Chemical Engineering Journal 254 (2014) 623–634

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

The uptake of radionuclides from aqueous solution by poly(amidoxime) modified reduced graphene oxide

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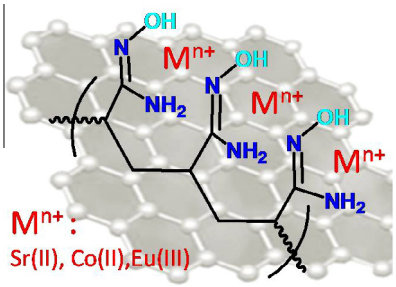
HIGHLIGHTS

- PAO-g-rGO was synthesized via an in-situ polymerization method.
- PAO-g-rGO had fine adsorption capacities of Co(II), Sr(II) and Eu(III).
- PAO-g-rGO could be an ideal adsorbent for radionuclides uptake from aqueous solutions.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 April 2014
Received in revised form 16 May 2014
Accepted 19 May 2014
Available online 27 May 2014

Keywords:
Radionuclide
Amidoxime
Graphene oxide
Acrylonitrile
Adsorption

ABSTRACT

Poly(amidoxime) (PAO) was grafted on the surface of reduced graphene oxide (rGO) via an in situ polymerization reaction to fabricate poly(amidoxime) grafted graphene (PAO-g-rGO) complexes. The as-prepared composites exhibited improved hydrophilicity and were characterized by scanning electron microscopy (SEM), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and thermal gravimetric analysis (TGA). The applications of the synthesized PAO-g-rGO to remove radionuclides, Sr(II), Eu(III) and Co(II), from aqueous solution were investigated with the maximum adsorption capacities of 99.4 mg/g, 296.4 mg/g and 177.6 mg/g, respectively. The adsorption reached equilibriums within 4 h and the kinetics could be well fitted by a pseudo-second-model. Effects of contact time, pH, ionic strength and temperature on radionuclides adsorption onto PAO-g-rGO were studied, indicating high dependences on pH and ionic strength. Adsorption isotherms fitted with Langmuir models well and the adsorption processes were spontaneous and endothermic. Experimental results exhibited a potential application of PAO-g-rGO in radionuclides cleanup.

1. Introduction

With the development of nuclear technology, numerous nuclear power plants were built to generate electricity. As a sustainable solution to global energy shortage, nuclear technology also brought side effects: the nuclear waste. In 2011, the disclosure of Fukushima nuclear power plant aroused global terror; in Russia and United States, large quantity of soil and groundwater were contaminated by the previous nuclear weapon tests, for instances. These contaminations made the radionuclide cleanup, especially from aqueous solution, a great challenge to human society [1].

Adsorption technology has been proven to be an effective method for radionuclides enrichment, and a series of material,

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http://dx.doi.org/10.1016/j.cej.2014.05.091
1385-8947/

such as carbon nanotubes, zeolite, porous alumina and etc., were investigated as adsorbents [2–4]. However, the reported low adsorption capacity cannot satisfy the universal application of unclear technology and new adsorbent possesses with high adsorption capacities for radionuclides are required for practical applications.

Graphene, a type of two-dimensional carbon material, has attracted extensive concerns in academic circles for its ideal physicochemical properties. The extremely high surface-to-volume ratio, ~2600 m^2/g theoretically [5], makes graphene an ideal adsorbent. However, graphene tends to aggregate and forms precipitations in aqueous solution, which severely restricts its practical applications. To enhance the dispersion property in aqueous solution, graphene oxide (GO), the precursor of graphene, is utilized as an adsorbent to enrich radionuclides. An example involves with the adsorption of radionuclides by pure GO, as reported by Romanchuk et al., which exhibited the maximum adsorption capacity of only 16.32 mg/g for Sr(II) [6].

Adsorption capacity is known as a surface process and controlled by the functional groups on the surface. The modification of graphene with suitable functional groups or anticoagulant [7] would reduce the self-aggregation and enhance the dispersion in aqueous solution, resulting in significant improvement of its adsorption capacity for pollutants. For example, Zhao et al. grafted amidoxime on magnetite/graphene oxide composites for the uptake of uranyl [8]; Sun et al. [9] studied the enrichment of radionuclides on graphene oxide-supported polyaniline and Yuan [10] investigated the removal of heavy metal ions by poly(amidoamine) modified graphene oxide. Amidoxime (AO), which has shown its special adsorption capacity to UO_2^{2+} [8,11], was studied extensively due to its numerous hydroxyl and amino groups and has been widely used to improve adsorbents' adsorption performance towards heavy metal ions in aqueous solution.

