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Superparamagnetic graphene oxide–magnetite nanoparticle composites for uptake of actinide ions from mildly acidic feeds

Trilochan Gadly[a], Prasanta K. Mohapatra[b,*], Dinesh K. Patre[c], Rajesh B. Gujar[b], Alka Gupta[d], Anand Ballal[d], Sunil K. Ghosh[e]

[a] Bio-organic Division, Bhabha Atomic Research Centre, Trombay, Mumbai, 400085, India
[b] Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai, 400085, India
[c] Radiations Safety Systems Division, Bhabha Atomic Research Centre, Trombay, Mumbai, 400085, India
[d] Molecular Biology Division, Bhabha Atomic Research Centre, Trombay, Mumbai, 400085, India
[e] Food Technology Division, Bhabha Atomic Research Centre, Trombay, Mumbai, 400085, India

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ABSTRACT

Super paramagnetic graphene oxide (GO) – Fe_3O_4 nanoparticle composites were prepared and characterized by conventional techniques such as XRD, SEM, EDX, FT-IR, Raman, XPS, DLS and zeta potential, etc. TEM studies have confirmed nanoparticle nature of the composites. The GO-magnetic nanoparticle composites can be dispersed in mildly acidic aqueous solutions and get concentrated in a small volume under application of an external magnetic field. The composites were evaluated for the uptake of actinide ions such as Am^{3+}, UO_2^{2+}, Th^{4+} and Pu^{4+} from mildly acidic aqueous solutions. Am^{3+} sorption sharply increased with pH as the K_d values increased from about 10 at pH 1 to about 10^5 at pH 3 beyond which a plateau in the K_d values was seen. Eu^{3+} displayed nearly comparable uptake behaviour to that of Am^{3+} while the uptake of other metal ions followed the trend: Pu(IV) > Th(IV) » UO_2^{2+}. The adsorption behaviour of Am^{3+} onto the graphene oxide – Fe_3O_4 nanoparticle composites fitted very well to the Langmuir as well as Temkin isotherm models. The desorption rate (using 1 M HNO_3) was fast and reusability study results were highly encouraging. The very high uptake values suggest possible application of the magnetic nanoparticles in radioactive waste remediation in natural ground water.

1. Introduction

There is an ever increasing risk of environmental contamination with long lived radionuclides including the actinides due to an increase in activities such as testing of nuclear devices and accidental release of radioactivity due to stray incidents such as Chernobyl, Fukushima Daiichi, etc. In a closed fuel cycle, the fissile content is separated from the spent fuel by a well known reprocessing technology based on the PUREX process [1]. The PUREX raffinate contains most of the fission and activation products and is subsequently concentrated to yield the high level waste which is immobilized in vitrified glass blocks [2]. There is a possibility of environmental contamination due to the leakage of radionuclides from these vitrified waste blocks as a result of geological disturbances such as volcanic eruption, earth quakes, etc. The cleanup of such localized contaminated ecosystem which includes ground water, rock and soil will require efficient separation methods such as membrane separations and solid phase extraction [3]. Solid phase extraction methods include ion exchangers and variants of carbon compounds such as carbon nano tubes and activated carbon [4,5].

Recently, graphene oxide (GO) [6] has been reported to be an efficient sorbent of radionuclides [7–10] possibly due to its one atom thickness and two dimensional geometry. In view of the large surface area and the multitude of functional groups, GO sheets have been found to be quite effective sorbents for many heavy metal ions such as Pd, As, Hg, etc. [11–16]. Recently, Romanchuk et al. [6] reported very high sorption of actinide ions in GO and sorption capacities of ca. 0.76 m mol and 0.12 mmol per gram of GO were reported for the uptake of Eu(III) (Eu is considered as a homolog of Am, the actinide ion of interest) and U(VI), respectively at pH 5.0. Higher Eu(III) loading was reported by Sun, et al., [17] who used GO nano sheets and investigated the mechanism of binding of the metal ions by extended X-ray absorption fine structure (EXAFS) and surface complexation modelling. A recent study on the surface complexation modelling of Eu(III) with GO suggested binding to

* Corresponding author.
E-mail address: mpatra@barc.gov.in (P.K. Mohapatra).

