Waste Management 79 (2018) 385–394

Contents lists available at ScienceDirect

Waste Management

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

Production, characterization and adsorption studies of bamboo-based biochar/montmorillonite composite for nitrate removal

Eva Viglašová [a,d,*], Michal Galamboš [a], Zuzana Danková [b], Lukáš Krivosudský [c], Christian L. Lengauer [e], Rebecca Hood-Nowotny [d], Gerhard Soja [d], Annette Rompel [c], Marek Matík [b], Jaroslav Briančin [b]

[a] Comenius University in Bratislava, Faculty of Natural Sciences, Department of Inorganic Chemistry, Ilkovičova 6, 842 15 Bratislava, Slovak Republic
[b] Institute of Geotechnics, Slovak Academy of Sciences, Watsonova 45, 040 01 Košice, Slovak Republic
[c] University of Vienna, Faculty of Chemistry, Department of Biophysical Chemistry, Althanstraße 14, 1090 Vienna, Austria
[d] Austrian Institute of Technology GmbH, Energy Department, Environmental Resources and Technologies, Konrad-Lorenz-Straße 24, 3430 Tulln, Austria
[e] University of Vienna, Faculty of Geosciences, Geography, and Astronomy, Department of Mineralogy and Crystallography, Althanstraße 14, 1090 Vienna, Austria

ARTICLE INFO

Article history:
Received 1 April 2018
Revised 29 June 2018
Accepted 4 August 2018

Keywords:
Biochar
Montmorillonite
Composite
Characterization
Nitrate

ABSTRACT

Biochar is a promising immobilization tool for various contaminants in liquid wastes, aqueous solutions and soils. To further improve the sorption characteristics, a biochar/montmorillonite composite was produced and synthesized in an experimental pyrolysis reactor, using bamboo as biomass feedstock. The composite was characterized by physico-chemical and structural methods (FTIR, SEM, SEM/EDX, SSA, Low temperature nitrogen adsorption method). Based on these methods, the successful preparation of a bamboo based biochar/montmorillonite composite preparation has been demonstrated. The particles of montmorillonite were distributed across the biochar surface. The adsorption studies for removal nitrates from aqueous solutions were investigated by a batch method at laboratory temperatures. The experimental data were fitted by three adsorption models (Langmuir, Freundlich and DR; $R^2 > 0.93$). The maximum adsorption capacity achieved by biochar at pH 4, was about 5 mg g^{-1} and by biochar/montmorillonite composite 9 mg g^{-1}. The results suggest that the bamboo-based biochar/montmorillonite composite can be used effectively in the treatment of industrial effluents or waste water containing anionic pollutants such as nitrates.

1. Introduction

Biochar (BC) is a carbon rich product, synthesized through carbonization of biomass in an oxygen limited environment (Lehmann and Joseph, 2009), it has been recognized as a multifunctional material for energy and environmental applications. A variety of applications include: carbon sequestration (Kuzyakov et al., 2009; Woolf et al., 2010), greenhouse gas emission reduction (Singh et al., 2010), land remediation, contaminant immobilization (Ahmad et al., 2014; Mohan et al., 2014) and soil fertilization (Chan et al., 2008; Yong et al., 2016).

In addition to extensive scientific work on the use of biochar for tackling environmental issues, several methods have also been developed to modify biochar, to achieve novel structures and surface properties, in order to enhance its remediation efficacy and environmental benefits (Ok et al., 2015; Yong et al., 2016; Thinnes et al., 2017; Li et al., 2017a,b). The chemical and physical properties of biochar mainly depend on the type of feedstock and pyrolysis conditions (e.g. residence time, temperature, heating

Abbreviations: BC, biochar; BCA, bamboo based biochar; BCD, bamboo based biochar composite with montmorillonite K10; BET, Brunauer-Emmett-Teller; BJH, Barrett Joyner Halenda; CHNS, Carbon, Hydrogen, Nitrogen and Sulphur analysis; DI, deionized water; DR, Dubinin-Radushkevich isotherm; EDX, Energy dispersive X-ray detector; FE/SEM, Field emission scanning electron microscope; FTIR, Fourier transform infrared spectroscopy; IBI, International biochar initiative; IUPAC, International union of pure and applied chemistry; MK10, Montmorillonite K10; OECD, Organization for Economic Co-operation and Development; SSA, Specific surface area; TG, Thermogravimetric analysis; UV, Ultraviolet spectroscopy.

