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Research paper

Removal mechanism of selenite by Fe_3O_4-precipitated mesoporous magnetic carbon microspheres

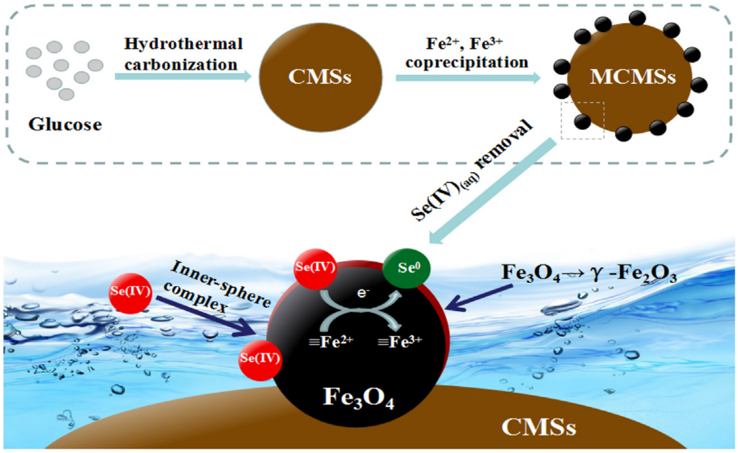
Jianwei Lu, Fenglian Fu*, Zecong Ding, Na Li, Bing Tang

School of Environmental Science and Engineering and Institute of Environmental Health and Pollution Control, Guangdong University of Technology, Guangzhou 510006, China

HIGHLIGHTS

- MCMSs were prepared via green hydrothermal carbonization and coprecipitation.
- MCMSs displayed effective removal of Se(IV) from wastewater.
- Se(IV) formed inner-sphere complexes with MCMSs and was reduced to insoluble Se^0.
- MCMSs can be easily separated and recycled by an external magnetic field.

GRAPHICAL ABSTRACT



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ABSTRACT

A mesoporous composite of magnetic carbon microspheres (MCMSs) was synthesized via introducing Fe_3O_4 nanoscale particles to the surface of carbon microspheres (CMSs) by coprecipitation. Scanning electron microscopy and transmission electron microscopy showed the Fe_3O_4 nanoscale particles were dispersedly immobilized on the surface of CMSs. The MCMSs demonstrated effective removal of selenite (Se(IV)) from wastewater. MCMSs showed the regular pattern where the lower pH value, the lower residual Se(IV) concentration. The coexisting sulfate, nitrate, chloride, carbonate, and silicate had no significant effect on Se(IV) removal, whereas phosphate hindered the removal of Se(IV) by competing with Se(IV) and formed inner–sphere complexes with Fe_3O_4 on the surface of MCMSs. Through X–ray photoelectron spectroscopy analysis, Se(IV) can not only form inner–sphere complexes with MCMSs, but also be reduced to insoluble elemental selenium (Se^0) by Fe_3O_4 which was oxidized and formed $\gamma\text{–}Fe_2O_3$. Moreover, the superparamagnetic MCMSs can be easily separated from solution by means of an external magnetic field. The high removal efficiency for Se(IV) and rapid separability of MCMSs made them promising materials for the application in the practice.

1. Introduction

Selenium (Se), a non–metal element, occurs in the environment naturally as an essential micronutrient for animals and human. It

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* Corresponding author.
E-mail address: fufenglian2006@163.com (F. Fu).

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is significant that Se owns a toxic and beneficial feature to health. At low concentration, Se plays an important role in strengthening the immune system, and has an anticarcinogenic effect. However, if taken in excess, it appears to be cancerigenic and genotoxic [1]. The range between essential and toxic concentrations in humans is narrow: the concentration below 40 μg/d will lead to Se dietary deficiency, while above 400 μg/d can reach a toxic level. Se can accumulate in the aquatic environment, which influences the propagation and health of fish and waterfowls [2]. Thus it is vital to control the content of Se in water. World Health Organization (WHO) has set a guideline at 40 μg/L for Se in drinking water [3]. Although selenium can naturally exist in the environment, the human anthropogenic activities including the combustion of coal, mining, production of insecticide, glass manufacture, and photocells aggravate the selenium contamination [4]. Taking mining wastewater for example [5], the containing Se can be found in a rather high concentration which was several hundred times over the guideline of WHO.

In environment, Se presents in five oxidation states: −2, −1, 0, +4, and +6 with the forms of selenide (Se^{2-}), elemental selenium (Se^0), selenite (Se(IV), SeO_3^{2-}, $HSeO_3^-$), selenate (Se(VI), SeO_4^{2-}), and organic selenium [6]. These different oxidation states strongly influence the chemical and toxicological properties of Se. In aqueous media, Se^0 and metal selenides are much insoluble, while selenite and selenate prevail as mobile aqueous oxyganions [7]. However, selenite and selenate in environmental water reveal more than 40 times higher toxicity than their organic selenium [8]. Moreover, the acute toxicity of Se(IV) is nearly 10 times higher than Se(VI) according to the U.S. EPA report (FRL–5649–7) [9].

