



Comparative study of calcium alginate, activated carbon, and their composite beads on methylene blue adsorption



A.F. Hassan^{a,*}, A.M. Abdel-Mohsen^{b,d}, Moustafa M.G. Fouda^{c,d,**}

^a Chemistry Department, Faculty of Science, Damanhour University, Damanhour, Egypt

^b Central European Institute of Technology (CEITEC), Brno University of Technology, Czech Republic

^c Chemistry Department, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia

^d Textile Research Division, National Research Center, Dokki, P.O. 12622, Giza 12522, Egypt

ARTICLE INFO

Article history:

Received 16 October 2013

Received in revised form 29 October 2013

Accepted 30 October 2013

Available online 27 November 2013

Keywords:

Alginate beads

Composite

Activated carbon

Coconut shells

Methylene blue

ABSTRACT

Three adsorbents, calcium alginate beads (AB), sodium hydroxide activated carbon based coconut shells (C), and calcium alginate/activated carbon composite beads (ACB) were prepared. Their textural properties were characterized by N₂-adsorption at −196 °C and scanning electron microscopy. The porosity, surface area and total pore volume of C > ACB > AB, but AB adsorbent was more acidic function groups more than the other adsorbents. Adsorption experiments were conducted to examine the effects of adsorbent dosage, pH, time, temperature and initial concentration of methylene blue. Methylene blue adsorption on C, AB and ACB was observed at pH > 6 to avoid the competition of H⁺. The amount of dye adsorbed increases as the adsorbent dosage increase. Adsorption of dye follows pseudo-second order mechanism. Thermodynamic studies show spontaneous and endothermic nature of the overall adsorption process.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

The output of production of dyes generates colored wastewaters, which has aroused peoples concern regarding the environmental safety. The recycling from the manufacturing sectors and the textile industries into seas and rivers, alter the biomedical stability of the surrounding (Sheng, Xie, & Zhou, 2009). Removal of dyes and pigments from the waste has been fully considered over the last decade.

Methylene blue is one of the most commonly dyes used for industrial applications. Although the dye is not considered as highly toxic, methylene blue has various dangerous effects on human and animals. It can cause heart rate increasing, nausea and vomiting. Therefore, many different ways are available in order to eliminate these dyes from the industrial wastes. The most common used are degradation (El-Sheekh, Gharieb, & Abou-El-Souod, 2009), flocculation–coagulation (Cañizares, Martínez, Jiménez, Lobato, & Rodrigo, 2006), oxidation (Salem & El-Maazawi, 2000) and adsorption. Among these ways, adsorption has been proven more effective

and attractive for the treatment of dye-bearing industrial wastes (Yao, Xu, Chen, Xu, & Zhu, 2010). Adsorption is also cheap and highly effective method in the removal of methylene blue from wastewaters.

The adsorption of methylene blue by using different adsorbents, such as activated carbon (AC), wastes from agriculture, silicate, clay, solid wastes from the industry (Rafatullah, Sulaiman, Hashim, & Ahmad, 2010) etc., have been investigated. Among these adsorbents, perhaps activated carbon is one of the most common used adsorbent for methylene blue removal, based on the highly adsorption capacity and the fast removal rate because of their higher specific surface area and surface reactivity too (Park & Kim, 1999). But it is prohibitively expensive. The wastewater materials and agriculture wastes are assumed to be low-cost adsorbents due to their most abundance in nature and with many surface functional groups. The raw agricultural wastes such as leaves (Han et al., 2009; Weng, Lin, & Tzeng, 2009), fibers (Kavitha & Namasivayam, 2007), peels (Hameed, 2009), seeds (Hameed & Ahmad, 2009) and waste materials from forest industries such as sawdust (Hamdaoui, 2006) etc. have been used as adsorbents for the purifications and removing of dyes and pigments.

