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Adsorption of nicotine in aqueous solution by a defective graphene oxide

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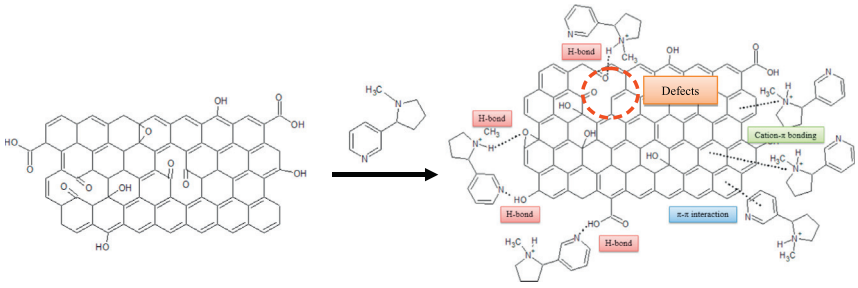
HIGHLIGHTS

- GO and modified GO were prepared by a simple wet-chemical method.
- The defective GO-COOH has superior adsorption capacity and stability toward nicotine.
- This may be due to the formation of defective sorption sites on the defective GO-COOH.
- The surpassing performance and cost-effectiveness enable adsorbents practical applications.

GRAPHICAL ABSTRACT



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ABSTRACT

Extensive concerns have been focused on the emerging contaminants including nicotine in the aquatic system recently. Graphene oxide (GO) and modified graphene oxides (GO-COOH and defective GO-COOH) are used as effective adsorbents to remove nicotine from aqueous solution. The adsorption isotherms and kinetics of the adsorbents all fit well with Langmuir model and pseudo-second-order model, respectively. The thermodynamic studies show that the adsorption is an exothermic and spontaneous process. The influence of pH and ionic solution strength on the adsorbents is also investigated. The maximum adsorption capacity can be observed at pH value of ca. 8. The adsorption capacities of nicotine are decreased upon the increase of sodium ion concentration. Among all the adsorbents, the defective GO-COOH adsorbents possess the maximum adsorption capacity of nicotine of 196.5 mg g^{-1} obtained from Langmuir isotherm. In regeneration experiments, the defective GO-COOH adsorbents can maintain 95.1% of adsorption capacity after five times of cyclic adsorption-desorption processes. The adsorbents are identified by Fourier transform infrared, ^{13}C solid-state magic-angle spinning nuclear magnetic resonance, X-ray photoelectron and Raman spectroscopies to determine the adsorption mechanisms and structure on the adsorbents. It can be deduced that the surpassing performance of defective GO-COOH may be ascribed to the unique adsorption mechanism of defects, the enhanced π–π interaction and cation-π bonding. The highly-efficient and stable features enable the defective GO-COOH a promising adsorbent to eliminate nicotine from water.

1. Introduction

Emerging contaminants (ECs) which may cause serious and chronic effects on ecosystems were frequently found in the environment these years (Barrios-Estrada et al., 2018). Nicotine which is mainly from tobacco plants also considered as an EC. A substantial amount of nicotine released to aqueous environment is mainly from the processing of tobacco and its corresponding products. Therefore, the nicotine has been discovered in industrial wastewater, surface and ground water, and even bottled water (de Franco et al., 2014). The studies show that the negative impacts of nicotine on human health contain heart disease,

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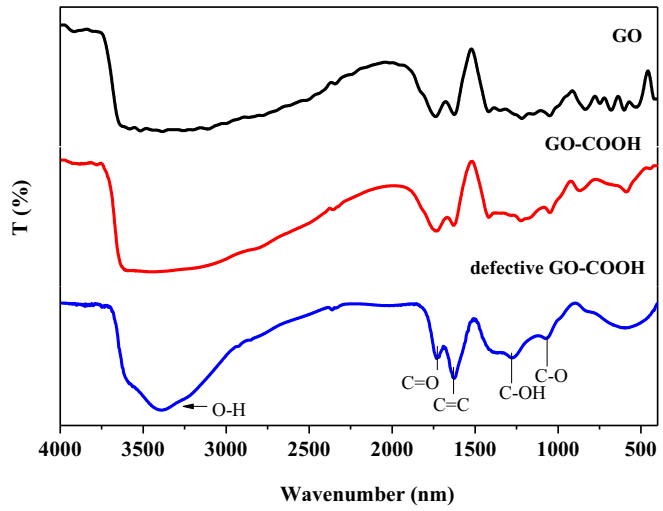

Fig. 1. FTIR spectra of various samples.

cancer and respiratory disorders (Cheng et al., 2003). It was estimated that the lethal dosage for adult is ca. 40–60 mg of nicotine which is one of highly toxic compounds in the alkaloids (Rakić et al., 2010).

A series of technologies have been investigated to remove nicotine such as adsorption (Akcay and Yurdakoc, 2008; Cai et al., 2014; Girão et al., 2010; Lazarevic et al., 2011; Pi et al., 2015; Rakić et al., 2010; Shin et al., 2011), advanced oxidation (Klamerth et al., 2010; Rodriguez et al., 2011), photocatalytic degradation (de Franco et al., 2014), and biodegradation (Meng et al., 2010; Wang et al., 2009; Zhong et al., 2010). Among these methods, the most effective and widely used method is adsorption on solid adsorbents because of its availability, high performance and cost-effectiveness. Various adsorbents such as zeolites (Rakić et al., 2010; Lazarevic et al., 2011), ordered mesoporous organosilicas (Shin et al., 2011), bentonite (Akcay and Yurdakoc, 2008) and carbon-based materials (activated carbons, mesoporous carbons and carbon nanotube) (Pi et al., 2015; Cai et al., 2014; Girão et al., 2010) have been employed for decontaminating wastewater containing nicotine. In particular, carbon materials (Pi et al., 2015) reported to be the most effective adsorbents due to their textural and surface properties with various functional groups. Thus, it is still urgent to develop effective and economical carbon adsorbents for the elimination of nicotine.

