Chemical Engineering Journal 343 (2018) 371–378

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Adsorption of 17β-estradiol by graphene oxide: Effect of heteroaggregation with inorganic nanoparticles

Luhua Jiang[a,b], Yunguo Liu[a,b,*], Guangming Zeng[a,b], Shaobo Liu[c], Wei Que[d], Jiang Li[c], Meifang Li[a,b], Jun Wen[e]

[a] *College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China*
[b] *Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Changsha 410082, PR China*
[c] *School of Architecture and Art Central South University, Central South University, Changsha 410082, PR China*
[d] *Department of Economics and Trade, Hunan University, Changsha 410082, PR China*
[e] *College of Agriculture, Guangxi University, Nanning 530005, PR China*

HIGHLIGHTS

- The presence of INPs significantly inhibited the E2 adsorption on GO.
- E2 adsorption onto GO decreased with increase of INPs/GO ratios.
- The inhibitory effect of Al_2O_3 onto E2 adsorption by GO was greater than that of SiO_2.
- Electrostatic attraction between oppositely charged Al_2O_3 and GO favored their heteroaggregation.

ARTICLE INFO

Keywords:
Graphene nanomaterial
Inorganic nanoparticle
Adsorption
17β-estradiol
DLVO theory

ABSTRACT

Increasingly applications of graphene nanomaterials have resulted in their release into the water environments where lot kinds of chemicals and inorganic nanoparticles co-exist. In this work, the influences of two common inorganic nanoparticles (INPs), namely SiO_2 and Al_2O_3, on the adsorption of 17β-estradiol (E2) onto graphene oxide (GO) were examined by using batch adsorption experiments in combination with microscopic, spectroscopic, and computational methods. Results exhibited that the presence of INPs significantly inhibited the adsorption and increased the time to reach adsorption equilibrium for the adsorption of E2 onto GO. Besides, the impact of Al_2O_3 was greater than that of SiO_2 due to the enhanced electrostatic attraction between positively charged Al_2O_3 and negatively charged GO. Derjaguin-Landau-Verwey-Overbeek calculation revealed that GO tended to first homoaggregate and then heteroaggregate with SiO_2. However, oppositely charged Al_2O_3 and GO were likely to heteroaggregation rather than homoaggregation. This was also demonstrated by the zeta potential measurement, and scanning electron microscope. These observations highlighted the significant influence of INPs on the adsorption of contaminants onto GO, and also provided new insights into the fate and transport of GO and pollutants in natural water environments.

1. Introduction

Graphene, as the first available two-dimensional atomic crystal, is a single layer of sp^2-hybridized conjugated carbon atoms closely packed into a honeycomb lattice [1,2]. Since discovered in 2004, it has been receiving much scientific attention because of its unique physicochemical properties, e.g., superior thermal conductivity, excellent mechanical strength, high electron conductivity, and large specific surface area [3–5]. As it has been regarded as ideal candidate for a wide range of commercial applications, industrial scale production of graphene has been predicted to increase exponentially in the next decade [6,7]. Thus, graphene will be inevitably released into the environment, which may lead to various health and environmental risks for plants, animals and humans [8–10]. Estrogens, as one classes of endocrine disrupting chemicals, have been identified to possess serious endocrine-disrupting activity and can lead to negative effects on organisms, such as reproductive disorders, abnormal development (i.e., malformations, feminine), and cancers, even at low concentrations [11–13]. Some of the adverse effects of graphene might be increased due to adsorbing estrogen contaminants, and the fate and transport of estrogens in the

---

[*] Corresponding author at: College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China.
E-mail address: liuyunguo_hnu@163.com (Y. Liu).

https://doi.org/10.1016/j.cej.2018.03.026
Received 28 December 2017; Received in revised form 4 March 2018; Accepted 5 March 2018

environment could be altered.

Consequently, it is imperative to investigate the behavior of estrogens by graphene nanomaterial under environmentally relevant conditions, which is crucial to assess the environmental risks of this material when adsorbed estrogen contaminants. Until now, lots of researches have demonstrated that graphene oxide (GO) with large specific surface areas (SSA), abundant functional groups, and strong π–π interactions possessed high adsorption ability to estrogen contaminants from aqueous solution [14–19]. Our previous studies found that the estrogen adsorption capacity by GO depended on its physicochemical properties (e.g., SSA, pore, and surface functional groups) and solution chemistry (e.g., pH, background electrolyte, ionic strength, and natural organic matter) in real water environments [20,21]. Besides, GO showed higher or comparable adsorption abilities to carbon nanotubes, biochars, and activated carbons; and the effect of natural organic matter competition on the uptake of GNs was less severe [22].

Heteroaggregation of GO with inorganic nanoparticles (INPs) is inevitable once they are released into water environments, which is important to thoroughly investigate the fate and transport of GO. Recently, lots of studies have been devoted extensive efforts to determine the heteroaggregation or interactions between INPs and GO. Results indicated that the aggregation of GO would be affected by INPs such as metal oxides (Al_2O_3, ZnO, TiO_2, and MgO), clays (kaolinite, montmorillonite), minerals (SiO_2, layered double hydroxides, hematite, and goethite), and metal–organic frameworks [23–29]. However, to the best of our knowledge, very limited researches have been conducted to examine the impacts of INPs on estrogens adsorption onto GO. To date, only several studies illustrated that the presence of natural minerals (e.g., goethite, kaolin, and montmorillonite) and sediments in the heteroaggregation of GO inhibited the adsorption of estrogen contaminants onto GO due to the occupation of the adsorption sites on GO through electrostatic attraction and hydrogen bonding [18,30]. Engineering nanoparticles, e.g., SiO_2 and Al_2O_3, were widely applied in the fields of engineering materials, machinery, environmental remediation, electronic engineering, and medicine [31,32]. Besides, they are ubiquitous in almost all natural surface waters [33,34]. Previous studies indicated that engineering nanoparticles have great impact on the adsorption of pollutants by carbon nanotubes (CNTs) via altering the surface chemistry and morphology of CNTs [34–36]. Similarly, adsorption of estrogens onto GO is also likely affected by engineering nanoparticles.

