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Studies on the capability and behavior of adsorption of thallium on nano-Al_2O_3

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Abstract

A novel sorbent, nano-Al_2O_3 was employed for the removal of thallium from aqueous solution in batch equilibrium experiments, in order to investigate its adsorption properties. The removal percentage of thallium by the sorbent increased with increasing pH from 1 to 5. The adsorption capacities and removal percentage of Tl(III) onto nano-Al_2O_3 were evaluated as a function of the solution concentration and temperature. Results have been analyzed by the Langmuir, Freundlich adsorption isotherms. Adsorption isothermal data could be well interpreted by the Langmuir model. The mean energy of adsorption 9.32 kJ mol^{-1} was calculated from the Dubinin–Radushkevich (D–R) adsorption isotherm. The kinetic experimental data properly correlated with the second-order kinetic model. The thermodynamic parameters for the process of adsorption have been estimated. The ΔH^0 and ΔG^0 values of thallium(III) adsorption on nano-Al_2O_3 showed endothermic adsorption.

Keywords: Tl(III); Nano-Al_2O_3; Adsorption; Kinetics; Thermodynamics

1. Introduction

Thallium has been identified to be an environmentally significant element because of its toxic effects and is commonly found with lead, zinc, iron, tellurium and the alkalis. And thallium is a heavy metallic element that exists in the environment mainly combined with other element (primarily oxygen, sulfur and the halogens). Thallium is used as a catalyst, in making alloys, optical lenses, low temperature thermometers, dyes and pigments in scintillation counters. Thallium is also used as medicines, rodenticides and insecticides [1]. By exploiting and machining mineral, thallium enters and contaminates environment. Therefore, it is important to remove the trace amounts of thallium and strictly controlled for preventing its pollution to humans and environment [2].

At present, it has been reported that thallium can be effectively removed from aqueous solution by iron powder method [3], activated alumina and ion exchange [4], manganese dioxide, ferrihydrite adsorption [5], silica gel [6], polyurethane foam [7], active carbon [8], etc. Besides, John Peter et al. [9] indicated that modified Aspergillus niger biomass was also an emerging and attractive method for the removal of thallium from aqueous solutions. In this paper, nano-Al_2O_3 as sorbent was used to remove thallium from aqueous solutions for the first time.

The nanometer material is a new functional material [10], which has attracted much attention due to its special properties. Most of atoms on the surface of the nanoparticles are unsaturated and can easily bind with other atoms. Nanoparticles have high adsorption capacity. Besides, the operation is simple, and the adsorption process rapid. So there is a growing interest in the application of nanoparticles as sorbents [11].

2. Experimental

2.1. Apparatus

UV–vis-NIR Cary 5000(VARIAN Co., US) was used to measure the concentration of Tl^{3+}. A S-3C Model pH meter (Shanghai Precision Scientific Instrument Co., China) was used for measuring the pH of solutions. A model KQ-100B

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ultrasonic cleaner (Kunshan Ultrasonic Instrument Co., China) and a model TDL80-2B centrifugal machine (Shanghai Anting Scientific Instrument Co., China) were used throughout.

2.2. Reagents

A stock solution of Tl(III) (1.000 mg mL^{-1}) was prepared by dissolving 1.3030 g of $TlNO_3$ (Beijing NCS Analytical Instruments Co., China) with some doubly distilled water and 2 mL concentrated nitric acid, then oxidized by saturated bromine water, finally diluted to a 1 L volumetric flask with 0.12 mol L^{-1} HCl.

All of the other reagents including Triton X-100 solution (1%), Cadion 2B (5.0×10^{-4} mol L^{-1}), ammonia, ammonium chloride, hydrochloric acid, nitric acid and sodium hydroxide, were of analytical grade and obtained from Shanghai Xinzhong Chemical Reagent Co., China. Doubly distilled water was used throughout experiments. Nano-Al_2O_3 (γ-Al_2O_3) that was used as sorbent in this study was provided from Zhoushanmingri Nanometer Material Co., and its particle size was about 10 nm.

2.3. Procedure

The adsorption experiments were carried out in a series of 50 mL Erlenmeyer flasks containing 0.03 g nano-Al_2O_3 and 10.0 mL of 10.0 mg L^{-1} thallium solution at pH 4.5. If necessary, an appropriate volume of 0.1 mol/L HCl or NaOH solutions was used to adjust the pH of the solution after addition of nano-Al_2O_3. The soild/liquid phases were separated by centrifuging at 3000 rpm. The adsorption percentage (Ads.%) was calculated as

$$\text{Ads.\%} = \frac{(C_i - C_a)}{C_i} \times 100 \qquad (1)$$

where C_i and C_a are the initial and the final concentration of Tl(III) in solution phase, respectively.

