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Removing ammonium from water using modified corncob-biochar

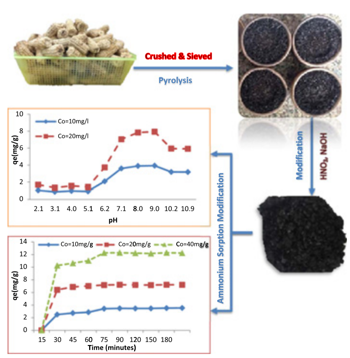
Thi Mai Vu [a], Van Tuyen Trinh [b], Dinh Phuong Doan [c], Huu Tap Van [d], Tien Vinh Nguyen [e,*], Saravanamuthu Vigneswaran [e], Huu Hao Ngo [e,*]

[a] Hanoi University of Natural Resources and Environment, Ministry of Natural Resources and Environment, 44 Phu Dien, Tu Niem, Ha Noi, Viet Nam
[b] Institute of Environmental Technology, Vietnam Academy of Science and Technology, A30, 18 Hoang Quoc Viet Street, Ha Noi, Viet Nam
[c] Institute of Materials Science, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet Street, Ha Noi, Viet Nam
[d] Faculty of Environment and Earth Science, Thai Nguyen University of Sciences, Tan Thinh ward, Thai Nguyen city, Viet Nam
[e] Faculty of Engineering and IT, University of Technology, Sydney (UTS), PO Box 123, Broadway, Sydney, Australia

HIGHLIGHTS

- Modified conditions for biochar prepared from corncob were studied.
- Materials' features before and after modification were determined by BET, FTIR, SEM.
- Highest adsorption capacity of NH_4^+-N on modified material is 22.6 mg/g.
- Adsorption kinetics of NH_4^+-N by MBCC2 followed the pseudo-second order kinetic model.
- Langmuir, Sips adsorption isotherm models could simulate well the adsorption behavior.

GRAPHICAL ABSTRACT



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ABSTRACT

Ammonium pollution in groundwater and surface water is of major concern in many parts of the world due to the danger it poses to the environment and people's health. This study focuses on the development of a low cost adsorbent, specifically a modified biochar prepared from corncob. Evaluated here is the efficiency of this new material for removing ammonium from synthetic water (ammonium concentration from 10 to 100 mg/L). The characteristics of the modified biochar were determined by Brunauer-Emmett-Teller (BET) test, Fourier transform infrared spectroscopy (FTIR) and Scanning electron microscopy (SEM). It was found that ammonium adsorption on modified biochar strongly depended on pH. Adsorption kinetics of NH_4^+-N using modified biochar followed the pseudo-second order kinetic model. Both Langmuir and Sips adsorption isotherm models could simulate well the adsorption behavior of ammonium on modificated biochar. The highest adsorption capacity of 22.6 mg NH_4^+-N/g modified biochar was obtained when the biochar was modified by soaking it in HNO_3 6 M and NaOH 0.3 M for 8 h and 24 h, respectively. The high adsorption capacity of the modified biochar suggested that it is a promising adsorbent for NH_4^+-N remediation from water.

1. Introduction

Ammonium is one of the major pollutants affecting both groundwater and surface water. Although the natural level of ammonium in surface water and groundwater is low (below 3 mg/L), the high

* Corresponding authors.
E-mail addresses: Tien.Nguyen@uts.edu.au (T.V. Nguyen), HuuHao.Ngo@uts.edu.au (H.H. Ngo).

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ammonium concentrations are found in some areas. In Vietnam, high ammonium concentrations of 70 mg/L and more than 55 mg/L were found in groundwater in Nam Du and Phu Lam villages, Hanoi (Lindenbaum, 2012; Vietnam Environment Agency, 2016). The high level of human activities such as intensive development of livestock farms or the severe usage of nitrogen fertilizers are the causes of the high levels of ammonium in these areas (Vietnam Environment Agency, 2016; WHO, 2016). High ammonium concentrations are also found in the surface water in Vietnam. Recent reports by the Hanoi Centre for Environmental and Natural Resources Monitoring and Analysis (2016) show that the ammonium concentration in Van Chuong lake in Hanoi was 15.5 mg/L, 31 times higher than surface water quality standards of Vietnam.

Current water treatment methods such as coagulation and filtration are not able to remove ammonium effectively, especially in decentralized water treatment systems. Adsorption is considered to be an economic and effective method for removing ammonium (Moradi, 2011; Yahaya et al., 2011). A number of adsorbents such as, biochar, activated carbon (AC), zeolite with and without modification have been trialed for removing ammonium via the water treatment process (Balci and Dinçel, 2002; Vassileva et al., 2008; Lin et al., 2009; Huang et al., 2010; Huo et al., 2012; Otal et al., 2013; Cui et al., 2016).

