Chemical Engineering Journal 281 (2015) 379–388

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

# Adsorption and coadsorption of organic pollutants and a heavy metal by graphene oxide and reduced graphene materials

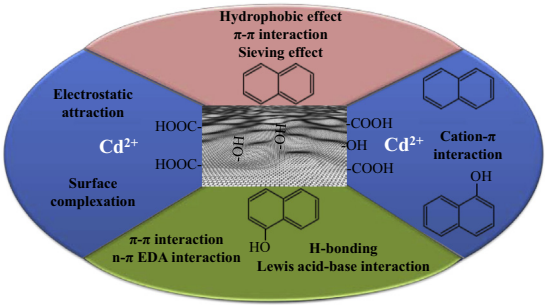
Jun Wang, Baoliang Chen *

*Department of Environmental Science, Zhejiang University, Hangzhou, Zhejiang 310058, China*
*Zhejiang Provincial Key Laboratory of Organic Pollutant Process and Control, Zhejiang University, Hangzhou, Zhejiang 310058, China*

## HIGHLIGHTS

- Adsorption of graphene nanosheets depend on their oxygen contents and conformation.
- Adsorption of 1-naphthol onto graphene is much stronger than that of naphthalene.
- $n$–π EDA interaction contributes to the adsorption of 1-naphthol onto graphene nanosheets.
- $Cd^{2+}$ and organic pollutants are coadsorbed by graphene via surface-bridging mechanisms.
- Multiple adsorption sites on graphene nanosheets favor the adsorption and coadsorption.

## GRAPHICAL ABSTRACT




## ARTICLE INFO

*Article history:*
Received 8 May 2015
Received in revised form 23 June 2015
Accepted 24 June 2015
Available online 27 June 2015

*Keywords:*
Graphene oxide
Reduced graphene oxide
Adsorption
Organic pollutant
Heavy metal
Mechanisms

## ABSTRACT

The adsorption and coadsorption of naphthalene, 1-naphthol and $Cd^{2+}$ onto graphene oxide (GO), chemically reduced graphene (CRG) and annealing reduced graphene (ARG) were compared to determine the unique adsorption properties of graphene nanosheets. The adsorption capability of organic pollutants followed the order CRG > ARG > GO, and all three adsorbents showed stronger adsorption to 1-naphthol than to naphthalene. In addition to a π–π interaction, the strong adsorption of 1-naphthol onto graphene nanosheets was mainly attributed to the $n$–π electron-donor–acceptor (EDA) interactions between the –OH groups of 1-naphthol and the electron-depleted sites on graphene nanosheets. The adsorption of 1-naphthol on reduced graphene materials increased with increasing pH and reached a maximum around its pKa, supporting the $n$–π EDA interaction mechanism. GO with more functional groups on the nanosheets over CRG and ARG exhibited a strong affinity with $Cd^{2+}$. The adsorption of $Cd^{2+}$ onto GO and CRG facilitated the coadsorption of naphthalene and 1-naphthol via surface-bridging mechanisms, such as cation–π interactions. Notably, though ARG showed no significant $Cd^{2+}$ adsorption, the suppressed coadsorption of naphthalene onto ARG may be attributed to the sieving effect by hydrated $Cd^{2+}$ binding to the micropore edges on ARG.



## 1. Introduction

Graphene, a one-atom-thick 2D layer of $sp^2$-bonded carbon [1], is the most intensively studied material in the world and possesses fantastic electrical, mechanical, optical and chemical properties,

* Corresponding author. Tel./fax: +86 571 8898 2587.
*E-mail addresses:* jwanges@163.com (J. Wang), blchen@zju.edu.cn (B. Chen).

http://dx.doi.org/10.1016/j.cej.2015.06.102
1385-8947/

such as high electrical conductivity, high strength, high transparency and facile modification [2,3]. Due to its planar structure and outstanding properties, graphene has a number of potential applications, especially in electronics and energy storage [4–6]. Recently, dozens of methods have been developed and used to prepare graphene structures of different shapes, dimensions and quality [7–12]. Graphene has sparked tremendous scientific interest in environmental applications [13,14], especially in the adsorption of pollutants, and the performance and mechanisms of these applications of graphene have been explored [15–30]. Graphene materials have already been investigated as efficient adsorbents for organic and inorganic pollutants, such as polycyclic aromatic hydrocarbons (PAHs) [15–18], phenolics [19,20], nitroaromatics [21], dyes [22–25], heavy metal ions [25–29] and anions [30]. Most adsorption characteristics of graphene materials have been conducted in single-solute systems, while few studies have considered bi-solute adsorptions of various adsorbates to graphene. However, a complex mix of organic pollutants and heavy metal ions often coexist in the environments [31]; their sorption would affect the fate and transport of contaminants [32]. Moreover, interactions with the coexisting heavy metal ions may affect the adsorption of organic pollutants to graphene. This adsorption behavior may provide further insight into the structure and mechanisms of the adsorptive sites of graphene materials. Therefore, the elucidation of the coadsorption behavior of organic pollutants and heavy metal ions is significant for evaluating the environmental impact of graphene materials and for developing novel functional materials for pollution management.

Due to its hydrophobic properties and strong π–π interactions of its aromatic 2D structure, graphene nanosheets exhibit superior adsorption capacities for persistent aromatic pollutants [15–18]. However, oxygen-containing functional groups, such as —COOH, —OH and —C=O, are formed on the surface of graphene nanosheets as a result of the incomplete reduction of graphene oxide (GO) [7]. These functional groups could significantly alter the adsorption of organic and inorganic pollutants. The adsorption of phenolics generally increased with an increasingly reduced GO [20], whereas the reduction of GO decreased the adsorption of heavy metal ions [29]. The reduction of GO eliminated the oxygen-containing functional groups and restored a $sp^2$-hybridized structure [7], which resulted in strengthened π–π interactions between the organic pollutants and graphene nanosheets, reduced water molecule competition with organic pollutants at the oxidized sites [15,19,20], and weakened surface complexations between heavy metal ions and the oxidized sites [26–29]. Therefore, by regulating the varieties of oxygen-containing functional groups on graphene nanosheets, graphene materials have great potential for applications in pollution control, especially for complex mixes of organic and inorganic pollutants. In addition, the conformation of graphene nanosheets has been demonstrated to have significant impact on the adsorptive sites for PAHs [15]. Because the conformations of graphene materials with different oxygen contents are not the same [15,20], it is worthwhile to explore the effect of graphene conformation on the interfacial behavior of organic molecules.

The main objective of this study was to recognize the unique adsorptive and coadsorptive properties of graphene nanosheets. Specific experiments were designed to investigate: (i) the interfacial behaviors of organic and inorganic pollutants adsorbed on graphene as affected by the oxygen content and conformation of graphene materials; and (ii) the effect of the presence of coexisting heavy metal ions on organic adsorption to graphene materials. Naphthalene and 1-naphthol with different polarities were selected to determine their adsorption capacity on graphene materials with and without the presence of $Cd^{2+}$, while $Cd^{2+}$ was selected as a typical toxic metal ion because it is commonly found in surface and underground waters which poses a threat to human health. The effects of pH on adsorption were also examined. Graphene oxide (GO), chemically reduced graphene (CRG) and annealing reduced graphene (ARG) were selected as adsorbents to better understand the adsorption characteristics of graphene materials with different oxygen contents and microstructures.

## 2. Materials and methods

### 2.1. Preparation of graphene materials

GO was synthesized from natural graphite flakes (325 mesh, 99.8%, Alfa Aesar) via a modified Hummers Method [33]. Then, the graphene oxide was exfoliated by sonication and dialyzed to remove acids and other impurities. CRG was obtained by the reduction of exfoliated GO with hydrazine hydrate [7]. ARG was achieved by a 500 °C expansion under $N_2$ using GO as the precursor [8]. GO, CRG and ARG of different oxygen contents were used as graphene-based adsorbents. Briefly, graphite powder (24 g) was mixed with an 80 °C solution of concentrated $H_2SO_4$ (96 mL), which contained $K_2S_2O_8$ (20 g) and $P_2O_5$ (20 g), and was kept at 80 °C for 4.5 h. Pre-oxidized graphite was obtained after careful washing and drying. The pre-oxidized graphite powder (20 g) and $NaNO_3$ (10 g) were added to cold (0 °C), concentrated $H_2SO_4$ (460 mL) in an ice bath. Then, $KMnO_4$ (60 g) was slowly added under continuous agitation. The reaction was kept at 35 °C for 2 h. Then, deionized (DI) water (920 mL) was gradually added, producing much heat. Afterward, the mixture was kept at 98 °C for 15 min, and 50 mL 30% $H_2O_2$ solution was slowly added to reduce the residual $KMnO_4$. The resultant brilliant yellow mixture was rinsed with 10% HCl solution (7.2 L) to remove residual $SO_4^{2-}$ and metal ions, followed by centrifugation at 8000 rpm. Then, the solid product was dissolved in DI water using vigorous agitation and ultrasonication for 30 min at 250 W. The centrifugation and ultrasonication steps were repeated several times. Then, the solution was dialyzed to remove residual acids and other impurities. After vacuum drying at 60 °C for 24 h, the GO sample was obtained and stored as a suspension in water. Chemically reduced graphene (CRG) was produced via the hydrazine reduction of GO. A certain amount of GO dispersion (1 mg/mL) was ultrasonicated (250 W) and pelleted at 3000 rpm for 5 min. The supernatant was decanted and loaded in a round-bottom flask; the pH was adjusted to 10 using ammonia hydroxide. Then, 10 mL hydrazine hydrate (98%, Aladdin Co., Ltd.) was added and the solution was heated in a 98 °C water bath under a water-cooled condenser for 24 h. The resultant black solid was isolated by filtration through a 0.22-μm membrane filter, and washed with deionized water and methanol to remove excess hydrazine. After freeze drying, the CRG was obtained as a black powder. Annealing reduced graphene (ARG) was produced via a 500 °C expansion under $N_2$ gas using GO as the precursor. A certain amount of GO powder was placed in a tube furnace under $N_2$ gas. The tube temperature was increased to 500 °C at a rate of 5 °C/min and kept at this temperature for 2 h. Annealing reduction carried out at 500 °C was to remove as many surface oxygen groups as possible, while ensure the adequate exfoliation of GO. Afterward, the tube was cooled down and the ARG was obtained.

### 2.2. Characterization of graphene materials

The structure and surface morphologies of graphene materials were characterized by elemental (C, H, and N) analyses, BET-$N_2$ specific surface areas, Raman spectra, and scanning electron microscopy (SEM). The surface functional groups were analyzed by Fourier transform infrared spectroscopy (FTIR), and the surface electrical properties were measured from duplicate samples using