



Effect of water chemistries on adsorption of Cs(I) onto graphene oxide investigated by batch and modeling techniques



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HIGHLIGHTS

- Maximum adsorption capacity of GO for Cs(I) pH 3.0 and 298 K was 32.53 mg/g.
- Inner-sphere surface complexation dominated Cs(I) adsorption on GO.
- Double layer model give the better fits for Cs(I) adsorption on GOs.

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ABSTRACT

Effect of water chemistries (i.e., reaction time, pH, ionic strength and temperature) on Cs(I) adsorption on graphene oxide were investigated by batch techniques. The characterized results indicated that graphene oxide synthesized by the modified Hummers method presented a variety of oxygen-containing functional groups such as epoxy, carbonyl, carboxyl and hydroxyl groups. The adsorption kinetics of Cs(I) on graphene oxide can be satisfactorily fitted by pseudo-second-order kinetic model with such high correlation coefficient ($R^2 > 0.9999$). The adsorption isotherm can be fitted by Langmuir model very well ($R^2 > 0.995$) compared to Freundlich model ($R^2 < 0.985$). The maximum adsorption capacity of graphene oxide calculated from Langmuir mode at pH 3.0 and 293 K was 40.00 mg/g. The thermodynamic parameters showed that the adsorption of Cs(I) on graphene oxide was an exothermic and spontaneous processes. The results of surface complexation modeling indicated that the diffuse layer model can give an excellent fits with SOHCs^+ and $\text{SOCs}(\text{OH})^-$ species, which indicating that adsorption of Cs(I) on graphene oxide was outer- and inner-sphere surface complexation at $\text{pH} < 4.0$ and $\text{pH} > 5.0$, respectively. The findings presented herein revealed that graphene oxide was a promising adsorbent for the removal and immobilization of radionuclide from aqueous solutions in environmental cleanup.

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1. Introduction

The earthquake and then tsunami of Japan was occurred on 11 Mar. 2011, which lead to abundant long-lived radionuclides (e.g., ^{238}U , ^{90}Sr , ^{137}Cs and ^{129}I) were released into the environments [1]. These long-lived radionuclides could be posed the potential threat for human health and biodiversity [2]. Therefore, it is extraordinarily urgent to remove these radionuclides from aqueous solutions under the scope of the permit before being discharged. In the last several decades, a variety of approaches have been extensively employed to remove these radionuclides such as redox [3–5], co-precipitation [6–8], and adsorption [9–12]. Among these approaches, adsorption has been demonstrated a very efficient method due to its low-cost, ease operation and envi-

ronmental friendly [13]. Recently, numerous studies have been investigated the adsorption of radionuclides on a variety of adsorbents such as clay minerals [14–16] and heavy (hydr)oxides [17–20]. In these studies, the effect of water chemistry on the adsorption of radionuclides had been extensively elaborated by batch techniques, whereas the low adsorption capacities of these adsorbents limited the practical application of radionuclides from aqueous solutions in environmental cleanup.

Graphene oxide (GO), a novel 2D nanomaterial prepared from natural graphite, has recently attracted significant attention as a high adsorbent in wastewater treatment [21–23]. GO displays the stable suspension in water due to the abundant hydrophilic oxygen-containing functional groups on its basal planes ($-\text{O}-$, $-\text{OH}$) and edges ($-\text{COOH}$, $-\text{OH}$) [24], which are responsible to the high efficient adsorption towards radionuclides. It is demonstrated that GO presents high effective enrichments of radionuclides under the different environmental conditions. Although the interaction

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mechanism between radionuclides and GO by using surface complexation modeling are observed [25–28], the more insights towards the different radionuclide on GO should be detailed.

Monovalent cesium (Cs(I)) as a chemical analogues of radionuclides was selected in this paper. The objectives of this paper were (1) to synthesize GO by modified Hummers method and characterize it using scanning electron microscope (SEM), transmission electron microscope (TEM), Fourier transmission infrared (FTIR) and X-ray photoelectron spectra (XPS); (2) to investigate the effect of water chemistries (e.g., reaction time, pH, ionic strength and temperature) on Cs(I) onto GO by batch techniques; (3) to determine the adsorption mechanism between Cs(I) and GO in terms of surface complexation modeling. The highlights of this paper is that the potential application of GO towards the removal of radionuclides from aqueous solutions in environmental remediation strategy.

2. Materials and methods

2.1. Synthesis and characterization of GO

GO was synthesized by a modified Hummers method [29]. In a typical procedure, 2.0 g of flake graphite with an average particle size of 100 μm and 1.5 g NaNO_3 (as co-solvent) were added into 500 mL tee round bottom flask, then 230 mL concentrated sulfuric acid were slowly added under an ice batch and vigorous stirring conditions. Then 9.0 g potassium permanganate was slowly added and then mixture was kept at room temperature for 5 days. The suspension was heated to 98 $^\circ\text{C}$, and then 460 mL of deionized water was gradually added and the reaction was maintained at this temperature for 30 min in order to increase their oxidation degree. The residual MnO_4^- ions of resultant suspension were further reduced by H_2O_2 solution (30 mL, 30%). The remnant salt was washed by 500 mL 0.1 mol/L HCl and 1.5 L deionized water and followed by centrifugation at 3600 rpm for 30 min. The precipitate was removed and supernate was ultrasonically treated at 140 W for 2 h in order to exfoliate GO nanosheets from graphite oxide aggregates.

