



Magnetic prussian blue/graphene oxide nanocomposites caged in calcium alginate microbeads for elimination of cesium ions from water and soil

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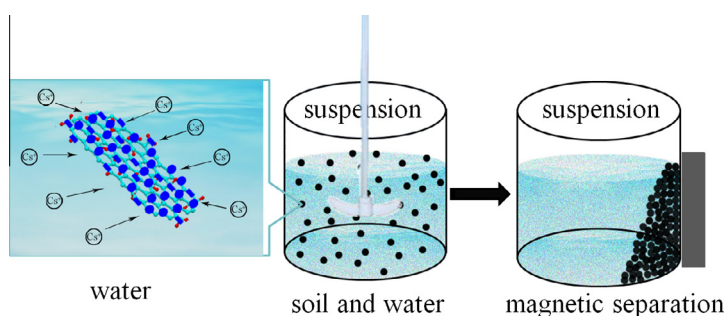
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HIGHLIGHTS

- Magnetic prussian blue/graphene oxide–calcium alginate microbeads were prepared.
- Microbeads could be separated rapidly by an external magnetic field.
- Adsorption properties for Cs⁺ of microbeads were studied.
- The microbeads present high efficiency and good selectivity to Cs⁺.
- The microbeads are convenient for treatment of cesium-contaminated water and soil.

GRAPHICAL ABSTRACT



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ABSTRACT

To remove cesium ions in water and soil, magnetic prussian blue/graphene oxide (PB/Fe₃O₄/GO) nanocomposites encapsulated in calcium alginate microbeads (PFGM) were designed and fabricated. The protocol was processed with environment-friendly and low-cost precursors at ambient temperature and pressure. The adsorbents presented high selectivity to Cs⁺ and could extract it even in trace amounts. Sorption of 80% Cs⁺ to the new adsorbent were fulfilled in less than 2 h, and maximum adsorption capacities were 43.52 mg/g. Cesium ions were absorbed primarily by both of chemisorption (K⁺/H⁺-exchange) and physisorption (ion trapping). The saturation adsorption and adsorption kinetics fitted well with the Langmuir isotherm and the pseudo-second-order kinetic model. Both the temperature and pH value would affect the sorption performance, meanwhile, the microbeads were stable in natural water, seawater, and pH value of solutions ranging from 4 to 10 without collapse of microbeads and leaching of prussian blue. Most importantly, these microbeads could be separated effectively from aqueous solution (or soil suspensions) by an external magnetic field, which was convenient for large-scale treatment of cesium-contaminated water (or soil).

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1. Introduction

As energy demands worldwide increase and more concerns over climate change, countries are looking for various cheap and

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carbon-free materials for alternate energy. Nuclear energy, which supplied about 9.7% energy of the world (2013) [1], is one of the most promising way. The weak point of this process is that it causes about 2000–2300 metric tons of nuclear waste releasing into the environment each year [2]. Especially, when the nuclear power plant accidents happened, more radionuclides leaked out. After Japan's 2011 Fukushima Daiichi nuclear disaster, an estimated

630,000–770,000 TBq (terabecquerel) radioisotopes left the region with contaminated soil, air and water [3–5]. Presently, an effective solution to deal with radioactive pollution is to store the waste in a place so that the environment would not be contaminated. However, the volume of radioactive water and soil is so huge that could not be stored long time safely. Therefore, many approaches are developed to decrease waste volumes effectively, and the selective separation of radionuclides from nuclear waste solutions is an effective method for the minimization of nuclear waste volumes for final disposal.

Among the nonactinide radioactive pollution, radio-isotopes of ^{134}Cs and ^{137}Cs with 2.06 and 30 years half-life, respectively, are principal source of radioactivity and the highest safety risk to the site by emitting beta-particles and strong gamma rays. Due to the radiation stability and high ion-exchange capacity, many inorganic cation exchangers, such as zeolites, clay minerals, chalcogenido clusters, crystalline silicotitanates and metal oxides have been already studied for separation of radioactive cesium from nuclear wastewater [6–10]. However, the low affinity for Cs^+ and high cost have hindered their practical application. Thus, an effective and low-cost method is necessary to solve the problems above mentioned.

Prussian blue (PB, ferric hexacyanoferrate), which is considered to be the first synthetic coordination compound [11], has ever been effectively used to treat cesium exposure after the Chernobyl nuclear reactor disaster and the Goiânia accident [12] because of its low-cost and high ion-sieving functionality for Cs^+ [13]. However, PB prepared by precipitation is usually ultra fine powder, which is difficult to be separated by centrifugation or filtration after Cs^+ sorption. Magnetic separation, which has been used in the treatment of heavy metal and organic pollutants [14–18], is a convenient method to recover adsorbent from wastewater. However, these nanomaterials are easily aggregated due to small size and active surface [19,20]. In order to improve the stability and expand the application of magnetic nanoparticles, anchoring onto matrix and surface coating is an efficient strategy. Graphene oxide (GO), which has a large theoretical surface area, has been proven to be non-toxic and biodegradable [21] and could be produced in bulk quantities. In addition, recently Romanchuk reported that GO could rapidly eliminate radioactive long-lived anthropogenic radionuclides from contaminated water [22]. Thus, anchoring Fe_3O_4 magnetic nanoparticles (MNPs) onto large surface area of GO and *in situ* coating Fe_3O_4 MNPs with PB might be a promising method to overcome the above difficulties. Our group has reported the *in situ* controllable synthesis of magnetic prussian blue/graphene oxide nanocomposites [23] recently. But it is still impractical to directly use magnetic nanoparticles for large-scale water treatment because of the complex substrate encountered in environmental applications, especially for soil. So a powerful immobilising approach is needed for the safe use of nanoparticles. Calcium alginate, which constitutes a polymer “cage” by cross-linking, is a water-insoluble and versatile immobilizer. It has been widely used for entrapment of enzymes (or microbial cells) and adsorbents in the biological and environmental applications [24,25].

