Batch and column adsorption of methylene blue by graphene/alginate nanocomposite: Comparison of single-network and double-network hydrogels

Yuan Zhuang[a], Fei Yu[a,c], Junhong Chen[a,b], Jie Ma[a,*]

[a] State Key Laboratory of Pollution Control and Resource Reuse, School of Environmental Science and Engineering, Tongji University, 1239 Siping Road, Shanghai 200092, PR China
[b] Department of Mechanical Engineering, University of Wisconsin–Milwaukee, Milwaukee, WI 53211, USA
[c] College of Chemistry and Environmental Engineering, Shanghai Institute of Technology, Shanghai 2001418, PR China

ARTICLE INFO

ABSTRACT

The alginate nanocomposite prepared by immobilizing nanomaterials into alginate has been widely studied to remove pollutants from water. However, how to prepare the alginate beads with better stability and reusability is important to its practiclal application. In this study, a new kind of porous graphene/alginate double network nanocomposite beads (GAD) are prepared and compared with graphene/alginate single network nanocomposite beads (GAS). The results show that GAD has higher specific surface area and better thermal stability than GAS. Moreover, GAD is more stable than GAS in NaCl solution. Furthermore, both batch and column adsorption experiments of methylene blue (MB) were applied to evaluate its adsorption performance. The obtained results indicated that GAD has better potential than GAS to be applied as adsorbent for the removal of organic pollutants.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

For the toxic effects of dye to aquatic biota and humans, release of dyes to the environment has aroused serious concerns all over the world. Therefore, removing the dyes from wastewater to an acceptable level before discharging into the natural environment is necessary [55]. Photo-catalytic degradation [8], biodegradation [44], filtration [5] and adsorption [3] have been applied in dye removal. Among these methods, adsorption is considered as an attractive and favorable technique because its low costs, easy operation and high efficiency [10,55].

Alginate is a binary heteropolymer consists of a linear chain of (1–4)-linked β-D-mannuronic acid (M) and α-L-guluronic acid (G). As a kind of natural polysaccharide, it can be extracted from seaweeds and is hydrophilic, biocompatible and nontoxic [29]. Alginate could chelate with divalent cations to form hydrogels through the tightly held junctions formed between G-blocks and divalent cations [46]. With a carboxylate function per unit, alginate is a negatively charged polyelectrolyte making it a suitable agent to remove cationic pollutant such as methylene blue (MB) driven by

both electrostatic and hydrophobic strong interactions [39]. It is now accepted that the addition of nanoparticles, such as nanospheres, nanotubes and nanosheets, to a polymer melt can result in significant improvement in thermomechanical, optical, and electrical properties of the material [24]. To improve the adsorption ability of alginate, one of the most effective method is to add nanomaterials into the alginate, such as carbon nanotubes [30], Fe_2O_3 nanoparticles [41], TiO_2 nanoparticles [40] and graphene oxide (GO) [28] to form composite materials.

In last decade, nanocarbonaceous materials such as carbon nanotubes (CNTs) and graphene have grown as promising adsorbents to sequester dyes and heavy metal ions from aqueous phase. Moreover, the production cost of graphene is comparatively lower than CNTs and resins, while their adsorption capacities are similar [61]. GO is consist of one carbon-atom-thick planar nanosheet which is known for its remarkable mechanical, electrical, and thermal properties and graphene-based hydrogels can be formed from self-assembly process [9]. There are various functional groups on GO sheets such as hydroxyl, epoxy and carboxyl groups, allowing GO to be functionalized or be hybridized with other materials to form composite materials [45]. Numerous biopolymers such as DNA, chitosan and protein, have been studied to be efficient to promote GO gelation through influencing the hydrophobic interactions, electrostatic repulsion, and hydrogen

bonding in GO [60]. It is noted that molecules which contain multiple nitrogen containing functionalities are able to bind with the —OH or —COOH groups on GO through hydrogen-binding or acid–base-type electrostatic attraction, leading to the assembly of GO sheets [27]. Thereby a series of covalent and non-covalent interactions enable GO to bridge with kinds of external ions, molecules or even bulk materials, such as π–π stacking, hydrogen bonding, and cation–π bonding [47]. The incorporation of GO in the usual adsorbents makes large-scale production of functionalized GO at low cost possible, which would result in good adsorbents for water purification [25]. GO and alginate both contain negative ions which causes electrostatic repulsions between them and promotes GO to be well dispersed [20]. Moreover, GO could cross-link the polymer chains through hydrogen interaction and surface grafting. The increase of GO content resulted in an enlargement in crosslinking [15]. There have been investigations which prepared composite materials using GO and alginate [2,28,54], however, in these studies, GO was only used as nanoparticle to be loaded on alginate which can be defined as single networks.

