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Recovery of tellurium from aqueous solutions by adsorption with magnetic nanoscale zero-valent iron (NZVFe)

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ABSTRACT

Waste tellurium cadmium solar cells, as one of the world's fastest growing electronic waste, contain abundant valuable rare elements, offering potential for the prospects of resource exploitation and separation. Herein, we proposed a facile magnetic adsorption separation of tellurium from aqueous solutions by nanoscale zero-valent iron. As the precursor of tellurium adsorbents, the nanoscale FeOOH were first prepared by facile hydrothermal reaction. Then, magnetic nano zero-valent iron NZVFe was obtained by thermal reduction of FeOOH in the hydrogen atmosphere. The physical and chemical properties of magnetic NZVFe were characterized by a number of analytical techniques including scanning electron microscopy (SEM), transmission electron microscopy (TEM), powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and N_2 adsorption-desorption. The results indicated that the obtained NZVFe exhibit high specific surface areas (64.43 m^2/g), uniform pore sizes (2.80 nm), and high pore volumes (0.045 cm^3/g). XPS results indicated that the surfaces of NZVFe were covered by a layer of tellurium, implying the successful extraction of tellurium. Parameters such as initial tellurium concentration, solution pH, interfering ions, adsorption times and adsorption temperatures that affect the adsorption efficiency of tellurium were studied. Due to the highly accessible surface and fully exposed active sites of NZVFe, the samples exhibit excellent adsorption capacity of 190 mg/g towards tellurium in water, and separation efficiency can reach $>$ 95%. As a clean and high-efficient adsorbent, NZVFe has tremendous potential to handle and recycle cadmium telluride solar cells waste.

1. Introduction

A variety of photovoltaic (PV) materials with excellent performance have been existed and have made a significant contribution for the global energy crisis, such as the polycrystalline silicon (Kim et al., 2012), monocrystalline silicon (Chen et al., 2016b), single-walled carbon nanotubes (Mallakpour and Khadem, 2016), cadmium telluride (CdTe) (Zeng et al., 2010), gallium arsenide (GaAs) et al. (Chen et al., 2018). Among them, the development of cadmium telluride (CdTe) thin film solar cells is gaining more and more attention due to its ideal band gap, high optical absorption coefficient, high conversion efficiency, and stable battery performance (Rocchetti and Beolchini, 2015). Compared to traditional photovoltaic materials, cadmium telluride solar cells have a low manufacturing cost (Candelise et al., 2013) and currently have a maximum efficiency of 16% (Ferekides et al., 2000) which is lower than monocrystalline silicon solar cells. But the cadmium telluride photovoltaics have better cost structure than other thin film solar materials, taking into account factors such as conversion efficiency and the cost of raw materials.

While the photovoltaic industry has brought many conveniences to people's lives, it has also caused a series of problems (Eltawil and Zhao, 2010). Waste tellurium cadmium solar cells are toxic electronic pollutant and can cause a serious, long-term and hidden effect which is hard to deal with (Zhong et al., 2018). Once this substance penetrates into soil or groundwater, and accumulates to a certain extent, it will be a great threat to people's health (Lu et al., 2017). In addition, tellurium has a high commercial value not only in the photovoltaic industry, but also in many other industries such as metallurgy (Makuei and Senanayake, 2018), petrochemical (Fan et al., 2013), electronics and electrical (Zhang et al., 2017), glass ceramics (Binnemans et al., 2015) and medicine (Gupta et al., 2016). Most of the world's recyclable tellurium is associated with copper deposits, and each ton of copper contains 0.065 kg tellurium so that tellurium reserves are only around 22,000 tons all over the world (Marwede and Reller, 2012). According

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to the statistics, the annual tellurium production is far behind the market demand. Therefore, it is necessary to recycle tellurium in photovoltaic waste for both environmental protection and resource utilization.

At present, several methods that can extract tellurium from tellurium-containing materials have been proposed. Currently, the foundational extraction methods can be broadly divided into three kinds: pyrometallurgy (Etschmann et al., 2016), biohydrometallurgy (Rajwade and Paknikar, 2003) and hydrometallurgy (Randhawa et al., 2016). Usually, owing to the calcination is required in tellurium separation, pyrometallurgy has several disadvantages such as low efficiency, high energy consumption and high operation costs. In addition, during the process of pyrometallurgy, large quantities of solid and gas pollutants are discharged and if handled improperly, it can easily cause environmental pollution. Therefore, the methods of pyrometallurgy are not environmentally recommended. Biohydrometallurgy is one of the ideal direction for future development of metallurgical industry which just utilizes the bio-oxidation of microorganism to make the ores soluble without causing pollutions. Microorganism requires appropriate temperature, appropriate amounts of oxygen and the presence of organic species (Zhang et al., 2017). So, how to develop the corresponding microorganism becomes the key technical problem. Compared to pyrometallurgy and biohydrometallurgy, hydrometallurgy is considered to be one of the most cost-effective methods because it is readily available, low-energy and environmentally friendly. A comparative study shows that this method is the most appropriate for it can leach copper and tellurium simultaneously from a variety of metal elements in the industrial waste (Sun and Zheng, 2011). In this respect, several functional adsorbents such as nano-TiO_2 (Zhang et al., 2010), *N*-*n*-octylaniline (Sargar et al., 2011), and ion-exchange resins (Wang and Fthenakis, 2005) have been used to separate tellurium from aqueous solution by hydrometallurgy. The tellurium can be recovered by the adsorption of functional materials which greatly shortens the process and will not introduce new impurity. However, adsorption capacities of adsorbents are not satisfactory and the reaction rate is relatively slow that hinder the practical applications in tellurium separation.

