



Alginate/calix[4]arenes modified graphene oxide nanocomposite beads: Preparation, characterization, and dye adsorption studies

Abbas Mohammadi ^{a,*}, Amir Hossein Doctorsafaei ^a, Khalid Mahmood Zia ^b

^a Department of Chemistry, University of Isfahan, Isfahan 81746-73441, Iran

^b Institute of Chemistry, Government College University, Faisalabad 38030, Pakistan

ARTICLE INFO

Article history:

Received 6 July 2018

Received in revised form 27 August 2018

Accepted 22 September 2018

Available online 24 September 2018

Keywords:

Alginate beads

Graphene oxides

Calix[4]arenes

Surface modification

Dye adsorption

ABSTRACT

The present study reports the preparation of novel alginate/calix[4]arenes modified graphene oxide nanocomposite beads (alginate/C4As-GOs) based on *p*-*tert*-butyl calix[4]arene and sodium *p*-sulfonatocalix[4]arene modified GO nanosheets (CGO and SGO). Different properties of alginate/GO and alginate/C4As-GOs nanocomposite beads were investigated by FTIR, XRD, TGA, SEM, and swelling ratio analysis. The alginate beads containing SGO nanosheets (ABSGO) showed a thin layered structure, high porosity, and high swelling ratio compared to other samples. Moreover, the batch adsorption studies on methylene blue exhibited that ABSGO beads act as a high-performance adsorbent among samples and can be introduced as a novel and efficient dye adsorbent. In the case of ABSGO adsorbent, the equilibrium adsorption data were modeled using the Langmuir and Freundlich isotherms. According to Langmuir isotherm equation, the maximum adsorption capacity of ABSGO was obtained 170.36 mg/g. The kinetic adsorption studies confirmed that the adsorption of MB onto ABSGO well obey the pseudo-second-order kinetic model.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

Artificial dyes are extensively utilized in the synthesis, textile, printing, food, and cosmetic industries. The dyes in wastewaters can cause harmful effects on human beings and the environment. Therefore, in order to decrease these problems, extensive efforts have been devoted to removing the dye effluents before being discharged to the environment [1–3].

Several methods have been extended for dye removal from aquatic mediums, including flocculation, precipitation, electro-kinetic coagulation, ion exchange, electro-flotation, irradiation, ozonation, membrane filtration, ultra-filtration, electrochemical destruction, photo-oxidation, and adsorption [4,5]. Among them, adsorption as a convenient, high efficiency, and inexpensive method has desirable performance in separation of a wide range of pollutants from industrial effluents [4,6].

Methylene blue (MB) dye is a cationic heteroaromatic compound with wide industrial applications and can adversely impact on the quality of water. MB can cause permanent injury to the eyes of humans and animals. On ingestion through the mouth, it can produce a burning sensation and may cause nausea, vomiting, profuse sweating, mental confusion, and methemoglobinemia [7]. In the literature, some adsorbents, such as activated clay [8], coir pith carbon [9], pyrolyzed petrified sediment [10], activated desert plant [11], garlic peel [12], rice husk [13], carbon nanotubes [14], palm kernel fiber [15], Graphene [16], and graphene oxide [17] have been reported for MB removal from aqueous mediums.

Sodium alginate (SA), as a water-soluble natural polysaccharide, is a linear copolymer of (1–4) linked β -D-mannuronic acid (M units) and α -L-guluronic acid (G units) [18]. Alginate has many advantageous features such as the cheap price, lots of resources, hydrophilicity, biocompatibility, biodegradability, and strong ion-exchange property [19–21].

Alginate has gel-forming ability due to its readily crosslinking with divalent metal ions where each divalent metal ion binds to two carboxyl groups of adjacent alginate molecules [22,23]. In this regard, the alginate hydrogel beads have been extensively developed and introduced as an adsorbent for removal of some dye effluents from aqueous solution [24–26]. Meanwhile, alginate beads have some limitations including dense gel layer, unsuitable porosity, and poor mechanical strength [27–29]. Therefore, overcoming these problems is mechanical to increasing the adsorption capacity of alginate beads.

