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INORGANIC NITROGEN CONTAMINANT REMOVAL FROM RUNOFFS BY BIOMASS-DERIVED ADSORBENT

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Abstract

Inorganic nitrogen contaminants (INCs) pose a great risk to the ecosystems since they are harmful to many organisms and are stable in the environment. Agricultural runoffs are widely blamed for environmental pollution due to the presence of INCs, as substantial amounts of unutilized nitrogenous compounds applied as fertilisers eventually enter the environment and contaminate ground and surface water bodies. These excess nutrients lead to eutrophication, water quality degradation, and numerous health issues which emphasises the need of efficient removal strategies. Incorporating waste to value approache is one of the principal objectives of current water treatment strategies. Hydrochar is a carbon-rich, value-added solid product derived from hydrothermal carbonisation (HTC) of biomass, which can be used in environmental remediation. Hydrochar's physiochemical properties are affected by HTC process conditions, which in turn affects the optimum nutrient removal. This paper introduces the study conducted to optimise surface chemistry of hydrochar, derived from waste biomass, for efficient removal of ammonium.

Introduction

Unutilised nitrogenous compounds contaminate the water bodies and other compartments of the environment. These are applied to agricultural lands via fertiliser application. (Nancharaiah et al., 2016). Ammonium is the most common form of reactive nitrogen, among all the forms of nitrogen contaminants, in water and wastewaters (Conley et al., 2009; Cui et al., 2016), which can cause various pollution issues. Hence, it is important to research effective ammonium removal methods. As most of the conventional water treatment methods suffer from complicated configuration or maintenance, high-cost involvement, low removal rates or

other drawbacks (Hung et al., 2003; Bódalo et al., 2005), physical removal via contaminants adsorption is a popular method among practitioners (Jorgensen and Weatherley, 2003; Tekerlekopoulou et al., 2013). Among the wide-ranging variety of adsorbents present, hydrochar derived from biomass waste is gaining considerable attention recently as it can overcome most of the aforementioned challenges (Fang et al., 2015; Flora et al., 2013; Takaya et al., 2016).

Hydrochar is a carbon-rich, energy-dense, value-added solid material processed via hydrothermal carbonisation of biomass and waste streams (Berge et al., 2011; Libra et al., 2011; Sevilla et al., 2011; Titirici et al., 2007). It is produced in the presence of subcritical water and an oxygen-free environment, subjected to autogenous pressure in the range of 2–10 MPa and temperatures 200–300 ^{0}C (Funke and Ziegler, 2010; Libra et al., 2011; Takaya et al., 2016). Various types of biomass waste are being utilised as the feedstock material. It mainly consists of three basic polymers; cellulose $(C_6H_{10}O_5)_x$, hemicelluloses $(C_5H_8O_4)$m and lignin $[C_9H_{10}O_3(COH_3)_{0.9\text{-}1.7}]$n with small extractives fats, proteins, sugars, arrowroots, water, ash, besides additional mixtures (Fatih Demirbas et al., 2011; Dukua et al., 2011; Verma et al., 2012). These components undergo structural rearrangement during HTC process and produce the resulting hydrochar (Libra et al., 2011).

Ammonium adsorption onto carbon adsorbents

Adsorption mechanism can be either physical or chemical. Adsorption process may involve several adsorbent-adsorbate interactions such as electrostatic attraction, ion exchange, surface complexation, and physical adsorption (Tan et al. 2015). Physical adsorption is caused due to Van der Waals forces occurring on the planes of surfaces (Atkas and Ferhan, 2011) while chemisorption occurs on edges in the presence of heterogeneous surface functional groups forming intermediate products (Atkas and Ferhan, 2011; Figueiredo and Pereira, 2010). Physiochemical properties of the material are important for adsorption process and further, studies report that chemical properties of the functional groups on chars' surface influence NH^{+}_{4} adsorption more than physical properties (Spokas et al. 2012). Yang and his colleagues have reported that a larger surface area is not significant for adsorption of ammonium which indicates physical adsorption is not significant in ammonium adsorption (Yang et al., 2018). Some other researchers have also stated that char surface groups may play a more important role than surface area and porosity in both biochars and hydrochars (Bargmann et al., 2014; Spokas et al., 2011). Hence, it is important to study the physiochemical properties of hydrochar

to develop an adsorbent which can efficiently remove ammonium. As the HTC conditions affect the physiochemical properties of hydrochar, it is important to have an understanding on how variations in these parameters affect the ammonium adsorption by altering the HTC conditions.

Effect of HTC conditions

During the HTC process, the rate of destruction of the polymeric structure of biomass typically depends upon the reaction time, temperature, and reaction medium. Among all of them, temperature is the most influential factor (Kambo and Dutta, 2015). A study conducted on HTC of plant biomass at different temperatures (200^0C, 250^0C and 300^0C) has reported a decrease of hydrochar yield with increasing production temperature, due to greater degree of biomass dissolution occurring at higher temperatures (Fang et al., 2015). With the increase of processing temperature, hydrochar yield is decreased due to greater degree of biomass dissolution occurring at higher temperatures (Fang et al., 2015).

Moreover, higher temperatures generate HTC carbons with a higher degree of aromatisation, resulting in enhanced chemical stability and structural order (Camilo Falco et al., 2013). During HTC, cleavage and cracking of weak oxygen and hydrogen bonds occur at higher temperatures, resulting in carbon content increase while hydrogen and oxygen content decrease (Qian et al., 2013). This can be confirmed by conducting the elemental analysis of the sample. Higher H/ C and O/C ratios suggest more presence of functional groups and present a possibility of chemical bonding of polar compounds such as NH_4^+. Studies confirm that hydrochar have got higher content of hydrogen and oxygen on surface which indicates the presence of more activated sites and stable carbon-oxygen complexes (Guerrero et al., 2005). Also, more oxygen on the surface is directly correlated with the Cation Exchange Capacity (CEC) which in turn indicates the presence of oxygen-containing functional groups which are crucial for ammonium adsorption.

Relationship of HTC temperature with surface area and pore volume of hydrochars is different. The decrease in surface area of hydrochar is due largely to the pore wall collapse as a result of deformation, melting, and fusion at high-temperature (Wagner, 1973). Reaction time influences the HTC process until a certain time, after which it does not have any specific effect on the process (Sasaki et al., 2003). Carbon content increases while the O and H content decreases as the reaction time increases (Zhang et al., 2019). As the reaction severity increases

O-H, C=O C-O groups decrease due to dehydration while the C==C bond increases indicating aromatic nature of the hydrochar (Zhang et al., 2019).

Results and Discussions

In this study, waste-biomass was subjected to different HTC conditions, including changes in temperature and reaction times, presence of different acids and bases during HTC, single stage and two-stage Hydrothermal Processing (HTP), adjustment of pH *etc*., to vary the surface chemistry of resulting hydrochar in order to determine optimal ammonium removal conditions. Our results show that ammonium adsorption on hydrochar was mainly chemisorption and optimal ammonium removal obtained was up to 10 times the benchmark adsorption efficiency of biochar derived from the same source material. A manuscript submission to a journal is under process and hence, detailed discussion about Materials and Methods and Results and Discussion could be available soon through science search databases.

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