Therefore, in this work, the influence of engineering nanoparticles (SiO_2 and Al_2O_3) on the adsorption of estrogens on GO was investigated. One commonly estrogens in natural waters, 17β-estradiol (E2), was selected as target estrogen pollutants. Adsorption kinetics and isotherms of E2 by GO were conducted at different INPs/GO ratios. The underlying influencing mechanisms were discussed according to zeta potentials, scanning electron microscope (SEM), and Derjaguin-Landau-Verwey-Overbeek (DLVO) calculation.

2. Materials and methods

2.1. Chemicals and materials

E2 (98%) was obtained from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA). GO was prepared through exfoliation of graphite flakes via using the modified Hummers' method [37–39]. Detailed preparation method for GO is provided in the Supplementary material. SiO_2 (purity > 99.9%, particle size 15 nm) was purchased from Aladdin Bio-Chem Technology Co., LTD (Shanghai, China). Al_2O_3 (purity > 99%, γ-phase, particle size 20 nm) was provided by Rhawn Reagent (Shanghai, China). NaOH, HCl, NaCl, and methanol were obtained from Sinopharm Chemical Reagent Co., Ltd., China and were analytical reagent grades. Ultrapure water generated by a Milli-Q water filtration system (Millipore, Billerica, MA) was used to all of the experiments.

2.2. Characterization methods

The Brunauer–Emmett–Teller (BET) surface area and the pore size distribution were examined by using N_2 adsorption and desorption (Micromeritics, Tristar II 3020) at 77 K over a relative pressure ranging from 0.0955 to 0.993. The C, H, O, N contents of GO were obtained by using an elemental analyzer (Vario EL III, Elementar, Germany). X-ray photoelectron spectroscopy (XPS) was determined by using an ESCALAB 250Xi X-ray photoelectron spectrometer (Thermo Fisher, USA) with the scanning range of 0–1000 eV. Fourier transform infrared spectrum (FT-IR) was investigated by a spectrophotometer (Nicolet 5700 Spectrometer) using the KBr pellet technique with the range from 400 to 4000 cm^{-1}. The surface morphologies were examined by a SEM (Zeiss EVO MA10, Germany) operated at 20 kV. The zeta potentials were recorded on dynamic light scattering measurements using a Zetasizer (Nano ZS90, Malvern Instruments Ltd., Malvern, UK).

2.3. Batch adsorption experiments

The E2 stock solutions were prepared through dissolving in methanol. The desired concentrations of E2 work solution were further obtained by dissolution of stock solutions in ultrapure water and successive dilutions. For the adsorption experiments on GO at different INPs/GO ratios, various amounts of INPs were added into a series of pre-dispersed suspensions of GO in amber glass bottles to obtain INPs/GO ratios of 0:1, 10:1, 50:1 and 100:1, respectively. The suspensions were then placed on a rotary shaker for 24 h at 160 rpm and 25 °C to achieve sufficient mixing. After that, E2 solutions were added into the suspensions to obtained initial concentrations of 4 mg/L. All batch adsorption experiments were conducted in pH 6.5 and 0.01 M NaCl placing in a temperature controlled water bath shaker for 24 h with a shaking speed of 160 rpm at 25 °C. For adsorption kinetic experiments, initial E2 solutions (4 mg/L) were taken at specific time intervals from 0 to 48 h. For adsorption isotherm experiments, the initial E2 concentrations were in the range of 0.2–8 mg/L. Subsequently, the suspensions were centrifuged at 8000 rpm for 10 min and then the filtered through 0.45 μm membrane filters. The E2 concentrations were measured through means of a fluorescence quenching method using a F-4500 fluorescence spectrophotometer (Hitachi, Japan) as illustrated in previous studies [19,20]. The adsorbed E2 quantity was calculated from the difference between the initial and equilibrium concentrations.

2.4. Model of data analysis

The adsorption kinetic data were analyzed by the pseudo-first-order, pseudo-second-order, and intra-particle diffusion model, which are commonly presented as follows [40–42]:

$$\text{Pseudo-first-order model: } q_t = q_e - q_e e^{-k_1 t} \tag{1}$$

$$\text{Pseudo-second-order model } q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{2}$$

$$\text{Intra-particle diffusion model } q_t = k_d t^{0.5} + L \tag{3}$$

where q_e (mg/g) and q_t (mg/g) are the amount of E2 adsorbed at equilibrium and different time, respectively; k_1 (1/min), k_2 (g/mg min), and k_d (mg/g·min$^{0.5}$) are the rate constants of the pseudo-first-order model, pseudo-second-order model, and intra-particle diffusion model, respectively; L (mg/g) is the thickness of boundary layer.

Langmuir and Freundlich model were used to fit the isotherm experimental data, and their mathematical expressions are given as follows [43–45]:

$$\text{Langmuir equation } q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \tag{4}$$