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Research article

Evaluation of the effectiveness and mechanisms of acetaminophen and methylene blue dye adsorption on activated biochar derived from municipal solid wastes

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ABSTRACT

The adsorption potential and governing mechanisms of emerging contaminants, i.e. acetaminophen or acetyl-para-aminophenol (APAP) and methylene blue (MB) dye, on activated carbon derived from municipal solid waste were investigated in this work. Results showed that MB adsorption was significantly more effective, with a maximum removal of 99.9%, than APAP adsorption ($\%R_{max}$ = 63.7%). MB adsorption was found to be unaffected by pH change, while the adsorption capacity of APAP drastically dropped by about 89% when the pH was adjusted from pH 2 to 12. Surface reactions during APAP adsorption was dominated by both physical and chemical interactions, with the kinetic data showing good fit in both pseudo-first order (R^2 = 0.986–0.997) and pseudo-second order (R^2>0.998) models. On the other hand, MB adsorption was best described by the pseudo-second order model, with R^2>0.981, denoting that chemisorption controlled the process. Electrostatic attractions and chemical reactions with oxygenated surface functional groups (i.e., −OH and −COOH) govern the adsorption of APAP and MB on the activated biochar. Thermodynamic study showed that APAP and MB adsorption were endothermic with positive ΔH° values of 16.5 and 74.7 kJ mol^{-1}, respectively. Negative ΔG° values obtained for APAP (−3.7 to −5.1 kJ mol^{-1}) and MB (−11.4 to −17.1 kJ mol^{-1}) implied that the adsorption onto the activated biochar was spontaneous and feasible. Overall, the study demonstrates the effectiveness of activated biochar from municipal solid wastes as alternative adsorbent for the removal of acetaminophen and methylene blue dye from contaminated waters.

1. Introduction

Emerging contaminants, such as pharmaceuticals, personal care products, surfactants and pesticides, are becoming a growing global environmental concern because of the difficult-to-degrade molecular structures of these compounds. These chemical species are not completely removed by conventional wastewater treatment technologies thus resulting in the subsequent contamination of surface waters (Álvarez et al., 2015; Malakootian et al., 2016).

Acetaminophen, also known as paracetamol or acetyl-para-aminophenol (APAP), is the main ingredient of analgesic, antipyretic and anti-inflammatory drugs and is considered as one of the most widely sold and used over-the-counter pharmaceutical compound across the globe (de Luna et al., 2013a). Because of the high consumption of this drug, significant concentrations of the compound are detected in water bodies which poses risks to environment quality, and animal and human health (De Laurentiis et al., 2014; Stamatis and Konstantinou, 2013).

Synthetic dyes also raise significant issues due to the wide use of dye-containing polymers in medicines (Ghobashy and Elhady, 2017). These compounds can bring about serious environmental and health risks because of their complex aromatic structures, high organic content, non-biodegradability, and stability to light, heat, water or chemicals (de Luna et al., 2013b; Ngulube et al., 2017). They can also affect the aesthetic nature of water bodies even at low concentrations because of the colors they impart to the receiving waters, and more importantly, they can cause various illnesses

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because of their carcinogenic and mutagenic properties (Hanafiah et al., 2012).

Adsorption is considered an ideal technology for the removal of organic compounds from aqueous media because it is inexpensive, simple to operate, can tolerate toxic substances, and can produce high quality effluents (Kulkarni et al., 2017; Wu et al., 2017). Conventional adsorption processes, however, use commercial activated carbon because of its excellent adsorption capabilities (Macías-García et al., 2017). However, the expensive and complex production of commercial activated carbon limits its wide application (Fan et al., 2016). Thus, more recent studies have explored the use of various waste biomass, such as agricultural wastes (Ding et al., 2016) and sludge (Fan et al., 2017), to make cost-effective activated carbon with high surface areas and adsorption capacities.

Biochar, a carbonaceous product of biomass thermal conversion in oxygen-limited conditions, is a promising alternative to commercial activated carbon because of its low cost, high surface area, good cation exchange capacity and strong affinity to organic and inorganic contaminants (Wang et al., 2015). Its properties are dependent on the type of feedstock used, and the process conditions during thermal conversion, such as oxygen level, temperature, residence time and pressure (Ahmad et al., 2014). The biochar surface is normally negatively-charged because of the dissociation of several oxygen-containing functional groups, such as carboxylate, carbonyl and hydroxyl groups, which makes it effective in the removal of organic and heavy metal pollutants from wastewater (Zhou et al., 2017b). Nearly all biomass can be transformed into biochar; however, waste-derived biomass is the preferred feedstock to make the thermal conversion process more environmentally and economically feasible (Jin et al., 2016).