* Corresponding author at: Comenius University in Bratislava, Faculty of Natural Sciences, Department of Inorganic Chemistry, Ilkovičova 6, 842 15 Bratislava, Slovak Republic.

E-mail addresses: eva.viglasova@fns.uniba.sk (E. Viglašová), michal.galambos@fns.uniba.sk (M. Galamboš), orolinova@saske.sk (Z. Danková), lukas.krivosudsky@univie.ac.at (L. Krivosudský), christian.lengauer@univie.ac.at (C.L. Lengauer), Rebecca.Hood@boku.ac.at (R. Hood-Nowotny), Gerhard.Soja@ait.ac.at (G. Soja), annette.rompel@univie.ac.at (A. Rompel), matik@saske.sk (M. Matík), briancin@saske.sk (J. Briančin).

https://doi.org/10.1016/j.wasman.2018.08.005
0956-053X/

Nomenclature

b	the adsorption ratio of adsorption/desorption rates	S_{BET}	the specific surface area
C_0	the initial concentration	S_T	the external surface area
C_{eq}	the equilibrium concentration	V	the volume of aqueous solution
C_s	the adsorption capacity (Langmuir isotherm)	V_{micro}	the volume of micropore
C_{smax}	the maximum of adsorption capacity/ site saturation	V_{tot}	the volume of total pore volume
K_{ad}	the DR isotherm constant	ε	the DR isotherm constant
K_F	the Freundlich isotherm constant		
Q_e	the adsorption capacity (calculations)		
q_s	the theoretical isotherm saturation capacity		

rate, and reactor type) (Lehmann and Joseph, 2009). Recently a new concept, engineered biochar has gained interest, in which engineered biochar is prepared by impregnation of minerals (e.g. clays) onto the biochar surface (Rajapaksha et al., 2016).

Clay minerals have been studied extensively for contaminant immobilization as they play a significant role in the field of environmental and toxic waste management (Jenne, 1998). Layered silicate is a low cost high abundance mineral, which consists of layers of tetrahedral silicate sheets and octahedral hydroxide sheets (Zilg et al., 2011). Clays are potentially good adsorptive material as a result of their large surface areas, high cation exchange capacity, chemical and mechanical stability, and layered structure (Rozić et al., 2000). The adsorption of heavy metals onto natural clays has recently been studied by various researchers (Abou-El-Sherbini and Hassanien, 2010; Bhattacharyya and Gupta, 2006; Ma et al., 2004; Orhan and Kocaoba; Sihrvani et al., 2015; Taghipour and Jalali, 2018; Vieira et al., 2010; Zhou et al., 2017; Xu et al., 2017; Wu et al., 2011). Therefore, clays have been used in many studies, mainly montmorillonite, to demonstrate their effectiveness for the removal of metal ions mainly in cationic forms from aqueous solutions. However, anionic compounds (e.g. phosphate, nitrate, sulphate, As-, Cr- compounds) do not sorb very well to unmodified clays, or onto unmodified biochar. It is posited that that it is possible to improve the removal efficiency by modification of biochar surface (Chen et al., 2017; Mazarji et al., 2017; Rajapaksha et al., 2016).

As a result, recently, layered silicates have been investigated for the modification of various materials (Dehouche et al., 2012; Yu et al., 2007), including biochar (Li et al., 2017,a,b; Mumme et al., 2018; Rawal et al., 2016; Ying et al., 2014; Zhang et al., 2018). These co-products contribute to the development of such innovative low-cost sorbents for the improvement of the environmental quality in contaminated regions and in an attempt to decrease eco-toxic effects of anionic pollutants in developing countries.

