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Superior adsorption of thallium(I) on titanium peroxide: Performance and mechanism

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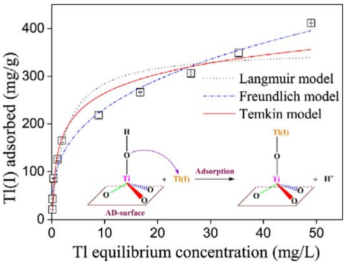
GRAPHICAL ABSTRACT



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ABSTRACT

Thallium is a highly toxic pollutant to mammals and its removal from water is increasingly gaining attention. In order to effectively remove thallium(I), a much more mobile and difficult to be removed thallium species, nanostructured titanium peroxide was facilely synthesized via an oxidation coupled with precipitation process in this study. The morphology and surface properties of the titanium peroxide were analyzed by TEM, XRD, BET, FTIR and XPS techniques. The obtained amorphous peroxide consists of nanoparticles, with a surface area of 13.6 m^2/g. The adsorption of Tl(I) is pH-dependent and increases with increasing pH-value. The titanium peroxide is very effective in removing Tl(I) from water, with a maximal adsorption capacity of 412 mg/g at pH 7.0. The present Ca^{2+}, Mg^{2+}, $K^+_,$ Cu^{2+}, Zn^{2+}, fulvic acid and humic acid had no significant effect on Tl(I) adsorption, indicating the high adsorption selectivity of Tl(I) on titanium peroxide. Furthermore, Tl(I) uptake might be mainly achieved through ion-exchange reaction between Tl(I) ions and hydroxyl groups on the surface of the peroxide, resulting in the formation of inner-surface complex of Ti–O–Tl(I). The as-prepared titanium peroxide could be a promising alternate for thallium removal from water, due to its excellent Tl(I) removal performance, high selectivity and facile synthesis process.

1. Introduction

Thallium is a rare heavy metal element, but it occurs extensively in the natural environment [1–3]. In natural freshwater, thallium concentration is very low and the average values are 1–410 ng L^{-1} in lakes, 13–1350 ng L^{-1}in rivers, and 1–550 ng L^{-1} in groundwater [4,5]. However, elevated levels of thallium in natural waters were reported because of anthropogenic activities such as mining, smelting and coal combustion, ranging from dozens of μg L^{-1} to several mg/L [2,6]. Thallium is well known due to its remarkable toxicity to mammals,

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which is higher than many other heavy metals such as mercury, lead, cadmium, copper and zinc [7–9]. Chronic thallium poisoning can cause anorexia, headache, pains in abdomen, alopecia, blindness and even death [2,10]. To minimize these health risks, a maximum contaminant level (MCL) of 2 μg L^{-1} was set as drinking water standard by the US Environmental Protection Agency (USEPA) [11], while a more stringent limit of 0.1 μg L^{-1} was adopted in China [12].

In water, thallium exists in two oxidation states: thallium (I) and thallium (III) [13,14], but Tl(I) was found to be dominant species in terms of pH and Eh [15]. In addition, Tl(I) is much more mobile and difficult to be removed than Tl(III) [16]. Tl(I) is therefore considered to be more undesirable and its removal has gained more attentions. Several techniques such as chemical precipitation [8], oxidation/coagulation, ion exchange [17], solvent extraction [18] and adsorption [16,19], have been employed to remove thallium from water or wastewater. In contrast to others, adsorption is believed to be one of the most promising methods, because it is highly efficient, cost-effective and easy to handle.

Many materials such as Prussian Blue [20], sawdust [21], eucalyptus leaves powder [9], modified *aspergillus niger* biomass [22], modified sugar beet pulp [23], activated carbon [24], carbon nanotubes [25], nano-Al_2O_3 [26] and manganese dioxide [16,27], have been used as adsorbents for thallium removal. Recently, titania-based materials have attracted increasing attention, due to their high efficiency in removing thallium and stability in water. For examples, Zhang et al. examined the sorption of Tl(III) by titanium dioxide nanoparticles [19]. Liu et al. synthesized titanate nanotubes via hydrothermal method, which exhibited a rather high sorption capacity towards thallium [28]. Titanium peroxide, a titanium compound containing peroxide anion (O_2^{2-}), has been used as catalyst for oxidation of organics [29] and adsorbent for cationic dyes [30]. It demonstrated highly selective adsorption performance for cationic dyes such as methylene blue (MB), malachite green (MG) and neutral red (NR) [30]. Heavy metal ions such as lead and thallium are positively charged, similar to cationic dyes. From the view of electrostatic interaction, the titanium peroxide might be a potential adsorbent for thallium sorption. However, to our best knowledge, no information is available on the removal of thallium using titanium peroxide from water.