Gong et al. [18] reported the a kind of composite, double network hydrogels, for the first time which has better mechanical properties than single network gels. Other investigations also proved that double network hydrogels has higher strength than single networks [12]. Commonly, double network gel is a kind of composite gel which consists of two interpenetrating polymer networks. The primary network, which is densely cross-linked and highly stretched, is stiff and brittle. The second network, which is sparsely cross-linked and flexible, is soft and stretchable. In most of the previous studies, both the two networks are formed by covalent bonds in order to get gels with higher bond energy [17]. However, previous studies mainly paid attention to the mechanical properties of the double network; few studies focused on the adsorption performance of the double network and even less studies compared the adsorption ability between single networks and double networks [14,58,57].

In this study, a functional double network gel (GAD) consisted of GO and alginate was prepared. GO/alginate single network (GAS) gel was also prepared for comparison with GAD. Adsorption of MB on GAD was studied through batch and column adsorption. In batch adsorption, isotherms and kinetics models were investigated. In column study, influence of time, flow rate and NaCl was investigated and the adsorbent reuse was also studied through 10 cycles.

2. Experimental

2.1. Materials

All chemicals used in this study were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) in analytical purity. All solutions were prepared using deionized water.

2.2. Preparation of GO/alginate gels

GO was prepared using the modified Hummers' method [21,35,56]. Briefly, graphite (2.0 g) and NaNO$_3$ (1 g) were placed in a 250 mL beaker. Then, 46 mL of sulfuric acid (98%) was added with stirring in ice bath. While maintaining the temperature below 283 K, 6 g KMnO$_4$ and 1 g NaNO$_3$ were slowly added to the suspension with vigorous stirring. After stirred for 2 h in icebath, the mixture was stirred at 303 K for 30 min. As the reaction proceeded, the color of the mixture gradually changed to brownish paste. Next, the paste was diluted with 92 mL ultra-pure water under vigorous agitation, heated to 368 K and then maintained for 30 min. By then the color of the suspension changed to bright yellow. When the suspension was cooled to room temperature, 10 mL H$_2$O$_2$ (30 wt.%) solution was added to the mixture to terminate the reaction and the mixture was stirred for 2 h at room temperature. After centrifugation, the precipitate was washed repeatedly with 5% HCl to remove residual metal ions, and then with de-ionized water to remove the sulfate ion. Finally, the precipitate (graphite oxide) was bath sonicated and dried under vacuum. Then the graphite oxide was dispersed in deionized water, and then sonicated in an ultrasonication bath for 12 h to obtain a GO solution.

Next, 1 g sodium alginate was dissolved into 100 mL 2 mg/mL GO solution and stirred for 5 h, and then 100 mL sodium alginate/ GO solution was slowly dropped into 200 mL 10 mg/mL CaCl$_2$ solution using a peristaltic pump accompanied by magnetic stirring to obtain the alginate/GO single network beads. The beads were washed with deionized water several times and the product is the GAS. To obtain double-network beads, the GAS beads were placed into 2 mg/mL ascorbic acid solution (which is a reductant for GO) and heated in water bath of 85 °C for 12 h under normal pressure to get GAD.

2.3. Characterization methods

A field-emission SEM (Hitachi, S-4800) was used to investigate the surface morphologies of GAS and GAD. The specific surface area, pore volume (PV) and pore size distribution were tested by nitrogen adsorption/desorption at 77.4 K using an Accelerated Surface Area and Porosimetry system (Micromeritics, ASAP 2020), and all the beads were degassed at 373 K for 8 h before the measurements. The MB concentrations in adsorption studies were measured by an ultraviolet spectrophotometer (Tianmei UV-2310 (II)) at 664 nm.

2.4. Batch adsorption studies

The adsorption isotherms were studied in a thermostatic shaker in pH 8 at 298 K at 150 rpm for 24 h under solid to liquid ratio 1 mg/ mL. The initial concentrations were set as 1 mg/mL to 3000 mg/mL. All the samples were operated in 3 duplicates with presented data in equal ($R^2 > 0.98$). After adsorption, GAS and GAD were separated by a 0.45 μm membrane. Eq. (1) was used to calculate the adsorption capacity (mg/g) [55].

$$q_t = (C_0 - C_t) \times \frac{V}{m} \qquad (1)$$

where C_0 and C_t are the initial concentration and the concentration after a period of time t (mg/L); V is the initial solution volume (L); and m is the adsorbent dosage (g).

Four adsorption isotherms (Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D–R)) were used to evaluate the adsorption equilibrium as in Eqs. (2)–(6).

The Langmuir isotherm assumes that there is a monolayer formed by adsorbate around the homogenous surface of the adsorbent and there is no interaction between the adsorbed adsorbate molecules [26].

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \left(\frac{a_L}{K_L}\right) C_e \qquad (2)$$

where K_L (L/g) and a_L (L/mg) are the constants of Langmuir isotherm, respectively, and a_L relates to the adsorption energy. C_e is the equilibrium concentration. The maximum adsorption capacity q_m of the adsorbent is numerically equal to K_L/a_L.

The Freundlich model is empirical which assumes that adsorption occurs on a heterogeneous surface, it proposes multilayer sorption and there is interaction among the adsorbed