



Fabrication of Carbonaceous-Modified Halloysite Nanotubes for the Removal of Metal Ions from Aqueous Solution

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Abstract: Halloysite nanotube-carbonaceous (HNT-C) composites were fabricated through one-pot hydrothermal carbonization of fructose and sodium carboxymethyl cellulose for use as an adsorbent for the removal of Pb(II), Zn(II), and Cu(II) from wastewater. The composites were chemically treated with sulfuric acid after carbonization. The acidic treatment of HNT-C structures contributed to a larger specific surface area and surface functionality, which was favorable for adsorbing more metal ions. Carbonaceous-modified HNTs were characterized by elemental analysis, FT IR, XRD, and BET analysis. Metal ion adsorption experiments were conducted with solutions containing low and high total metal ion concentrations (Cu, Zn, Pb) by mixing with HNT-C composites at a solid/liquid ratio of 1.0 and 10.0 g/L. The results indicated that the HNT C composites exhibited promising Zn(II) adsorption up to 94%, while no Zn(II) adsorbed onto unmodified HNTs. The amount of Pb(II), Zn(II), and Cu(II) ions that were taken up increased as the amount of adsorbent was increased up to 10 g/L in an aqueous solution. The HNT-C composites exhibited the highest adsorption efficiency for Pb(II) ions.

Keywords: Adsorbent, adsorption, halloysite nanotube, heavy metal, wastewater.

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1. INTRODUCTION

Water pollution, which increases due to different factors day by day, is very dangerous not only for living things in the water but also for humans and plants in nature. Therefore, it is important to provide preventive measurements against water pollution and to create a culture in this regard. The main reason for the pollution of water is the different pollutants that are drained into nature without any treatment. These pollutants mix with the surface and groundwater and both disrupt their chemical formula and affect it physically (1). Water may become contaminated by the accumulation of heavy metals such as lead, copper, zinc, cadmium, and mercury through emissions from rapidly expanding industrial areas, mine tailings, disposal of high metal wastes, leaded gasoline and paints, pesticides, wastewater irrigation, and electronic waste (2). Heavy metal accumulation is the most dangerous dimension of chemical water pollution. Heavy metals have toxic effects when they exceed their concentration limits in both water and living organisms. They can cause health problems by affecting the psychological structure, even at very

low concentrations. The negative effects of polluted water on people are investigated by many disciplines, and the importance of measures to prevent pollution is emphasized. The World Health Organization (WHO) recommends 1.5, 0.015, and 5.0 mg/L as the maximum tolerable levels of copper (Cu (II)), lead (Pb (II)), and zinc (Zn (II)) ions in drinking water, respectively (3).

Halloysite nanotube (HNT) is a nanoclay with a tube-like morphology, and is composed of a bilayer aluminosilicate structure with a 1:1 Al:Si ratio (4). It has been shown that HNTs are good adsorbents used to remove metal ions from wastewater (5) due to the specific crystal formations, and the electrical and chemical characteristics of the external and internal surfaces of HNT. The applications of HNT structures are developing, particularly because HNTs are environmentally friendly, inexpensive, and have compatible behavior in preparing composites (6-10). Modified HNTs usually exhibit increased stability, due to reduced agglomeration and increased zeta potential values (11). HNTs can be used to adsorb various compounds and contaminated substances (12, 13). Kiani et al.

utilized the Taguchi technique to identify the optimal conditions for HNTs to remove Zn (II) from aqueous solutions (14).

In this study, HNT-carbonaceous composite adsorbents have been successfully synthesized through hydrothermal carbonization using two different carbon precursors and used to remove metal ions from wastewater. Functionalization of HNTs by incorporation of carbonaceous structure followed by acid treatment enhances the adsorption ability of the clay mineral, thus making the nanoclay a good candidate for metals' removal from aqueous solutions.

2. MATERIALS AND METHODS

2.1. Materials

Halloysite nanotube (HNT) (nanopowder, 1.26-1.34 mL/g pore volume) and sodium carboxymethyl cellulose (average mw ~90000) were supplied from Aldrich Chemistry. Sulfuric acid (98.0%) was purchased from Merck, d-fructose was purchased from VWR Chemicals, and ethanol (>99.9%) was supplied from ISOLAB.

