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Improving the surface properties of municipal solid waste-derived pyrolysis biochar by chemical and thermal activation: Optimization of process parameters and environmental application

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ABSTRACT

Biochar produced from the slow pyrolysis of municipal solid waste was activated with *KOH* and thermal treatments to enhance its surface and adsorptive properties. The effects of *KOH* concentration, activation temperature and time on the specific surface area (*SSA*) of the activated biochar were evaluated and optimized using central composite design (CCD) of the response surface methodology (RSM). Results showed that the activation of biochar enhanced its *SSA* from 402.8 ± 12.5 to 662.4 ± 28.6 $m^2 g^{-1}$. The adsorptive capacities of the pristine biochar (PBC) and activated biochar (ABC) were compared using methylene blue (MB) dye as model compound. For MB concentrations up to 25 mg L^{-1}, more than 99% dye removal was achieved with ABC, while only a maximum of 51% was obtained with PBC. Results of the isotherm study showed that the Langmuir model best described MB adsorption on ABC with adsorption capacity of 37.0–41.2 mg g^{-1}.

1. Introduction

Municipal solid waste (MSW) management and disposal is one of the major global concerns especially for countries with small land area, high population growth rate, and rapid industrialization and urbanization. The scarcity of suitable landfill sites and the growing public awareness on various environmental, aesthetic and social issues that accompany landfill disposal are compelling legislators and researchers to find alternative strategies to reduce the amount of landfilled wastes to a minimum. One approach is to transform MSW into high value products i.e. liquid or gaseous fuel (Lonappan et al., 2016). This waste-to-fuel conversion is usually done via a thermochemical process (Taherymoosavi et al., 2017) in an oxygen-free or oxygen-limited environment and at a specified temperature range depending on the preferred product, e.g. torrefaction (200–300 °C), pyrolysis (300–600 °C) or gasification (>600 °C) for solid, liquid and gaseous fuels, respectively (Nam et al., 2015, 2016).

Biochar is the carbonaceous solid byproduct of MSW thermochemical conversion. It is usually rich in nutrients and stable aromatic carbon which makes it suitable for various applications, such as soil amendment, carbon sequestration, pollution mitigation and energy production (Genuino et al., 2017; Hung et al., 2017). Depending on the raw biomass composition and process conditions, the resulting biochar can be environmentally stable and can have an extensive pore network, high surface area and surface functional groups that are important to a specific application (Lian et al., 2016; Randolph et al., 2017; Taheran et al., 2016; Zhou et al., 2017). Hence, biochar is becoming a popular and practical alternative to expensive activated carbon particularly for adsorption applications. However, the typical sorption capacity of biochar remain inferior to that of commercial activated carbon due to the underdeveloped pore network of the former which is attributed to relatively low pyrolysis temperature and the absence of an activation process (Guzel et al., 2017; Lian et al., 2016). In recent years, various biochar certification programs such as International Biochar Initiative (IBI, 2015) and European Biochar Certificate (EBC, 2012) have been established to standardize biochar products and its applications. These certifications provide guidelines and information on the minimum quality parameters and characterization protocols for biochar materials (Llorach-Massana et al., 2017). Thus, activation methods to improve the adsorptive performance of biochar have recently been investigated and these methods mainly increase the surface area and porosity of the bio-

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char and form oxygenated functional groups on its solid surface (Vaughn et al., 2017; Wang et al., 2017).

Biochar activation can be accomplished by physical and/or chemical methods. Physical activation is usually done at high temperatures (800 to >1000 °C) in the presence of oxidizing gas compounds such as CO_2 or steam (Islam et al., 2015). Chemical activation, on the other hand, involves the impregnation of the biochar with a chemical reagent, usually a Brönsted or Lewis acid or a strong alkali, such as H_3PO_4, HNO_3, *KOH* or *NaOH*, and then followed by carbonization at a temperature range of 450–900 °C (Contreras et al., 2010). Chemical modifications other than acid and alkaline treatment have also been done on biochar, such as magnetic treatment with $FeCl_3$ and impregnation with metal ions, like $ZnCl_2$ and $KMnO_4$ (Arami-Niya et al., 2011; B. Li et al., 2017a). Though both activation treatments increase the aromatic condensation and improve the porosity and structure of the biochar, chemical activation is still usually preferred to physical activation because of the lower temperature and shorter time requirements of the former (Yargicoglu et al., 2015).

