Journal of Molecular Liquids 198 (2014) 334–340

Contents lists available at ScienceDirect

Journal of Molecular Liquids

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

Preparation and utilization of anaerobic granular sludge-based biochar for the adsorption of methylene blue from aqueous solutions

Li Shi [a], Ge Zhang [b], Dong Wei [b], Tao Yan [b], Xiaodong Xue [b], Shusheng Shi [b], Qin Wei [a,*]

[a] *Key Laboratory of Chemical Sensing and Analysis in Universities of Shandong, School of Chemistry and Chemical Engineering, University of Jinan, Jinan 250022, PR China*
[b] *School of Resources and Environment, University of Jinan, Jinan 250022, PR China*

ARTICLE INFO

Article history:
Received 3 June 2014
Received in revised form 15 July 2014
Accepted 19 July 2014
Available online 31 July 2014

Keywords:
Anaerobic granular sludge
Biochar
Methylene blue
Adsorption mechanisms

ABSTRACT

In this study, a novel anaerobic granular sludge-based biochar (AGS-BC) was synthesized and utilized to remove methylene blue (MB) from aqueous solutions. The AGS-BC was characterized by scanning electron microscope (SEM), zeta potential, Brunauer–Emmett–Teller (BET) surface area, Boehm's titration, Fourier transform infrared spectroscopy (FTIR) analysis and X-ray photoelectron spectroscopy (XPS). Adsorption results were analyzed by the adjustment of various experimental parameters, including contact time, adsorbent dosage and pH values. In addition, the adsorption mechanism was investigated by adsorption isotherms, adsorption kinetic and adsorption thermodynamics. It was found that MB adsorption by AGS-BC fitted well the Langmuir isotherm model and pseudo-second order kinetics model. Based on the values of activation parameters including Gibbs free energy (ΔG^0, −9.20 to −11.10 kJ/mol), enthalpy (ΔH^0, 19.95 kJ/mol) and entropy (ΔS^0, 0.095 kJ/mol · K), we concluded that the adsorption process of MB onto AGS-BC was endothermic and spontaneous in nature. The result of this study could provide strong evidence of the potential of AGS-BC for removing MB from aqueous solutions.

1. Introduction

Dye is one of the major constituents of the wastewater discharged in many industries including dying, textile, leather, paint and plastic industry [1]. Most of the dyes were used in textile processing, in which the degree of fixation of dyes to fabrics is hardly never complete, 10–15% of the used dyes enter the environment through wastes, resulting in dye-containing effluents [2]. The wastewater containing dyes and pigments was quite stable, which makes it difficult to biodegrade because of the complex aromatic structures of dyes. Thus, the extensive uses of dyes cause not only a severe public health concern but also many serious environmental problems.

During the last few years, many researches have been conducted on physical–chemical methods of removing dyes from textile effluent, including coagulation [3,4], oxidative degradation [5], photocatalytic degradation [6,7], ultrafiltration [4,8], electro-chemical [9–11], adsorption [4,12] and combined electro-chemical and adsorption [13–15] techniques. Adsorption is recognized as a more effective and economic technology among above those methods. Since the adsorption efficiency mainly depends on the adsorbent properties, developing an effective adsorbent is of importance for the wide application of dye adsorption in water treatment.

In recent years, many kinds of carbon materials have been prepared and used for the removal of dyes and heavy metal ions due to their low cost, acid and alkali corrosion resistance, high specific surface area and enhanced adsorption capacity [16]. However, the applicability of carbon materials is limited and the available carbon materials are usually prepared from expensive or nonrenewable materials. Biochar (BC) is produced by oxygen-limited pyrolysis of carbon-rich biomasses, which has been developed as a novel and value-added solid adsorbent compared with conventional activated carbons. Additionally, biomass materials are appropriate for biochar production including crop residues (both field residues and processing residues such as nut shells, fruit pits, bagasse, etc.), as well as yard, food and forestry, and animal manures. But the utilization of anaerobic granular sludge to produce biochar has not been reported.

Anaerobic granular sludge has been widely applied for wastewater treatment. It has advantages of lower energy consumption, higher loading, and less amount of residual sludge especially when treating high concentration of organic wastewater. Due to its unique granule attributes, anaerobic granular sludge contains lots of bacteria, protozoa and extracellular polymeric substances (EPS). Furthermore, the functional groups on bacteria, protozoa and EPS including carboxyl and hydroxyl groups and other components provide binding sites for dye biosorption [17]. Anaerobic granular sludge is potentially suitable for the production of biochar because of rich biomasses and functional groups. However, the utilization of anaerobic granular sludge as a biochar adsorbent is rarely reported.

This study applied the anaerobic granular sludge-based biochar (AGS-BC) as the adsorbent for adsorption of methylene blue (MB). To achieve this purpose, effects of different parameters including contact

---

* Corresponding author. Tel.: +86 531 82767872; fax: +86 531 82765969.
E-mail address: sdjndxwq@163.com (Q. Wei).

http://dx.doi.org/10.1016/j.molliq.2014.07.023
0167-7322/© 2014 Elsevier B.V. All rights reserved.

time, adsorbent dosage, and pH values were studied to optimize the adsorption process. In order to further understand the interaction between AGS-BC and organic dyestuff molecules, the adsorption isotherms and kinetic and thermodynamics studies on MB adsorption by AGS-BC were also investigated.