Water soluble sodium alginate, is linear polysaccharide, natural occurring polymer composed of α -guluronate and β -mannuronate residues. Alginate has some unique properties such as, its hydrophilicity, biocompatibility and it is considered to be non-toxic substance (Liu, Chen, Zhong, & Wu, 2009). The gelation properties of sodium alginate is mainly affected by the confirmed exchange

* Corresponding author. Chemistry Department, Faculty of Science, Damanhour University, Damanhour, Egypt.

** Corresponding author at: Chemistry Department, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia. Tel.: +966 560773127.

E-mail addresses: asmz68@yahoo.com (A.F. Hassan), mmfoudah@ksu.edu.sa, m.gaballa@yahoo.com (M.M.G. Fouda).

of sodium ions from the guluronic acid residues with different divalent cations such as Ca^{2+} , Sr^{2+} , Ba^{2+} , etc. All divalent cations connect to the α -L-guluronic acid blocks between two different chains resulting in 3D network (Sarmiento et al., 2006). Calcium alginate is widely used in immobilization of activated carbon (Kim, Jin, Park, Kim, & Cho, 2008), carbon nanotubes (Li et al., 2010), titanium nanoparticles (Mahmoodi, Hayati, Arami, & Bahrami, 2011) and magnetite nanoparticles (Rocher, Siaugue, Cabuil, & Bee, 2008) to create different adsorbents in order to remove wastes like dyes, pigments and metals from aqueous solutions.

The main objectives of this research work are: (i) preparation of NaOH-activated carbon from coconut shells, calcium alginate beads from sodium alginate solution, and calcium alginate/activated carbon composite beads, (ii) textural and chemical characterization of the prepared adsorbents using N_2 adsorption at -196°C , SEM, FTIR and pH_{PZC} (iii) adsorption of methylene blue from all solutions, which are previously prepared by the solid adsorbents, taking into account the kinetic and thermodynamic parameters, (iv) comparative studies between the three adsorbents toward organic pollutants.

2. Materials and methods

2.1. Materials

Calcium chloride, sodium hydroxide, methylene blue, sodium alginate, hydrochloric acid, sodium chloride were all purchased from Sigma–Aldrich (USA) and Loba Chemie Pvt. Ltd. (India). All other chemicals were used without any further purification. Deionized water was used for the preparation of all the required solution.

2.2. Preparation of adsorbents

2.2.1. Preparation of NaOH-activated carbon (C)

Coconut shells collected from coconut are obtained from Egyptian local markets and were used as precursor. Firstly, they were washed with distilled water to remove any adhering impurities, and then dried at 110°C for 24 h followed by grinding and sieving in order to use a particles size ranged between 1 mm and 2 mm. NaOH/activated carbon sample (C) was prepared via two steps: carbonization of dried precursor at 600°C for 4 h in absence of air using a stainless steel reactor (600 mm \times 40 mm) at a rate of $10^\circ\text{C}/\text{min}$ up to 600°C . The carbonized sample was cooled and soaked with certain weight of NaOH (40 g of carbonized sample with 120 g of solid NaOH) in 50 ml distilled water for 48 h at room temperature, followed by drying at 110°C and finally activated at 750°C for 4 h. Prepared sample was washed several times with distilled water till neutral filtrate and then dried at 110°C to constant weight and finally stored in a clean dry glass bottle.

2.2.2. Preparation of calcium alginate beads (AB)

A solution of 1% sodium alginate and 3% calcium chloride were prepared separately in deionized water. For preparation of AB beads, 1% sodium alginate solution was added drop wise to calcium chloride solution. The water-soluble sodium alginate was converted to water-insoluble calcium alginate beads. All beads were then washed with deionized water several times to remove the excess of unbounded calcium chloride from the bead surfaces. The washed beads were then dried at 70°C for 24 h and stored in a clean dry glass bottle.