Strong alkaline compounds, such as *KOH*, have been widely employed as chemical activation agents (Dehkhoda et al., 2016; Ding et al., 2016; Jin et al., 2016, 2014; B. Li et al., 2017a). Several researchers proposed the overall stoichiometric reaction (Eq. (1)) between *KOH* and surface carbon during chemical activation (Huang et al., 2015; Lillo-Rodenas et al., 2003; Lozano-Castello et al., 2007; Wang and Kaskel, 2012). This chemical reaction has a positive standard Gibbs free energy, $\Delta G°$, at $T = 25$ °C, which becomes negative and, thus, spontaneous at around $T = 570$ °C (Lozano-Castello et al., 2007). However, according to Wang and Kaskel (2012), compounds, such as K_2O and K_2CO_3, are produced through simultaneous and consecutive chemical reactions between *KOH* and the surface carbon starting at 400 °C. Three main *KOH* activation mechanisms have been proposed: (1) etching of the solid structure due to chemical reactions between the carbon and potassium species (*KOH*, K_2O and K_2CO_3) which mainly generate the pore network; (2) dehydration of *KOH* leading to the formation of H_2O and CO_2 which both contribute to porosity development via carbon gasification; and (3) intercalation of the produced metallic *K* into the carbon framework causing irreversible expansion of carbon lattices and thus creating more micropores in the solid structure upon the removal of the metallic *K* by washing.

$$6KOH + 2C \rightarrow 2K + 2K_2CO_3 + 3H_2 \quad (1)$$

The surface areas and pore volumes of activated carbons are critical properties in adsorption applications (Sigmund et al., 2017). Although an overall reaction has already been adopted, generalization of the resulting pore structure and surface area of the activated biochar remains difficult because of several factors contributing to its surface properties, such as type of feedstock and the parameter conditions set during activation i.e. carbonization temperature, duration and activating agent (Zhou et al., 2017). A thorough understanding of how these process parameter conditions interact to produce the most favorable biochar surface properties is highly important.

Response surface methodology is a powerful tool used not only to quantify the influence of different process parameters and their interactions on the response variables, but also optimize the process variable conditions to obtain the maximum response values (Yavari et al., 2017). It also minimizes the number of experimental runs resulting to reduced overall costs, low process variability and short experiment durations (Lin et al., 2015; Roshan et al., 2013). This technique helps determine which among the parameters, including quadratic and interaction effects, have the most significant effect on the response. It also generates a low-order polynomial model equation to describe the relationship of the input and response variables, and is used to approximate the response within a given range of parameter conditions (Podstawczyk et al., 2015).

Based on the authors' extensive literature review, no optimization study of MSW pyrolysis biochar activation has been published. In this work, the effects of *KOH* and thermal activation of MSW pyrolysis biochar were investigated. Optimization study using CCD was done to determine the optimum specific surface area of ABC by varying key process parameters, such as *KOH* concentration, activation temperature and time. Furthermore, this study compared the general adsorptive potential of PBC and ABC based on methylene blue dye adsorption experiments. Methylene blue was used as a representative organic pollutant because of its strong affinity with solid materials (Sun et al., 2013). The effects of initial dye concentration and adsorbent dosage were also investigated. Adsorption isotherm studies were carried out using Langmuir, Freundlich and Temkin models. PBC and ABC were characterized by scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET) and X-ray diffraction (XRD) analyses.

2. Materials and methods

2.1. Biochar production

Biochar samples were prepared from MSW obtained from the Brazos Valley Recycling Facility (College Station, TX) and contained paper, textiles and yard wastes. The particle size of the MSW was reduced to less than 2.0 mm and then pyrolyzed at 400–500 °C for 30 min using a pressure batch reactor (Parr Instrument Series 4580 HP/HT) with a heating rate of 3 °C per min. After pyrolysis, the reactor was cooled down to 25 °C and the biochar was collected and stored in air-tight containers for future use. This biochar sample will be referred to as pristine biochar (PBC) in this study.

2.2. Chemical and thermal activation of biochar

Activation experiments were done by soaking 10 g of biochar with 300 mL of *KOH* solution with varying concentrations (0.25–0.75 M). The mixture was then placed in an incubator shaker (New Brunswick Scientific G25) maintained at a temperature of 30 °C and a shaking speed of 150 rpm. After 24 h, the *KOH*-activated biochar was filtered and washed with deionized (DI) water until the filtrate reached a stable pH = 7. The biochar was then dried overnight at 105 °C, collected and stored in air-tight containers.

Thermal activation was carried out by placing the *KOH*-activated biochar in a tube furnace (Carbolite Gero Ltd.) maintained under an inert N_2 condition and set at the desired temperature (600–800 °C) and time (30–90 min). After cooling to room temperature, ABC was collected and soaked in 0.1 M HCl solution for 2 h to remove ash and other inorganic impurities. It was then filtered and washed with DI water until the filtrate had a stable pH = 7. Finally, the ABC was dried at 105 °C for 24 h and then stored in air-tight containers for future use.

2.3. Experimental design and numerical optimization

The effect of activation conditions, i.e. *KOH* concentration, activation temperature and duration on the specific surface area (*SSA*) of the ABC was determined using central composite design (JMP Pro 12.2 software, SAS Institute, Inc.) with 3 blocks and 6 central points. Furthermore, CCD was used to find the conditions that will yield the optimum *SSA* of ABC. Table 1 shows the low (−1) and high (+1) levels of each design parameter used to generate a table of fully randomized runs to minimize any error arising from run sequence.

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