Graphene oxide (GO), a two-dimensional layer of sp^2 bonded carbon atoms, can be used as a potential adsorbent for aromatic compounds via π–π interaction. In addition, many reports (Chen et al., 2018; Kyzas et al., 2015; Ersan et al., 2016; Tanhaei et al., 2018; Wang et al., 2018; Yu et al., 2015; Zhou et al., 2016) have indicated that GO can be a promising adsorbent to remove pollutants from aqueous phase because of its hydrophilicity, high surface area and abundant functional groups. In the earlier studies, GO has been used as adsorbents for removal of inorganic ions (e.g., Cu(II), Zn(II), Cd(II) and Pb(II)) (Sitko et al., 2013), organic compounds (endocrine disrupting chemicals and antibiotics) (Gao et al., 2012; Jiang et al., 2016) and various dyes (e.g., methylene blue and triphenylmethane dyes) (Kingori et al., 2014; Yan et al., 2014) from wastewater. However, the potential application for eliminating nicotine from polluted water by using GO and modified GO is limited.

In this study, the possibility of nicotine adsorption by GO and modified GO was evaluated for the first time. A variety of adsorption isotherms, kinetic and thermodynamic studies was fully investigated. Moreover, the effects of pH values and ionic strength on the removal of nicotine via GO and modified GO were also studied. Five cyclic runs of adsorption-desorption process were also tested to assess the durability of adsorbents. Most importantly, the chemical structure and adsorption mechanism of GO and modified GO toward nicotine were identified by using Fourier transform infrared (FTIR), ^{13}C solid-state magic-angle spinning NMR (^{13}C ssNMR), X-ray photoelectron (XPS) and Raman spectroscopies.

2. Experimental sections

2.1. Adsorbents preparation

Graphene oxide (GO) was prepared by using a modified route described earlier (Liu et al., 2016). Typically, 3 g of graphite and 1.5 g of $NaNO_3$ were introduced into 75 mL of concentrated H_2SO_4 under ice bath. Then, 9 g of $KMnO_4$ was slowly added and stirring continuously at room temperature for 45 min. Next, 138 mL of deionized (DI) water was mixed with the resulting solution and then stirred for another 60 min. Afterwards, 30 mL of 30% H_2O_2 and 420 mL of DI water were added to the above solution. At last, the resultant solids (denoted as GO) were washed repeatedly with 5% of HCl and dried at 333 K. In terms of graphene oxide with rich carboxylic acid groups (GO-COOH), 1 g of graphite powder was mixed with 46 mL of concentrated sulfuric acid at the temperature of <283 K. Then, 3 g of $KMnO_4$ was slowly added to the above solution which was kept at the temperature of the <293 K. Next, the solution was ramped to 313 K and continuously stirred for 3 h. Afterwards, 100 mL of DI water was slowly added to the reaction system, followed by increasing the temperature of the

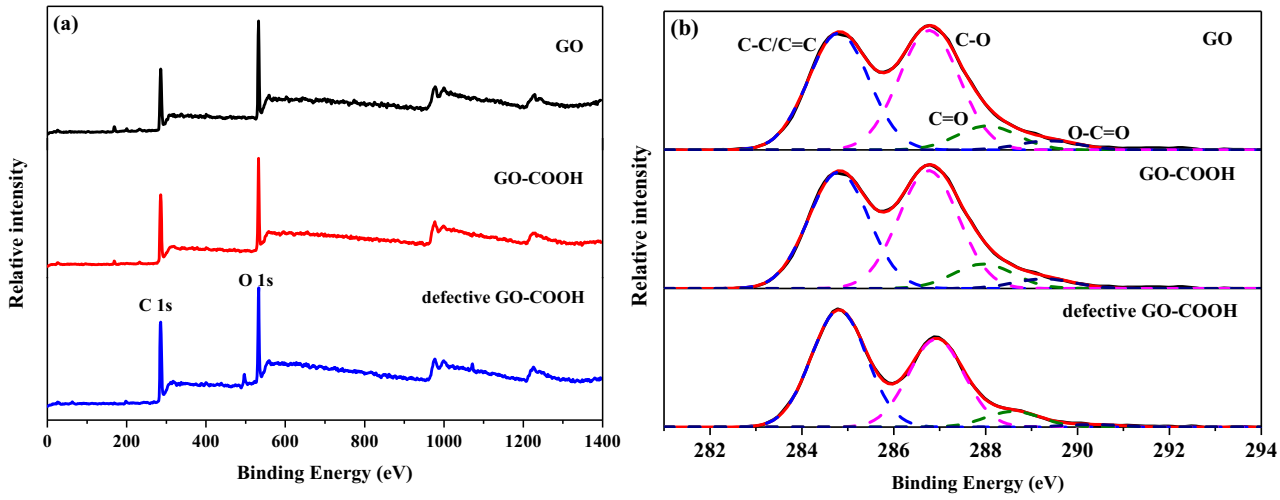

Fig. 2. (a) XPS survey and (b) carbon 1s spectra of various samples.