2.2. Preparation and Characterization of HNT-C Composites

0.40 g of carbon precursor (fructose, sodium carboxymethyl cellulose) was dissolved in 40 mL DI water, and 0.50 g of HNT was added to the solution and stirred at a speed of 200 rpm at 25 °C for 12 h. The prepared mixture was heated in a 100 mL Teflon-lined stainless steel reactor at 160 °C for 48 h. The cooled sample was filtered through a 0.45 µm Teflon filter, washed sequentially with water and ethanol, and dried in a vacuum oven at 60°C (15). For acid treatment; 0.50 g of HNT-C composite was dispersed in 12.5 mL of a 4.0 M H₂SO₄ solution. The dispersion was heated at 85 °C under stirring for 8 h, then allowed to cool to 25 °C and again stirred for 16 h at room temperature. The obtained powder was filtered, washed with ethanol, and dried in a vacuum oven at 60 °C (16). The fructose and sodium carboxymethyl cellulose-modified HNTs were abbreviated to HNT-FC and HNT-CC, respectively. For comparison, unmodified-HNTs were also used in adsorption experiments.

The carbon contents of composites were determined using a Thermo Scientific FlashSmart Elemental Analyzer. The total surface area and pore size of the composites were obtained from N₂ adsorption-desorption analysis using a Micromeritics Gemini VII instrument, and prior to the analysis, the samples were outgassed for 10 h at 473 K. The pore volume data were obtained using the Barrett-Joyner-

Halenda (BJH) method, and the surface areas were obtained using the Brunauer, Emmet, and Teller (BET) method. The X-ray diffraction patterns were obtained using a PANalytical Empyrean XRD diffractometer with Cu K α radiation (0.1540 nm) at 45KV. Scanned data was detected in the 2 θ =7° to 60° range. The FT-IR spectra of composites were collected using a JASCO FT-IR spectrophotometer using ATR from 4000 to 400 cm⁻¹.

2.3. Adsorption Experiments

Metal ion adsorption experiments were conducted with a solution containing 1.0 (low) and 10.0 (high) ppm total metal ions' concentration (Cu, Zn, Pb) mixed with HNT-C composites at a solid/liquid ratio of low and high amounts of adsorbents (1.0 and 10.0 g/L). The mixture was stirred continuously for 24 h at 21 °C to determine the adsorption capacity. The amounts of ions adsorbed on HNT-C composites were calculated from the concentrations in the solution before and after adsorption. An inductively coupled plasma atomic emission spectroscopy (ICP-OES, Perkin Elmer Optima 7000) method was used to determine the content of the following elements in the solution: zinc (Zn), copper (Cu), and lead (Pb).

3. RESULTS AND DISCUSSION

3.1. Characterization of HNT-Carbonaceous Composites

It can be observed from the result of the elemental analysis that carbonaceous structure was successfully incorporated into the HNTs after the carbonization process (Table 1). The specific surface area and pore structure are both crucial factors affecting adsorption performance. The specific surface area and pore volume values of raw HNTs decreased after the carbonization process (HNT-FC*). After the acid treatment, the specific surface areas and the pore volumes of the HNT-C composites increased (HNT-FC and HNT-CC) suggesting that the acid treatment significantly contributed to the specific surface area and pore volume increment without affecting the carbon ratio on the HNT structure. It was notable that the C loading ratio was higher for the composite prepared with fructose (HNT-FC) than for the one prepared with sodium carboxymethyl cellulose (HNT-CC). The use of fructose as a carbon precursor was more effective than the use of carboxymethyl cellulose as a hydrothermal carbonization precursor probably due to its simple structure, which makes it easier to incorporate and disperse into the HNT structure. The lowest C loading detected for HNT-CC can be attributed to the polymeric structure of the precursor.

Table 1: Specific surface areas, pore characteristics, and carbon contents of HNT and HNT-C composites.

Samples	BET Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Pore width (nm)	Carbon (%)
HNT	64.0	1.26-1.34	-	-
HNT-FC*	40.7	0.34	30.2	8.5
HNT-FC	117.9	0.44	16.2	9.9
HNT-CC	126.6	0.60	20.3	7.5

* HNT-C composite sample prepared without sulfuric acid treatment.

