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High-rate adsorption of acetaminophen from the contaminated water onto double-oxidized graphene oxide

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HIGHLIGHTS

- Double-oxidized graphene oxide (DGO) was prepared.
- Acetaminophen (ACT) adsorption of onto the DGO was examined.
- Efficient ACT adsorption obtained at neutral pH and low DGO concentration.
- High ACT adsorption capacity (704 mg/g) on DGO was achieved.
- DGO was found to be an efficient and promising adsorbent for pharmaceuticals.

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ABSTRACT

A double-oxidized graphene oxide (DGO) was prepared and characterized. The DGO was the planar and layered sheets with the smooth surface with the BET specific surface area of 51.2 m^2/g and an average pore size of 9.7 nm. A high density of oxygen-containing functional groups was developed on the surface of DGO. Adsorption of acetaminophen (ACT) was investigated on the prepared DGO. The maximum adsorption obtained at $pH \leqslant 8$. The experimental adsorption data was well fitted with the pseudo-second-order kinetic model. The Langmuir isotherm model had better fitness with the equilibrium adsorption results with the maximum adsorption capacity of 704 mg/g. Thermodynamic analysis indicated that adsorption of ACT onto DGO is a physical spontaneous and exothermic process. Accordingly, the DGO has a very high capacity for adsorption of pharmaceuticals from the contaminated water and can be considered as a promising alternative of conventional activated carbon adsorbent.

1. Introduction

Pharmaceuticals are among the main important emerging water contaminants which are frequently found at low to high concentrations in many of the water sources [1,2]. Acetaminophen (ACT) is one of the most widely consumed analgesic and antipyretic pharmaceutical which has been frequently found in all sorts of waters all around the world [3,4]. Releasing of these micropollutants to the environment has led to their accumulation in the water bodies including those used in public water supplies which negatively affect the ecosystem as well as posse the adverse chronic effect on the human health [5,6]. To improve the water quality and protect the human health, the water contaminated with the emerging contaminants including pharmaceuticals has to be efficiently treated using an appropriate technique before being supplied for consumption.

Adsorption is one the most widely used process for the removal of organic contaminants including pharmaceutics from the contaminated waters. This is due to its unique features including simplicity in design, construction and operation, high removal efficiency without producing treatment byproducts, and low setup and operation cost [1,2,7]. Activated carbon is the main conventional adsorbent used in this process. Several studies e.g., [3,4,8,9]have been published on adsorption of ACT form the contaminated water with the maximum adsorption capacities of 268 mg/g [4]. However, the activated carbon has a high production and regeneration costs. Moreover, the size of pores in the activated carbon is irregular and the biofilm growth or particles may clog the pores; these features restrict the pore distribution leading to kinetically variable adsorption onto the activated carbon [7]. Therefore, many efforts have been focused on developing new adsorbents with higher adsorption capacity in order to make the process more cost-effective. Graphene oxide (GO) is a single sheet form of graphite with a high specific surface area which contains various oxygenated surface functional groups without pore diffusion

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restrictions [7,10,11]. These unique structural properties presented the GO as an efficient adsorbent to be used for the remediation of waters contaminated with both organic and inorganic contaminants e.g., [7,10]. It has been shown that the adsorption property of the GO depends on the extent of its oxidation degree [12].

Accordingly, the novelty of the present investigation is as follows: (1) the preparation of the double-oxidized GO (DGO), (2) the investigation of the DGO for the adsorption of the ACT from the contaminated solutions at various conditions including solution pH, DGO and ACT concentrations, contact time, and solution temperature and (3) modeling of the kinetic, isotherm and thermodynamic of ACT adsorption onto DGO.

2. Materials and methods

2.1. Preparation and characterization of highly oxidized graphene

The DGO was prepared from the natural graphite powder by a modification in Hummers and Offeman's method [13]. Briefly, 2.5 g of $K_2S_2O_8$ and 2.5 g of P_2O_5 were put into a 100 mL flask. Thereafter, 12.5 mL of concentrated H_2SO_4 (98%) was added into the flask and the mixture was stirred by a magnet stirrer at room temperature. After all the reactants were completely dissolved, 2.5 g of graphite powder was added slowly to the flask. Then, the reaction system was transferred to an oil bath (80 °C) and stirred for 8 h under reflux. Heating was then stopped and the mixture was cooled to room temperature naturally. After that, the mixture was diluted with 500 mL water and was stirred overnight. Such prepared solution was finally washed with deionized water to remove acid and then, the bottom solid product named graphene oxide (GO) was dried in air at room temperature.