Abbreviations: SA, sodium alginate; C4As, calix[4]arenes; BC4A, *p*-*tert*-butyl calix[4]arene; SC4A, sodium *p*-sulfonatocalix[4]arene; GO, graphene oxide; AB, alginate beads; FTIR, Fourier-transform infrared spectroscopy; XRD, X-ray diffraction; FESEM, field emission scanning electron microscopy; TGA, thermogravimetric analysis; q_e , equilibrium adsorption capacity; Q_m , equilibrium mass swelling ratio; q_m , maximum adsorption capacity; ΔH , enthalpy change; ΔS , entropy change; ΔG , free energy change.

* Corresponding author.

E-mail address: a.mohammadi@sci.ui.ac.ir (A. Mohammadi).

Addition of nanostructures to alginate is an effective approach to develop its pore structure as well as improvement in its mechanical property [30,31]. Graphene oxide (GO) is a two-dimensional sheet-like carbon structure which contains a random distribution of hydroxyl, epoxy, and carboxyl groups on its surface and edges [32]. These structural features impart excellent dispersibility in aqueous mediums and also provide superior secondary interactions with adsorbates through hydrogen bondings and electrostatic interactions [32–34]. Because of these advantages, GO has proven to be a promising adsorbent for removal of dyes pollutants from water and exhibit high adsorption capacities [35]. However, after adsorption, separation of GO from the water is very difficult and must be separated via high-speed centrifugation [36]. To solve this problem, incorporating of the GOs into alginate beads as a facile strategy have been reported [37–39]. Besides, because of high surface area and strong Van der Waals interaction, GO nanosheets tend to agglomerate in polymeric matrices. In this regard, the most convenient strategy to enhance the dispersion quality is chemical modification of GOs [40,41].

Calix[4]arenes (C4As) are macrocyclic and cavity-like compounds with some outstanding properties such as tailor-made structure, host-guest property, and high thermal stability. These features make them favorite candidates as a potential adsorbent for some dye effluents and heavy metals in the environment [42–44]. It is anticipated that modification of GOs with calix[4]arenes derivatives, not only overcome to their agglomeration tendency but also make them more efficient adsorbents due to providing the host-guest property and enhanced interactions with adsorbates.

This study focused on the preparation and characterization of novel alginate/graphene oxides nanocomposite beads based on *p*-*tert*-butyl calix[4]arene (BC4A) and sodium *p*-sulfonatocalix[4]arene (SC4A) modified GO nanosheets (CGO and SGO). To our knowledge, the preparation of novel alginate beads incorporated with calix[4]arene modified graphene oxides and also evaluate them to adsorb the MB dye from aqueous solution has not been reported. Structural, thermal, and morphological properties of pure alginate beads (AB) and GO, CGO, and SGO incorporated nanocomposite beads (ABGO, ABCGO, and ABSGO) were studied. The adsorption efficiency of prepared ABCGO and ABSGO beads in the removal of methylene blue from aqueous solution was also evaluated and the results were compared with AB and ABGO beads. The dye adsorption studies were carried out in terms of equilibrium (by applying Langmuir and Freundlich isotherms) and also by using pseudo-first-order and pseudo-second-order kinetic models.

2. Experimental

2.1. Materials

The sodium alginate (SA, $M_w = 120$ kDa, and $M/G = 1.56$) and methylene blue (MB) were purchased from Sigma Aldrich. The calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) was obtained from Merck. All these materials were used directly without any purification. BC4A-GO (CGO) and SC4A-GO (SGO) nanosheets were also prepared based on our previously reported method [45].

