Comparative studies on copper adsorption by graphene oxide and functionalized graphene oxide nanoparticles

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ABSTRACT

In this study, the graphene oxide (GO) was made from graphite powder via a modified Hummers method, then carboxylated to GO–COOH in a mixture of a strong basic pH from mixing in the chloroacetic acid with NaOH. The GO and GO–COOH were characterized by means of the HR-TEM, FTIR, XRD and zeta potential. On this basis, the Cu(II) was adsorbed onto the GO and GO–COOH in aqueous solutions using the simple batch-adsorption mode. The amount of thus-removed Cu(II) was successfully varied, depending on the pH values, initial copper concentration, reaction time and reaction temperature. Under the ambient temperature at pH 6 over 60-min adsorption time, the highest removal efficiency of Cu^{2+} are 97 and 99.4%, respectively. The experimental data agree well with the Langmuir isotherm in both cases, and the maximum adsorption capacities of GO and GO–COOH are 277.77 and 357.14 (mg/g), respectively. The metal adsorption of the GO–COOH is better than other carbonaceous adsorbents, and is exothermic and spontaneous from the calculations of chemical thermodynamics. The effect of competing cations on adsorption of Cu(II) ions on GO and GO–COOH was evaluated by mono and divalent metals. The reusability of GO and GO–COOH were estimated and it was found that both adsorbents have good regeneration properties.

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Introduction

Copper is one of a toxic heavy metal which does not break down in the environment, and can be effect on human health and is not easily metabolized in human body [1]. The copper waste sources are come from electroplating industries, textile industries or washing effluents for remediation of soil contaminated with copper and may be contain up to 500 mg/L of copper, according to environmental regulations worldwide (ERW). So, these waste sources must be controlled to an acceptable level before being discharged to the environment [2].

Several treatment processes have been demonstrated for the removal of copper from aqueous media by new adsorbent materials, such as adsorption on different biogenic oyster shell structures [3], amino modification of biochar [4], soil minerals [5], chitosan-coated cotton gauze [6], ion-imprinted hydrogel [7], graphene oxide-CdS composite [8], activated charcoal [9], bio-sorption such as marine algae [10], ion exchange on zeolites [11], chelating resins [12,13], flotation-microfiltration [14] and chemical precipitation [15,16].

Graphene oxide, which is considered as one of a good adsorbent material for heavy metal removal which contains a range of reactive oxygen functional groups, e.g., epoxides, hydroxyl, ketones, and carboxyl groups [17]. In addition, GO has high surface area up to (2620 m^2/g) (theoretical value) and can be readily obtained from cheap natural graphite in large scale [18]. Graphene oxide (GO), or Graphene is a new type of carbon nanomaterials, have attracted many research interests not only in biological fields, and electronics, but also in wastewater treatment [17,19,20]. For example, adsorption of fluoride ions [21], heavy metals such as, As, Pb and Cd [22,23], and exhibited as a good adsorption material.

Functionalization is a method to change the chemical properties of a material by adding new features or function groups or capabilities by changing the surface chemistry of the material. In general, functionalization is performed by attaching nanoparticles or molecules to the surface of a material, and may be takes place by a chemical or just through adsorption. Functionalization or Modification of graphene oxide surface is only possible due to the presence of oxygen containing functional groups [24]. Two common ways for functionalization of GO or carbon based graphene oxide have been done using covalent and non-covalent

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methods. Functionalized GO was prepared by several authors for different application, for example, Shen and Chen were prepared sulfonated graphene nanosheets as a superb adsorbent material for various environmental pollutants in water [25], Yan et al. were prepared chitosan-functionalized graphene oxide and used it as a potential immunoadjuvant [26] and He et al. were prepared 3-aminopropyl- triethoxysilane -functionalized graphene oxide for Effective removal of Cr(VI) from aqueous solution [27].

This paper is aims compares the adsorption behavior of copper on GO and GO–COOH based on pH effect, kinetic studies, equilibrium adsorption capacity, and temperature effect. Graphene oxide (GO) was obtained by modified Hummers method and then convert it to carboxylated graphene oxide (GO–COOH) using chloroacetic acid under strong basic conditions. The differences in the physico-chemical properties of both adsorbents were demonstrated using different analytical techniques such as HR-TEM, FTIR, XRD and zeta potential.

1. Materials and methods

2.1. Chemicals and equipment

Graphite (particle size < 20 μm) was purchased from Sigma-Aldrich Company, USA. Potassium permanganate, (KMnO$_4$), concentrated sulfuric acid (H$_2$SO$_4$, 98%) and hydrogen peroxide were purchased from CAMEO Chemical Reagent Corporation, USA. Deionized water was used for preparation, dilution and analytical purposes.

