



## Molecular insights into the role of fulvic acid in cobalt sorption onto graphene oxide and reduced graphene oxide



Kaikai Chang<sup>a</sup>, Xue Li<sup>b</sup>, Qing Liao<sup>a</sup>, Baowei Hu<sup>a</sup>, Jun Hu<sup>c,d</sup>, Guodong Sheng<sup>a,\*</sup>, Wensheng Linghu<sup>a</sup>, Yuying Huang<sup>e</sup>, Abdullah M. Asiri<sup>f</sup>, Khalid A. Alamry<sup>f</sup>

<sup>a</sup> College of Chemistry and Chemical Engineering, Shaoxing University, Zhejiang 312000, People's Republic of China

<sup>b</sup> College of Yuanpei, Shaoxing University, Zhejiang, Shaoxing 312000, People's Republic of China

<sup>c</sup> School of Electronic Engineering, Dongguan University of Technology, Guangdong 523808, People's Republic of China

<sup>d</sup> Institute of Plasma Physics, Chinese Academy of Sciences, P.O. Box 1126, Hefei 230031, People's Republic of China

<sup>e</sup> Shanghai Synchrotron Radiation Facility (SSRF), Chinese Academy of Sciences, Shanghai 201204, People's Republic of China

<sup>f</sup> Chemistry Department, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

### HIGHLIGHTS

- Sorption of FA on RGO was mainly controlled by  $\pi$ - $\pi$  interaction.
- Sorption of FA on GO was mainly governed by polar interaction.
- FA enhanced Co(II) sorption on RGO but showed little role in its sorption on GO.
- Co(II) sorption on GO mainly by coordination with O-bearing functional groups.
- The presence of FA could inhibit the formation of Co(II) precipitation on RGO.

### ARTICLE INFO

#### Article history:

Received 4 June 2017

Received in revised form 18 June 2017

Accepted 19 June 2017

Available online 20 June 2017

#### Keywords:

Graphene oxide

Reduced graphene oxide

Co(II)

Fulvic acid

Extended X-ray absorption fine structure

### ABSTRACT

The role of fulvic acid (FA) in the sorption of Co(II) onto reduced graphene oxide (RGO) and graphene oxide (GO) were investigated using batch equilibrium method and extended X-ray absorption fine structure (EXAFS). The results showed that FA could be adsorbed on both RGO and GO via different interaction mechanisms, and thus exert different roles in Co(II) sorption. The sorption of FA on RGO was mainly controlled by  $\pi$ - $\pi$  interaction, and the adsorbed FA introduced negative charges and O-bearing functional groups on RGO, facilitating Co(II) sorption due to electrostatic attraction and complexation. Meanwhile, the sorption of FA on GO was mainly governed by polar interactions, and the adsorbed FA can not only introduce new sites for enhanced Co(II) sorption, but also shield the surface of GO and occupy parts of sorption sites, which decreased Co(II) sorption. So, FA had little role in Co(II) sorption onto GO. EXAFS results suggest that O-bearing functional groups of RGO and GO were the main sorption sites for Co(II). Compared to GO, a portion of Co(II) precipitate on RGO surfaces at pH 8.78 due to fewer O-bearing functional groups. The introduction of FA provides lots of sorption sites on RGO, which makes Co(II) be adsorbed on RGO as RGO-FA-Co ternary surface complexes. The results of this work indicated that both RGO and GO exhibited great potential in pollution control applications, even in mixed organic and inorganic pollutants.

© 2017 Elsevier B.V. All rights reserved.

### 1. Introduction

Recently, industrialization and urbanization has increasingly resulted in the discharge of a large number of toxic heavy metal ions in natural surface water bodies, including Pb(II), Hg(II), Cd

(II), Cr(VI), Ni(II), Co(II) and so on, which could be widely detected in the effluents of metallurgy, tanning, mining and other industries [1–8]. It is well known that these metal ions have been regarded as one of the main environmental concerns owing to their mobility and persistency in the natural environmental systems. Thereby, a variety of studies has been focused on the efficient scavenging of these metal pollutants from aqueous solutions such as by chemical precipitation, adsorption, electrolysis and so on [8–16]. Among these important approaches, sorption method has been reported

\* Corresponding author.