2. Materials and methods

2.1. Preparation of AGS-BC

AGS was provided by the sewage treatment plant of Dezhou Corporation in Shandong Province of China. In order to dehydrate the sludge, the raw sludge was dried at 105 °C for 24 h, until constant weight was achieved, then comminuted and sieved into a uniform size of 0.5–2.0 mm. Ten grams of the dehydrated sludge (DS) samples were added into 25 ml of 5 mol/L $ZnCl_2$ solution, and stood for 24 h. When supernatant was removed, the samples were subjected to vacuum drying at 105 °C for 24 h. The resulting chemical loaded samples were then pyrolyzed in a quartz tube in N_2 atmosphere. The heating rate was kept at 15 °C/min and held temperature at 650 °C for 120 min. After cooling down to room temperature, the carbonized products were washed with 3 mol/L HCl solution, followed by filtration. At last, the products were rinsed with deionized water and dried at 105 °C for 24 h.

Table 1
Concentrations of surface functional groups of the AGS-BC and commercial activated carbon.

Samples	Acidic groups (mmol/g)				
	Carboxylic	Lactonic	Phenolic	Total acidic	Basic
AGS-BC	1.284	0.129	0.080	1.493	0.281
CAC	0.636	0.128	0.068	0.832	0.054

2.2. Characterization

The surface physical morphology of AGS-BC was observed by a scanning electron microscope (SEM, JEOL JSM-6700F microscope, Japan). Brunauer–Emmett–Teller (BET) analysis was performed on Micromeritics ASAP 2020 surface area and porosity analyzer (Quantachrome, United States). Pore distributions and pore volume were calculated by using the adsorption branch of the N_2 isotherms based on the BJH model. Zeta potential was measured by a Malvern zetameter (Zetasizer 2000). Boehm's titration method [18] was used to quantify the amount of acidic and basic functional groups on the carbon's surfaces. The Fourier transform infrared spectroscopy (FTIR) of AGS-BC was recorded on VERTEX70 FTIR spectrometer (Bruker Co.,

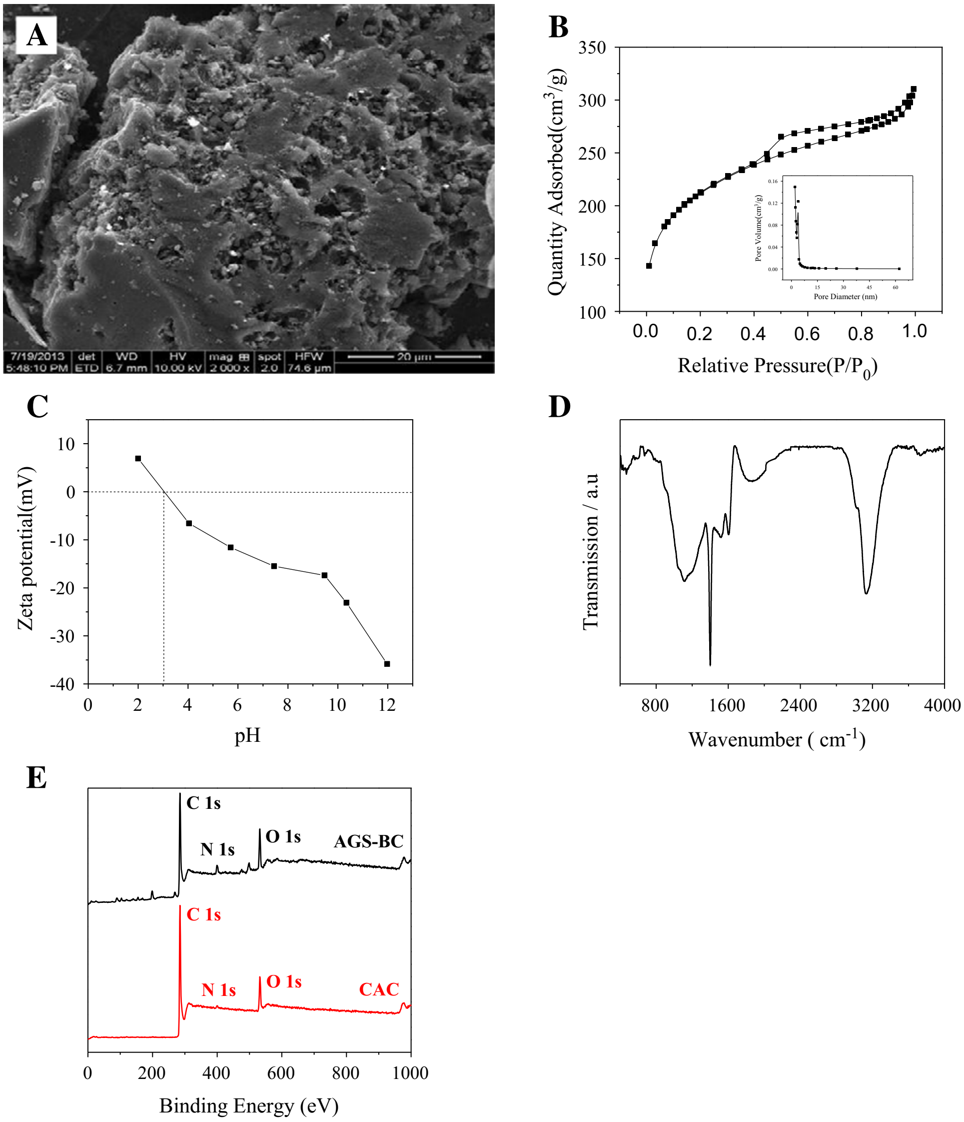

Fig. 1. SEM (A), BET analysis (B), zeta potential (C), the FTIR spectra analysis (D) and XPS survey spectra (E) of AGS-BC.