In this study, the effectiveness of activated biochar produced from municipal solid waste for the adsorption of emerging contaminants, such as acetaminophen and methylene blue dye, was investigated. Several dye removal studies have been done using methylene blue as the representative compound because of its hard-to-degrade nature and strong adsorption onto solids (Sun et al., 2013; Zhou et al., 2017a). The present study also aims to evaluate the properties of the activated biochar and explore the governing interaction mechanisms and adsorption behaviors of the model organic compounds on the biochar surface.

2. Materials and methods

2.1. Activated biochar preparation

The biochar was obtained from the slow pyrolysis of municipal solid waste (MSW) collected from the Brazos Valley recycling facility in College Station, Texas, USA. The MSW was composed of 60% paper, 25% yard wastes and 15% textiles. The MSW was ground to a particle size <2.0 mm and was pyrolyzed at a temperature range of 400–500 °C using a pressure batch reactor (Parr Instrument Series 4580 HP/HT) heated at a rate of 3 °C min^{-1} and operated isothermally for 30 min. Before the pyrolysis run, the reactor was purged with nitrogen gas at 10 psi for 15 min to ensure the absence of oxygen during the reaction.

Optimization experiments for biochar activation were done (Genuino et al., 2018) and the resulting optimum activation parameters were used to prepare the activated biochar in this study. The biochar was mixed with 0.50 M KOH solution and placed in an incubator shaker (New Brunswick Scientific G25) maintained at 30 °C and 150 rpm for 24 h. The KOH-activated biochar was then filtered and washed with deionized water until a stable pH of the filtrate was reached. Then, the samples were dried overnight at 105 °C. After drying, the biochar was thermally activated using a tube furnace (Carbolite Gero Ltd.) heated at 683 °C under an inert N_2 condition for 53 min. Then, the MSW activated biochar (MAB) was soaked in 0.1 M HCl solution for 2 h to remove ash and other inorganic impurities, followed by washing with deionized water until neutral or stable pH, and drying at 105 °C for 24 h. Finally, MAB was collected and stored in air-tight containers for future use.

2.2. Adsorbent characterization

Elemental composition analyses of the raw and spent activated biochar were done based on ASTM standard D5373 and using an elemental analyzer (Vario MICRO, Elementar Analysensysteme GmbH). The changes in the surface functional groups of the MAB before and after adsorption with APAP and MB were investigated by Fourier transform infrared spectroscopy (FTIR, Shimadzu IRAffinity-1) within the wavenumber range of 2800–600 cm^{-1}. The surface chemistry was further evaluated by determining the pH at point of zero charge (pH_{PZC}) based on the method used by Essandoh et al. (2015). Using 15-mL centrifuge tubes, 50 mg MAB was mixed with 10 mL 0.01 M NaCl aqueous solutions at different pH levels ranging from 2 to 12. The pH was adjusted using HCl and NaOH solutions. The samples were then placed in an incubator shaker operated at 30 °C and 150 rpm for 24 h. After, the samples were centrifuged at 4000 G for 10 min, decanted, and the final pH of the supernatant was measured by pH/ion meter (Accumet 25, Fisher Scientific). The change in pH was plotted against the sample initial pH to obtain the point of zero charge. Other adsorbent characterization data, namely surface area and porosity, scanning electron micrographs and X-ray diffraction (XRD) patterns were obtained and reported in the previous work of the authors (Genuino et al., 2018).

2.3. Adsorbate and batch adsorption experiments

Analytical grade acetaminophen (APAP) and methylene blue (MB) dye were purchased from Sigma-Aldrich and used without further purification. Table 1 summarizes the physico-chemical characteristics of APAP and MB used in this study. Stock solution, with a concentration of 500 mg L^{-1}, of each compound was prepared using deionized (DI) water and stored for future use. All dilution requirements were also done using DI water.

The batch adsorption experiments were done by mixing 20 mg of MAB with 10-mL solutions of APAP and MB, at 50 mg L^{-1}, in separate 50-mL glass containers with covers. The initial pH of the mixtures was adjusted accordingly using 0.1 M NaOH and HCl solutions. The samples were then agitated using an 18-L water bath shaker (VWR International) operated at 100 rpm and maintained at 30 °C for 24 h to ensure equilibrium. Then, the MAB was separated from the solution using a 0.45-μm syringe filter. The final concentration of the APAP and MB solutions were measured by UV–Vis analysis at λ_{max} 243 and 664 nm, respectively. Calibration curves (5–500 mg L^{-1}) for both APAP and MB, with $R^2 > 0.98$, were initially established to determine the relationship between absorbance (A) and concentration (C), which are given in Eqs. (1) and (2).

$$C_{APAP} = 15.31 * A_{\lambda=243\ nm} \quad (1)$$

$$C_{MB} = 5.63 * A_{\lambda=664\ nm} \quad (2)$$

2.4. Adsorption kinetics and modeling

The experiment on adsorption kinetics was done by placing 20 mg MAB into 10-mL solutions of APAP and MB at an initial concentration of 10 and 50 mg L^{-1}, respectively. Samples were