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sulphonate groups at lower pH while stronger carboxylate binding was suggested at higher pH values [18]. These results, though encouraging, cannot be used for actual applications due to two demerits, viz. it may be difficult to determine an accurate K_d value in view of the fine dispersion of GO in the aqueous medium (the counts in the aqueous phase may be partly due to the counts on the dispersed GO particles) and stripping of the loaded metal ions was a real challenge. Furthermore, column mode operations with the GO nano sheets, for any viable application, may not be feasible as choking of the column can affect the flow rate due to the fine nature of the sorbent material. There are reports suggesting modification of GO with polyaniline (PANI) [19] or polyacrilamide (PAM) [20] for better settling properties. However, the results are not so encouraging as the % Eu uptake values are reported to be <80% which in real term can be considered quite ineffective [20]. Alternatively, polymeric composite beads containing GO can be used for the uptake studies. This was attempted by us with reasonably good success where porous polyethersulphone (PES) beads containing GO were prepared by a phase inversion technique [8].

Another possibility is to use composite GO-Fe_3O_4 magnetic particles which can be settled easily by using a magnet. Such magnetic GO composites have been used for controlled targeted drug carriers [21]. In a recent publication by Yang et al., [22] the GO-Fe_3O_4 composite has been tagged with Prussian blue for the effective separation of radio-cesium from mildly acidic to alkaline feeds. In another recent study, Eu(III) uptake from environmental samples has been reported using a nanocomposite of graphene oxide and silane modified magnetic nanoparticles which form dendritic structures [22]. However, a comparative evaluation of actinide ions was lacking. To our knowledge, the GO-Fe_3O_4 composite magnetic particles have not been used for actinide ion uptake studies and the present paper gives the first report on the tri-, tetra- and hexa-valent actinide ions which are important from environmental sample point of view. Furthermore, such studies from slightly acidic feeds (low pH solutions) have great relevance in the remediation of contaminated ground water or even the radioactive effluents emanating from radioactive laboratories. In the present study, GO-Fe_3O_4 magnetic particles were prepared and characterized by a host of techniques and were subsequently studied for the uptake of actinide ions from aqueous feeds.

2. Experimental

2.1. Materials

High Density Graphite (HDG, 1.96 g/c.c., 99.99% purity) was obtained from Nickunj Exim Enterprises Pvt. Ltd., Mumbai. $KMnO_4$ (AR; Merck), H_2O_2 (30%; Merck), $FeSO_4{\cdot}7H_2O$ (AR; Aldrich), $FeCl_3{\cdot}6H_2O$ (AR; Aldrich) and $NaNO_3$ (99%; BDH) were used as procured. Concentrated sulphuric acid (Thomas Baker), dilute nitric acid (Merck) and Suprapur hydrochloric acid (Merck) were used as obtained. GO was prepared as given below. Water was obtained from Milli-Q System (Millipore) has typically the resistivity of > 18 MΩ cm at 25 °C.

2.2. Radiotracers

^{241}Am, Pu (mainly ^{239}Pu) and ^{233}U were taken from laboratory stock and were used after purification from their corresponding daughter products [23–25]. ^{234}Th was separated from ^{238}U by a reported method [26]. ^{152}Eu was purchased from BRIT (Board of Radiation and Isotope Technology), Mumbai. All radionuclides were used after checking their radiochemical purities. The concentrations of the radionuclides used in the present study were 10^{-7} M for ^{241}Am, 10^{-6} M for Pu, 10^{-5} M for ^{233}U and ^{152}Eu and <10^{-10} M for ^{234}Th. ^{241}Am, ^{234}Th and ^{152}Eu were assayed by gamma ray spectroscopy using a NaI(Tl) scintillation detector (Para Electrincs) coupled to a multi-channel analyzer (ECIL, India) while Pu and ^{233}U were assayed by alpha liquid scintillation counting system (Hidex, Finland) using Ultima Gold (Perkin Elmer) scintillator cocktail.

