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Removal of ammonium from groundwater using NaOH-treated activated carbon derived from corncob wastes: Batch and column experiments

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ABSTRACT

High ammonium concentration in groundwater represents a major public health concern in Hanoi, Vietnam. In this study, mesoporous activated carbon was prepared from corncob using H_3PO_4 through a one-stage chemical activation process. Corncob activated carbon (CCAC) was subsequently treated with NaOH to enhance its cation exchange capacity. The results showed that this NaOH-modified corncob activated carbon (M-CCAC) exhibited a large specific surface area (1097 m^2/g) and high total pore and mesopore volumes (0.804 cm^3/g and 0.589 cm^3/g, respectively). The batch experiments indicated that the NH_4^+-N removal was strongly dependent on the coexisting cations and pH of the solution, while in the kinetic experiments adsorption equilibrium was quickly reached within 60 min. The activation energy was calculated to be 49.7 kJ/mol. The maximum Langmuir adsorption capacity of M-CCAC exhibited the following order: 17.03 mg/g at 20 °C > 15.4 mg/g at 35 °C > 11.99 mg/g at 50 °C. The NH_4^+ adsorption process was spontaneous ($-\Delta G^\circ$) and exothermic ($-\Delta H^\circ$), and it increased the randomness ($+\Delta S^\circ$) in the system. The column experiments were conducted using real underground water to analyze the effects of different flow rates (1–3 mL/min), influent concentrations (10–40 mg/L), and bed heights (8.07–23.9 cm) on the adsorption capacity. The maximum adsorption capacity (8.69 mg/g) was achieved at a flow rate of 2 mL/min, an initial concentration of 40 mg/L, and a column height of 15.8 cm. Ion exchange was found to be the principal mechanism that controls ammonium adsorption, while pore-filling and electrostatic attraction played minor roles in the process. This study proved that M-CCAC is an effective adsorbent to remove ammonium from real groundwater.

1. Introduction

Excessive presence of ammonium could affect the quality of groundwater and surface water. In addition, high NH_4^+ concentrations in water bodies disrupt the natural nutrient cycles and increase eutrophication. Some areas in Hanoi, Vietnam were reported to have higher ammonium levels than the allowable limits, e.g., Hanoi Centre for Environmental and Natural Resources Monitoring reported that the ammonium concentration in the Van Chuong Lake in Hanoi (15.5 mg/L) was approximately 31 times higher than the surface water quality standards in Vietnam. Results of previous studies reported extremely high ammonium concentrations in the groundwater of Nam Du (approximately 70 mg/L) and Phu Lam (more than 55 mg/L) villages in Hanoi, Vietnam (Lindenbaum, 2012). The high levels of ammonium found in these areas resulted from accelerated anthropogenic activities, such as intensive development of livestock farms or excessive usage of nitrogen fertilizers (Vu et al., 2017). Vietnam has abundant surface and ground water resources (the average total runoff is 848 km^3/year); however, approximately 6 million Hanoi inhabitants receive 80% of

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their drinking water from groundwater. Therefore, high ammonium levels in water bodies represent a challenge for Hanoi.

Numerous techniques have been applied to remove NH_4^+ ions from water and wastewater (Table S1), such as ion exchange, membrane technology, adsorption, nitrification-denitrification processes, chemical precipitation, and electrochemical separation. Of these, adsorption is considered an effective, inexpensive, and simple technique for removing NH_4^+-N from waterbodies, especially at a low NH_4^+ concentration. Activated carbon (AC) has been widely used to remove numerous contaminants, including ammonium, because of its large surface area, high total pore volume, and excellent chemical stability. However, the maximum adsorption capacity of pristine AC for ammonium is relatively low, such as approximately 5.4 mg/g for avocado seed-derived AC (Zhu et al., 2016), 3.2 mg/g for rice husk-derived AC (Zhu et al., 2012), 2.3 mg/g for coconut shell-derived AC (Boopathy et al., 2013), and 0.5 mg/g for commercial AC (Shi et al., 2013). This is because the adsorption mechanism related to pore filing might play an insignificant role in the adsorption process of NH_4^+-N onto AC compared to the others (i.e., ion exchange and electrostatic attraction). Therefore, it is necessary to apply further treatment or modification to the surface of AC in order to enhance its adsorption capacity to NH_4^+ ions. According to Statistical Yearbook of Vienam 2015, the planted area and maize production in Hanoi were approximately 21,100 ha and 102,300 tons, respectively, while the corresponding data for the whole country were 1,179,300 ha and 5,281,000 tons, respectively. Therefore, corncob wastes can be considered an abundant, renewable, and cheap feedstock to prepare AC.

