Journal of Hazardous Materials 337 (2017) 27–33

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Research Paper

Facile preparation of 3D GO/CNCs composite with adsorption performance towards [BMIM][Cl] from aqueous solution

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HIGHLIGHTS

- A three-dimensional crumpled graphene oxide adsorbent (GO/CNCs) was synthesized.
- The loading of CNCs onto GO provides more chance for the sorption of [BMIM][Cl].
- GO/CNCs shows a maximum sorption capacity of 0.455 mmol/g for [BMIM][Cl].

ARTICLE INFO

Article history:
Received 4 December 2016
Received in revised form 4 April 2017
Accepted 3 May 2017
Available online 3 May 2017

Keywords:
Graphene oxide
Corncob
Cellulose nanocrystals
Three-dimensional structure
[BMIM][Cl] removal

ABSTRACT

A novel three-dimensional crumpled graphene oxide/cellulose nanocrystals (GO/CNCs) composite was successfully synthesized and firstly used as adsorbent for the removal of ionic liquid [BMIM][Cl] from aqueous solution. The 3D crumpled structure and abundant oxygen of the functional groups on GO/CNCs composite can provide more chance for the sorption of [BMIM][Cl] compared with CNCs and GO, respectively. Therefore, a series of batch experiments were carried out to evaluate the adsorptive property of 3D GO/CNCs composite towards [BMIM][Cl], such as the GO mass content, the pH value and contact time. The results showed that pseudo-second-order kinetic model and Eovlich model were well fitted with the sorption kinetic. The isotherm adsorption data indicated that it was better described by Langmuir model, with the maximum sorption capacity of 0.455 mmol/g. This work provides a facile method for the preparation of 3D structure adsorbent from graphene oxide and cellulose nanocrystals which has high adsorption capacity of [BMIM][Cl] in aqueous solution.

1. Introduction

Graphene oxide (GO) as a novel two-dimensional (2D) carbon nanostructure has attracted a large amount of attention due to its unique physical and chemical properties. Until now, various graphene oxide and graphene oxide composites have been widely used in different areas, such as supercapacitors [1,2], gas storage [3,4], catalysis [5,6], lithium storage [7,8] and sensors [9,10]. Recently graphene oxide and its composites have been developed to be a promising adsorbent for adsorption of heavy metal ions and organic pollutants [11–14] from aqueous solution, because the 2D structure, large surface area, and abundant oxygen-containing groups (epoxy, hydroxyl and carboxyl groups) of graphene oxide can strongly enhance the combination between the pollutant and graphene oxide composite. In addition, graphene oxide can be stacked into three-dimensional (3D) graphene oxide composites through various methods and the composites have been applied in supercapacitors, sensors and adsorbents [15–18]. The three-dimensional structure can provide more area for the diffusion of pollutant molecules into the 3D structure [19]. Therefore, it is interesting and challenging to develop 3D graphene composite as high efficient adsorbent for the removal of pollutant from wastewater.

Ionic liquids (ILs) mostly made of organic cations and organic/inorganic anions at room temperature have been widely applied as catalysts and green solvents in chemical reactions and processing [20]. With the release into the environment, ionic liquids exhibit toxicities on organisms, bacteria and algae [21]. It has gained much attention because of its toxicities towards water as well as organisms and it was considered as a new kind of pollutant to environment. Thus how to remove or recover the ionic liquids

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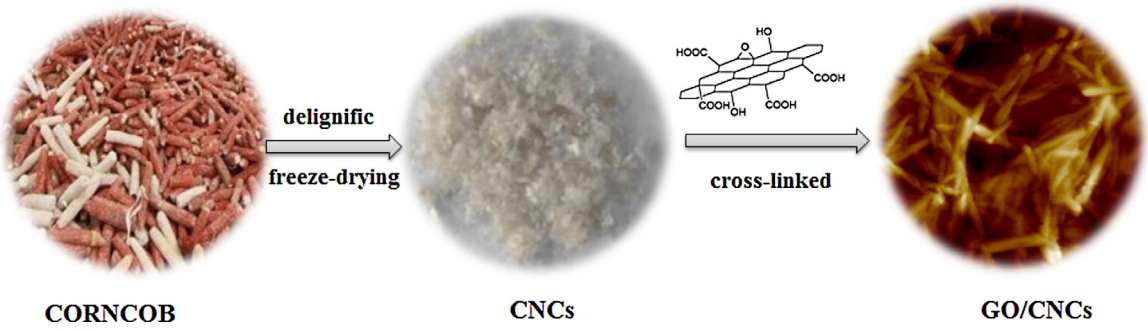
http://dx.doi.org/10.1016/j.jhazmat.2017.05.002
0304-3894/



Scheme 1. The synthesis of GO/CNCs.

from wastewater has become an important topic. Some methods have been reported about disposing the ILs-containing wastewater, including photocatalysis [22], biodegradation[23], electrodialysis [24], and adsorption [25,26]. Among the available methods, adsorption has been considered as a cost-effective, non-destructive and eco-friendly way for removing ILs from aqueous solution. Therefore, it is an urgent need to develop new adsorbents with high adsorption capacity of ILs in aqueous solution.