In this study, titanium peroxide was synthesized using a facile oxidation coupled with precipitation method at room temperature and characterized with a variety of techniques. The adsorption kinetics and adsorption isotherm of Tl(I) were investigated. The influences of solution pH, ionic strength and coexisting cations on Tl(I) adsorption were also examined. In addition, a possible mechanism of Tl(I) removal was proposed.

2. Materials and methods

2.1. Materials

All chemicals including titanium sulfate, hydrogen peroxide (30%), ammonia, sodium nitrate and thallium(I) nitrate were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China) and were analytical grade without further purification. Tl(I) stock solution (500 mg/L) was prepared with thallium(I) nitrate and deionized water. Tl(I) working solutions were freshly prepared by diluting Tl(I) stock solution with deionized water.

2.2. Synthesis of titanium peroxide

Titanium peroxide was synthesized according to a modified method reported in the literatures [29,30]. Briefly, under vigorously stirring, 100 ml H_2O_2 (30%) was added to a solution of 10% $Ti(SO_4)_2$ (250 ml). Then, 10% ammonia was dropwise added into this solution until the solution pH increased to about 7.0. The color of the suspension turned into yellow gradually in the process of neutralization. The formed precipitates were washed for several times, then filtrated and dried at 55 °C for 24 h. The dried titanium peroxide was crushed and stored in a desiccator for use. Additionally, titanium dioxide was prepared in a similar procedure, without H_2O_2 addition.

2.3. Characterization of synthesized titanium peroxide

The specific surface area was measured by nitrogen adsorption using the BET method with a Micromeritics ASAP 2020 surface area analyzer (Micromeritics Co., USA). X-ray diffraction (XRD) analysis was carried out on a D/Max-3A diffractometer (Rigaku Co., Japan) using Ni-filtered copper Ka1 radiation. The morphology of the particles was characterized by a transmission electron microscope (TEM) (JEM-1230, Japan). The Fourier transform infrared (FTIR) spectra of titanium peroxide before and after treatment with Tl(I) solution were collected on a Nicolet IS10 FTIR spectrophotometer (Thermo scientific, USA) using a transmission model. Samples for FTIR determination were ground with spectral grade KBr in an agate mortar. FTIR spectra were obtained from dry samples in KBr pellets corresponding to 5 mg of sample in approximately 200 mg of KBr. All FTIR measurements were carried out at room temperature. A laser particle size analyzer (Mastersizer 2000F, Malvern, UK) was used to determine the distribution of particle size of titanium peroxide. A zeta potential analyzer (Zetasizer 2000, Malvern, UK) was used to analyze the zeta potential of titanium peroxide particles before and after Tl(I) adsorption. The content of titanium peroxide in the solution was 200 mg/L and Tl(I) concentration was 20 mg/L. $NaNO_3$ was used as background electrolyte to maintain an approximately constant ionic strength of 0.01 M. After mixing for 72 h to ensure the achievement of adsorption equilibrium, 10 mL of the suspension was transferred to a sample tube. Zeta potential of the suspension was then measured by electrokinetic analysis. X-ray photoelectron spectra (XPS) were collected on an ESCALab-220i-XL spectrometer with a monochromatic Al Ka X-ray source (1486.6 eV). C1s peaks were used as an inner standard calibration peak at 284.7 eV. For wide-scan spectra, an energy range of 0–1100 eV was used with pass energy 80 eV and step size 1 eV. The high-resolution scans were conducted according to the peak being examined with pass energy 40 eV and step size 0.05 eV. The XPS results were collected in binding energy forms and fitted using a nonlinear least-squares curve-fitting program (XPSPEAK41 Software).

2.4. Batch adsorption tests

Batch tests of Tl(I) adsorption by titanium peroxide were all performed in triplicate at room temperature (25 ± 1 °C). The average values were reported, together with error bars represented.

2.4.1. Adsorption kinetics

Determined amount of Tl(I) stock solution was added in a 2000-ml glass vessel and then corresponding amount of deionized water was added to make 1500 ml 18.5 mg/L or 31.5 mg/L, or 47.5 mg/L thallium solution. Additionally, a certain amount of sodium nitrate (1.276 g) was added to the solution, to maintain the ionic strength as 0.01 M. The solution pH was adjusted to 7.0 ± 0.1 by adding 0.1 M HNO_3 and/or NaOH. Then, titanium peroxide powder (0.3 g) was added to obtain a 0.2 g/L suspension. The suspension was mixed with a magnetic stirrer at an agitation speed of 170 rpm, and the pH was maintained at 7.0 ± 0.1 throughout the experiment by addition of dilute acid and/or base solutions. Approximately 5-ml aliquots were taken from the vessel at predetermined times. The samples were immediately filtered through a 0.45-μm membrane filter. The concentrations of residual thallium were determined using an inductively coupled plasma mass spectrometry machine (ICP–MS).

2.4.2. Effect of solution pH and ionic strength

To examine the effect of solution pH on Tl(I) sorption, batch tests