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Adsorption of methylene blue on biochar microparticles derived from different waste materials

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ABSTRACT

Biochar microparticles were prepared from three different types of biochar, derived from waste materials, such as pine wood (BC-PW), pig manure (BC-PM) and cardboard (BC-PD) under various pyrolysis conditions. The microparticles were prepared by dry grinding and sequential sieving through various ASTM sieves. Particle size and specific surface area were analyzed using laser particle size analyzer. The particles were further characterized using scanning electron microscope (SEM). The adsorption capacity of each class of adsorbent was determined by methylene blue adsorption tests in comparison with commercially available activated carbon. Experimental results showed that dye adsorption increased with initial concentration of the adsorbate and biochar dosage. Biochar microparticles prepared from different sources exhibited improvement in adsorption capacity (7.8 ± 0.5 mg g^{-1} to 25 ± 1.3 mg g^{-1}) in comparison with raw biochar and commercially available activated carbon. The adsorption capacity varied with source material and method of production of biochar. The maximum adsorption capacity was 25 mg g^{-1} for BC-PM microparticles at 25 °C for an adsorbate concentration of 500 mg L^{-1} in comparison with 48.30 ± 3.6 mg g^{-1} for activated carbon. The equilibrium adsorption data were best described by Langmuir model for BC-PM and BC-PD and Freundlich model for BC-PW.

1. Introduction

Disposal of solid waste materials is a cause for concern throughout the world. Recent developments in environmental technology focused on the use of sustainable materials and advanced management practices for waste materials such as production of value-added products from waste materials. Biochar is a carbon-rich solid obtained by the pyrolysis of organic material. The organic materials can be waste materials of municipal or agricultural origin. The unique and specific properties of biochar include large surface area, highly porous structure, enriched surface functional groups and mineral components. These unparalleled properties make biochar an effective material for mitigating global warming, soil amendment, enhancement of crop yield, carbon storage and removal of contaminants from water (Tan et al., 2015). Besides, biochar is being considered as a waste disposal and recycling option (Gupta et al., 2009). The specific properties of biochar, such as surface area and porous structure will depend upon the source material and method of production, such as pyrolysis temperature, thermochemical conversion technology and residence time (Tan et al., 2015).

Due to its economic feasibility and environmental relevance along with its physico-chemical properties, biochar can be used for the removal of contaminants. The adsorption potential of biochar is widely acknowledged with adsorption of wastewater pollutants, such as phenol (Tan et al., 2009), dye (Cheng et al., 2013) and heavy metals (Kołodyńska et al., 2012; Mohan et al., 2007). Relatively recently, biochar without any activation was identified as a 'supersorbent' for neutral organic compounds (NOCs) (Yang and Sheng, 2003). A copiousness of polar functional groups on biochar surface enhanced NOC adsorption by biochar compared to

Abbreviations: ASTM, American Society for Testing Materials; BC-PD, biochar-paper derived; BC-PM, biochar-pig manure; BC-PW, biochar-pinewood; MB, methylene blue; SEM, scanning electron microscope.

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activated carbon (Yang et al., 2004). Thus, biochar offers good opportunities for removal of various organic contaminants.

The behavior of microparticles is unique and quite different since microparticles have a larger surface-to-volume ratio than at the macro scale (Vert et al., 2012). According to International Union of Pure and Applied Chemistry (IUPAC) guidelines "Terminology for biorelated polymers and applications (IUPAC Recommendations 2012)", microparticles are defined as particles with dimensions between 1×10^{-7} and 1×10^{-4} m, even though the lower limit between micro sizing and nanosizing is still a matter of debate since nanoparticles cover only the range of particle dimensions with 0.1–100 nm (Vert et al., 2012). This study followed the IUPAC guidelines for microparticles. Generally, biochar prepared via pyrolysis process are of larger dimensions, such as millimeters and micrometers depending upon the source material and method of production and are used as obtained from the process (Demirbas, 2004; Lei et al., 2009). The effort to classify micro particles according to size is uncommon except for nanoparticles (Kambo and Dutta, 2015; Yan et al., 2013). Hence, lacuna still exists in this field of research. Most of the previous studies were carried out on crude biochar (Banerjee et al., 2014; Shih, 2012; Yao et al., 2012). Maximum removal efficiencies for methylene blue observed in these studies were 4.58 mg g^{-1} for untreated saw dust biochar (Banerjee et al., 2014), 8.07 mg g^{-1} for rice husk biochar (Shih, 2012) and 16.75 mg g^{-1} for pine sawdust biochar (Cheng et al., 2013). Few recent studies evaluated the efficiency of biochar nanoparticles in combination with other nanomaterials used for various applications, such as a catalyst (Saxena et al., 2014; Yan et al., 2013). No study data exists, to the best of our knowledge for biochar nanoparticles as a standalone adsorbent for methylene blue. In a recent study, magnetic Fe_3O_4 nanoparticles coated with sub-nano biochar exhibited excellent adsorption capacity of 349.40 mg g^{-1} for crystal violet (Sun et al., 2015). Crystal violet is a dye such as methylene blue, used for the adsorption capacity characterization of newly synthesized adsorbents. It is expected that nano biochar might exhibit excellent adsorption capacity over raw biochar or micro biochar because of its largest surface area; however production costs and fouling at times can limit the advantages. On the other hand with microparticles, an increase in adsorption potential can be expected in comparison with biochar in as obtained form without a vast increase in production cost. Moreover, synthesis and characterization of biochar microparticles for adsorption is a relatively untouched area and further research is needed in this field. In general, nanoparticles agglomerate in liquid and which will reduce the adsorption capacity since agglomeration will reduce the effective surface area of the nanoparticles (Kalia et al., 2011). In the case of biochar microparticles, the possibility for agglomeration can be ruled out in comparison with nanoparticles. In addition, because of its unique environmental properties, carbon nanoparticles are toxic to many organisms (Brar et al., 2010; Firme Iii and Bandaru, 2010). Hence, disposal of nanoparticles after utilization can be a major issue. While considering biochar as a waste management option and further producing "toxic nanoparticles", is not an effective method for waste reduction. Hence, biochar microparticles can be used as an effective non-toxic adsorbent as well as a waste management option.