Figure 1 exhibits the FT-IR spectra of unmodified-HNTs and HNT-C composites. The double absorption peaks at 3695.2 and 3622.5 cm⁻¹ were attributed to

the stretching vibration of the inner-surface hydroxyl group of HNTs (17-19). The small peak in unmodified-HNTs spectra occurred at 3543 cm⁻¹ for

O-H with an intermolecular hydrogen group, but it disappeared in HNT-C composite spectra. One possible reason for the disappearance of this peak is the breakage of bonds due to the acid treatment (19). The in-plane stretching vibration of the Si-O bonds as indicated by peaks in the HNTs spectra in the fingerprint region between 2000 and 500 cm^{-1} ,

at 1027 and 911 cm^{-1} , respectively, while symmetric stretching of Si-O-Si was seen at 794 cm^{-1} . The band at 1116 cm^{-1} , which is indicative of Si-O stretching vibrations of SiO_2 , was still observed in the spectra of HNT-composites despite the modification (Figure 1) (20).

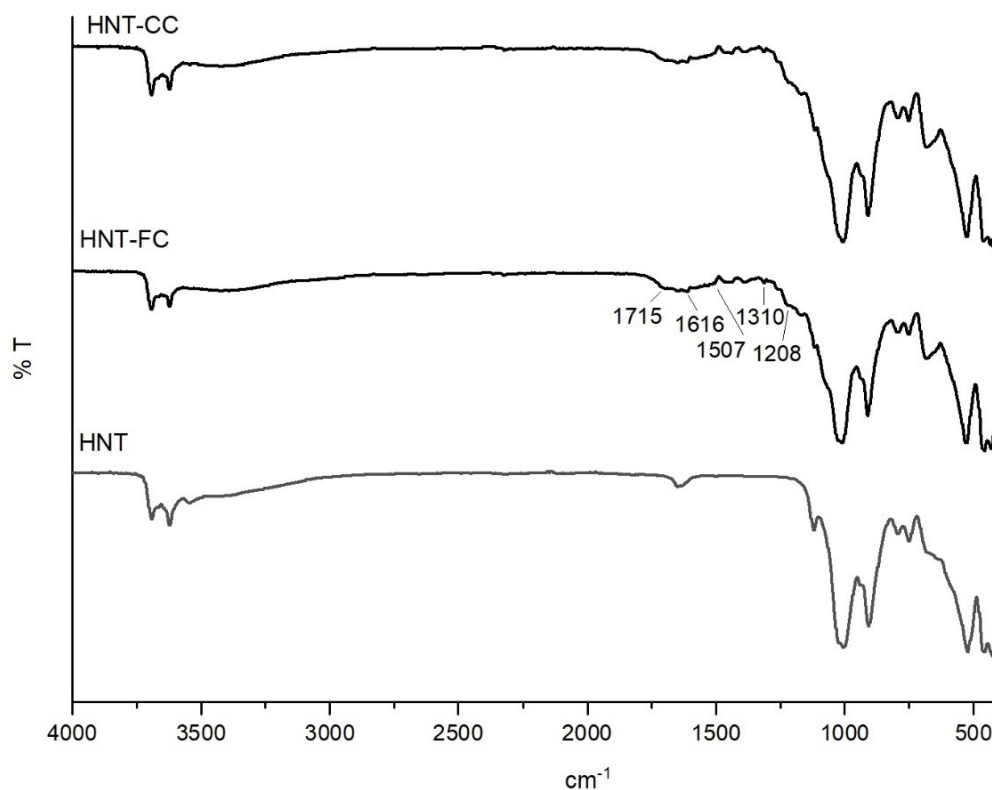


Figure 1: The FT-IR spectra of unmodified HNT and HNT-C composites.

Compared to the unmodified-HNTs some new peaks appeared around 1700 cm^{-1} , 1300 cm^{-1} , 1600 cm^{-1} , and 1200 cm^{-1} on the spectra of HNT-C structures. The peak at 1715 cm^{-1} is assigned to C=O stretching vibrations, while the peaks at 1310 cm^{-1} and 1208 cm^{-1} are attributed to C-O stretching vibrations. The peaks at 1616 cm^{-1} and 1507 cm^{-1} are ascribed to C=C stretching vibrations (21). These results indicated that carbonaceous materials were successfully introduced into the HNT structure.

