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Facile synthesis of pectin-stabilized magnetic graphene oxide Prussian blue nanocomposites for selective cesium removal from aqueous solution

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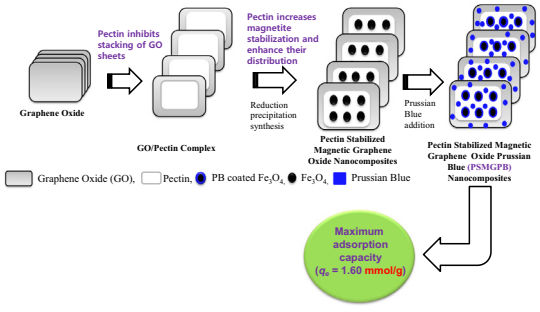
HIGHLIGHTS

- PSMGPB nanocomposites were synthesized by low cost facile method for cesium removal.
- The PSMGPB nanocomposites were characterized by XPS, XRD, MPMS, TEM, and SEM.
- Pectin-stabilized separation of graphene oxide sheets enhanced the cesium adsorption.
- Based on nonlinear regression, Langmuir model gave the best fit to experimental data.
- Thermodynamic study indicated the spontaneous and exothermic nature of adsorption.

GRAPHICAL ABSTRACT



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ABSTRACT

This work focused on the development of pectin-stabilized magnetic graphene oxide Prussian blue (PSMGPB) nanocomposites for removal of cesium from wastewater. The PSMGPB nanocomposite showed an improved adsorption capacity of 1.609 mmol/g for cesium, compared with magnetic graphene oxide Prussian blue, magnetic pectin Prussian blue, and magnetic Prussian blue nanocomposites, which exhibited adsorption capacities of 1.230, 0.901, and 0.330 mmol/g, respectively. Increased adsorption capacity of PSMGPB nanocomposites was attributed to the pectin-stabilized separation of graphene oxide sheets and enhanced distribution of magnetites on the graphene oxide surface. Scanning electron microscopy images showed the effective separation of graphene oxide sheets due to the incorporation of pectin. The optimum temperature and pH for adsorption were 30 °C and 7.0, respectively. A thermodynamic study indicated the spontaneous and the exothermic nature of cesium adsorption. Based on non-linear regression, the Langmuir isotherm fitted the experimental data better than the Freundlich and Tempkin models.

1. Introduction

Nuclear power is a carbon-free energy source and an alternative to power generated from fossil fuels. Nuclear power generates about 5.7% of the world's energy and 13% of the world's electricity. Radioactive cesium (Cs) is a significant fraction of the radioactive liquid waste generated from the reprocessing of nuclear fuel (Chang et al., 2008). Radioactive Cs is a strong gamma emitter with a long half-life ($T_{1/2}$ = 30.17 years). Cs is also very soluble in water, which enables its migration through ground water to the biosphere, which causes serious environmental and human health threats (Dwivedi et al., 2013). The biogeochemical behavior of Cs

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is similar to that of potassium, a major nutrient for plants and animals, signifying that radioactive Cs has the potential to rapidly transfer into the food chain (Liu et al., 2014). Recent accidents, such as at the Fukushima Daiichi nuclear power plant in Japan and the contamination of water in nuclear reactors, have been highlighted along with the significant need for effective treatment methods for radioactive Cs-contaminated water (Chen et al., 2015). Various treatment technologies, such as solvent extraction, chemical precipitation, membrane processes, evaporation, and adsorption have been used for the removal of radionuclides from aqueous solutions (Mahmoud and Seliman, 2014). Conventional coagulation–sedi mentation processes can effectively remove particle-bound Cs from waters, but it cannot easily remove soluble Cs ions (Liu et al., 2014). Adsorption is the one treatment technology in the above list that has been successfully applied to the treatment of radioactive Cs-contaminated water (Mahmoud and Seliman, 2014).

Prussian blue ($Fe_7(CN)_{18}$) is a dark blue color pigment, which has a simple face-centered crystal structure with eight water molecules forming a unit cell. The Prussian blue crystal has a cage size similar to the hydration radius of Cs^+ (3.25 Å), which is smaller than the cage size for Na^+ (3.6 Å), Ca^{2+} (4.1 Å), and Mg^{2+} (4.25 Å) (Liu et al., 2014). Hence, in recent years, much attention has been given to the selective removal of Cs by Prussian blue and its analogues (Jang and Lee, 2016; Olatunji et al., 2015). However, due to the fine powder morphology of Prussian blue, it is very difficult to separate it from treated solutions. The Prussian blue coating on iron oxide (Fe_3O_4) magnetic nanoparticles gives a unique nanocomposite, which can be separated after the adsorption of radioactive Cs from water. The average particle size of Fe_3O_4 is in the range of 5–10 nm, which results in a very high total surface area for agglomeration (Yang et al., 2014b). However, anchoring the magnetic Prussian blue-coated Fe_3O_4 nanocomposites onto a unique matrix, for example graphene sheets, is an ideal method to prevent agglomeration. Graphene is a very popular material in numerous applications due to its excellent electronic, thermal, and mechanical properties (Novoselov et al., 2012). Graphene sheets, however, tend to irreversibly agglomerate because of the favorable van der Waals interactions between them, which limits their application (Devasenathipathy et al., 2014). Attaching polymer sheets to the graphene sheets is a facile approach to maintain graphene as individual sheets so that its excellent properties can be accessed (Devasenathipathy et al., 2014; Latif et al., 2013). Biopolymer pectins, also known as pectic polysaccharides, are rich in galacturonic acid, and are reported to be bioactive, biocompatible, and biodegradable. The pectin structure also contains hydroxyl (–OH) and carboxyl (–COOH) groups like graphene oxide that allows enhanced attachment of Prussian blue. This better attachment may lead to enhanced Cs adsorption, providing an extra advantage for the nanocomposite (Mollea et al., 2007). Evidence in the literature tells that pectin as a stabilizer for graphene oxide sheets enhances its properties (Devasenathipathy et al., 2014).

