Graphene-prussian blue nanocomposite impregnated in alginate for efficient removal of cesium from aquatic environment

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ABSTRACT

Simple hydrothermal reaction followed by displacement reaction was used for preparation of prussian blue graphene oxide alginate (PB-GO-Alg) composite in beads form for highly efficient removal of Cs isotopes from aquatic environment. The optimum composition of the beads was 5% loading of PB (Prussian blue)-GO (Graphene Oxide) nanoparticles into 4% Ca-alginate matrix. GO upon functionalization with PB which is a zeolite-like inorganic materials capable of exchange of its K ions for Cs ions. Due to the combined effects of GO, PB and host alginate matrix, the hybrid beads showed excellent removal efficiency (> 98%) for Cs isotopes from different aquatic environments. Sorption isotherm followed the Langmuir model (linear regression correlation = 0.95) and the maximum sorption capacity of Cs was calculated to be 290.6 mg g^{-1}. Kinetic study showed that the uptake was following the pseudo second order rate law. The beads were effective at pH5-7 (uptake > 98%) for Cs removal and the equilibrium time required was 6 h.Mechanism of sorption was proposed based on the zeta potential values of the GO and PB-GO nanocomposites at different pH. The developed hybrid beads hold great promise to be used in case of any nuclear eventualities to decontaminate Cs contaminated water without disturbing the water quality parameters.

1. Introduction

Growing demand of clean energy can be meet by making the use of nuclear energy. In recent times, many countries are looking for nuclear energy to meet their power requirement [1,2]. Most of the nuclear reactors use uranium as a fuel where ^{235}U undergoes fission. ^{137}Cs is one of the high yield fission products of ^{235}U. ^{137}Cs is radioactive and undergoes decay with the release of beta and gamma radiation. The half-life of ^{137}Cs is 30 years Other major source of release of ^{137}Csinto the environment are nuclear weapon tests, nuclear accidents like Chernobyl, USSR (March, 1986) and catastrophic incidents like Dai ichi Nuclear Power Plant Fukushima, Japan (11 March, 2011) [3–6]. Once the radioactive ^{137}Cs enters the terrestrial environment, its probability of causing large scale potable water contamination is very high. Considerable attention has therefore been devoted in recent years to decontaminate water from radioactive ^{137}Cs. Various materials and methods like filtration, coagulation, co-precipitation, centrifugation, chemical precipitation, ultra and nano filtration, reverse osmosis, adsorption, ion exchange etc. are reported in literature for removal of cesium from aquatic bodies [7–9]. Most of the reported solid state adsorbent materials are not suitable for ambient pH and for sea water with high salt content [10] except very few [11].

Research on composite materials as a new generation sorbent is one of the emerging topics in environmental science and engineering. Enabling incorporation of molecular components into a base or support matrix lead to formation of multi component composites with novel functionality and enhanced performance. The multi component materials are generally known as hybrid materials or simply as composites [12–15].

PB in recent years has gained attention because of its unique properties and wide range of application [9,16]. Prussian blue (PB) has shown excellent sorption ability for Cs and is a potential candidate to be used as a component for composite sorbent for cesium. PB is a blue pigment consisting of iron cations, cyanide anions, and water. The empirical formula without the water of crystallization is $Fe_4[Fe(CN)_6]$. But the PB particles formed by precipitation method is in fine powder form. Its separation from the aqueous medium becomes very difficult as sedimentation rate is very slow.

Graphene oxide (GO) can be a good supporting material for PB due to the paper like monolayer of sp2 hybridised carbon atoms patterned in a hexagonal structure with presence of surface functional groups. Its properties like high electrical conductivity, thermal conductivity, high surface area etc. prompted scientist to show interest to utilise it for electronic applications, use as sensing materials, as catalysts etc.

[17–19]. Potential of GO to be used as a sorbent as individual or as a component of composite material is being studied worldwide [20–22].

Since GO forms a stable colloidal suspension, it is difficult to separate and then functionalise with PB. So in-situ synthesis of PB over GO network is advisable [23–25].Combining PB and GO may yield enhanced performance due to synergistic effects [26].

Although PB-GO composite can be selective for cesium, actual treatment plant deserves the sorbent in the beads form and preferably suitable to be packed in a column as separation of powder or suspended particles is an issue. Immobilising the sorbent into the second medium not only is helpful in terms of ease the separation but also reduces the probability of leaching of its constituents into water [27,28]. Alginate which is a natural polymer extracted from brown algae is a good candidate for immobilization to form the hybrid beads [29–31]. It is a sequence of β-D-mannuronate (M block) and its epimer α-L-guluronate (G block) rresidues with a molecular weight of 10–600 kDa [32–34]. The use of alginate as immobilizing agent rests in its ability to form heat-stable strong gels. These gels can be developed at room temperatures and are quiet stable [35–38]. Sodium alginate is soluble, Na$^+$ ions dissociate from the polysaccharide strands and divalent cations (e.g. Ca^{2+}) bind with two different alginate networks simultaneously, causing cross linking and formation of ionotropic hydrogels [39–42].

In the present study, we report the synthesis and characterization of PB-GO nanocomposite and its impregnation into calcium alginate matrix to form hybrid material PB-GO-Ca-Alg. This hybrid material (PB-GO-Ca-Alg) was used for the uptake of cesium after optimizing various parameters like pH, equilibrium time, initial concentration of cesium. Developed material exhibits strong affinity for the removal of cesium from aquatic bodies and the mechanism was proposed based on the zeta potential of GO and PB-GO at different pH.