Low-cost bamboo biomass as feedstock has lot of advantages, it is a fast-growing material with high strength-weight ratio, it also has enormous potential for alleviating many environmental problems to which the world is facing today (Chen et al., 2017; Li et al, 2014). Biochar acts as a good porous carrier to support and host the distributed fine clay particles on the surface and within the pore matrix. The most commonly used guest clay minerals are montmorillonite, gibbsite and kaolinite (Li et al., 2017a,b; Mumme et al., 2018; Zhang, 2013).

All over the world, groundwater plays a crucial role as a source of drinking water in rural communities and urban areas. Unfortunately, industrial and agricultural activities increased the formation of inorganic pollutants and other contaminants, which has raised public concern about groundwater quality. A number of inorganic anions such as nitrates (NO_3^-), have been found at potentially harmful concentrations in numerous drinking water sources. (Bhatnagar and Sillanpa, 2011). Higher concentration of NO_3^- in drinking water poses a potential risk to the environment and public health. Nitrates can stimulate eutrophication of surface waters including extreme algal growth, if nitrates are the rate-limiting nutrients for the process. Nitrate contaminated water supplies have also been linked to outbreaks of infectious disease (Bhatnagar and Sillanpa, 2011; Loganathan et al., 2013).

A fundamental understanding of the changes in the biochar structure as function of mineral additives is therefore crucial for the implementation of strategies to design biochar with superior properties, tailored to enhance performance. For this purpose, the biochar/montmorillonite composite was synthesized and a detailed analysis of structure was described. Prepared and characterized materials were tested for removal of nitrates from aqueous solutions. The objective of this study was to test the efficacy of these composites as a viable tool in wastewater treatment and to relate the nitrate sorption capacity to the product characteristics.

2. Materials and methods

2.1. Materials

All chemicals and solvents used during experiments were of analytical grade quality. Agricultural bamboo waste from green way golden bamboo (*Phyllostachys viridiglaucescens*), was used as biomass input for bamboo-based biochar (BC-A) and bamboo-biochar/montmorillonite composite preparation (BC-D). Prior to use, the bamboo was crushed and chopped into a particle size 2 cm × 2 cm × 2 cm, washed several times with deionized water (DI) (<0.4 μS cm^{-1}), to remove various impurities and oven dried at 60 °C for 5 h. The clay mineral Montmorillonite (MK10; chemical formula $(Na, Ca)_{0.33}(Al, Mg)_2(Si_4O_{10})(OH)_2{\cdot}nH_2O$, purchased from Sigma Aldrich -Merck Millipore) was used in this study to prepare mixture of pre-treated biomass feedstock. Adsorption studies were performed with solutions of $NaNO_3$ from Sigma Aldrich.

2.2. Biochar/montmorillonite composite production

The feedstock of bamboo biomass for samples preparation was pyrolyzed at 460 °C with a residence time of 120 min in a rotary furnace. To ensurean oxygen-free environment and uniform heating conditions, nitrogen (N_2) was used as flush gas. After pyrolysis the biochar product was ground and sieved to a particle size of 0.5–1 mm. The material was rinsed several times with DI water, oven dried at 80 °C for 24 h and stored at 22 °C in polypropylene boxes for characterization and adsorption experiments.

Bamboo-biochar composite with montmorillonite (BC-D) was produced from bamboo feedstock prepared by steps described above. A clay suspension was prepared by adding 2 g of clay material MK10 powder to 500 mL of DI water followed by sonication of the suspension with sonicator (Branson ultrasonic bath). Prepared bamboo feedstock (10 g) was immersed in suspension with MK10 and this mixture was stirred for 2 h. The feedstock was than separated from mixture and dried at 80 °C for 24 h. The pre-treated bio-