Herein, we graft AO groups on the surface of reduced graphene oxide (rGO) via an in situ polymerization reaction to fabricate poly(amidoxime) grafted graphene (PAO-g-rGO) composites. Scanning electron microscopy (SEM) presents an uniform fine structure for the as-prepared composites, which are further applied to remove radioactive Sr(II), Eu(III) and Co(II) from aqueous solution. Experimental results give much higher maximum capacities in removal of toward radioactive Sr(II), Eu(III) and Co(II) by the PAO-g-rGO composites, as compared with the previous adsorbents [12–14]. The adsorption process is heavily impacted by the pH and ionic strength of the suspension. Langmuir model is preferred to simulate the adsorption isotherm. Kinetic and thermodynamic studies indicate a spontaneous and endothermic process. Possible adsorption mechanisms are also investigated. This paper provides a potential application of PAO-g-rGO composite in radionuclide treatment.

2. Materials and methods

2.1. Materials

Graphite powder (70 μm, Qingdao Graphite Company), 98% H_2SO_4, $KMnO_4$, $NH_2OH{\cdot}HCl$, NaOH, H_2O_2, acrylonitrile and all other chemicals were reagent grade and purchased from Sinopharm Chemical Reagent Co., Ltd., Milli-Q (Millipore, Billerica, MA, USA) water was used in all experiments.

2.2. Preparation of PAO-g-rGO

GO was fabricated from graphite powder via a modified Hummers' method [15]. NH_2OH solution was prepared by dissolving 140 g $NH_2OH{\cdot}HCl$ into a mixed solution of methanol and water (volume ratio 5:1, total volume 800 ml) and neutralized by adding concentrated NaOH solution until pH = 10.0. Then, the solution was filtrated to remove NaCl precipitation.

PAO-g-rGO composites were prepared via an in situ polymerization method. Briefly, 0.8 g acrylonitrile monomer was dispersed in 200 ml Milli-Q water under agitating, 100 mL 2 g/L GO were added into the solution and the mixture was stirred overnight. Then, the mixture was preheated to 50 °C, followed by adding equal moles of $(NH_4)_2S_2O_8$ aqueous solution (0.1 M) and proper amount of Milli-Q water to reach a totally 400 mL solution [16]. Polymerization of acrylonitrile monomer on GO surface was initiated by the addition of $(NH_4)_2S_2O_8$ at 50 °C under electromagnetic stirring. After 3 h reaction, the suspensions were centrifuged and rinsed several times with 5:1 methanol/water solution and Milli-Q water to remove excess $(NH_4)_2S_2O_8$ and acrylonitrile monomer. The derived composites were dispersed in 100 mL previously prepared NH_2OH solution and then the reaction vessel was placed in a 70 °C bath under constant stirring for 3 h. During this period, GO in solution was reduced into rGO by NH_2OH [17,18]. The products were rinsed according to the previous process. After drying in oven at 50 °C for one week, PAO-g-rGO composites were obtained. The same method was also used to synthesize rGO without the addition of AO.

2.3. Characterization

PAO-g-rGO composites were characterized by scanning electron microscopy (SEM), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and thermal gravimetric analysis (TGA). To achieve the SEM images, samples were dispersed in ethanol and ultrasonic for 10 min, then the sample suspension was smeared on a copper sheet by a capillary. The SEM measurements were conducted on a JEOL JSM-6330F operated at the beam energy of 15.0 kV. Raman spectroscopy analyses of GO and PAO-g-rGO composites were obtained by using a LabRam HR Raman spectrometry at the excitation of 514.5 nm by Ar^+ laser. XPS spectroscopy measurements were performed with an ESCALab220i-XL surface microanalysis system (VG Scientific) equipped with a 300 W Al $K\alpha$ ($h\nu$ = 1486.6 eV) source at a chamber pressure of 3×10^{-9} mbar. The surface charging effects were corrected with C 1s peak at 284.4 eV as a reference. TGA curves measurements were examined by using a Shimadzu TGA-50 thermogravimetric analyzer from room temperature to 800 °C at the heating rate of 10 °C/min with a nitrogen rate of 50 mL/min.

2.4. Batch adsorption experiments

Adsorption experiments were carried out by batch technique in 10 ml polyethylene centrifuge tubes. 0.12 g PAO-g-rGO powders were dispersed in 100 ml Milli-Q water and a 1.2 g/L stock adsorbent concentration was achieved. The radionuclides stock solution, NaCl solution, PAO-g-rGO stock solution and Milli-Q water were added in the 10 ml polyethylene test tubes respectively to achieve the desired concentrations of different components. Negligible amount high-concentrated HCl or NaOH was added into the suspensions to adjust pH to desired values. The tubes were placed in an oscillator and kept shaken. In kinetic study, the adsorption solutions in the centrifuge tubes at different reacting time were separated from the suspension by centrifugation at 9000 rpm for 15 min. In the effect of pH, ionic strength and temperature sections, the adsorption suspension was shaken for 24 h to guarantee the achievement of adsorption equilibrium. Concentrations of radionuclide in solution were analyzed by liquid scientific counting using a Packard 3100 TR/AB Liquid Scintillation analyzer (PerkinElmer). The amount of radionuclides adsorbed on the PAO-g-rGO composites was calculated from the difference between the initial concentration (C_0) and the equilibrium one (C_e). Adsorption