E-mail address: [gdscheng@usx.edu.cn](mailto:gdscheng@usx.edu.cn) (G. Sheng).

to be superior to other techniques owing to its high efficiency, low-cost and easy of operation.

Graphene (G) is a two-dimensional structure which mainly consists of  $sp^2$  hybridized carbons with only one atomic thickness, and has attracted considerable attention in the environmental application as superior adsorbent due to their remarkable electronic properties, large specific surface area and high ability of modification [17–24]. Therefore, G and its modified composites have been widely utilized for the efficient scavenging of various organic and inorganic contaminants from water [25–32]. For example, it was found that polyaniline decorated graphene oxide (GO) exhibited highly efficient enrichment of radionuclides from water [23]. Zhao et al. [24] reported that sulfonated graphene (G) was one of the most effective adsorbents for persistent aromatic pollutant. Besides, few-layered GO nanosheets could be also used as superior adsorbents for heavy metal ion pollution management, where the amount of O-bearing functional groups on GO is an important factor affecting the scavenging of heavy metal ions [26]. In addition, in individual studies, Per et al. [29] and Wang et al. [30] revealed the high adsorption of polycyclic aromatic hydrocarbons, 1,2,4-trichlorobenzene, 2,4,6-trichlorophenol, 2-naphthol and naphthalene on both graphene and graphene oxide.

Humic substances (HSs) like fulvic acid (FA) and humic acid (HA) are ubiquitous in natural water and soil environments and have been generally reported to show strong interaction with adsorbents in the environment systems [33–36]. The interactions between HSs and adsorbents could not only change the surface properties and environmental impact of these adsorbents, but also alter the adsorption kinetic and performance of co-existing contaminants [26,37]. Generally regarding, HSs could be coated on the surfaces of adsorbents including metal oxide nanoparticles, as well as carbon nanomaterials, which makes scavenging of heavy metal ions from water more effective [26,34–38]. Although knowledge about HS interaction with various adsorbents is noteworthy, which can help interpret the effect of HS interaction on metal scavenging, compared to other adsorbents, GO-based materials with open layered structure, contain C atoms with different saturation degrees and oxidation states, and thus the differences in physiochemical properties among GO materials are pronounced. Therefore, it is necessary to investigate the interaction between HSs and GO-based materials of different properties, and to reveal its effect on the scavenging of co-existing contaminants. In a previous work, Yang et al. [37] examined the effects of HA on Cu(II) uptake on few-layer GO and reduced graphene oxide (RGO), using extended X-ray absorption fine structure spectroscopy (EXAFS) that is useful to identify the microstructures of metal ions onto surfaces [39–42]. However, according to our literature survey, no attention has been paid to the comparison roles of FA interaction in metal uptake on RGO and GO.

Therefore, in this work, we will examine the interactions of FA with RGO and GO of different O-bearing functional groups and  $\pi$ -electron density, as well as their roles in Co(II) sorption. Herein, cobalt element (Co(II)) is an essential nutrient in trace amounts for life since it is a main component of vitamin B<sub>12</sub> complex. Nevertheless, Excessive oral doses of Co(II) can result in a variety of adverse effects on human beings. When Co(II) ions are released into the natural environment, they can lead to many disease and thus cause mutations in living cells [43–45]. The aims of this study were (a) to compare the sorption of FA on GO and RGO, (b) to examine the sorption of Co(II) on GO and RGO in the absence and presence of FA, and (c) to provide an insight into the mechanisms of Co(II) sorption on GO and RGO via use of extended X-ray absorption fine structure spectroscopy (EXAFS).

