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Adsorption of emerging contaminant metformin using graphene oxide

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HIGHLIGHTS

- Rapid and efficient removal of metformin can be achieved during the adsorption process.
- Sorption kinetic, isothermal and thermodynamic characteristics of metformin are explored.
- The adsorption capacity of GO for metformin is influenced in the presence of NaCl and background electrolyte.
- The adsorption mechanism is believed to be so-called π−π interactions and hydrogen bonds between GO and metformin.

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ABSTRACT

The occurrence of emerging contaminants in our water resources poses potential threats to the livings. Due to the poor treatment in wastewater management, treatment technologies are needed to effectively remove these products for living organism safety. In this study, Graphene oxide (GO) was tested for the first time for its capacity to remove a kind of emerging wastewater contaminants, metformin. The research was conducted by using a series of systematic adsorption and kinetic experiments. The results indicated that GO could rapidly and efficiently reduce the concentration of metformin, which could provide a solution in handling this problem. The uptake of metformin on the graphene oxide was strongly dependent on temperature, pH, ionic strength, and background electrolyte. The adsorption kinetic experiments revealed that almost 80% removal of metformin was achieved within 20 min for all the doses studied, corresponding to the relatively high k_1 (0.232 min^{-1}) and k_2 (0.007 g mg^{-1} min^{-1}) values in the kinetic models. It indicated that the highest adsorption capacity in the investigated range (q_m) of GO for metformin was at pH 6.0 and 288 K. Thermodynamic study indicated that the adsorption was a spontaneous ($\Delta G^0 < 0$) and exothermic ($\Delta H^0 < 0$) process. The adsorption of metformin increased when the pH values changed from 4.0 to 6.0, and decreased adsorption were observed at pH 6.0–11.0. GO still exhibited excellent adsorption capacity after several desorption/adsorption cycles. Besides, both so-called π−π interactions and hydrogen bonds might be mainly responsible for the adsorption of metformin onto GO.

1. Introduction

Pharmaceutical and Personal Care Products (PPCPs) were a series of compounds including analgesics, antibiotics, contraceptives, lipid regulators, in addition to the active ingredients in soaps, detergents, perfumes, and skin, hair, and dental care products (Rice and Mitra, 2007). In recent years, their increasing consumption and adverse effects on ecological or human body have been attained extensive attention. The emission of these emerging contaminants has emerged as an environmental problem and rather poor wastewater management could not effectively eliminate these compounds (Terzić et al., 2008). Therefore, there is a widespread demand that this kind of contamination requires effective

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elimination.

Metformin has become a worldwide first-line pharmaceutical for type 2 diabetes mellitus since the late 1950s (Viollet et al., 2012), the medicinal use was well characterized, but the effect it had on the environment was still uncertain. It was found that there were some threats in intersex gonads in male fish, fecundity and the overall size of male fish after exposing fathead minnows in wastewater effluent with metformin (*Pimephales promelas*), and the juvenile *Pimephales promelas* were more susceptible to the estrogenic effects of metformin than older, sexually mature male one (Niemuth and Klaper, 2015; Crago et al., 2016). Metformin was not structurally hormone-like chemical compound, and could not cause estrogenic activity (Escher et al., 2011). However, it has been proved that metformin was an effective medicine to treat endocrine disorder polycystic ovarian syndrome (PCOS) (Tang et al., 2012). The results suggested that metformin might be a potential endocrine disruptor in the environment (Niemuth and Klaper, 2015). Thus, metformin would be one of the nontraditional endocrine disrupting chemicals (EDCs) in the environment. Despite a large conversion in wastewater treatment plants (WWTPs) before discharge, metformin was still one of the most abundant pharmaceuticals found in WWTP effluent and surface-waters, and it could usually reach 6 tons per year in individual WWTPs of urban areas (Blair et al., 2013; Oosterhuis et al., 2013). Therefore, metformin has become an emerging contaminant in the environment. It is necessary to find a way to decontaminate metformin.