2.2. Preparation of pure and alginate/GOs nanocomposite beads

In order to prepare the alginate/GOs nanocomposite beads (ABGO, ABCGO, ABSGO) containing 2 wt% of GOs, a 2.5 wt% sodium alginate solution which previously loaded with suitable amounts of GO, CGO and SGO nanosheets, were dropwise added to calcium chloride solution (0.2 mol/L) using a syringe at a flow rate of 60 drop/min. After cross-linking reactions, the prepared gel beads were allowed to remain in the calcium solution under slow agitation for 1 h. Afterward, the mixtures were stored overnight at 4 °C without any agitation. The prepared beads were subsequently removed and washed three times with distilled water and finally dried according to a method developed by Ma et al. [46]. Herein, the beads were frozen at –10 °C for 12 h, then immersed three times in ethanol for about 2 h at room temperature, and finally dried at 60 °C for 3 h. For comparative purposes, pure alginate beads (AB) with no GOs incorporation, were also prepared similarly to the mentioned procedure. Schematic illustration of chemical routes for the synthesis of Alginate/C4As-GOs beads is shown in Fig. 1. In addition, the code designation and composition of prepared samples are given in Table 1.

2.3. Measurements

2.3.1. Characterization of the prepared beads

FTIR spectroscopy of AB and alginate/GOs nanocomposite beads was performed on a JASCO FTIR-4600 spectrophotometer. XRD measurement was carried out at room temperature on a Bruker D8 Advance diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.540598$ Å) with a scan rate of 1°/min between $2\theta = 5^\circ$ and $2\theta = 70^\circ$. The morphology of gold covered beads was evaluated by a Tescan Mira FESEM. TGA analysis was performed on a Mettler-Toledo TGA1 thermal gravimetric analyzer from

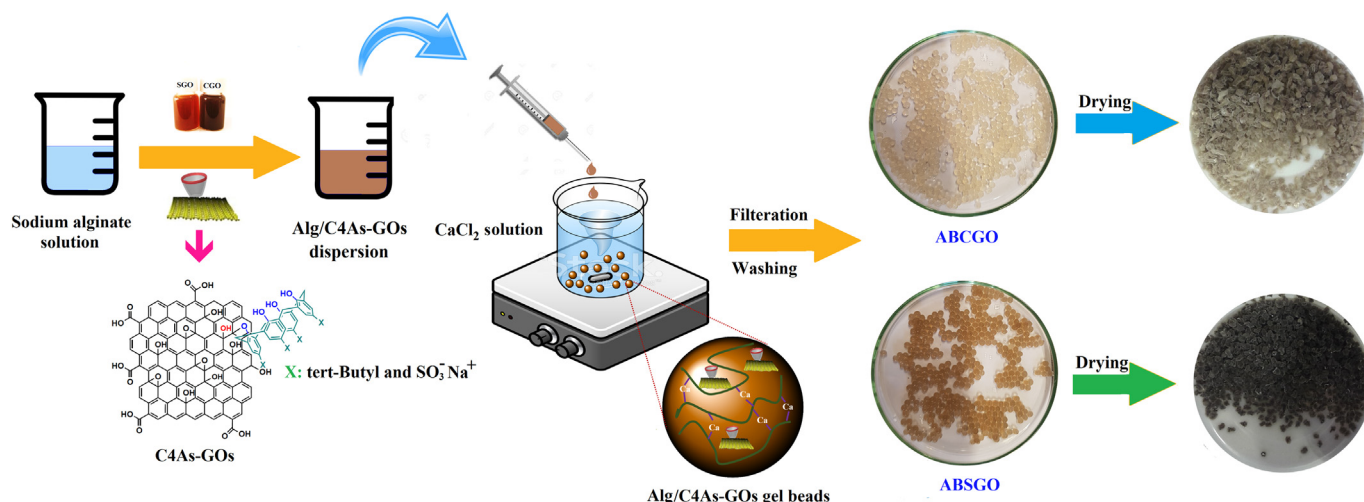


Fig. 1. The synthesis schematic of ABCGO and ABSGO nanocomposite beads.

Download English Version:

<https://daneshyari.com/en/article/11026030>

Download Persian Version:

<https://daneshyari.com/article/11026030>

[Daneshyari.com](https://daneshyari.com)