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Research article

Fast and efficient adsorption of methylene green 5 on activated carbon prepared from new chemical activation method

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ABSTRACT

Activated carbon (AC) was synthesized from golden shower (GS) through a new chemical activation process. The three-stage process comprised (1) hydrothermal carbonization of GS to produce hydrochar, (2) pyrolysis of hydrochar to produce biochar, and (3) subsequent chemical activation of biochar with K_2CO_3 to obtain GSHBAC. The traditional synthesis processes (i.e., one-stage and two-stage) were also examined for comparison. In the one-stage process, GS that was impregnated with K_2CO_3 was directly pyrolyzed (GSAC), and the two-stage process consisted of (1) pyrolytic or hydrothermal carbonization to produce biochar or hydrochar and (2) subsequent chemical activation was defined as GSBAC and GSHAC, respectively. The synthesized ACs were characterized by scanning electron microscope, Brunauer–Emmett–Teller (BET) surface area analysis, Fourier transform infrared spectrometry, point zero charge, and Boehm titration. The adsorption results demonstrated that the MG5 adsorption process was not remarkably affected by neither the solution pH (2.0–10) nor ionic strength (0–0.5 M NaCl). Kinetic studies showed that the adsorption equilibrium was quickly established, with a low activation energy required for adsorption (*Ea*; 3.30–27.8 kJ/mol), and the ACs removed 50–73% of the MG5 concentration from solution within 01 min. Desorption studies confirmed the adsorption was irreversible. Thermodynamic experiments suggested that the MG5 adsorption was spontaneous ($-\Delta G^{\circ}$) and endothermic ($+\Delta H^{\circ}$), and increased the randomness ($+\Delta S^{\circ}$) in the system. Although the specific surface areas of the ACs followed the order GSAC (1,413) > GSHAC (1,238) > GSHBAC (903) > GSBAC (812 m^2/g), the maximum adsorption capacities determined from the Langmuir model (Q^o_{max}) at 30 °C exhibited the following order: GSHBAC (531) > GSAC (344) > GSHAC (332) > GSBAC (253 mg/g). Oxygenation of the ACs' surface through a hydrothermal process with acrylic acid resulted in a decrease in MG5 adsorption and identified the importance of π-π interactions to the adsorption process. The primary interactions in MG5 adsorption were π-π interactions and pore filling, while hydrogen bonding and n-π interactions were minor contributors. The three-stage process can be regarded as the effective preparation method of AC with a high adsorption capacity toward the cationic dye.

1. Introduction

Activated carbon (AC) with exceptionally large specific surface area, high pore volume, well-developed internal porous structure, relative chemical stability, high thermal stability, and abundant surface functional groups, has been widely applied in various industrial processes. In water treatment, ACs can be considered as effective adsorbents for the removal of various organic and inorganic contaminants. According to an industry market research report (Freedonia, 2014), world demand for AC is estimated to increase 8.1 percent per year to 2.1 million metric tons in 2018.

ACs can be synthesized through two well-known processes: physical and chemical activation. The chemical activation process can be conducted using one or two stage process. One-stage process is the most common method in which the raw materials are directly mixed with certain activating reagents and then the resulting mixture is pyrolyzed. By contrast, the two-stage process comprises (1) a precarbonization process (i.e., pyrolysis or

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hydrolysis) and (2) chemical activation. For pyrolysis process, the material is subjected to high temperatures (400–1200 °C) in an inert atmosphere (i.e., N_2 or Ar atmosphere), under vacuum conditions, or in non-circulated air atmosphere (i.e., within lid-enclosed crucible). In hydrolysis, the raw materials are dispersed in an autoclave containing a given solution. Subsequently, the autoclave temperature is controlled (150–350 °C) for 2–24 h at a specific pressure to produce hydrochar (Gaspard et al., 2014; Tran et al., 2016a).

ACs produced from the two-stage chemical activation have a larger surface area and higher adsorption capacity than those prepared using the one-stage chemical activation process as reported in the literature (Oh and Park, 2002; Kennedy et al., 2004; Basta et al., 2009; Sevilla et al., 2011; Huang et al., 2014; Fernandez et al., 2015; Bedin et al., 2016; Tran et al., 2016a).

Notably, activating reagents highly affect AC characteristics. For example, Hayashi et al. (2000) prepared commercial lignin-derived activated carbons by chemical activation. It was concluded that ACs activated by K_2CO_3 show the highest S_{BET}, nearly 2,000 m^2/g, compared with those activated by KOH (approximately 1,400 m^2/g), NaOH (1,200 m^2/g), $ZnCl_2$ (1,000 m^2/g), Na_2CO_3 (800 m^2/g), and H_3PO_4 (700 m^2/g). In another comparison study on the efficiency of chemical agents (i.e., K_2CO_3 and KOH) in the synthesis of grape seed–derived ACs (Okman et al., 2014), ACs activated by K_2CO_3 and KOH through the optimal carbonization process exhibited similar yields, S_{BET}, and micropore volumes. Furthermore, environmentally friendly chemical agents play a major role in industrial and environmental applications. In particular, K_2CO_3 is not a deleterious chemical, and it is frequently used in food additives. Therefore, K_2CO_3 was used as an activating agent in the current study.