A previous study by Moreno-Castilla et al. (2000) confirmed that the surface chemistry plays a more important role than the BET surface area of adsorbents and the pore structure in adsorbing inorganic compounds from groundwater. The modification strategy is a popular method to change the surface chemistry and improve the adsorption efficiency of adsorbents. The oxidation process with H_3PO_4, HNO_3, H_2O_2 or $KMnO_4$ has been applied for modifying the AC's surface characteristics (Moreno-Castilla et al., 2000; Soto-Garrido et al., 2003; Vassileva et al., 2008; El-Wakil et al., 2014). Soto-Garrido et al. (2003) investigated the chemical modification of activated carbon made from peach stones in adsorbing ammonium. Their results indicated that modified activated carbon with HNO_3 6 M was more efficient in ammonium adsorption than when applying H_2O_2 6 M. More recently, El-Wakil et al. (2014) analyzed the removal of Pb^{2+} from groundwater by modified activated carbon generated from hyacinth. In their study, hyacinth was sequentially impregnated with H_3PO_4 and HNO_3 solutions (impregnation ratios of 1:3 and 1:1 w/v, respectively). Halim et al. (2013) also found that the activated carbon modified by HNO_3 (37%) and NaOH 1 M had better ammonium adsorption capacity than the original activated carbon. Each gram of this material could adsorb 19.34 mg ammonium, four time higher than the original one (4.5 mg/g) when treating groundwater of 685–735 mg NH_4^+/L.

Biomass recently has been used to produce AC for removing different pollutants from water due to its low cost and wide availability. Corncob waste is generally used as a food source for livestock and the excess can be burnt. In Vietnam, million tons of agricultural by-products like corn cob, rice straw, etc., are burnt every year in the field which causes air, soil and water pollution. The reuse of these low cost agricultural by-products as new adsorbents for wastewater treatment will contribute to the reduction of green-house emissions. To improve their value, corncob should be used to produce AC which can then be applied to removing pollutants such as ammonium from water. Because the adsorption capacity of AC prepared from corncob is still limited, this AC needs to be modified to improve its adsorption capacity. Thus, in this study corncob was firstly carbonized at 400 °C to produce corncob biochar (BCC). The BCC was then modified by HNO_3 and NaOH to produce a modified corncob-biochar which could very efficiently adsorb ammonium to a high degree. The objective of this paper is to: (i) determine the best conditions for preparing a modified corncob biochar; and (ii) evaluate the performance of this material in removing ammonium from water through the equilibrium and kinetics studies.

2. Materials and methods

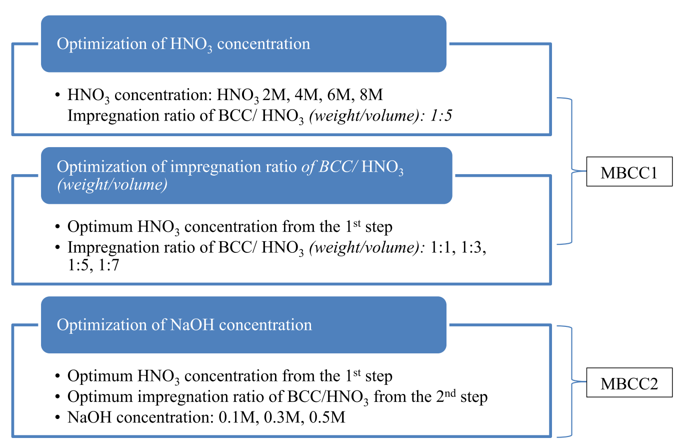
2.1. Materials

A stock solution of NH_4^+-N with a concentration of 1.0 g/L was obtained by dissolving accurately weighed 3.82 g NH_4Cl (analytical grade) in 1000 mL of deionized, distilled water in a volumetric flask. The corncob sample used in this study was collected from Da Bac district, Hoa Binh province, Vietnam. Its average moisture and ash contents were 15.71% and 8.81%, respectively.

2.2. Optimization of biochar modification

The corncob was firstly washed three times with tap water, three times with distilled water and dried in an oven at 100 °C for 2 h. The dried corncob was then crushed and sieved to a size of 0.5–2 mm. The corncob biochar BCC was prepared by heating it under slow pyrolysis at 400 °C for 1 h in a furnace (Nabertherm, model L3/11/B170, Germany). BCC was then modified by soaking it in a solution of HNO_3 for 8 h. Following that, the biochar was washed three times with distilled water. This is the first modified corncob biochar –the MBCC1. For optimizing the modified conditions for MBCC1, the HNO_3 concentration and impregnation ratio (weight/volume) of BCC/HNO_3 were varied from 2 M to 8 M and 1:1 to 1:7, respectively. The MBCC1 was then soaked in NaOH solution for 24 h, and then was washed several times with distilled water until a pH of 7–8 was reached. The dried product was referred to as the second modified corncob-biochar - MBCC2. Here the NaOH concentration was varied from 0.1 M to 0.5 M and the impregnation ratio (weight/volume) of MBCC1/NaOH of 1:20 was used. The impregnation ratio of 1:20 was selected following the findings of Trinh (2009). The HNO_3, NaOH concentrations and impregnation ratio of BCC/HNO_3 that led to the highest NH_4^+-N adsorption amount were chosen as the optimum scenario for preparing modified corncob biochar.

The experimental conditions for optimization are summarized in the following flowchart.



2.3. Characteristics of modified corncob biochar

The MBCC1 and MBCC2 samples produced at the optimizated conditions and BCC were used for characterization. The textural characteristics of samples were determined by N_2 adsorption at 77 K with an accelerated surface area and porosimeter (ASAP-200, Micromeritics). Specific surface area was calculated from the isotherms using the Brunauer–Emmett–Teller (BET) equation. SEM images were recorded using an electron microscope S-4800 (FE-SEM, Hitachi).

The surface chemical group of BCC, MBCC1, MBCC2 in terms of both quantity and quality was assessed by Boehm titration. Titration