Herein, a 3D crumpled structure GO/CNCs composite was designed and used as adsorbent for the removal of ionic liquid [BMIM][Cl] from aqueous solution. Firstly, the one-dimensional rod-like CNCs was prepared from waste corncob via Soxhlet extraction and freeze drying. Then, it was cross-linked with GO nanosheets, receiving a 3D structure adsorbent with abundance of functionality groups for adsorption. Finally, a range of experiments were carried out to evaluate the adsorption abilities of the 3D structure GO/CNCs adsorbent onto [BMIM][Cl] in aqueous solution. More importantly, the loading of CNCs onto GO sheets can improve the adsorption capacity towards [BMIM][Cl] compared with CNCs and GO, respectively. Through this study, we attempt to develop a new 3D structure GO composite and investigate its excellent performance as adsorbent.

2. Experiment

2.1. Materials

Corncob was received from Kaifeng of Henan Province. 1-butyl-3-Methylimidazolium Chloride ([BMIM][Cl]) was purchased from Henan Lihua Pharmaceutical Co., Ltd. Graphite was obtained from Sinopharm Chemical Reagent Co., Ltd., China. All reagents used in this study were of analytical grade. Deionized water was used throughout the experiments.

2.2. Instrumentation

Fourier transform infrared spectroscopy (FT-IR) was performed on an AVATAR360 (American Nicolet Instrument Corporation) FT-IR spectroscopy in the form of KBr pellets. X-ray diffraction (XRD) analysis was performed on a Philips X-PertPro automatic powder diffractometer using Cu Kα radiation. The scanning electron microscope (FE-SEM) was carried out by a NOVA NanoSEM450 (American FEI corporation) scanning electron microscope. Atomic Force Microscopy (AFM) was performed on NT-MDT Solver P47H-PRO (Russia NT-MDT corporation) in a tapping mode.

2.3. Preparation of CNCs from corncob

CNCs were synthesized according to our previous work [27]: 20.0 g of corncob power was extracted by soxhlet's extracter, receiving the pure cellulose. Then 10.0 g of the pure cellulose was mixed with 85 ml of sulfuric acid under vigorous mechanical stirring. The CNCs were obtained after washed by deionized water and freeze-dried.

2.4. Preparation of three dimensional GO/CNCs composite

GO was prepared by the Hummers' method [28] and was ultrasonically dispersed in deionized water to acquire GO dispersion with a concentration of 5.5 mg/ml. Then 97 ml of 16.0 mg/ml CNCs solution was added into 120 ml of GO dispersion, receiving a brown mixture solution. The brown solution was ultrasound for 1 h and stirred for 2 h at ambient temperature. The solid adsorbent GO/CNCs composite (with 30% GO in mass) was obtained by freeze-drying the final solution. Then a series of GO/CNCs composites were prepared by the same procedure with different GO content of 10%GO, 20%GO, 40%GO, 50%GO (Scheme 1).

2.5. Adsorption experiments of [BMIM][Cl]

Adsorption studies were performed by adding 20 mg of each adsorbent to 50 ml polyethylene flask with 20 ml of [BMIM][Cl] at a constant speed of 190 rpm in a thermostatted shaker bath. After centrifuged, the supernatants were determined at 211 nm for [BMIM][Cl] on UV–vis spectrophotometer. The pH was adjusted by 0.1 mol/l HCl and NaOH. The adsorption kinetic experiments were investigated by mixing the adsorbent and [BMIM][Cl] at different reaction time in the range of 0.5–25 h. All the experiments were carried out in triplicate and the average values were reported. The amount of adsorbed [BMIM][Cl] and removal percentage were calculated as follows [29]:

$$\text{Removal percentage} = \frac{C_o - C_e}{C_o} \times 100\% \quad (1)$$

$$q = (C_o - C_e)\frac{V}{m} \quad (2)$$

Where C_0 and C_e (mmol/l) are the initial and equilibrium concentration of [BMIM][Cl] respectively, q (mmol/g) is the adsorption capacity of adsorbent towards [BMIM][Cl], V (l) is the volume of solution, and m (g) is the mass of the adsorbent.

3. Results and discussion

3.1. Characterization of the 3D GO/CNCs structures

The FTIR spectrum of CNCs, GO and GO/CNCs were shown in Fig. 1a. The peaks emerging at 3300–3500 and 2918 cm^{-1} were attributed to the stretching of —OH and —CH bonds of CNCs according with our previous work [30]. The peaks appeared at 1726, 1400 and 3422 cm^{-1} were related to the —COOH, C=O and the C—O stretching vibrations of GO, indicating the carboxylic acid groups on the surface of GO consisted with literatures [31,32]. The bands