In this study, pectin-stabilized magnetic graphene oxide Prussian blue (PSMGPB) nanocomposites were sequentially synthesized by graphene oxide pectin complexation, reduction precipitation, and Prussian blue attachment for selective removal of Cs from water. The PSMGPB nanocomposite was thoroughly characterized by high-resolution transmission electron microscopy (HR-TEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), thermal gravimetric analysis (TGA), and scanning electron microscopy (SEM). Stabilization of magnetite and graphene oxide sheets by pectin resulted in enhanced distribution of Prussian blue, which ultimately caused an increase in Cs removal.

2. Materials and methods

2.1. Materials

All chemicals used herein were analytical grade, the highest purity available. Cesium nitrate, pectin, and calcium chloride were purchased from Sigma-Aldrich (USA). Ferric chloride, potassium ferrocyanide, ethanol, acetone, ammonia, and sodium sulfate were acquired from Junsei (South Korea).

2.2. Synthesis

The PSMGPB synthesis was carried out in three steps. In the first step, complexation of pectin and graphene oxide was done by mixing a graphene oxide solution 15 mL (0.33%) with 10 mL of pectin (0.5%). This mixture was ultrasonicated (Powersonic 605) for 15 min followed by 10–15 min of stirring at room temperature. In the second step, pectin complexed with graphene oxide was used to synthesize the pectin-stabilized magnetic graphene oxide nanocomposite by the reduction precipitation method. Pectin complexed with graphene oxide was added dropwise with continuous stirring to 35 mL of $FeCl_3$ solution (3.2% $FeCl_3$ in 0.12 N HCl). Once this mixture was stirred well, 25 mL of Na_2SO_3 solution (0.7%) was added. As soon as the color of this mixture changed from red to yellow, 12 mL of 14% ammonia was added. A black-colored precipitate resulted, to which was added 5 mL of $CaCl_2$ (1%). The mixture was stirred continuously at room temperature for 2 h. The resulting pectin stabilized magnetic graphene oxide nanocomposite was collected by an adscititious magnet, and then washed sequentially and thoroughly with water, ethanol, and acetone. In the third step, Prussian blue (PB) was attached to the pectin stabilized magnetic graphene oxide nanocomposite to form the nanocomposite PSMGPB. Well-washed pectin stabilized magnetic graphene oxide nanocomposites were placed in 200 mL distilled water and dispersed for 1 h using an ultrasonicator (Powersonic 605). The well-dispersed nanocomposite was transferred to a 500 mL reaction vessel and stirred continuously at 90 °C for 10 min. Then, 85 mL of potassium ferrocyanide (42.6 mmol) was added to the mixture, and this mixture was stirred for 2 h at 90 °C. After stirring, 170 mL of $FeCl_3$ (56.8 mmol) solution was dropwise-added to the mixture. The resulting blue-colored mixture was aged by stirring for 3 h at 90 °C. The PSMGPB nanocomposites were removed using an adscititious magnet and washed thoroughly with distilled water. The resulting PSMGPB particles were freeze-dried and ground to form uniform size particles for use in further studies.

The synthesis of magnetic graphene oxide Prussian blue (MGPB), magnetic pectin Prussian blue (MPPB), and magnetic Prussian blue (MPB) nanocomposites was done as per above mentioned method, by using the respective component. In case of MGPB and MPPB synthesis, graphene 15 ml (0.33%) and pectin 10 mL of pectin (0.5%) was taken, and proceeded for reduction precipitation synthesis and prussian blue attachment, respectively. For the synthesis of MPB, the reduction precipitation synthesis was followed by the prussian blue attachment. The obtained respective nanocomposites were washed thoroughly, freeze-dried, and ground to form a uniform size for the further use.

2.3. Characterization

XRD analysis was performed using an X-ray diffractometer (Rigaku, D/Max-2500) with Cu Kα radiation (λ = 1.5406 Å) over a scanning range of 10°–80° (2θ). The magnetic properties of the PSMGPB nanocomposite were analyzed by a SQUID-VSM QM02 magnetometer at room temperature with an applied field between