carried out to determine the optimum parameters of the adsorption process (contact time, pH, initial concentration, adsorbent dose and temperature). 50 ml of 25 mg/L of uranium(VI) solutions with a range of pH values from 3 to 10 was transferred in a conical glass flask with 100 mg of AONP. The mixture was agitated at 200 rpm in a thermostatic shaker water bath for different time intervals at different temperatures (303, 313, 323 and 333 K). The samples were withdrawn and centrifuged at 5000 rpm for 5 min and the supernatant solutions were analyzed spectrophotometrically using Shimadzu UV-VIS-1601 spectrophotometer. Adsorption capacity (q) of U(VI) was defined as:

$$q = \frac{(C_0 - C_e)V}{M} \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentration of U(VI) in the aqueous solution (mg/L), respectively. V and M are the volume of solution (L) and mass of adsorbent (g), respectively. In addition, the removal efficiency (R_e) is calculated according to the following equation:

$$R_e(\%) = \left(\frac{C_0 - C_e}{C_0}\right) \times 100 \quad (2)$$

The adsorption selectivity of AONP for U(VI) ion was carried out using a multi-metal solution containing Pb(II), Cd(II), Zn(II), Ni(II) prepared from metal salts. The inlet solution consisted of 25 mg/L U(VI) and 10 mg/L of other interfering ions. The adsorption was carried out at the optimum conditions. The adsorption selectivity coefficient (SC) is defined as follows (Chen et al., 2011):

$$SC = \log\left[\frac{(q_e/C_e)_{\text{uranium}}}{(q_e/C_e)_{\text{other metals}}}\right] \quad (3)$$

Desorption of U(VI) from loading AONP was carried out using different concentrations of HCl, HNO_3 and H_2SO_4 solution. Then U(VI) ion in the eluent solution was measured and desorption percent (De%) was calculated from to the following equation:

$$De\% = \frac{C_e}{C_0} \times 100 \quad (4)$$

2.4. Adsorption isotherms study

Equilibrium studies are described by Freundlich, Langmuir and Dubinin–Radushkevich (D–R) isotherms, which are important to explain the relation between the quantity of adsorbed ions and that remained in the solution at equilibrium.

2.4.1. Langmuir isotherm

The Langmuir equation is used to estimate the maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface and is expressed by (Langmuir, 1918):

$$q_e = \frac{q_{max}K_L C_e}{1 + K_L C_e} \quad (5)$$

where q_e and C_e are the amount of U(VI) adsorbed per gram of adsorbent (mg/g) and the U(VI) concentration (mg/L) in the aqueous solution at equilibrium, respectively. q_{max} and K_L are constants related to the maximum adsorption capacity (mg/g) and the intensity of adsorption (L/mg), respectively. The linear form of the above equation after rearrangement is given by:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \quad (6)$$

The constants q_{max} and K_L can be determined from the slope and intercept of plotting C_e/q_e against C_e, respectively.

2.4.2. Freundlich isotherm

Freundlich model (Denise et al., 2012), is used to estimate the adsorption intensity of the adsorbent toward the adsorbate and is given by:

$$q_e = K_F C_e^{(1/n)} \quad (7)$$

where K_F is the constant of Freundlich model and n gives an indication about the favorability of the adsorption process. The above equation is conveniently used in linear form as:

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \quad (8)$$

A plot of $\ln C_e$ against $\ln q_e$ yielding a straight line indicates the conformation of the Freundlich adsorption isotherm. The