2. Materials and methods

2.1. Chemical and reagent

All the reagents and chemicals used for the experimental work were of analytical grade and were used without pre-treatment. MILLIQ water having resistivity 0.01 μS cm^{-1} and DOC (Dissolved Organic Carbon) less than 5 ng mL^{-1} was used for the preparation of the reagents throughout the experiment.

2.2. Synthesis of the prussian blue-graphene oxide (PB-GO) composite

Graphene oxide was first synthesized by chemical exfoliation of graphite powder using modified Hummers method [43,44]. In a typical process 1 g graphite powder was added to 50 mL ice cooled H$_2$SO$_4$ (< 5 °C). Then 4 g KMnO$_4$ was added slowly under constant stirring and the mixture was kept for 3 h at a temperature below 10 °C. The mixture was diluted with deionized water keeping inside an ice bath. To remove the remaining KMnO$_4$,30% H$_2$O$_2$ was added drop wise to the mixture. The mixture was filtered and solid residue collected was washed with 5% HCl followed by deionized water and finally the residue was dried at 50 °C for 24 h. Thus, obtained graphene oxide (GO) was suspended in water [500 mg in 100 mL water] using an ultrasonic bath (model. The pH was adjusted to 3–4 and a freshly prepared 1 mM ferrous sulfate solution was added drop wise under constant stirring. Fe (II) was oxidised followed by hydrolysis to form goethite (iron oxyhydroxide, α-FeOOH) over the GO particles. The mixture was then reacted with 10 mM potassium ferrocyanide to form Prussian blue (PB) attached to the suspended GO particles [9,16]. The obtained composite (PB-GO) was filtered, washed and dried.

2.3. Impregnation of prussian blue-graphene oxide (PB-GO) composite in calcium alginate (PB-GO-Ca-Alg)

Measured quantity PB-GO composite was mixed thoroughly in 4%

Sodium alginate solution. of Then the mixture was stirred (900 rpm) for 3 h to make it homogeneous. Mixture was added drop wise into 4% calcium chloride solution using a flow controlled peristaltic pump. Sodium alginate reacted with calcium chloride to form beads of Ca alginate, entrapping the PB-GO within it. The beads of PB-GO-Ca-Alg were homogenous, stable and permeable to water.

2.4. Characterization of the sorbent

The size distribution and zeta potential and of GO and PB-GO composite were measured using He-Ne laser (633 nm) based dynamic light scattering (Melvern: Zeta sizer nano ZS). The zeta potential of the GO and PB nanoparticles were measured using the laser Doppler velocimetry (LDV) technique. Zeta potential was recorded at different pH values using auto titration system attached to the zeta sizer. Structural and functional group characterization of synthesized GO and PB-GO was done by XRD and Attenuated Total Reflectance Fourier Transform Infra Red spectrometer (ATR-FTIR) respectively. XRD was recorded using "InXitu BTX 194″system having scanning range of 5-55°. ATR-FTIR spectra were collected in the wavelength range of 500–4000 cm^{-1} with a spectrum resolution of 4 cm^{-1}using ATR-FTIR spectrometer equipped with the universal ATR as an internal reflection accessory having composite zinc selenide (ZnSe) optics and diamond crystal (ATRFTIR; Make Bruker, Model ALPHA-P). The morphology of the sorbent was recorded by using Scanning Electron Microscope - Energy Dispersive X-ray Spectrometry system (SEM-EDS) (Instrument Model No. VEGA MV 2300 T).

2.5. Sorption study

The sorption studies of cesium using PB-GO-Ca-Alg beads were performed in batch process. The glassware and polypropylene bottles used for the experiment were cleaned, rinsed thoroughly with demineralized water and dried in an oven before use. Water samples were contaminated with cesium (0.1–1000 mg L^{-1}) using standard stock solutions (10,000 mg L^{-1}) of cesium in acidic medium. Known cesium solutions of predetermined concentration were poured into polypropylene bottles and known weight of PB-GO-Ca-Alg beads was added into it. Shaking was done intermittently till equilibrium time using Spinix orbital shaker (Tarson). Groundwater samples used in the study were collected from the western region of India having latitude 19.0760 °N and longitude 72.8777 °E in polypropylene bottles and filtered through 0.45 μm filter paper fitted into a Millipore suction filtration assembly. The pH of the solutions was adjusted using nitric acid and sodium hydroxide as per the requirement of the experiment. The effect of pH and contact time on sorption was examined by varying pH and contact time while keeping dose rate of sorbent (10 mgmL^{-1}) and initial concentration of cesium (100 μg mL^{-1}) constant.

After the PB-GO-Ca-Alg beads were separated, the concentration of cesium was determined. The following equation was used to calculated the amount of Cs sorbed (Eq. (1)),

$$Q_e = \frac{(C_o - C_e)^* V}{W} \qquad (1)$$

Where,

C$_o$= the initial equilibrium concentrations of cesium (mg L^{-1}),
C$_e$= the final equilibrium concentrations of cesium (mg L^{-1}),
Q$_e$= the sorption capacity (mg g^{-1}) at equilibrium,
V = the volume (mL) of solution,
W = the mass (g) of beads.

2.6. Determination of cesium concentration

Concentration of cesium (^{133}Cs) was determined by using Flame atomic absorption spectrometer (FAAS, model SAVANTAA Σ, Australia) with PMT (photomultiplier tube) detector to cover entire wavelength