## 2. Materials and methods

### 2.1. Chemicals and materials

All the chemicals and materials applied in our experiments including cobalt nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), sodium nitrate ( $\text{NaNO}_3$ ), sodium hydroxide ( $\text{NaOH}$ ), nitric acid ( $\text{HNO}_3$ ) and so on, were purchased from Shanghai chemical Co. Ltd., China, with analytic purity, and used without further purification. All the solutions were prepared by using de-ionized water under ambient conditions. The graphene oxide (GO) was prepared according to a modified Hummers method [46–48], and the reduced graphene oxide (RGO) was prepared via a thermal exfoliation/reduction process by applying graphite oxide as a precursor [49–51]. The detailed process has been provided in previous reports [47–50]. The fulvic acid (FA) was isolated from the soil of Hua-Jia county (Gansu, China) according to the process of the international humic substances society, and had been characterized in our previous studies [33–35]. Before use, the as-isolated FA was dried, pulverized gently in a mortar to pass through a 0.25-mm sieve at room temperature, and stored in a glass vial.

### 2.2. Macroscopic experiments

The macroscopic experiments for the sorption of FA or Co(II) onto RGO and GO were conducted under ambient conditions in 50-mL glass vials, in triplicate using a batch equilibrium method. The FA solution was prepared in a 0.01 mol/L  $\text{NaNO}_3$  solution, and filtered through a 0.22- $\mu\text{m}$  membrane filter before use. The sorption of FA on RGO and GO as a function of pH was carried out by mixing a certain amount of RGO or GO with 30.0 mL of 0.01 mol/L  $\text{NaNO}_3$  containing 12.5 mg/L FA. The suspension pH was adjusted from 3.0 to 9.0 by using 0.01 mol/L  $\text{HNO}_3$  or  $\text{NaOH}$ , and the suspension was continuously rotated for 1 d. After sorption equilibrium was reached, the suspension was centrifuged for 30 min, and filtered with a 0.22- $\mu\text{m}$  membrane filter, and the filtration FA concentrations in the filtrate were determined. Prior to the initiation of Co(II) sorption, a certain amount of RGO or GO was mixed with 10.0 mL of FA solution in 50-mL glass vials, and rotated continuously for 1 d. Afterwards, the Co(II) stock solutions were added to the glass vials. The final volume of the solution was adjusted to 30.0 mL with 0.01 mol/L  $\text{NaNO}_3$  solution. The suspension pH was adjusted from 3.0 to 9.0 by using 0.01 mol/L  $\text{HNO}_3$  or  $\text{NaOH}$  for the pH effect experiments. For sorption isotherm determinations, the pH of suspension was adjusted to  $5.1 \pm 0.1$ . The suspension was continuously rotated for 1 d to ensure complete sorption. After centrifugation and filtration, the concentrations of Co(II) in the filtrate were determined. Preliminary experiments indicated no significant loss of FA or Co(II) after centrifugation and filtration. The adsorbed FA or Co(II) was calculated from the differences between initial ( $C_0$ ) and equilibrium ( $C_e$ ) concentrations. The sorption percentage and adsorbed capacity was calculated according to:

$$\begin{aligned} \text{sorption (\%)} &= 100\% \times (1 - C_e/C_0), \text{ and } q_e(\text{mg/g}) \\ &= (C_0 - C_e)/m \times V, \end{aligned}$$

where  $m$  is GO mass (g), and  $V$  is suspension volume (L). To confirm data repeatability accuracy, the experiments data was measured in triplicate [39–41].

### 2.3. Analytical methods

The concentrations of FA were determined by UV-vis spectrometer (Shimadzu UV-2550). The concentrations of Co(II) were determined by inductively coupled plasma atomic emission

Download English Version:

<https://daneshyari.com/en/article/6465028>

Download Persian Version:

<https://daneshyari.com/article/6465028>

[Daneshyari.com](https://daneshyari.com)