In this study, the focus was to evaluate the general adsorption potential of biochar microparticles (derived from various sources) based on methylene blue (MB) adsorption experiments. MB was considered as a model for visible pollution as a result of its strong adsorption onto solids and toxicity to humans and animals (Sun et al., 2013). The equilibrium data of the adsorption process were used to study the adsorption mechanism of the MB molecules. This study also aimed to check the adsorption behavior of biochar microparticles.

2. Materials and methods

2.1. Materials

Case studies of three biochar samples are presented. The first biochar sample (BC-PW) was obtained from Pyrovac Inc. (Quebec (Qc), Canada). BC-PW was derived from pine white wood (80% v/v) purchased from Belle-Ripe in Princeville and the rest was spruce and fir (20%). BC-PW was produced at 525 °C under atmospheric pressure for 2 min in the presence of nitrogen and used as obtained from the reactor outlet. The second biochar sample (BC-PM) was obtained from "Research and Development Institute for Agri-Environment" (IRDA), Quebec (Qc), Canada. This biochar was derived from solid fraction of pig slurry and prepared at 400 °C for 2 h at 15 °C/min increase in temperature in the presence of nitrogen at a flow rate of 2 L min^{-1} during heating. The third biochar sample (BC-PD) was prepared at INRS – ETE (Quebec (Qc), Canada) and it was obtained from cardboard waste material via pyrolysis technique. Pyrolysis was performed at 500 °C at 15 °C/min in the presence of nitrogen at a flow rate of 2 L min^{-1} and for 2 h. Pine wood, pig manure and cardboard materials are commonly produced waste materials in Canada and which can be used for the production of biochar without any further pre-treatment. Powdered activated carbon (AC) was used as positive control for the adsorption studies to compare the adsorption results and was purchased from Fisher scientific (Ottawa, Canada).

Methylene blue dye (MB) shows strong adsorption to solids and it is widely recognized for its usefulness in characterizing materials (Cheng et al., 2013; Inyang et al., 2014) and the dye was purchased from Fisher scientific (Ottawa, Canada). A stock solution of 1000 mg L^{-1} MB was prepared in an amber colored volumetric flask and diluted to the required concentrations (500–10 mg L^{-1}) in deionized water. MB used in this study was analytical grade

2.2. Biochar microparticles preparation

Biochar microparticles were prepared from all the aforementioned biochar samples with a series of size reductions using mortar and pestle. Subsequently, the particles were sequentially sieved through ASTM 20, 50 and 200 numbered sieves for 10 min and particle size obtained was 850–300 μm (S1-large sized), 300–75 μm (S2-medium sized) and less than 75 μm (S3-microparticles). The particle size and size distribution were further confirmed using Horiba particle size analyzer (LA-950 Laser Particle Size Analyzer). In comparison with other methods, such as vapor deposition method for nanoparticle production, dry grinding method does have its own advantage, such as cost-effectiveness and simplicity.

2.3. Biochar and microparticles characterization

Particle size distribution analysis of microparticles was performed using a Horiba particle size analyzer (LA-950 Laser Particle Size Analyzer, HORIBA, Edison, NJ, USA). The analysis was carried out in triplicate and the mean value was taken. The specific surface area of each sample was also obtained from microparticle size analyzer and was expressed in cm^2/cm^3 of water. The surface characteristics, such as porosity and pore distribution were analyzed using field emission-scanning electron microscopy. Particles were coated with gold (plasma state) prior to the analysis to minimize sample charging. The ash and moisture content of BC-PW, BC-PM, and BC-PD was analyzed as per ASTM methods (ASTM D1762–84).

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