Adsorption mechanism of emerging and conventional phenolic compounds on graphene oxide nanoflakes in water

Hepsiba Niruba Catherine [a,b], Ming-Han Ou [b], Basavaraju Manu [a], Yang-hsin Shih [b,*]

[a] Department of Civil Engineering, National Institute of Technology Karnataka, Surathkal 575025, India
[b] Department of Agricultural Chemistry, National Taiwan University, Taipei 106, Taiwan

HIGHLIGHTS

- Graphene oxide nanoflakes we synthesized have a high suspension stability in water.
- Graphene oxide (GO) surface was studied by several spectroscopic methods.
- Adsorption mechanisms of emerging compounds (ECs) on GO were illustrated.
- π–π interactions and hydrophobic interactions dominate the adsorption process.
- GO with ECs could lead to their spread in aquatic environment.

GRAPHICAL ABSTRACT
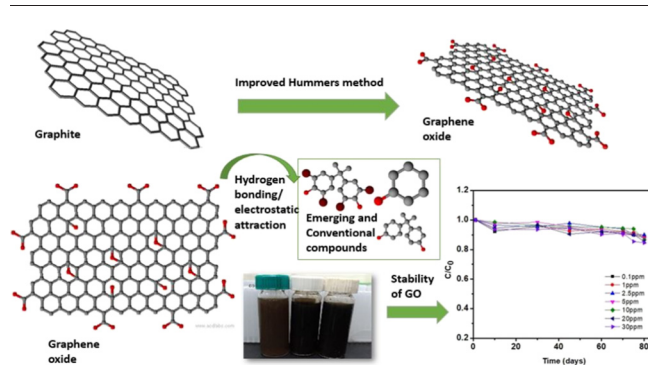
ABSTRACT

Emerging contaminants (ECs) such as bisphenol A (BPA), 4-nonylphenol (4-NP) and tetrabromobisphenol A (TBBPA) have gained immense attention worldwide due to their potential threat to humans and environment. Graphene oxide (GO) nanomaterial is considered as an important sorbent due to its exceptional range of environmental application owing to its unique properties. GO was also considered as one of ECs because of its potential hazard. The adsorption of organic contaminants such as phenolic ECs on GO affects the stability of GO nanoflakes in water and the fate of organic contaminants, which would cause further environmental risk. Therefore, the adsorption behaviors of emerging and common phenolic compounds (PCs) including phenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 4-NP, BPA and TBBPA on GO nanoflakes and their stability in water were studied. The adsorption equilibrium for all the compounds was reached <10 h and was fitted with Langmuir and Freundlich isotherms. In addition to hydrophobic effect, adsorption mechanisms included π-π bonding and hydrogen bonding interactions between the adsorbate and GO, especially the electrostatic interactions were observed. Phenol has the highest adsorption affinity due to the formation of hydrogen bond. GO has a good stability in water even after the adsorption of PCs in the presence of a common electrolyte, which could affect its transport with organic contaminants in the environment. These better understandings illustrate the mechanism of emerging and common PC interaction with GO nanoflakes and facilitate the prediction of the contaminant fate in the aquatic environment.

© 2018 Elsevier B.V. All rights reserved.

* Corresponding author.
  E-mail address: yhs@ntu.edu.tw (Y. Shih).

1. Introduction

Emerging contaminants (ECs) are a new class of identified compounds of rising concern that have been investigated in the past 20 years, mainly comprising pharmaceuticals, surfactants, flame retardants, hormones, and nanomaterials. They are widely detected in many environmental media and raise public concerns because they are toxic and have no regulatory standards (Petrie et al., 2015; Sophia and Lima, 2018; Zhu et al., 2017). ECs are widely found in water supplies and persistent, which could cause an adverse effect to humans (Rivera-Utrilla et al., 2013). These chemicals present in the environment are of more concern as they do not appear individually but mostly as a complex, which lead to synergistic effect (Petrie et al., 2013). ECs like bisphenol A (BPA), 4-nonylphenol (4-NP), tetrabromobisphenol A (TBBPA) and some relative phenolic compounds (PCs) exist in water due to their discharge from industrial, domestic, and agricultural wastewater.

Graphene oxide (GO) nanosheet is a derivative of graphite that contains oxygen bearing functional groups at the edges of the carbon layer. The presence of oxygen-carrying functional groups and high surface area make GO a promising tool for adsorption. Graphene nanomaterials and their derivate reveal excellent performance in the environmental contaminant removal of dyes, organic, inorganic pollutants and heavy metal due to the large theoretical surface area, fast electron transfer and the presence of functional groups (Jiang et al., 2015; Shen et al., 2015). GO has the potential for the elimination of organic compounds containing benzene ring due to strong interaction with π-π system. Its high affinity of PAHs to graphene material was also dominated by π-π stacking (Chowdhury and Balasubramanian, 2014; Wang et al., 2014b).

GO has gained recent attention among researchers due to its significant electronic, mechanical and chemical properties. The huge application of GO has led to the growing concerns of transport of GO in the natural water bodies during the life cycle process (Doudrick et al., 2015). The large-scale usage and production of nanomaterials such as GO have unavoidably lead to its release into the environment, posing a potential threat to health and also increasing its possible interaction with the contaminants in the environment (Johra et al., 2014; Peng et al., 2016). For the toxicity of GO, many biological activities were hampered in the presence of GO in the activated sludge (Ahmed and Rodrigues, 2013). The antibacterial properties of GO to pure bacterial cultures were observed (Mejias Carpio et al., 2012). Furthermore, GO can suspend well in water and hence form colloidal suspension due to the electrostatic repulsion originating by the presence of carboxylic and hydroxyl groups on the GO sheets. It is necessary to examine the colloidal stability and its environmental transport to evaluate its fate and health risk (Li et al., 2008; Yao et al., 2015). Once GO releases into the environment, their adsorption of organic contaminants further influences the fate of both pollutants. The sorption could lead to the enhanced mobility of adsorbed ECs on GO nanomaterials causing an environmental risk. The properties of ECs such as the dissociation constant (pK_a), aromatic ring substitution and solubility will affect its interaction with GO surface. Therefore, the adsorption of organic compounds by GO nanoflakes is required to understand the fate of these organic pollutants in water (Liu et al., 2016; Wu et al., 2014; Zhang et al., 2013).

In the present study, the synthesized GO was used to examine the adsorption behavior of ECs in water and their adsorption mechanism. Conventional phenolic contaminants such as phenol, 4-CP, 2,4, DCP, 2,4,6 TCP were chosen to compare their adsorption behaviors. The chemical compositions and surface morphologies of self-synthesized GO nanoflakes were analyzed. Sorption experiments of on GO nanoflakes were performed to study their sorption behavior and interaction mechanism. A better understanding of the sorption of ECs and PCs with GO will lead to the fate prediction of these contaminants in the environment.

2. Materials and methods

2.1. Chemicals and reagents

Graphite flakes (<20 mm) and potassium permanganate ($KMnO_4$) were purchased from Sigma-Aldrich. Hydrochloric acid (HCl, 37%), sulfuric acid (H_2SO_4, 98%) and phosphoric acid (H_3PO_4, 85%) with Grade AR were purchased from Merck. Phenol, 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP), bisphenol A (BPA), 4-nonylphenol (4-NP), and tetrabromobisphenol A (TBBPA) were obtained from Acros. Hydrogen peroxide (30–32%) Grade AR was purchased from Acros chemical company. All solutions were prepared using deionized (DI) water (Millipore, Temecula, CA, USA).

2.2. Preparation of graphene oxide

GO was synthesized by following improved Hummers method (Dreyer et al., 2010; Sahu et al., 2017). In brief, 2.0 g of graphite flakes were added to a mixture 225 mL of sulfuric acid and 25 mL phosphoric acid maintained at a temperature of 35 °C. 5.0 g of potassium permanganate was gradually added to the solution that was maintained at 35 °C and stirred continuously for 10 h. The resultant mixture was cooled in an ice bath, diluted with 225 mL of DI water, then 3 mL of 30% hydrogen peroxide was added to the mixture to remove the residual permanganate. A large number of bubbles will be released and the solution color will be changed to brilliant yellow. The suspension was centrifuged several times and washed with 0.1 N hydrochloric acid and phosphate buffer to remove extra manganese ion. The final solution was washed with DI water to lower the pH value to around 5–7 and then dried in rotary vapor at 45 °C. The GO suspension was prepared by sonication GO sheets in DI water for 2 h.

2.3. Characterization of graphene oxide

The properties of the GO sample were characterized by using Fourier-transform infrared spectroscopy (FTIR), Raman spectroscopy, and X-ray diffraction (XRD). All experiments were performed at different beamlines in National Synchrotron Radiation Research Center (Taiwan). The surface elemental composition was also accomplished by using X-ray photoelectron spectroscopy (XPS). The morphological characterization was performed by using scanning electron microscopy (SEM, JOEL JSM-7600F) and transmission electron microscopy (TEM, JEOL JEM-200CX). SEM/TEM images of the GO were captured digitally for further size analysis.

The electrophoretic mobility of GO samples at different pH values was measured by Zetasizer Nano ZS dynamic light scattering (DLS, Malvern, MA) and their zeta potentials were calculated according to the Helmholtz-Smoluchowski equation. The sedimentation of GO nanoflakes was determined according to time-resolved optical absorbance by using an ultraviolet-visible spectrophotometer (UV–Vis, CT-2200, Chrom Tech, Inc., Apple Valley, MN, USA) at 230 nm.

2.4. Adsorption experiments

Sorption batch experiments of phenol, 4-CP, 2,4-DCP, 2,4,6-TCP, 4-NP, BPA and TBBPA were all performed in a shaker at 150 rpm at 25 °C in the dark. 4 mL amber vials with PTFE screw cap were added one sorbate and the background solution containing 0.01 M $CaCl_2$ in DI water and 200 mg/L NaN_3 as bio-inhibitor. The physiochemical properties of the pollutants considered in our study are listed in Table 1. The kinetic studies were performed by using 20 mg/L sorbate and 5 mg GO nanoflakes to determine the equilibrium time for each sorbate. The time-dependent adsorption experiments were determined by varying the time from 5 to 1440 min. For isotherms, the vials were prepared as the above by adding various concentrations of sorbate and shaking for >48 h. All experiments were repeated at least three times. The vials