The XRD patterns of the HNT-C composites and unmodified- HNTs are shown in Figure 2. All samples showed the typical characteristic diffraction angles of HNTs at $2\theta=12.2^\circ$, 20° , 24.8° , 26.6° , 30° , 35° , and 55.4° as marked in Figure 2 (22, 23). The main diffraction at 2θ , which is associated with the planes at $12^\circ(001)$, is visible in the XRD pattern of HNTs. But similar peaks were visible at a slightly shifted angle ($2\theta=9^\circ$) in unmodified HNT. It has been proven that HNT can continue to be structurally stable even after chemical changes (24). After the modification and following acid treatment, there was no significant change in the XRD peaks, implying that the crystal structure of HNTs was not damaged. The diffraction spectrum of the produced HNT-C composites has a broad peak at $2\theta=24.8^\circ$

which is the typical peak of the 002 crystal plane of carbon (25).

3.2. Adsorption Performance of HNT-Carbonaceous Composites

Adsorption experiments were carried out to compare the adsorption capacities of HNT-C composites and unmodified-HNTs on the removal of heavy metals from water. To determine the effect of total ion concentration on the adsorption behavior of HNT-C composites, adsorption experiments were first achieved with a constant low dosage of adsorbent (1.0 g/L) at total ion concentration ranges of 1.0 and 10.0 ppm. As can be seen from Figure 3.a., HNT-FC and HNT-CC have a higher adsorption capacity than unmodified-HNTs at 1.0 ppm total ion concentration. It was interesting that there was a significant difference in the adsorption of Zn^{2+} . While unmodified-HNTs have no capability to adsorb Zn^{2+} , the adsorption of Zn^{2+} was significantly increased up to 19.0% by using the HNT-FC composite. After modifying the HNT structure by hydrothermal carbonization of fructose or carboxymethyl cellulose, a carbonaceous layer was introduced on the HNTs with organic functional groups (-OH and -COOH) that play an important role in the adsorption of ions. On the other hand, before

the acid treatment, the specific surface area of HNT-FC was only 40.7 m²/g, a small specific surface area for adsorption, and this value reached 117.9 m²/g (or more) by the acid treatment. The results showed that acid treatment is an effective method of

improving the adsorption properties by increasing the surface area of the structures.

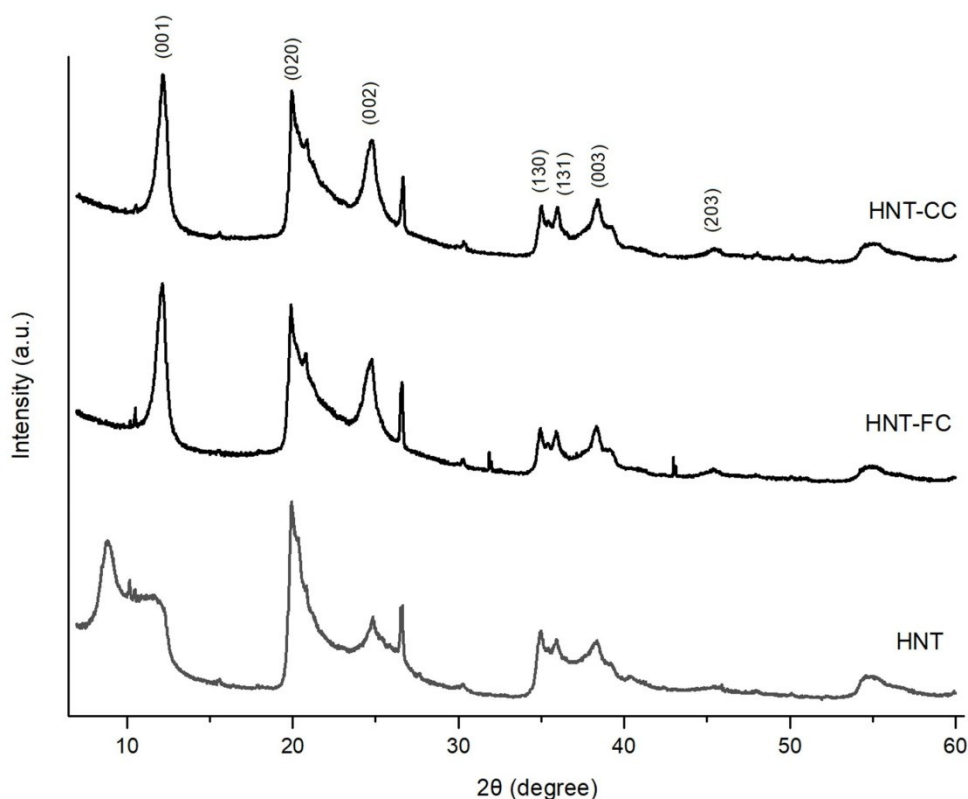


Figure 2: The XRD patterns of unmodified-HNT and HNT-C composites.

