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Removal of thorium (IV) ions from aqueous solution by a novel nanoporous ZnO: Isotherms, kinetic and thermodynamic studies

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ABSTRACT

The adsorption of thorium (IV) from aqueous solutions onto a novel nanoporous ZnO particles prepared by microwave assisted combustion was studied using batch methods under different experimental conditions. The effect of contact time, solution pH, initial concentration and temperature on adsorption process was studied. The ability of this material to remove Th (IV) from aqueous solution was characterises by Langmuir, Freunlinch and Temkin adsorption isotherms. The adsorption percent and distribution coefficient for nanoporous ZnO powders in optimum conditions were 97% ± 1.02; 8080 L $kg^{-1}$for Th (IV), respectively. Based on the Langmuir model, the maximum adsorption capacity of nanoporous ZnO for Th (IV) was found to be 1500 g kg^{-1}. Thermodynamic parameters were determined and discussed. The results indicated that nanoporous ZnO was suitable as sorbent material for recovery and adsorption of Th (IV) ions from aqueous solutions. The radioactive Th (VI) in surface water, sea water and waste waters from technologies producing nuclear fuels, mining (uranium and thorium) and laboratories working with radioactive materials (uranium and thorium) can be removed with this nanoporous ZnO.

1. Introduction

In terms of environmental protection, the removal of radioactive elements in waste waters is a major problem. This is accetunated when these are toxic to the environment and human health at very low concentrations and when they have long half lives (Ilaiyaraja et al., 2013a,b). These pollutants appear in water from some industrial activities such as mining, nuclear power plants, nuclear weapons and laboratory activities (Humelnicu et al., 2014).

Thorium in the earth's crust is three times more abundant than uranium. It can be used as a nuclear fuel. Thorium (Th-232) is not itself fissile. However, after absorbing a neutron, it produces atoms of U-233, which is an excellent fissile fuel material. The primary benefits of utilizing thorium in a nuclear fuel are safe, clean energy production, enhanced proliferation resistance, and potential fuel cycle cost savings. Furthermore, thorium reactors produce far less waste and the waste that is generated is much less radioactive and much shorter-lived. Although direct toxicity of thorium is low because of its stability at room temperature, since the liquid wastes of these industrial applications may leak to the surface and can mix with the underground waters, it is increasingly becoming a concerning environmental issue (Sheng and Hu, 2013). Thorium-232 is long-lived with a suite of radioactive daughter products which can pose a human health and ecosystems risk (Höllriegl et al., 2007).

Therefore, the removal and recovery of Th (IV) from waste water are is an urgent and essential work. Several methods have been developed to recover metals from waste product such as solvent extraction, ion exchange, biosorption and adsorption (Liu et al., 2011; Nazari et al., 2011; Agrawal et al., 2000). Adsorption is the most popular, efficient and convenient method because of its cost effective treatment, high capacity, low cost, easy of regeneration, and no sludge produced, and has been widely practiced in industrial waste product for the removal of radioactive elements (Rahmati et al., 2012).

Natural and synthetic adsorbents such as perlite (Talip et al., 2009), organoclay (Şimşek et al., 2014), alumina (Guo et al., 2005), activated carbons (Kutahyali and Eral, 2004), bentonite (Guerra et al., 2009; Song et al., 2013), and nanoporous materials (Sadeghi et al., 2012) have been tested for adsorption of Th (IV) from wastewaters. Nanotechnology is nowadays one of the most important trends in material science. The term nanomaterial is normally used to emphasize nanoporous structures in which at

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least one of its phases has one or more dimensions (length, width or thickness) in the nanometer size range (1–100 nm) (Tian et al., 2013).

Nanoparticles have the features of large specific surface area, potential for self assembly, high specificity, high reactivity, high adsorption and desorption capacity, and low temperature modification ability for water treatment applications (Tian et al., 2013; El-Nahhal et al., 2013; Yan et al., 2008; Yusan et al., 2014). The use of nanoparticles in the environmental applications has been increased due to these features (Wang and Zhang, 1997; Xu and Zhang, 2000; Schrick et al., 2002). For example, nanomaterials with promising sorptive and reactive properties have been used in water and air purification, hazardous waste treatment, and environmental remediation. This trend points to a considerable increase in the rate of usage of nanomaterials in environmental technologies (Li et al., 2006).

Carbon nanotubes are used for the removal of arsenate from water (Peng et al., 2005) as well as other toxic metals such as Pb^{2+}, Cu^{2+} and Cd^{2+} (Li et al., 2003). They show a high capacity for adsorption of lead (Li et al., 2002) and are able to remove chemicals of concern such as bisphenol A (Cai et al., 2003). Nanoparticles of magnetite (Fe_3O_4) coated with mesoporous silica can be used in the removal of many harmful agents present in the environment (Wu et al., 2004).