In this paper, PB/ Fe_3O_4 /GO nanocomposites encapsulated in calcium alginate microbeads (PFGM) were synthesized for removing cesium ions from water and soil. PB/ Fe_3O_4 /GO nanocomposites were prepared by an anchoring Fe_3O_4 MNPs onto surface of GO and *in situ* coating Fe_3O_4 MNPs with PB nanocrystal layer. In comparison with that, PB/ Fe_3O_4 nanocomposites encapsulated in calcium alginate microbeads (PFM) were also prepared in similar way. The chemical and physical characterization of the synthesized adsorbents was conducted, and the applicability in Cs^+ removal was evaluated in view of the sorption kinetic and capacity, mechanism, effects of water matrices, and the material stability. Moreover, the removal capacity of Cs^+ from soil was also investigated.

2. Experimental

2.1. Synthesis of PB/ Fe_3O_4 and PB/ Fe_3O_4 /GO nanocomposites (Fig. 1)

Fe_3O_4 nanoparticles sized 8–12 nm were synthesized by a slightly modified Massart Method [26]. Graphene oxide (GO) nanosheets were obtained from natural graphite flakes by a modified Hummer's method [27]. In a typical synthesis, GO (30 mg in 50 mL, aq.) and magnetite (0.3 g in 300 mL, aq.) were dispersed by ultrasonication, respectively. The two suspensions were then mixed together and stirred vigorously for 10 min. The brown precipitate was collected with a magnet and rinsed with water three times. Subsequently, the precipitate was redispersed in 300 mL of water. 100 mL of FeCl_3 (28.4 mM, aq.) was added to the precipitate suspension under stirring, and then 50 mL of $\text{K}_4[\text{Fe}(\text{CN})_6]$ (42.6 mM, aq.) was slowly dropped in. The color of the mixture gradually changed from brown to dark cyan, suggesting the formation of PB/ Fe_3O_4 /GO nanocomposite. The mixture was stirred for another hour. The precipitate was recovered with a magnet, and then washed with water three times. Finally, the powder was dried in oven at 50 °C.

Control studies indicated that the addition of GO improved the adsorption capacity against cesium ions. Nanocomposites with high adsorptive efficiency were obtained by using the optimized concentrations for 1.6% (GO), 39.0% (Fe_3O_4) and 59.4% (PB) for PB/ Fe_3O_4 /GO.

The preparation of PB/ Fe_3O_4 nanocomposites is similar as that of PB/ Fe_3O_4 /GO but without adding GO.

2.2. Preparation of the PB/ Fe_3O_4 (or PB/ Fe_3O_4 /GO)-encapsulated calcium alginate microbeads

3.5 g of PB/ Fe_3O_4 (or PB/ Fe_3O_4 /GO) powder was added into the solution of sodium alginate (87.5 mL, 2%, w/v) and intensely stirred for 20 min. PFM (or PFGM) (Fig. S1) were prepared by the dropwise addition of the aqueous PB/ Fe_3O_4 (or PB/ Fe_3O_4 /GO)-sodium alginate colloidal solution into a beaker containing calcium chloride solution (5%, w/v) under mechanical stirring. The hydrogel microbeads were stirred in the solution about 2 h for maturation. They were then collected by an external magnet, washed three times with deionized water. Followed that, they were dealt with by two ways. One is dried in oven at 50 °C (denoted as PFMd or PFGMd), the other is stored in calcium chloride solution (1%, w/v) (denoted as PFMw or PFGMw). Moreover, the Fe_3O_4 /GO encapsulated-calcium alginate microbeads and pure microbeads were prepared and named as AFGM and M, respectively. Large-scale bead production was possible with the help of a small pump and flow controller (Fig. S2).

2.3. Adsorption experiments

Inactive cesium (cesium-133) was used to study adsorption behaviors. About 0.05 g (dry weight) of the PB-based adsorbent (denoted as PFM or PFGM) were added into 20 mL of cesium chloride solution (ranging from 25 to 150 ppm) in a sealable plastic tube. The test tubes were shaken at 200 rpm on a vortex shaker. The concentration of cesium that remained in solution was quantified with an atomic absorption spectrophotometer (AA-6300C, Shimadzu). The adsorption of each sample was tested in triplicate, and averages were used to evaluate the adsorbent capabilities. The elimination efficiency ($E\%$) and adsorption capacity at equilibrium (q_e) of cesium ions can be calculated by using Eqs. (1) and (2), respectively [28,29].

$$E(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

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