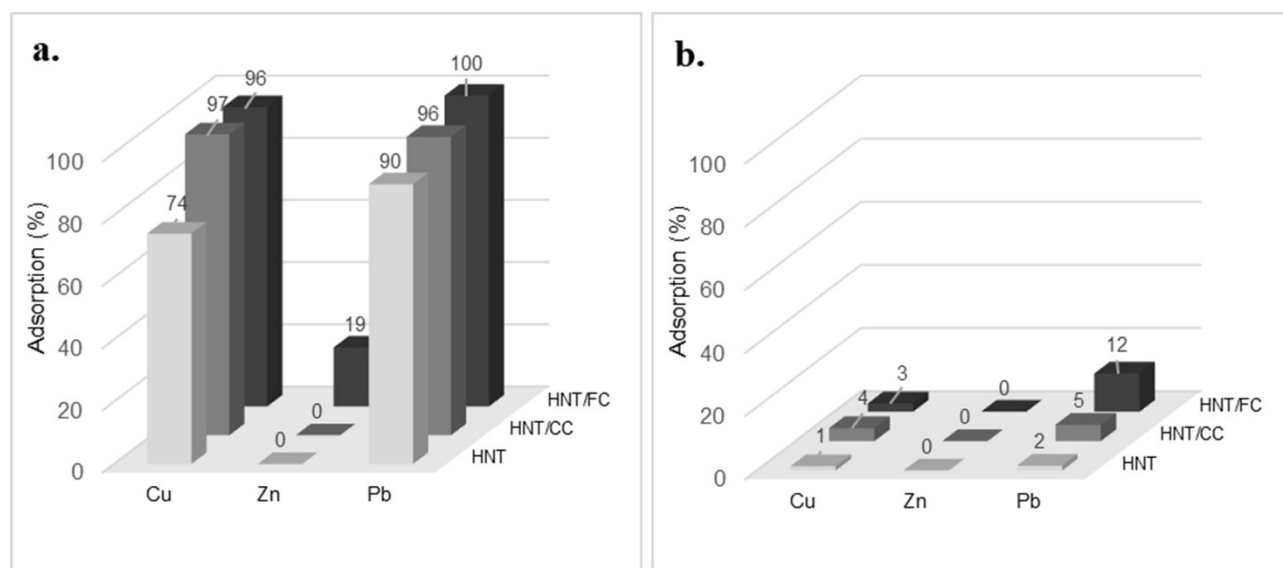


Figure 3: Effect of metal concentration a. 1.0 ppm, b. 10.0 ppm at a 1.0 g/L adsorbent dosage.

As can be seen in Figure 3. b., the removal efficiency of adsorbents decreased with the increase in total ion concentration. For instance, the removal ratio of Pb(II) with HNT-FC from the solution decreased from 100% to 12% when the total ion concentration increases from 1.0 to 10.0 ppm. The overall reduction in the removal efficiency of ions was probably due to the saturation of adsorption

sites with the increase in the quantity of ions in the solution. Zn(II) absorption was not observed on unmodified-HNTs and HNT-CC structures, regardless of initial total ion concentration. The sorption capacity of HNT-FC for Zn(II) was higher than that of HNT-CC probably due to the higher carbon content that provides more active acidic sites for metal adsorption.

