Chemical Engineering Journal 240 (2014) 565–573

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Graphene oxide captured for green use: Influence on the structures of calcium alginate and macroporous alginic beads and their application to aqueous removal of acridine orange

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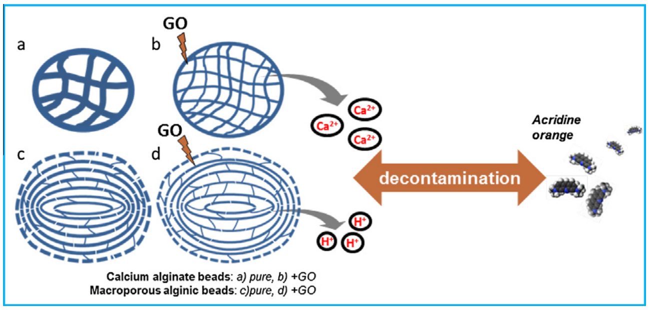
HIGHLIGHTS

- GO was well encapsulated inside alginate-based matrix as hybrid adsorbents for green use.
- Alginate matrix became porous with the addition of GO.
- Encapsulated GO demonstrated to have enhanced performance towards the dye removal as an example.
- GO played dominantly in adsorption under highly acidic condition.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 20 August 2013
Received in revised form 25 October 2013
Accepted 28 October 2013
Available online 6 November 2013

Keywords:
GO
Alginate beads
Acridine orange
Porous structure

ABSTRACT

To investigate the influence of immobilized graphene oxide (GO) on host structures, it was incorporated into calcium alginate and macroporous alginic beads, and acridine orange (AO) was used as a typical dye pollutant to eliminate. Characterizations demonstrated GO was well encapsulated and had promoted both beads more porous yet to a varying extent. Kinetics studies exhibited the addition of GO resulted in adsorptions with shorter equilibrium time and faster initial adsorption rate, and the adsorbents with higher equilibrium capacities. Isotherm studies indicated the hybrid absorbents following Langmuir-type adsorptive behavior had higher maximum adsorption capacities than those without GO. In addition, GO would contribute dominantly to the removal of AO under highly acidic condition whereas alginate/alginic part became failure.

1. Introduction

Increasing porosity is admittedly a critical factor influencing the absorbent performance. To form stable 3D porous gel absorbents, a conventional method is using the abundant seaweeds- and bacteria-derived alginate, a heteropolysaccharide composed of β-D-mannuronic acid and α-L-guluronic acid, of which the molecular chains rich in hydroxyl and carboxyl groups. It is therefore easily cross-linked by various multivalent cations, such as Ba^{2+}, Ca^{2+}, and Fe^{3+}. In the past few years, this feature as well as its biosafety, easy processing and high adsorptive selectivity, has been extensively applied to the aqueous decontamination of various metal ions [1–3], dyes [4,5]. It is noteworthy that these absorbents could possess more unique properties with immobilizing guest materials. For instance, active carbon-entrapped calcium alginate beads showed the selectivity of removal towards positively charged methylene blue and neutral *p*-chlorophenol, while the ferric alginate mostly adsorbed negatively charged humic acid [6]. And carbon nanotube-encapsulating biocompatible barium alginate had

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http://dx.doi.org/10.1016/j.cej.2013.10.083

an affinity-based selectivity among the ionic dyes of acridine orange, ethidium bromide, eosin bluish, and orange G [7]. However, in regard to the low porosity, measures are much desired to promote alginate more porous with the purpose of allowing substance diffusions into the interior structure and thus enhancing the sorption kinetics properties [8].

Graphene oxide (GO) in nature inherits the 2D carbon backbone from graphene. It has large surface area with random distributed hydroxyl, epoxy, ketone, carboxyl groups at edges and basal planes. 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 pi–pi stacking, hydrogen bonding, and cation–pi bonding. Thus it is highly available not only for direct decontamination, like removing Cd^{2+}, Co^{2+}, and Pb^{2+} [9,10], tetracycline antibiotics [11], acridine orange (AO, ~3.3 g g^{-1}) [12], etc., but also to prepare novel composites/hybrids as supporter, immobilizer, etc., such as GO-composited magnetic chitosan to adsorb methylene blue [13]. Both alginate and GO are highly water dispersible, resulting from the functional group ionization as well as the resultant negatively charged property; mixing them together is also available to get homogeneous solution, owing to mutual electrostatic repulsion and the hydrogen bonding. Importantly, involving GO may carry an effect to promote the hybrid composite with high porosity [14]. In addition, regarding to the GO's bio-hazardousness incompletely unveiled [15,16], it demonstrated necessary for environmental application. Herein we investigated the influence of incorporated GO on the structures of alginate-based adsorbents, namely, calcium alginate and macroporous alginic beads. The subsequent impact on removal of AO from water was then demonstrated as an example in terms of time and concentration dependences. In the meantime, the adsorptive kinetics, isothermal behavior and mechanism were also discussed.