Nanoscale zero-valent iron particles NZVFe have been studied since mid-1990s for its both excellent physical and chemical properties (Tosco et al., 2014). The most basic form of NZVFe is composed of spherical iron nanoparticles with individual dimensions < 100 nm (Hao and Zhang, 2017). In addition, NZVFe also possesses optical, electrical and gas sensitive properties which allow it broad application in the technical fields of magnetic fluid, high gradient magnetic separator, absorbing material, high density magnetic recording medium, gas sensor, and ceramic toughening technology (Danish et al., 2017). Moreover, because of its special nano-sized structure, NZVFe shows larger specific surface area and more reactive chemical activity than conventional ZVI and has been applied for environmental remediation and hazardous waste treatment since 2000 (Khalil et al., 2017). Large amounts of researches have reported the application of NZVFe in water treatment to degrade chlorinated solvents (Song and Carraway, 2005), phosphorus (Eljamal et al., 2016), trichloronitromethane (Chen et al., 2016a), organic dyes (Raman and Kanmani, 2016), and inorganic pollutants such as perchlorate, nitrate, and heavy metal ions (Ponder et al., 2000). Xiong et al. (2007) used stabilized zero-valent iron nanoparticles to destroy of perchlorate in water and ion-exchange brine. Watts et al. (2015) utilized NZVFe to treat chromite ore processing residue containing Cr(VI). Though the application of NZVFe in the field of environmental remediation and pollution control is evident by some research workers, there are no reports on the rare elemental separation from aqueous solutions using NZVFe.

This study is aimed to develop high-performance tellurium adsorbents and rapid separate tellurium from solution. The magnetic NZVFe, obtained by hydrogen reduction of FeOOH, was chosen as adsorbent for tellurium separation, and sodium tellurite was used as model targets. In order to optimize the optimal experimental conditions, several variables such as initial tellurium concentration, solution pH, interfering ions, adsorption times and adsorption temperatures that affect the adsorption efficiency of tellurium were controlled. The present work gives a new route to develop nanoscale zero-valent iron as magnetic adsorbents for the separation of tellurium from aqueous solution.

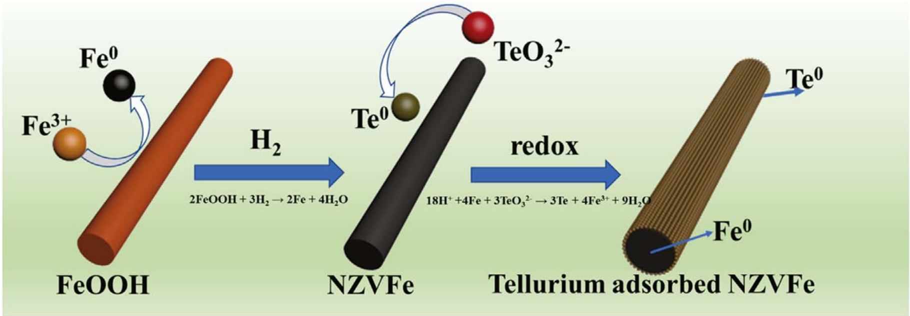
2. Materials and methods

2.1. Materials

Ferric chloride hexahydrate ($FeCl_3·6H_2O$), sodium nitrate ($NaNO_3$), sodium hydroxide (NaOH), sodium tellurite (Na_2TeO_3) and hydrochloric acid (HCl) were all purchased from Sinopharm Chemical Regent Co., Ltd. (Shanghai, China). Unless otherwise stated all above chemicals and reagents were of analytical grade and commercial available, and used without further purification. Distilled water was used in all experiments.

2.2. Fabrication of nanoscale zero-valent iron

In a typical synthesis, $FeCl_3·6H_2O$ (15 mmol) and $NaNO_3$ (150 mmol) were dissolved in deionized water (150 mL) and the pH was adjusted to 1.25 with 1% dilute aqueous hydrochloric acid solution. The mixture was dispersed by ultrasound at 40 kHz for 10 min, then the solution was transferred into a 150 mL teflon-coated stainless autoclave and reacted in an oven at 95 °C. After 12 h, the obtained FeOOH was filtered and washed three times with deionized water and ethanol respectively. After drying in an oven at 50 °C for 12 h, the dried FeOOH was grinded into a powder. Finally, the as-prepared products were transferred into a porcelain boat and placed in the tubular furnace. The whole process, including the initial heating from room temperature to 500 °C, was performed in a tube furnace with a constant flow of hydrogen at atmospheric pressure for 2 h, and the obtained NZVFe was sealed and stored to prevent oxidation in the air. The preparation process of NZVFe is shown in Scheme 1.



Scheme 1. The preparation and adsorption procedure of NZVFe.