In this study, corncob waste-derived activated carbon (CCAC) was prepared through one-stage chemical activation using H_3PO_4. To enhance the cation exchange capacity, CCAC was further treated with NaOH [Na-modified corncob activated carbon (M-CCAC)]. The adsorbents were characterized using nitrogen adsorption/desorption isotherm, pH at the point of zero charge (pH_{PZC}), scanning electron microscopy, Fourier transform infrared spectroscopy, and thermo-gravimetric analysis. Batch experiments were conducted to assess the effects of various operation conditions (i.e., the pH of the solution, coexisting cation, contact time, initial ammonium concentration, and temperature) on the NH_4^+ adsorption from an aqueous solution. In addition, the effects of relevant dynamic parameters, such as solution flow rate, adsorbent bed height, and influent ammonium concentration on the NH_4^+ removal from groundwater were examined in a fixed-bed column. Moreover, the adsorption mechanism was also investigated.

2. Materials and methods

2.1. Adsorbent preparation

Raw corncob materials were obtained from the local market in Hanoi, Vietnam, and they were washed with tap water at least twice and then with deionized distilled water to remove any adhering dirt or impurity. They were dried in an oven at 80 °C for 48 h. The dried corncob (CC biosorbent) was ground and sieved to obtain particles with sizes that ranged from 0.5 to 2 mm.

CCAC was prepared through one-stage chemical activation using H_3PO_4, in which a known mass of the dried raw CC materials was directly mixed with H_3PO_4 and pyrolyzed to obtain activated carbon. Figure S1 shows the optimal conditions of AC preparation: a pyrolysis temperature of 400 °C, a pyrolysis time of 90 min, an H_3PO_4 concentration of 50%, and an impregnation ratio (volume of H_3PO_4 per mass of corncob) of 1.5/1. The pyrolysis process was conducted in a non-circulated air atmosphere using a porcelain crucible covered with a lid at a heating rate of 15 °C/min. Following the carbonization process, the CCAC sample was thoroughly washed with 0.1 M HCl to dissolve the ash and inorganic salts. Finally, deionized distilled water was used to wash the samples until the pH of the filtrates stabilized. The CCAC yield was determined by calculating the difference between the dried masses before and after pyrolysis (approximately 81.5% ± 0.75; $n = 4$).

To improve the adsorption capacity, CCAC was treated with NaOH (0.3 M) at a constant ratio of 20/1 (v/w), and then it was vigorously stirred for 24 h at 30 °C. M-CCAC was then washed repeatedly with deionized water until the pH value of the filtrate reached 7.0, dried at 105 °C for 48 h, and stored in airtight plastics. The adsorbents (i.e., CC, CCAC, and M-CCAC) with 0.1–0.8 mm particle size were used in the adsorption experiments in this study.

2.2. Activated carbon properties

The textural properties of M-CCAC were measured using a sorptometer (Micromeritics ASAP, 2020) at 77 K, the morphology of M-CCAC was examined using scanning electron microscopy (SEM; Hitachi S-4800, Japan), and the thermal stability of corncob was measured by thermo-gravimetric analysis (TGA; DuPont TA Q50, USA). The experiment was carried out starting at room temperature until the temperature reached 900 °C at a heating rate of 10 °C/min in an inert nitrogen environment, i.e., in the absence of oxygen. The available functional groups on the adsorbent surface were detected using Fourier transform infrared spectroscopy (FTIR; NEXUS 670, Nicolet). The pH_{PZC} was determined using the drift method. More detailed information on this method can be found in the study of Tran et al. (2017). The acidic groups and basic sites on the adsorbent surfaces were determined through Boehm titration following the standardization protocol proposed by Goertzen and coworkers (2010). The numbers of moles of the functional groups on the adsorbent surface were determined from the equations reported in our recent publication (Tran et al., 2017).

2.3. Batch adsorption experiment

All the concentrations of ammonium solution used in the experiment were diluted from a 1.0 g/L NH_4^+-N stock solution, which was prepared by dissolving accurately weighed 3.819 g of NH_4Cl (analytical grade) in 1000 mL of deionized distilled water.

Approximately 0.1 g of the adsorbent was added to 50 mL of the solution with the predetermined ammonium concentration in a 125-mL Erlenmeyer flask. The initial pH of the solution was adjusted to the target values using 1 M NaOH or 1 M HCl. The flask was immediately covered with a parafilm and shaken at 150 rpm in a water bath isothermal shaker (GFL 1083, Germany) until the end of the contact time. Next, the adsorbent-adsorbate mixture was immediately separated using glass fiber filter. The ammonium concentration was determined via colorimetric method using UV-VIS spectrophotometer (DR5000, Hach) at $\lambda = 640$ nm. The operation conditions (i.e., pH value of the solution, contact time, temperature, and ammonium concentration) of the four adsorption experiments (i.e., pH dependence, the presence of other cations, kinetic, and isotherm) are provided alongside every figure.

The amounts of ammonium adsorbed at equilibrium (q_e; mg/g) and time t (q_t; mg/g) were calculated using the following mass balance equations:

$$q_e = \frac{(C_o - C_e)}{m}V \quad (1)$$

$$q_t = \frac{(C_o - C_t)}{m}V \quad (2)$$

where C_o (mg/L), C_t (mg/L), and C_e (mg/L) are the ammonium