Nano-sized metal oxides are highly active for a large number of reactions that are important in both pollution control and chemical synthesis (Peyghan and Bagheric, 2012). In recently studies, nanoporous ZnO particles have been used in adsorption studies (Prasad and Jha, 2009; Hua et al., 2012; Beheshtiana et al., 2012). As an adsorbent, ZnO was mostly applied to sorption of lead (Venkatesham et al., 2013). As far as we know, Th (IV) adsorption onto nanoporous ZnO has not been reported.

The aim of this work was to study the efficiency of nanoporous ZnO for removal of Th (IV) from aqueous solutions. The effect of contact time, solution pH, initial concentration and temperature on adsorption process was also studied. Equilibrium adsorption isotherms were analyzed to obtain the Langmuir, Freundlich and Temkin constants and thermodynamic parameters of the process were calculated.

2. Experimental

2.1. Materials and methods

The solutions of Th^{4+} (1 g L^{-1}) were prepared by dissolving the weighed amounts of thorium salt ($ThNO_3.5H_2O$) in millipore water. The initial pH of the working solutions was adjusted by addition of HNO_3 or NaOH solution. Other chemicals used in this work of analytical reagent grade.

The method used for the nanoporous ZnO material synthesis by microwave-assisted ignition reaction was given in detail in our previous study (Kaynar et al., 2014). The synthesis method of the adsorbent has been shown in Scheme 1. In that study, the crystallite structure accuracy and particle size of 52 nm were determined doing by XRD and SEM characterizations of the ZnO crystallites (Kaynar et al., 2014).

2.2. Determination of Th (IV)

Deionized water, obtained by passing water through pure water system (innovation Human Power I Scholar), was used to prepare all of the samples and solutions. The concentrations of Th (IV) in the solutions were measured by using a Perkin-Elmer Optima 2000 DV model Inductively Coupled Plasma-Optic Emission Spectrometry (ICP-OES) (Dastbaza and Keshtkar, 2014).

2.3. Adsorption experiments

The core method was to contact 0.1 g of nano-adsorbent with 25 mL of solutions (50 mg Th L^{-1}) in 50 mL polypropylene centrifuge tubes. Th (IV) solution with the given concentration, pH value and volume was added to plastic tube containing the nanoporous ZnO. The tubes were shaken on the controlled shaker (GFL 1083 model) at 300 rpm for 1 h at 20 °C. Samples of the suspension were collected at 15, 30, 60, 90 and 120 min for Th (IV) analysis. Then, the remaining mixture was centrifuged at 4000 rpm for 10 min at room temperature.

The amount of Th (IV) adsorbed was calculated at equilibrium (qe) and at time (qt) from the following Eq. (1)

$$q_{e,t} = (Co - Ce).(V/m) \quad \left(\text{g kg}^{-1}\right) \tag{1}$$

where C_o is the initial metal ion concentration (mg L^{-1}), Ce is the concentration of metal in the solution at equilibrium time t (mg L^{-1}), V is the volume of the contact solution (L) and 'm' is the dry weight of sample (g). The adsorption isotherms were investigated for varying Th (IV) concentrations between 25 mg L^{-1} and 125 mg L^{-1}.

The adsorption process, described by the ion distribution coefficient, Kd (L kg^{-1}), was calculated using Eq. (2)

$$K_d = \frac{(C_0 - C_e)}{C_e} \times \frac{V}{m} \tag{2}$$

The adsorption Th (IV) metals expressed in terms of adsorption percentage (Ads %) was obtained from Eq. (3)

$$Ads\% = \frac{C_o - C_e}{C_o} \times 100 \tag{3}$$

The effect of temperature on Th (IV) adsorption was studied between 293 K and 313 K. The thermodynamic parameters (ΔH°, ΔS° and ΔG°) were calculated.

3. Results and discussion

3.1. Effect of contact time

The effect of shaking contact time was studied using a fixed concentration of Th (IV) solution at 293 K in the range of (15–120) min. At the conditions of 0.1 g adsorbent, 25 mL volume, pH 3.5, 20 °C and 50 mg L^{-1} Th (IV), Th (IV) the time dependence is shown in Fig. 1. The Th (IV) absorption efficiency was over 91% at 30 min. After that, the absorption efficiency became constant.

3.2. Effect of initial pH values

The influence of pH was investigated using 25 mL of at 50 mg L^{-1} at pH 3.0–8.0 at 20 °C for 4 h (Fig. 2). The effect of pH on adsorption media is complex and also strongly influences the ionic state of metal ions on the surface of adsorbents (Sharma et al., 2013). It is well known that Th(IV) can exist in various chemical forms in solution as a function of pH such as Th (IV) at pH $\leq$ 3, $Th(OH)^{+3}$ around pH 3–5, $TH(OH)_2^{2+}$ around pH 4.5–5.5 and $Th(OH)_4$ above pH 6 (Anirudhan and Rejeena, 2011). The pH at the optimum sorption conditions was found to be 5. Similar results have been found by other researchers (Song et al., 2013; Bozkurt et al., 2011). The adsorption mechanism for Th (IV) is shown in Scheme 1.