The oxidation state of Pu was adjusted to the +4 state using 0.005 M $NaNO_2$ solution followed by the extraction of Pu^{4+} by 0.5 M TTA (2-thenoyltrifluoro acetone) in xylene for 30 min. The Pu^{4+} stock, thus prepared, was found to be stable for about one month. All experiments involving Pu^{4+} ion also used ammonium meta vanadate as the holding oxidant as per a previous report [27].

2.3. Synthesis of GO-Fe_3O_4 nanocomposite

2.3.1. Preparation of graphene oxide

Graphene oxide (GO) was synthesized using modified Hummers method [28,29]. Concentrated sulphuric acid (23 mL) was added to a mixture of high density graphite (HDG) powder (1 g) and sodium nitrate (0.5 g) and the mixture was stirred for 30 min. The reaction mixture was cooled on an ice-water bath and powdered $KMnO_4$ (3 g) was added slowly to it in portions with constant stirring while maintaining the temperature below 20 °C. After the addition was over, the reaction mixture was warmed to 35 °C and stirred for 30 min. The reaction mixture was slowly diluted with water (23 mL) and then heated to increase the temperature to 98 °C and stirred for 15 min. Subsequently, the reaction mixture was diluted with water (80 mL) followed by addition of H_2O_2 (10 mL, 30% V/V). The resulting dark brown suspension of graphitic oxide was filtered and the residue was washed with 1 N HCl (10 mL) followed by water several times to remove residual metal ions and acid. The graphitic oxide obtained was dried in oven at 80 °C for 6 h. The dried powder was re-dispersed in water by sonication for subsequent use as graphene oxide (GO). GO was characterized by elemental analysis and yielded 48.51% C, 2.21% H, 1.18% S and the balance being O. The synthesis is presented in Scheme 1.

2.3.2. Preparation of GO-Fe_3O_4 nano-composite

The GO-Fe_3O_4 composite was synthesized within the GO suspension using chemical co-precipitation method. Graphene oxide (0.9 g) was ultra-sonicated in 600 mL water for 1 h to form a homogeneous suspension. The suspension was transferred to a 1L three necked round bottomed flask with a mechanical stirrer and purged with nitrogen gas. Aqueous solution of $FeSO_4{\cdot}7H_2O$ (1.14 g, 4.01 m mol in 15 mL water) and $FeCl_3{\cdot}6H_2O$ (1.01 g, 3.74 m mol in 15 mL water) was [30] added to the mixture and heated at 80 °C. Ammonia solution (25%) was then added to the mixture to adjust the pH to 10 and the mixture was heated and stirred for 30 min. Tri-sodium citrate (1 g) was added to the mixture while the temperature was raised to 95 °C, which resulted in a black coloured suspension. The desired product was separated with a permanent magnet and rinsed with water several times and finally dried at 60 °C to afford the Fe_3O_4-graphene oxide nano-composite [2]. The composite was grinded to make fine power which appeared free flowing. The final product was dispersed in water and it could not settle to clear solution even after 6 h. However, a clear solution was obtained once the dispersed liquid was brought in contact with the magnet (*vide infra*).

2.4. Batch sorption studies

The composite GO-Fe_3O_4 nanoparticles were tested for actinide ion uptake by equilibrating with an aqueous solution containing the required radiotracer and the uptake value was measured by equilibrating a known quantity of the sorbent with an aqueous solution (at a phase ratio of 1:200 g/mL) of a pre-adjusted pH (using dilute nitric acid) spiked with the required radionuclide in stoppered