At the second oxidation step, 125 mL of concentrated H_2SO_4 was maintained at 0 °C using an ice water bath. The GO prepared in the previous step was added to the acid under constant stirring. 15 g of $KMnO_4$ was then gradually added to the mixture to keep the temperature of the mixture bellow 10 °C. The mixture was further stirred for 30 min in the ice bath and 2 h at room temperature. After that, the suspension was transferred to 35 °C water bath and stirred for more 2 h. Next, 250 mL of distilled water was slowly added to the mixture in the ice bath to prevent rapid boiling of the reaction mixture. Then the ice bath was removed and the mixture was again stirred for 2 h. The resulting mixture was further diluted by adding 750 mL of distilled water under vigorous stirring. After 15 min mixing, the reaction was terminated by dropwisely addition of 25 mL H_2O_2 (30%), resulting in a yellow–brown mixture. Then, the mixture was left undisturbed overnight. The nearly clear supernatant was then decanted and the bottom gel was washed with 0.1 N HCl followed by distilled water to remove the residual ions of oxidant and other impurities. This washing step was repeated several times until the pH of the decantate become neutral. The resulting product dried at room temperature was named as DGO. A stock suspension of DGO was prepared by adding 25 mg of DGO to 50 mL of distilled water (DW) and the mixture was ultrasonicated for 2 h at 20 k Hz in order to exfoliate the DGO sheets.

2.2. DGO characterization

The prepared DGO were analyzed for crystalline phase and size, specific surface area, volume and size of pores, surface morphology, elemental analysis, and surface functional groups. The structure of the DGO material was characterized by X-ray diffraction (XRD) (XPERT diffractometer) done at 30 mA and 40 kV using CuKα radiation (λ = 1.78897 nm) for 2θ between 10° and 80°. The average size of crystals in the prepared DGO was determined using the Scherrer's formula [14]. The specific surface area, volume, and pore sizes of DGO were determined from N_2 adsorption/desorption data carried out using a Belsorp mini II (Japan) at 77 K according to the BET isotherm model. The samples were degassed in a vacuum at 120 °C for 17 h before N_2 adsorption/desorption analysis. The surface morphology and shape of the DGO was observed using Ziess (Germany) scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (SDD detector, Oxford Instruments) for elemental analysis of the materials. The surface functional groups were determined using FTIR spectrometer [model Nicolet-6700].

2.3. Adsorption experiments

A 1 g/L stock solution of ACT ($C_8H_9NO_2$) was prepared by dissolving 0.5 g ACT in 500 mL of distilled water. The adsorption batch experiments of ACT on DGO were conducted in a glass flask. For each test, 10 mL of the known concentration of ACT solution was transferred to the flask and then 10 mL of the known concentration of DGO suspension was added to that and the whole content of the flask was then magnetically stirred for the specified time. At the end of the test period, the suspension was filtered using a 0.2 μm cellulose acetate filter to separate the DGO particles and the filtrate was analyzed for the residual ACT. The ACT adsorption efficiency was measured in terms of removal efficiency and adsorption capacity calculated from Eqs. (1) and (2), respectively.

$$\text{ACT removal efficiency } (\%) = \frac{\text{ACT}_0 - \text{ACT}_t}{\text{ACT}_0} \times 100 \tag{1}$$

$$\text{ACT adsorption capacity } (\text{mg/g}) = \frac{\text{ACT}_0 - \text{ACT}_t}{C_{\text{DGO}}} \times 1000 \tag{2}$$

where ACT_0 and ACT_t stand for the concentration (mg/L) of ACT in the test suspension at the beginning and end of the target adsorption experiment, and C_{DGO} represent the concentration (mg/L) of the DGO in the adsorption test suspension. For the equilibrium tests, the ACT_t represented the concentration (mg/L) of ACT in the filtrate at the equilibrium time (10 h contact time).

The effect of solution pH (2–11), DGO concentration (4–20 mg/L), ACT concentration (10–100 mg/L), contact time (2–120 min), solution temperature (15–45 °C) and salinity (0.5–5 g NaCl/L) was evaluated on the ACT removal efficiency by DGO. The kinetic and isotherm of ACT adsorption onto DGO was also investigated. The experimental runs and conditions are given in Table 1.

3. Results and discussion

3.1. DGO characterization

Fig. 1 shows the FTIR spectra in range of 4000–400 cm^{-1} of DGO. The strong bands at 3431 cm^{-1} are related to the O–H vibration in water absorbed on the surface of DGO [15]. The strong peak seen at 1632 cm^{-1} is attributed to the C=O stretching vibration [16]. The weak peaks at 1413 cm^{-1}, 1227 cm^{-1} and 1047 cm^{-1} are attributed to the symmetric stretching of COO– carbonyl [17], the C–O is corresponding to the peroxide group on the surface of DGO [18] and the C–O stretching vibration [15], respectively. Low radiation transmission (<20%) in FTIR spectra (Fig. 1) clearly indicates that the DGO contains a high density of oxygen-containing functional groups which promote the adsorption rate. The DGO had a BET specific surface area of 51.2 m^2/g with an average pore size of 9.7 nm. It indicates that the prepared DGO is a mesoporous material with a relatively high specific surface area. Chang et al. [19] reported a BET between 65.8 and 90.6 m^2/g with the mean pore size between 0.3 and 5.9 nm for GO prepared with