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ORIGINAL ARTICLE

Adsorption characteristics of graphene oxide as a solid adsorbent for aniline removal from aqueous solutions: Kinetics, thermodynamics and mechanism studies

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KEYWORDS

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Abstract The aim of this study is to investigate the possibility of graphene oxide (GO) as an alternative adsorbent for aniline removal from aqueous solution. Adsorption properties of GO for aniline removal were regularly investigated, including pH effect, adsorbent dose, temperature, contact time and initial concentration. The adsorption amount of aniline decreased with increasing pH. The experimental data were evaluated by Langmuir, Freundlich, Temkin and Harkins–Jura models in order to describe the equilibrium isotherms. Equilibrium data fitted well to the Langmuir model. The kinetic parameters achieved at different concentrations were analyzed using a pseudo first-order, pseudo second-order kinetic equation and intra-particle diffusion model. The experimental data fitted very well the pseudo second-order kinetic model. Thermodynamic parameters (free energy change, enthalpy change, and entropy change) announced that the removal of aniline from GO was endothermic and spontaneous. The study showed that GO could be used as an efficient adsorbent material for the adsorption of aniline from aqueous solution.

1. Introduction

The water is the most valuable natural resource, and because of its importance, it has become a dominant cause of concern. It has obtained more and more attention; the world became a foul with the maintenance and water purification. The petroleum refineries and the industries of plastics and paint are noxious sources for the sewage, which have the potential to destroy the receiving waters. Therefore, it is necessary to install convenience center for the treatment of the wastewater in places where these industries are posited.

Aniline is an important chemical compound which is well known for its abroad applications in the manufacture of dyestuffs, rubbers, pesticides, plastics and paints. However, the aniline-laden wastewater discharged from these industries has become a severe environmental difficulty as well. It is highly

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toxic and has adverse influences on human health and lentic life [10,4]. Moreover, aniline can be easily adsorbed in foulings, the fact that they can expand its insistence in the aquatic environment [24]. There are many processes, including biodegradation [21], oxidation by ozone [9], ligand exchanger [11], adsorption [30] and some other processes that can be used for the removal of aniline from wastewater. These processes can decompose or remove aniline from wastewater.

The adsorption phenomenon is probably the most widely employed manner in separation method [26], waste effluents treatment [23], refrigeration, environmental control and life support device in spacecraft, and obviously heterogeneous catalysis [8].

Graphene, a new carbon nanomaterial, has unique physical, chemical, electrical and mechanical properties [20,19,22,3] and is adequate for preparing nanodevices and advanced composite materials [2,27,25].

Recently, graphene and graphene oxide were used as adsorbents to remove methyl orange [14,15,16], naphthalene [31,32,33], 1-naphthol [31,32,33], arsenic [5], fluoride [14,15,16], heavy metals from aqueous solutions, and showed high adsorption amount and fast adsorption rates [6,7,29,31].

In this study, the removal characteristics of aniline were investigated using graphene oxide as the adsorbent. The adsorption isotherms and kinetics of the adsorbents were measured. The pH effect, adsorbent dose, temperature, contact time and initial concentration on aniline removal were also studied.

2. Materials and methods

2.1. Naive materials

Graphene oxide (GO) was prepared from natural graphite powder by the modified Hummers method [5]. A transmission electron microscopy (TEM, JEM-2100F HR, 200 kV) was used to characterize the size and shape of adsorbent. X-ray diffractometer (XRD) Philips X'Pert was used to characterize the adsorbent for its morphological information.

Aniline ($C_6H_5NH_2$) (molecular weight, 93.13 g/mol) was supplied by Merck, Germany (maximum available purity). Other chemicals, bought from Sigma Aldrich Co., Germany, are of analytical grade.

2.2. Batch experiments

Batch mode adsorption studies for aniline have been carried out to investigate the effect of different parameters such as adsorbate concentration, adsorbent dose, temperature and pH. Solution containing 20 mL adsorbate and 0.05 g adsorbent was taken in 250 mL capacity conical flask and agitated at 200 rpm in water bath shaker. The initial and final aniline concentrations remaining in solutions were analyzed by a UV spectrophotometer (Varian-Cary100 Bio), monitoring the absorbance changes at a wavelength of maximum absorbance λ = 280 nm. The equilibrium adsorption capacity was calculated from the relationship:

$$q(\mathrm{mg/g}) = \frac{(C_i - C)V}{C_i} \quad (1)$$

where C_i and C are the initial and residual concentrations of aniline in ppm, q is the adsorption capacity in mg/g, V is the volume of aniline solution in L, and m is the adsorbent mass in g. The data analysis was carried out using correlation analysis employing least-square method and the residuals sum of square is calculated using the following equation [34]:

$$RSS = \sum \left[q_{e,\mathrm{exp}} - q_{e,\mathrm{cal}}\right]^2 \quad (2)$$

3. Results and discussions

3.1. Characterizations of graphene oxide

Fig. 1A shows the XRD patterns of GO. In the pattern of GO, the peak at 2u = 26.58 was no longer detected and a new broader peak appeared at 2θ = 11°, demonstrated that the graphene structure with new oxygen containing groups was formed successfully by the strong oxidation reaction on the graphite.

The structure of GO was characterized by TEM and indicated in Fig. 1B. The TEM image of GO also corroborated that the GO existed in the sheet-like shapes. The BET analysis of the GO yielded a specific surface area of 305.8 $m^2\,g^{-1}$ [14,15,16].

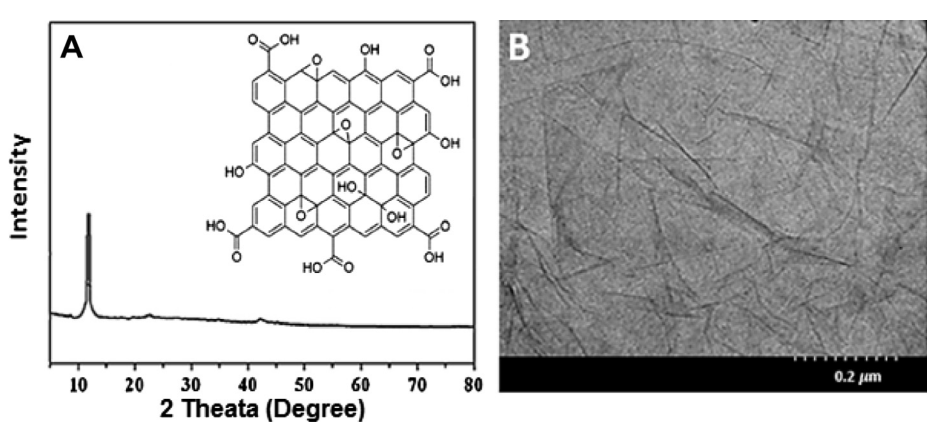

Figure 1 XRD (A) and TEM (B) images of purified GO.