Various researches have been reported that inorganic forms of Se species (Se(IV) and Se(VI)) can strongly bond with iron oxides such as maghemite (γ–Fe_2O_3), and magnetite (Fe_3O_4) [10,11]. Compared with other iron oxides, Fe_3O_4 carries out unique properties such as superparamagnetism and reducibility [12,13]. So Fe_3O_4 can be easily separated from the reaction medium with an external magnetic field, and it is possible to reduce Se(IV) and Se(VI) to a more insoluble Se^0 species. Nevertheless, the aggregation during the reaction leads to the decrease of the reaction activity of Fe_3O_4, hindering the extensive applications of Fe_3O_4 [14]. Therefore, some significant efforts for avoiding such limitation and significant efforts for avoiding such limitation of the Fe_3O_4 particles have been made in the recent years [15–17], which proved that immobilizing Fe_3O_4 particles on supports to form multifunctional composites can solve the problem of aggregation. Carbon materials have been regarded as ideal candidates for supporting Fe_3O_4 particles due to their excellent properties, including high specific surface area, high structural and chemical stability [18,19]. As an important form of carbon materials, carbon microspheres (CMSs) have attracted much attention recently [20,21]. CMSs have not only the advantages of the carbon materials but also the unique pore structure and size [20]. CMSs are attractive in interdisciplinary researches because of their characteristics of narrow pore size distribution and continuous adjustability [19,22].

To the best of our knowledge, the removal of Se(IV) by magnetic carbon microspheres (MCMSs) has not been studied to date. Thus, in the present work, the CMSs were synthesized via a green method of hydrothermal carbonization [23,24], and Fe_3O_4 nanoscale particles (NPs) were introduced to the surface of CMSs to form MCMSs by coprecipitation. Then, the MCMSs were used to investigate the ability in removing Se(IV) from aqueous solutions. The characterizations of MCMSs before and after reaction with Se(IV) were carried out by scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS) mapping, Fourier transform infrared (FTIR), X–ray diffraction (XRD), vibrating sample magnetometry (VSM), and X–ray photoelectron spectroscopy (XPS), aiming to elucidate the structure of MCMSs and the reaction mechanism. The residual concentrations of Se(IV) and the generated Se(VI) during the reaction at different pH values were determined. Finally, tests on the effect of coexisting anions and the recycling of MCMSs were also conducted.

2. Materials and methods

2.1. Materials and reagents

All chemicals were of analytical grade. Glucose ($C_6H_{12}O_6{\cdot}H_2O$) was purchased from KeLong Chemical Reagent Co., Ltd. (Chengdu, China). Ferrous chloride ($FeCl_2{\cdot}4H_2O$) was purchased from Guangzhou Chemical Reagent Co., Ltd. Ferric chloride ($FeCl_3{\cdot}6H_2O$) was purchased from Damao Chemical Reagent Co., Ltd. Ammonia was purchased from Shanghai Titan Scienctific Co., Ltd. Na_2SeO_3 was purchased from Xiya Chemical Reagent Co., Ltd. (Shandong, China). All stock solutions were prepared with distilled water. The Se(IV) stock solutions were prepared by dissolving Na_2SeO_3 in distilled water.

2.2. Preparation of CMSs

CMSs were synthesized according to the adapted method from Ryu et al. [24]. In brief, 7.92 g of glucose was dissolved into 80 mL of distilled water. Following ultrasonic dispersion for 5 min, the solution was transferred into a Teflon–lined autoclave with a 100 mL capacity (80% filling). Then the reactor was placed in a muffle furnace at a temperature of 180°C for 5 h. After hydrothermal reaction, the reactor was naturally cooled to room temperature. The brown precipitates were collected by filtration with a 0.22 μm pore diameter membrane, and washed with distilled water and ethanol for several times until the supernatant was colorless and transparent. The brown solids of CMSs were finally obtained after drying at 80 °C for 6 h.

2.3. Preparation of MCMSs

MCMSs were synthesized by chemical coprecipitation method [25]. 0.585 g of $FeCl_3{\cdot}6H_2O$ and 0.215 g of $FeCl_2{\cdot}4H_2O$ (mole ratio of Fe^{3+} and Fe^{2+} is 2:1) were firstly dissolved into 200 mL distilled water which had been bubbled with high purity nitrogen gas ($N_2 \geq 99.999\%$) for 30 min. Then, 0.2 g of CMSs was added into the flask with vigorous stirring. 1.0 M ammonia solution was added dropwise to precipitate Fe^{2+} and Fe^{3+} ions to synthesize Fe_3O_4 NPs till the pH value of the mixture reached 11.0. To avoid the oxidation of Fe^{2+} ions, the system was kept under nitrogen atmosphere throughout the entire synthetic process. After that, the black solution was applied by external magnetic field to separate the MCMSs. Finally, the MCMSs were washed to neutral pH with anaerobic distilled water for several times, and then dried under vacuum at 40 °C for about 12 h.

2.4. Batch experiments of Se(IV) removal

Batch experiments were conducted to examine the Se(IV) removal by MCMSs in a thermostatic shaker at 120 rpm. A definite amount of MCMSs was added to the Se(IV) wastewater with the initial concentration of 10.0 mg/L under ambient condition. The initial pH of the solution was adjusted to the designated values (3.0, 5.0, 7.0, 9.0, and 11.0) with HCl or NaOH. At a given time interval, 2.0 mL mixture was sampled, and filtered using 0.22 μm pore diameter membrane. Afterwards, the concentrations of Se(IV) and Se(VI) in the filtrate were measured. All experiments were carried out at least in triplicate, and average values along with one standard deviation were presented.