2.2. Synthesis of GO and carboxylated GO

Numerous researchers were prepared GO via modified Hammers method [28,29]. Briefly, graphite (5 g) NaNO$_3$ (5 g) and concentrated H$_2$SO$_4$ (100 mL) were first stirred together in an ice bath for 2 h The temperature of the solution mixture was controlled at approximately 10 °C using ice bath. Next step, KMnO$_4$ (30 g) was added slowly in portions to keep the reaction temperature below 10 °C. Afterwards, the solution mixture was transferred to a 35 °C water bath and stirred for 1 h and then, 500 mL of deionized (DI) water was slowly added into the solution and the solution temperature was increased to 98 °C. The solution mixture was reserved at this temperature by heating for 30 min. After that, 450 mL deionized water and 50 mL of hydrogen peroxide (30%) was added gradually to the solution to terminate the reaction. The color of the solution in this step is gradually turned from dark brown to bright yellow. Then, the resulting product (graphite oxide) was centrifuged and washed with HCl (5%) for 3 times and then washed by di-ionized water for 4 times. It was repeated washing until the pH value of the filtrate was close to 7 and no impurities appeared in the filtrate. Finally, the filtrate was dried in a vacuum oven at 50 °C for 3 days to obtain graphite oxide. The product powder was dispersed in water with sonication using an ultrasonic cell disruptor, for giving a solution of exfoliated GO. The suggested structure of GO is as shown in Fig. 1a.

Functionalization of GO by Carboxylation process has been reported in previous work and used it in different applications [30–32]. In the Carboxylation process, the hydroxyl groups on the surface of GO convert into carboxyl groups. For carboxylation, an aqueous suspension (5 ml) of GO (dispersed) was diluted by a factor of 2 to obtain a concentration of ∼ 2 mg/ml and was then bath sonicated for 1 h to obtain a clear solution. NaOH (1.2 g) and chloroacetic acid (Cl–CH$_2$–COOH) (1.0 g) were added to the G suspension and the mixture was bath-sonicated for 2 h to convert the –OH groups into –COOH via conjugation of acetic acid moieties to obtain GO–COOH. The resulting solution was neutralized with
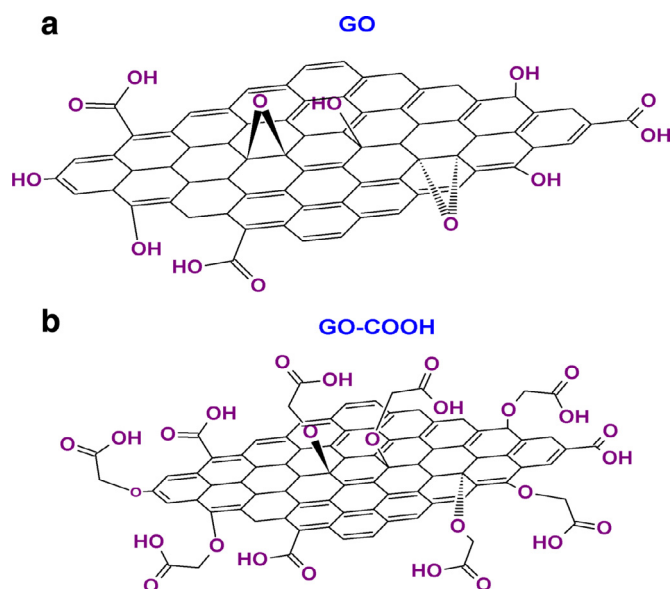

Fig. 1. Structure of graphene oxide (a) and carboxylated graphene oxide (b).

0.1 M HCl, and was then purified by repeated rinsing and filtration. The suggested structure of GO–COOH is as shown in Fig. 1b.

2.3. Characterization of GO and GO–COOH

The morphologies of GO and GO-COOH were evaluated using High resolution transmission electron microscope model JEOL JEM-1230 with acceleration voltage of 80 kV. The Fourier transformed infrared (FTIR) spectra for graphite, GO and GO-COOH were obtained from SHIMADZU Corporation, USA. The crystal structure of graphite, GO and GO-COOH were confirmed by X-ray diffractometry model Rigaku MiniFlex II. The surface area and porosity analyses were done using Gemini- VII Series, 2390, USA. Zetasizer model 2000/3000 was used for zeta potential measurements.

2.4. Adsorption procedure

The effects of experimental parameters of pH values (1.5–9.0), initial copper concentration (50 –700 mg/L) on the removal of copper were investigated in a batch technique of operation for 120 min. In these experiments, the samples of copper solution with known concentration was put in a 100 mL glass conical flask, and then the definite amount of adsorbent (GO, and GO–COOH) was added into the beaker. The beaker was shaken for 120 min in a thermostatic water bath oscillator at 25 °C to reach equilibrium. Subsequently, the adsorbent materials (GO and GO–COOH) were removed from the solutions after adsorption by centrifugation at 4000 rpm for 5 min. The concentration of copper in the solution was measured using a UV– vis spectrophotometer (model Hitachi UV spectrometer, No, U-0080D, Made in Japan). The measured samples were repeated three times and the results were taken by averaged. The adsorption capacity, Q$_e$ (mg/g), was estimated using Eq. (1) and the removal rate (%) was calculated by Eq. (2):

$$Q_e = (C_o - C_e) \times \frac{V}{m} \qquad (1)$$

$$Removal\ rate\ (\%) = \left(\frac{C_o - C_e}{C_o}\right) \times 100 \qquad (2)$$

where C_o and C_e are copper concentrations (mg/L) before and after adsorption respectively, V is the volume of adsorbate L and m is the weight of the adsorbent (g).