As a continuation of the study, HNT-C composites' adsorption experiments were also achieved with a constant high dosage of adsorbent (10.0 g/L) at a total ion concentration range of 1.0 and 10.0 ppm. As can be seen in Figure 4.a., Cu and Pb removal efficiency was nearly 100% at low initial metal concentrations for all adsorbents. The removal efficiency of Zn(II) ions increased sharply with increasing the adsorbent concentrations from 1 to 10 g/L for HNT-C composites, while no Zn(II) adsorbed onto unmodified HNT. The HNT-CC and HNT-FC composites exhibited a promising performance in the removal of Zn (II) ions. The percentage adsorption increased from 0% to 84.0% and from 19.0% to 94.0% for Zn(II) with HNT-CC and HNT-FC, respectively, over the same total ion concentration (Figure 3.a. and Figure 4.a.) It might

have been attributed to the fact that increasing the adsorbent dosage provided a larger surface area and more binding sites for the metal ions. On the other hand, according to Fig. 4.b., the percentage adsorption efficiency sharply decreased with increasing the total ion concentration to 10.0 ppm at 10.0 g/L adsorbent dosage, probably due to the adsorbent saturation. These three metal cations also have different sorption capacities for the adsorbents. The obtained HNT-C composites show good adsorption capacity, especially for Pb(II), a higher adsorption efficiency was obtained for Pb(II) compared to Cu(II) and Zn(II). This may be explained by the low hydration enthalpy of Pb(II) that permits the detachment of water molecules from cations and then lets the ion interact with the functional groups on adsorbents (26, 27).

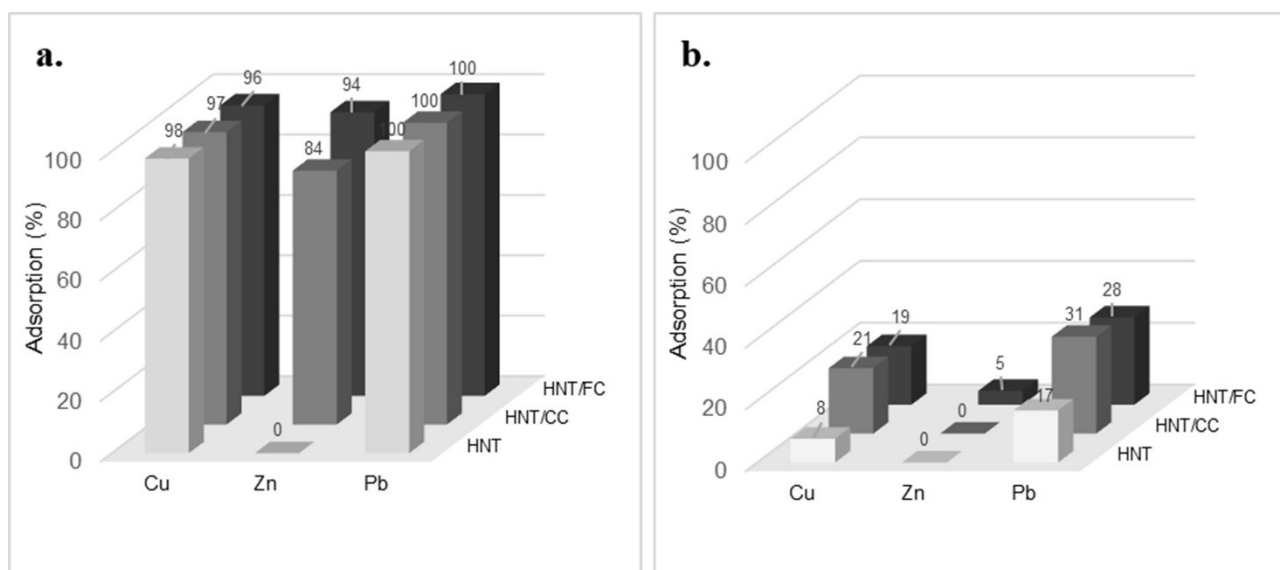


Figure 4: Effect of metal concentration a. 1.0 ppm, b. 10.0 ppm at a 10.0 g/L adsorbent dosage.

4. CONCLUSION

In the study, halloysite nanotubes, a naturally occurring clay mineral, were used as raw materials to produce functional HNT-C adsorbents for the removal of heavy metals, including Cu(II), Pb(II), and Zn(II), from wastewater. The experimental results demonstrate that the adsorption capacity of the HNTs increases significantly with the incorporation of carbonaceous layers into the structure. The acid treatment after the hydrothermal carbonization process provided significant enhancement of specific surface area and pore characteristics of HNT-C composites. HNT-C composites can be evaluated as a potential low-cost and eco-friendly adsorbent material.

5. CONFLICT OF INTEREST

No potential conflict of interest was reported by the authors.

6. ACKNOWLEDGMENTS

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