磁铁矿去除 Sb(V)的吸附实验研究

摘要

锑（Sb）是一种可长距离传输的全球性污染物，在水体中主要以五价锑[Sb(V)]的形式存在。如何高效去除水体环境中的Sb(V)是环境科学领域的研究热点之一。为评估磁性纳米材料对 Sb(V)的吸附效能，选择两种不同来源的磁铁矿（商业购买以及微生物合成）作为吸附剂开展室内研究，并探究其吸附机理。

本实验中，购买于 Sigma 公司的纳米磁铁矿是采用纯化学法工业合成的，而微生物合成的磁铁矿是经异化铁还原菌还原水铁矿途径合成所得。

通过 X-射线粉晶衍射（XRD）、透射电镜（TEM）、X-射线光电子能谱（XPS）等测试技术对两种磁铁矿进行矿物学表征。XRD 结果显示两种吸附剂都为磁铁矿且纯度较高。与商业购买的磁铁矿相比，微生物合成的磁铁矿结晶程度较弱。透射电子显微镜结果除进一步应证二者结晶度差异外，还揭示两种磁铁矿的粒径大小具有明显不同：商业购买的磁铁矿的颗粒平均粒径是 122.9 nm，而微生物合成材料的平均粒径为 15.8 nm。两种材料的 Fe 2p 光电子能谱测得的两个能量值与数据库 NIST XPS database 中给出的 Fe3O4 的 Fe 2p 结合能都很接近，由此可以进一步确认两种材料都是单一的磁铁矿。

通过开展批次吸附实验来研究吸附动力学、平衡等温吸附和不同 pH 值对磁铁矿吸附 Sb(V)的影响。吸附动力学结果显示，两种磁铁矿的吸附行为均可用准二级动力学方程描述，说明磁铁矿表面的吸附主要为化学吸附。平衡等温吸附中，微生物合成磁铁矿对 Sb(V)的最大吸附能力为 9.88mg/g，约为商业磁铁矿的 4.1 倍。在 pH 为 3-10 梯度下研究 pH 对吸附的影响，两种磁铁矿的吸附能力都随 pH 的升高而逐渐减弱，但微生物合成磁铁矿的吸附能力明显优于商业购买材料。

比较两种磁铁矿的合成方法、材料学特征以及吸附性能，最终我们认为微生物合成的磁铁矿是一种绿色环保和成本低廉的锑吸附材料，具有较大的应用潜力和广阔的应用前景。

关键词：Sb(V)吸附；磁铁矿；纳米材料；重金属修复

Abstract

Antimony (Sb) is a long-distance transported hazardous metalloid. In aqueous settings, Sb primarily exists in the form of Sb(V). Mitigation of Sb in water has become a significant research in environmental sciences. In order to assess the Sb adsorption capacity of ferromagnetic materials, two different kinds of nano-magnetite either purchased from Sigma company or synthesized with the aid of microorganisms, were selected to adsorb Sb(V) from solutions. Specifically, the commercial magnetite was synthesized abiotically using a hydrothermal method in industry. The biogenic

magnetite was made though bioreduction of ferrihydrite using a typical iron-reducing bacteria, *Shewanella oneidensis* MR-1.

Multiple approaches were employed to characterize the nano-magnetites, inculding X-ray powder diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). XRD results showed that two magnetites well crystallized and highly pure. Based on the calculation using MDI Jade (version 6.0), it could be found that the crystallinity of commercial one purchased was close to 100% calculated by MDI Jade6 software. Furthermore, the biogenic one had less crystallinity，as evidenced by it lower value ranging from (88% to 90%). These results are were further validated by TEM observations. TEM images also revealed that the crystal size between these two magnetites were significantly different. The average crystal size of commercial magnetite was 122.9 nm, while biogenic magnetite was approx 16.8 nm. The two energy values of Fe 2p measured by the photoelectron spectroscopy of the two materials are very close to the binding energy of Fe 2p in Fe_3O_4 given in the database NIST XPS database, which further confirms that both materials are made of Fe_3O_4. In addition, both materials have abundant surface-bound hydroxyl groups on their surfaces.

Batch adsorption experiments were performed to study the effects of adsorption kinetics, equilibrium isothermal adsorption and pH on the Sb adsorption of nano-magnetites. Potassium pyroantimonate ($K_2H_2Sb_2O_7 \cdot 4H_2O$) was used as Sb(V) source. Five different concentrations of Sb(V) in the range of 0.5-50 mg/L were prepared,and a certain amounts of adsorbent magnetite were used as adsorbent. The adsorption experiments indicated that Pseudo-second-order equation could better fit the adsorption data of Sb (V) solution by measuring the adsorption data of 0.5 and 1 mg/L Sb solution within 12 hours. It indicated that the adsorption occurring on the surface of magnetite was mainly chemical adsorption. The maximum adsorption capacity of microorganism to synthesize magnetite was 9.88 mg/g, which is about 4.1 times than that of industrial magnetite. The effect of pH on adsorption was studied under the condition of PH 3-10. The adsorption capacity of two magnetites decreased gradually with the increase of pH. , However, the adsorption capacity of biogenic magnetite was significantly higher than that of commercial magnetite.

Comparing the synthesis methods, material characteristics and adsorption properties of two kinds of magnetite, we conclude that biogenic magnetite is a kind of