Generally, the lignocellulose materials derived from agricultural wastes have been considered as the most common feedstock for the preparation of AC compared to other materials in the literature. The feedstock for preparation of AC comprised agricultural wastes (i.e., olive stone, cherry stone, coffee bean, pecan shell, and coir pith); wood industry (i.e., rubber wood sawdust, eucalyptus sawdust, cedar wood, and teak sawdust); and non-conventional wastes, such as *plastics* (PET and PVC), industrial wastes (Polymer, fly ash, acrylic fabric waste, pitch), and others (tire and sewage sludge) (Dias et al., 2007; Ioannidou and Zabaniotou, 2007).

Cassia fistula (commonly known as golden shower; GS) is a very popular ornamental plant in tropical and subtropical regions, and it can be used as a lignocellulose precursor for synthesizing ACs because it is relatively abundant, a renewable resource, and costs less. The application of raw GS as a biosorbent for removal of Ni(II), chromium(III), and chromium(VI) has been reported elsewhere (Hanif et al., 2007; Abbas et al., 2008). Recently, Sorokhaibam et al. (2015) prepared the AC from whole golden shower fruit through one-stage chemical activation with H_3PO_4 and applied it for the removal of sulfur and congo red. Therefore, in this study, raw GS pod is considered as the precursor for preparation of AC. Methylene green 5 (MG5) is a cationic phenothiazine dye and heterocyclic aromatic chemical compound that can be considered as a nitro derivative of methylene blue. In addition, MG5 is commonly used in various industries; therefore, it is selected as a target adsorbate in this study.

To the best of our knowledge, the three-stage process for the preparation of activated carbon has not yet been presented in the scientific literature. In this study, the golden shower-derived activated carbon was synthesized through the new three-stage process (GSHBAC) and applied for the adsorption of MG5 from an aqueous solution. The characterization and adsorption capacity of GSHBAC were compared with three ACs prepared from the traditional preparation methods (i.e., the one-stage and two-stage processes). The adsorption process of MG5 by the ACs was investigated in batch experiments under varying operating conditions—solution pH, ionic strength, contact time, initial MG5 concentration, temperature, and the presence of desorption agent. Lastly, we suggest a simple and efficient method for identification of the dominant interactions in an adsorption mechanism.

2. Materials and methods

2.1. Activated carbon preparation

Pods of GS were collected from Taipei in Taiwan, and the seeds were removed. The materials (Fig. S1) were washed with tap water at least thrice and then with deionized distilled water to remove any adhering dirt or impurity. They were then placed in an oven at 80 °C for 24 h. The dried GS was ground and sieved to obtain particles in the size range from 0.106 to 0.250 mm.

The one-stage and two-stage processes for AC preparation reported in the literature and our recent publication (Tran et al., 2016a) are illustrated in Fig. 1. In the one-stage process, approximately 30 g of the dried raw GS materials were directly mixed with K_2CO_3 and the mixture was pyrolyzed for obtaining GSAC. In the two-stage process, approximately 50 g of the dried powdered GS was pyrolyzed to prepare biochar (GSB), and then the mixture of GSB and K_2CO_3 was pyrolyzed for obtaining GSBAC. Meanwhile, approximately 20 g of dried GS was mixed with 120 mL of deionized distilled water in a 200 mL Teflon-lined autoclave, and subsequently used hydrothermal carbonization to prepare GSH. After that, the mixture of GSH and K_2CO_3 was pyrolyzed for achieving GSHAC.

The new three-stage process of AC preparation (GSHBAC) was described in Fig. 1. The first stage involves the preparation of hydrochar (GSH) through the hydrothermal carbonization process. The second stage regards the preparation of hydrochar-derived biochar (GSHB) through the pyrolytic process of GSH sample. The third stage relates to the chemical activation of GSHB with K_2CO_3.

In this study, the hydrothermal carbonization process was conducted at 190 °C for 24 h under self-generated pressure conditions in Teflon-lined autoclave, and the pyrolytic process was carried out in a limited-oxygen condition at 800 °C for 4 h in a porcelain crucible covered with a lid. The pyrolysis process has been described in elsewhere (Tran et al., 2015). Both hydrothermal and pyrolytic processes were undertaken in a muffle furnace (Deng Yng DF 40, Taiwan). The precursors (i.e., GS, GSB, GSH, and GSHB) were immersed in K_2CO_3 solution with a weight ratio of 1:1 (K_2CO_3: precursors, w/w). Before the mixture of the precursor and K_2CO_3 was pyrolyzed, it has been placed into a drying oven at 80 °C for 24 h.

After carbonization process, the samples were thoroughly washed with 0.1 M HCl for dissolving ash and inorganic salts. Finally, deionized distilled water was used to wash the samples until the pH of the filtrates reached a constant value. The samples were dried and sieved, and then were stored in tightly closed brown bottles.

2.2. Activated carbon properties

Textural properties of the ACs were measured using a Micromeritics ASAP 2020 sorptometer at 77 K. The morphology of the ACs was obtained using scanning electron microscopy (SEM; Hitachi S-4800, Japan).

The functional groups available on the ACs' surface were detected using Fourier transform infrared spectroscopy (FTIR; FT/IR-6600 JASCO); the AC particles were pelleted mixing with KBr. The pH value of the ACs at the point of zero charge (pH_{PZC}) was determined using the solid addition method, which is analogous to