Adsorption isotherm studies were carried out with different initial concentrations of Tl(III) while maintaining the sorbent dosage at constant level. In order to inspect any adsorption of thallium on the container surface, control experiments were carried out without the sorbent. It was found that no adsorption occurred on the container wall.

Kinetic experiments were conducted using a known weight of the sorbent dosage at the range 2–40 °C. After regular intervals of time, suitable aliquots were analyzed for thallium concentration. The rate constants were calculated using the conventional rate expression.

The thermodynamic parameters for the process of adsorption were determined at a particular temperature. This procedure was repeated at three different temperatures ranging from 2 to 40 °C. In this experiment, it was found that Tl(III) ions would be desorbed from nano-Al_2O_3, when the temperature of the system was more than 40 °C. Therefore, all the temperatures of the procedure were controlled at less than 40 °C.

3. Results and discussion

3.1. Effect of pH

In this study, knowledge of pH was important because the pH of solution influences the distribution of active sites on the surface of nano-Al_2O_3. At the higher pH, the OH^- on the surface of nano-Al_2O_3 provides the ability of binding cations. The decrease of pH leads to the neutralization of surface charge, and OH^- is displaced from the surface. When the surface of nano-Al_2O_3 carries positive charges, it begins to adsorb anions.

Fig. 1 shows the effect of pH on the adsorption of Tl(III) by nano-Al_2O_3, which indicates that the recovery of thallium increases with an increase in pH from 1 to 5. The effect of pH on Tl(III) adsorption can be explained by the following reasons. The surface charge is neutral at isoelectric point (IEP), which pH_{IEP} value is 9 for nano-Al_2O_3. The surface of sorbent carries positive charges at pH value lower than IEP, which enhances electrostatic force of attraction with $TlCl_4^-$ (In the studied system, the main chemical species of thallium(III) in solutions is $TlCl_4^-$ [12]). As a result, the process of sorption takes place more easily in pH 3–4.5, so the adsorption percentage of Tl(III) was higher. In pH 1–2, there is a balance reaction: $H^+ + HlC_4^- \rightleftarrows HTlCl_4$, the main chemical species of thallium(III) is $HTlCl_4$ [13,14], so the adsorption percentage of Tl(III) was lower.

However, at pH >5, with the increase of OH^- in solutions Cl^- in $TlCl_4^-$ was gradually replaced by OH^{-1}. And $[TlCl_2(H_2O)_3]^-$, $[Tl(H_2O)_4(OH)_2]^+$, $[Tl(H_2O)_5(OH)]^{2+}$ [15] and so on, were formed in solutions, which is not favor of adsorption of thallium(III). Therefore, pH 4.5 was chosen for adsorption of Tl(III) in the experiment, and the adsorption percentage was calculated to be 99.56% at pH 4.5.

3.2. Adsorption kinetic model

The models of adsorption kinetics were correlated with the solute uptake rate; hence these models are important in water treatment process design. In this study, for a batch of reactions,

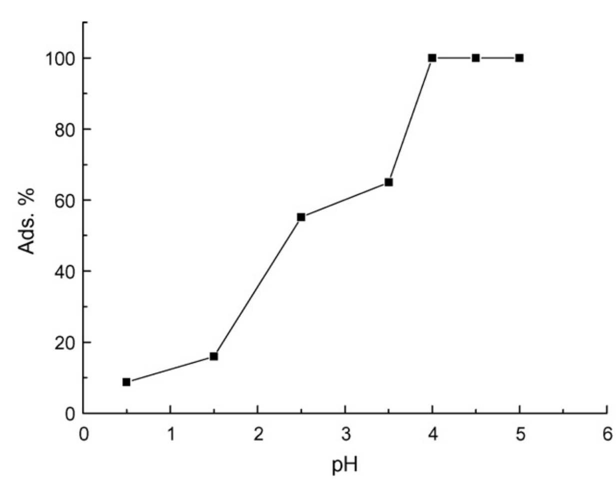

Fig. 1. Effect of pH on the adsorption efficiency of Tl(III) on nano-Al_2O_3; 30 mg of nano-Al_2O_3; $C_{Tl(III)}$ 10.0 mg L^{-1}; static time 10 min; temperature 20 ± 0.1 °C.