Adsorption has been proved to be an excellent and promising technique due to its low expenses, accessibility, excellent performance, and environmentally benignity. In recent years, various materials have been widely applied to the elimination of various contaminants, such as powdered activated carbon (PAC) (Yoon et al., 2003), ion exchange resin (Gupta et al., 2004; Wang et al., 2016), carbon nanotubes (Yao et al., 2010), chitosan (Hu et al., 2011a), bottom ash (Mittal et al., 2009a, 2009b, 2010a, 2010b), activated carbon (Gupta et al., 1998; Gu et al., 2009), biochar (Tan et al., 2015, 2016, 2017) and organic resin (Lu et al., 2016). However, these sorbents suffered the problem of either low sorption capacities or high-cost. Thus, there is a strongly desire to search for a high-performance, low-cost adsorbent. Graphene oxide (GO), a single atomic layer material derived from graphene, has inspired huge interests in adsorption, photocatalytic degradation and sensor, due to its excellent physical-chemical properties and high specific surface area (theoretical value of 2620 $m^2\ g^{-1}$) (Zhao et al., 2011b; Chang and Wu, 2013; Hu et al., 2016). It has confirmed that GO could be a promising adsorbent, because it had large surface area and abundant surface oxygen-containing groups (Hu et al., 2014a; Wu et al., 2017). In previous study, GO was used as an adsorbent to remove metal ions (copper, zinc, cadmium and lead), the maximum adsorption capacity of GO for Cu(II), Zn(II), Cd(II) and Pb(II) could reach 294, 345, 530, and 1119 mg g^{-1}, respectively (Sitko et al., 2013). It was demonstrated that GO could act as a good adsorbent in adsorbing tetracycline antibiotics from aqueous solution (Gao et al., 2012). GO could also be successfully applied for the removal of aniline (Fakhri, 2017), 17β-estradiol (Jiang et al., 2016). Moreover, GO could be an efficient adsorbent for the removal of various dyes such as methylene blue, methyl violet and Basic Red 12 (Ramesha et al., 2011; Moradi et al., 2015). It was reported that metformin was an emerging contaminant in the environment (Niemuth and Klaper, 2015; Crago et al., 2016), and effective removal was needed. Unfortunately, there were very little data available about the elimination of metformin, few articles about the reduction of metformin had been reported (Blair et al., 2013; Kim et al., 2014; Neamţu et al., 2014; Kyzas et al., 2015; Cui and Schröder, 2016), and the application of graphene oxide as an adsorbent in the removal of metformin from aqueous solution was still scarce.

In this study, GO was studied for the first time to remove metformin from aqueous solution and characterized by scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), Brunauer-Emmett-Teller (BET) and zeta potential to investigate its adsorption behaviors. Batch adsorption experiments were carried out to explore the effects of contact time, concentration, temperature, pH, and ionic strength on the removal of metformin by GO. The effects of electrolyte anions (Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-}) and electrolyte cations (Na^+, K^+, Mg^{2+} and Ca^{2+}) in aqueous solutions on the adsorption of metformin onto GO were also investigated.

2. Materials and methods

2.1. Materials

Metformin (97%) were purchased from Acceia ChemBio Co., Ltd and graphite powder was obtained from Tianjin Kermel Chemical Regent Ltd. All chemicals including $K_2S_2O_8$, P_2O_5, H_2SO_4, $NaNO_3$, $KMnO_4$, H_2O_2, NaCl, Na_3PO_4, KCl, Na_2SO_4, $MgCl_2$, $CaCl_2$ and HCl were supplied by Shanghai Chemical Corp. All compounds used in the experiment were analytical grade without further purification. All the solutions were prepared using high purity water (18.25 MΩ cm^{-1}) from a Millipore Milli-Q water purification system. A stock solution (40 mg L^{-1}) of metformin was prepared by dissolving 42 mg of metformin (97%) in 1 L of Milli-Q water. The working solution of desired metformin concentrations used in the following experiments was obtained by diluting the stock solution.

GO was prepared by using modified Hummers method from the natural graphite powder (Jiang et al., 2016). Briefly, 6 g graphite powder was firstly oxidized by 24 ml concentrated H_2SO_4 (98%), 5 g $K_2S_2O_8$ and 5 g P_2O_5, and stirred at 353 K for 4.5 h. Then, 1 L of Milli-Q water was added and left overnight. The mixture was washed thoroughly and dried under vacuum at 333 K. Next, 240 ml 273 K concentrated H_2SO_4 (98%), 30 g $KMnO_4$ and 5 g $NaNO_3$ were slowly added to oxidize the preoxidized graphite and stirred below 293 K for 4 h. Then, the reaction was carried out at 308 K for 2 h. Next, 500 ml Milli-Q water was added slowly and the mixture was stirred for another 6 h at 363 K. After that, 40 ml H_2O_2 (30%) was used to eliminate the surplus MnO_4^- and stirred for 2 h at room temperature. The products were finally washed by 10% (v/v) HCl and water several times. The resulting solution was sonicated for 2 h and freeze dried for further use.

2.2. Characterization of GO

The surface morphologies and structures of GO were observed by scanning electron microscope (SEM, JSM-7001F, Japan) and transmission electron microscope (TEM, JEM-3010, Japan). The fourier transform infrared spectroscopy (FTIR) of GO was conducted by using a Nicolet 5700 FT-IR Spectrometer (Thermo Scientific). The surface elemental composition analyses of GO were characterized based on the X-ray photoelectron spectroscopy (XPS) (Thermo Fisher, USA). The Brunauer-Emmett-Teller (BET) specific surface area of GO was measured by using automatic surface analyzer (Quantachrome, USA). The X-ray diffraction (XRD) patterns of GO was obtained by an X-ray diffractometer (Rigaku D/max-2500, Japan) with Cu Kα radiation (k = 1.541 Å). The zeta potentials of GO in water solutions at pH 4.0–11.0 (adjusted by NaOH or HCl) was detected by a zeta potential meter (Zetasizer Nano-ZS90, Malvern).