2.2. Characterization

The morphology and nanostructure of GO were characterized by SEM and TEM (JEOL JEM-2010 transmission electron microscope) operating at an accelerating voltage of 200 kV. The TEM samples were prepared by dripping a GO solution onto 400-mesh copper grids and dried them prior to test. The surface functional groups were determined by FTIR spectra prepared in KBr pellets, which were recorded on a Perkin-Elmer Specrum 100 spectrometer by accumulation of 64 scans with a resolution of 4.0 cm^{-1} . For the surface chemistry analysis, A Kratos Ultra XPS system was employed with a monochromatic Al K α X-ray source operating at 15 kV and 10 mA.

2.3. Batch adsorption experiments

The batch adsorption experiments as a function of reaction time, pH, ionic strength, initial concentration and temperature were carried out in triplicates in 10-mL polycarbonate centrifuge tubes in glove box ($P_{\text{CO}_2} = 0$ atm) purged using N_2 gas. Briefly, NaClO_4 (as electrolyte) was added into GO under vigorous stirring conditions, and then Cs(I) solution was added to the tubes to achieve the desired concentration. The pH values of suspensions were adjusted to desired pH values by adding ignore volume 0.01–1.0 mol/L NaOH or HClO_4 solutions. The samples were placed on a reciprocating shaker table. The solid phase was separated

from liquid phase by centrifuging it at 6000 rpm for 30 min. An aliquot of the supernatant was withdrawn and immediately filtered with a 0.45- μm syringe filter. The concentration of Cs(I) in the supernate was analyzed by atomic absorption spectroscope (AAS-6300C, Shimuzda). The amount of adsorbed Cs(I) can be calculated in terms of Eq. (1):

$$Q_e = \frac{(C_0 - C_e) \times V}{m} \quad (1)$$

where C_0 and C_e (mg/L) refer to the initial concentration and equilibrated concentration of supernatant after uptake equilibrium, respectively. m (g) and V (mL) are the mass of GO and the volume of the suspension, respectively. All experimental data were the average of double determinations and the relative errors were $\pm 5\%$.

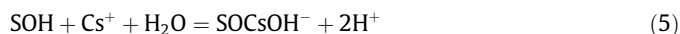
2.4. Surface complexation modeling

The surface complexation modeling of Cs(I) on GO are fitted by using diffuse layer model (DLM) with an aid of FITEQL v 4.0 codes [30]. The two surface acidity constants ($\log K^+$, $\log K^-$) can be calculated by the following protonation (Eq. (2)) and deprotonation reactions (Eq. (3)):



where SOH refers to the amphoteric hydroxide functional groups. The values of $\log K^+$ and $\log K^-$ were obtained by fitting the data of potentiometric titration of GO in the presence of 0.01 mol/L NaClO_4 and N_2 flow conditions.

In this study, two surface complexation reactions were described by Eqs. (4) and (5):



The equilibrium parameters of $\log K_{\text{SOHCs}^+}$ and $\log K_{\text{SOCsOH}^-}$ were optimized by similarity of fitted results with experimental data. During fitting processes, the site density (N_s , sites/ m^2) can be calculated by Eq. (6):

$$N_s = \frac{N_t \times N_A}{C_s \times S_{\text{BET}}} \quad (6)$$

where C_s (g/L) refers to solid concentration. N_A (sites/mol) and S_{BET} (m^2/g) are Avogadro constants and BET specific surface area, respectively. The concentration of total reactive sites (N_t , mol/L) can be obtained by fitting the potentiometric data. Hence, the site density for GO was calculated to be 15.8 sites/ nm^2 . The quality of the fitting results is evaluated by weighted sum of squares divided by degrees of freedom (WSOS/DF). A good fit to experimental data is indicated by a value of WSOS/DF between 0.1 and 20 [30].

3. Results and discussion

3.1. Characterization

Fig. 1A and B showed the SEM image and TEM image of GO, respectively. As shown in Fig. 1A, GO presented the multiplayer nanosheets aggregated randomly. According to TEM observation (Fig. 1B), GO displayed the wrinkly and sheet-like structures, which was consistent with the previous studies [21,25]. Fig. 1C showed the FTIR spectrum of GO. The broad peak at 3454 cm^{-1} was assigned to $-\text{OH}$ stretching vibration [22]. In low wavenumber range, the bands at 1750, 1660, 1400 cm^{-1} were attributed to stretching vibration of $\text{C}=\text{O}$, aromatic $\text{C}=\text{C}$, carboxyl $\text{O}=\text{C}-\text{O}$, and

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