2.2.3. Preparation of calcium alginate/activated carbon composite beads (ACB)

Calcium alginate/activated carbon composite beads (ACB) were prepared by ionic gelation method (Bée, Talbot, Abramson, & Dupuis, 2011; Fiol, Poch, & Villaescusa, 2004). Two grams of

powdered activated carbon (C) was dispersed in 100 mL deionized water and mixed with clear viscous 200 mL (1%, w/v) solution of sodium alginate. The mixture was stirred for 2 h. Once the mixture was homogenous, 50 ml of this solution is added to calcium chloride solution and the resulting black composite beads were collected and treated as the above prepared AB beads.

2.2.4. Adsorption procedure

The adsorption of adsorbate (methylene blue) was conducted in a static batch experiment. Aqueous solution of certain concentration of adsorbate was shaken in Stoppard Pyrex bottles of 100 mL capacity with 0.1 g of adsorbent (C, AB, or ACB) for 24 h. The supernatant liquid was filtered out, where the equilibrium concentration of the dye was determined using UV–vis spectra (Unicam 5625 UV/VIS spectrophotometer) at 662 nm. The adsorbed amount at equilibrium, q_e (mg/g) was calculated by:

$$q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

where C_o and C_e are the initial and equilibrium concentration (mg/L) of adsorbate solution, respectively; V is the volume of working solution (L) and W is the weight (g) of adsorbent used.

The effect of adsorbent dosage on the uptake was determined by shaking 1, 2, 3, 4, 5, 7, and 10 g/L of adsorbent with 75 mL of 1000 mg/L of methylene blue. All mixtures were shaken at 20°C and at pH 7.5. The reduction in adsorbate concentrations was measured.

Effect of pH was measured by carrying out the adsorption process at different pH values ranged between 2 and 12. Effect of time was carried out by contacting 0.1 g of adsorbent with 100 ml bottles of definite concentration of adsorbate (1000 mg/L of methylene blue). The concentration of adsorbate after recorded time intervals is determined; the adsorption capacity at time t , q_t (mg/g) was calculated using:

$$q_t = \frac{(C_o - C_t)V}{W} \quad (2)$$

where C_t (mg/L) is the liquid-phase concentration of adsorbate at time t . Effect of temperature was examined at 20 and 40°C and constant pH of 7.5. In these experiments, 0.1 g of adsorbents with 100 mL of 1000 mg/L of methylene blue was employed. After shaking, the adsorbed amount was measured; mg/g.

2.3. Characterization of solid adsorbents (C, AB, and ACB)

Fourier transform infrared spectra (FT-IR) were recorded on a Mattson 5000 FTIR spectrometer in the range between 4000 cm^{-1} and 450 cm^{-1} . Point of zero charge (pH_{PZC}) of solid adsorbents was carried out by: initially; 50 mL of 0.01 M NaCl solutions were put into several closed Erlenmeyer flasks. The pH within each flask was adjusted to a value between 2 and 12 by adding HCl (0.1 M) or NaOH (0.1 M) solutions, then a portion of the sample (0.15 g) was added to each flask, the flasks were agitated for 48 h and the final pH was then measured. The pH_{PZC} is the point where $\text{pH}_{\text{final}} = \text{pH}_{\text{initial}}$ (Hameed & Ahmad, 2009).

The morphological structure of the investigated samples was examined by scanning electron microscopy (SEM) using SEM model Quanta 250 FEG (Field Emission Gun) attached with EDX unit (Energy Dispersive X-ray Analyses), with accelerating voltage 30 kV, magnification $14\times$ up to 1,000,000 and resolution for Gun. Specific surface area (S_{BET} , m^2/g), total pore volume (V_T , mL/g), and average pore radius (r^- , nm) were determined via nitrogen adsorption at -196°C (outgassing was carried out at room temperature) using NOVA2000 gas sorption analyzer (Quantachrome Corporation, USA) system.

Download English Version:

<https://daneshyari.com/en/article/7792584>

Download Persian Version:

<https://daneshyari.com/article/7792584>

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