2. Experimental

2.1. Materials and reagents

Graphite (Commercial code: EC1000, average particle size 15 μm as manufactured) was purchased from Ito Kokuen Co., Ltd, Mieken, Japan. Unless specifically noted, other chemicals, such as sodium alginate (500–600 mPa s at 10 g L^{-1} at 293 K as marked), calcium carbonate, and calcium chloride were obtained from Wako Pure Chemical Industries, Ltd., or Sigma–Aldrich Inc., Japan.

2.2. Preparation of GO-encapsulating alginate beads

Sodium alginate of 2 wt% was prepared by dissolving it into deionized water. GO of 0.10 wt% was prepared from the graphite using a developed Hummers–Offeman method by our group [17].

Calcium alginate beads were prepared by the conventional $CaCl_2$-hardening method [7]. To prepare GO-encapsulating alginate beads (denoted as SA-GO-N), GO solution (50 g), sodium alginate solution (250 g) (mass ratio: GO/alginate ~1/100) was firstly mixed to be homogeneous. Then it was dropwise dripped into a magnetically stirred $CaCl_2$ solution (about 6 wt%) by virtue of a self-made apparatus comprising a 500-mL container, and an air pump with an airflow controller under a certain internal pressure. After gelation and maturation, the beads were rinsed with deionized water several times using a 100-μm mesh sieve. As compared, the beads without GO were prepared, denoted with Pure SA-N.

To prepare macroporous alginic beads, HCl (5 wt%) replaced $CaCl_2$ to harden the alginate. Commercial calcium carbonate was ball-milling ground ahead for 48 h to decrease the particle size. Then GO solution (50 g), $CaCO_3$ (2.5 g) and sodium alginate (250 g) (mass ratio: GO/$CaCO_3$/alginate ~1/50/100) were mixed in sequence and stirred vigorously. Next, alginic beads were prepared similarly by the above-mentioned wet process. During such, the reaction between $CaCO_3$ and HCl in situ produced a lot of CO_2 gas, what accumulated inside (initially the beads floated at water surface) and further expanded the inner pores, of which the walls became much thinner. These beads were marked as SA-GO-M. For comparison, the beads without GO (Pure SA-M) were also prepared. All beads were preserved in a fridge (4 °C). The weight was obtained by averaging over 60 air-dried beads in a 353 K oven.

2.3. Batch experiments

Time/concentration-dependent adsorptions were performed at room temperature (293 ± 2 K). Beads (6 mg) were mixed with AO (50 mL, 20 mg L^{-1}) and suffered shaking (300 rpm) until being the equilibrium. Concentrations of AO were determined by using a UV–Vis spectrometer (JASCO V-570 spectrophotometer). Each experiment above set in triplicate for determination.

The adsorption capacity (q_t, g g^{-1}) was calculated by the equation:

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

where V, is the volume of the suspension (mL); m, is the dry weight of beads used in the system (g); C_0, and C_t, mean the concentrations at the initial and at each interval (g L^{-1}). When the adsorption becomes equilibrated, we obtained the equilibrium concentration C_e, and subsequently the equilibrium capacity q_e.

2.4. Material characterization

The characterizations involved Atomic force microscopy (AFM, Agilent series 5500 AFM instrument in tapping mode at a scanning rate of 0.5 Hz), Fourier transform infrared spectroscopy (FTIR, FT/IR-6100 Spectrometer, JASCO), Scanning electro-microscopy (SEM, JSM-6300, JOEL), Thermo gravimetric analysis (TGA, TG/DTA 6200, SII Exstar6000, heating rate of 5 K per minute under N_2 atmosphere) and X-ray diffraction (XRD, Rigaku Denki RINT 2000, X-ray $\lambda_{Cu\ K\alpha} = 0.154$ nm). In addition, N_2 sorption isotherm at 77 K was used to calculate the specific surface area (SSA) using the Brunauer–Emmet–Teller (BET) equation (Yuasa Ionics Autosorb-6, samples were degassed at 353 K for 2 h prior to determination).

2.5. Data analysis

2.5.1. Adsorption kinetics

To study the sorption kinetics, we used the pseudo-first-order and pseudo-second-order rate models [18].

The pseudo-first-order rate equation of Lagergren is as follows:

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \tag{2}$$

Applying with the boundary conditions ($t = 0$, $q_t = 0$) and then integrating, we have:

$$q_t = q_e(1 - e^{-K_2 t}) \tag{3}$$

where q_e, q_t respectively represent the adsorption capacities at the equilibrium and as each sampling time (g g^{-1}); K_1 is the rate constant of the pseudo-first-order adsorption (min^{-1}).

The pseudo-second-order rate equation is written as:

$$\frac{dq_t}{dt} = K_1(q_e - q_t)^2 \tag{4}$$

By integration with the above-mentioned conditions, it is converted to: