Mesoporous Biopolymer Architecture Enhanced the Adsorption and Selectivity of Aqueous Heavy-Metal Ions

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ABSTRACT: Halloysite nanotubes (HNT) and ball-milled biochar (BC) incorporated biocompatible mesoporous adsorbents (HNT-BC@Alg) were synthesized for adsorption of aqueous heavy-metal ions. HNT-BC@Alg outperformed the BC, HNT, and BC@Alg in removing cadmium (Cd), copper (Cu), nickel (Ni), and lead (Pb). Mesoporous structure (∼7.19 to 7.56 nm) of HNT-BC@Alg was developed containing an abundance of functional groups induced from encapsulated BC and tubular HNT, which allowed heavy metals to infiltrate and interact with the adsorbents. Siloxane groups from HNT, oxygen-containing functional groups from BC, and hydroxyl and carboxyl groups from alginate polymer play a significant role in the adsorption of heavy-metal ions. The removal percentage of heavy metals was recorded as Pb (∼99.97 to 99.05%) > Cu (∼95.01 to 90.53%) > Cd (∼92.5 to 55.25%) > Ni (∼80.85 to 50.6%), even in the presence of 0.01/0.001 M of CaCl₂ and Na₂SO₄ as background electrolytes and charged organic molecule under an environmentally relevant concentration (200 μg/L). The maximum adsorption capacities of Ni, Cd, Cu, and Pb were calculated as 2.85 ± 0.08, 6.96 ± 0.31, 16.87 ± 1.50, and 26.49 ± 2.04 mg/g, respectively. HNT-BC@Alg has fast sorption kinetics and maximum adsorption capacity within a short contact time (∼2 h). Energy-dispersive X-ray spectroscopy (EDS) elemental mapping exhibited that adsorbed heavy metals co-distributed with Ca, Si, and Al. The reduction of surface area, pore volume, and pore area of HNT-BC@Alg (after sorption of heavy metals) confirms that mesoporous surface (∼2–18 nm) supports diffusion, infiltration, and interaction. However, a lower range of mesoporous diameter of the adsorbent is more suitable for the adsorption of heavy-metal ions. The adsorption isotherm and kinetics fitted well with the Langmuir isotherm and the pseudo-second-order kinetic models, demonstrating the monolayer formation of heavy-metal ions through both the physical sorption and chemical sorption, including pore filling, ion exchange, and electrostatic interaction.

1. INTRODUCTION

Water contamination from natural processes and anthropogenic activities has potential toxic effects due to rapid transportation, bioaccumulation, and biomagnification of organic and inorganic contaminants from abiotic to biotic ecosystems. The remediation of heavy metals from wastewater is challenging due to the lack of sustainable, feasible, and effective technologies. Adsorption is a widely accepted and low-cost remediation approach in comparison to other removal techniques, including oxidation, precipitation, coagulation, membrane-based separation, electro flotation, biofiltration, and electrodialysis. Various adsorbents, including biochar, clay, graphene oxides, carbon nanotubes, metal nanoparticles, nanomaterials, polymers, and nanocomposites have been widely utilized to remove organic and inorganic contaminants including heavy-metal ions over the past decade. The application of conventional adsorbents is limited in relation to selectivity, competitive sorption, and easy separation after sorption. Biocompatible stabilization of nanosized adsorbents in the form of beads can be utilized to overcome such problems. The polymerization of nano/micorsize adsorbents could immobilize and stabilize in and around biopolymer beads, stimulating easy separation of the adsorbents. Biopolymer bead synthesis in the form of hydrogel beads from natural biopolymer, including cellulose, nanocellulose, alginate, and chitosan, is receiving enormous scientific attention because of the facile synthesis procedure, functionality, biocompatibility, and tunability. However, polymer selection depends on the affinity toward the target contaminants, properties of the contaminants, desired active sites, and removal performance. Alginic polymer is hydrophilic in nature due to the presence of oxygen-containing functional groups over the molecular structure of alginic. Carboxyl and hydroxyl functional groups (hard bases) along

Received: March 26, 2021
Accepted: May 21, 2021
Published: May 31, 2021
the polymer skeleton allow high affinity toward hard and intermediate acid. The polysaccharide polymer consists of two 1,4-linked hexuronic acid residues, namely, β-D-mannuronopyranosyl (M) and α-L-guluronopyranosyl (G). Repeating M−M blocks, G−G blocks, and M−G blocks are arranged on alginate polymer’s molecular structure (Figure S1). Sodium alginate can quickly transform into polymer beads once it encounters divalent cations (Ca²⁺) or a cationic polymer. Sodium ions from G blocks are exchanged with divalent cations and generate hydrogel in the form of beads. Nevertheless, raw biopolymer beads have several limitations: low swelling/shrinkage capacity and rigid nonporous structure resulting in low surface area and limited porosity. Thus, raw polymer beads (nonporous) hinder the accessibility of heavy-metal ions or organic contaminants inside the polymer beads, resulting in limited adsorption with embedded functional groups. Thus, bare polymer beads’ robust and rigid structure impedes the mass transfer of heavy-metal ions from an aqueous solution because of the nonporous surface, which results in slow sorption kinetics and low adsorption performance. Additionally, bare polymer beads have low mechanical, structural, and chemical stabilities under high hydraulic pressure and wide solution pH ranges. Moreover, controlling the pore size of polymer beads continues to be challenging. The ionic and kinetics diameter of heavy-metal ions is below 0.2 nm. Thus, both microporous and mesoporous materials could be suitable for the adsorption of heavy-metal ions.

Our research target is to manufacture biochar (ball-milled)/nanotubes incorporated alginate composite beads that pose meso- or micropores with high mechanical and chemical stabilities as well as excellent adsorption performance. Mesoporous polymer architecture could be designed because of the tubular porous structure of halloysite nanotubes (HNT) (outer diameter: 50–70 nm, inner diameter: 10–20 nm) and microsized porous carbonaceous materials. Moreover, incorporating biochar (BC) and HNT into polymer beads could improve active sites, thermal stability, and the multifunctional properties of the adsorbents, promoting selective and fast adsorption of heavy-metal ions.

Considering the above discussion, polymer beads embedded with abundance of active sites will contribute toward heavy metals selectively. Thus, we develop and discuss mesoporous materials (static and stable) of biopolymer for the adsorption of heavy metals in this study. The counterpart of HNT-BC@Alg should help boost the performance of the heavy metals’ sorption and provide an additional stable porous framework to operate the structure and serve its target application. The primary objective of the experiment is to understand the influence of surface properties (surface area, pore diameter, and pore volume) of the HNT-BC@Alg in relation to the sorption of heavy-metal ions. The other objectives of the experiments are (i) understanding the physical and chemical properties of the mesoporous HNT-BC@Alg; and (ii) investigating the selectivity and removal efficiency of heavy-metal ions from a multicomponent mixture solution of cadmium (Cd), copper (Cu), nickel (Ni), and lead (Pb).
Table 1. Surface Properties of the Adsorbents

| Adsorbent                | surface area (BET) (m²/g) | surface area (SA) (m²/g) | external SA (m²/g) | micropore area (m²/g) | pore volume (cm³/g) | pore diameter (BJH adsorption) (nm) | pore diameter (D–H adsorption) (nm) |
|--------------------------|---------------------------|--------------------------|--------------------|-----------------------|---------------------|-------------------------------------|------------------------------------|
| HNT                      | 55.51                     | 144.14                   | 58.72              | 0.001                 | 6.21                | 6.62                                |                                    |
| HNT-BC@Alg (pre-sorption)| 16.00                     | 38.71                    | 13.10              | 2.90                  | 0.004               | 7.19                                | 7.93                               |
| HNT-BC@Alg (post-sorption)| 7.11                     | 15.71                    | 4.87               | 2.23                  | 0.001               | 7.56                                | 8.31                               |

Figure 2. Thermal stability (a) and derivative weight loss (b) of HNT, BC, HNT-BC@Alg, and bare alginate beads (alg).

The removal percentages of the adsorbent were evaluated in environmentally relevant concentrations in the presence and absence of background electrolytes and organic molecules to identify the ionic selectivity of the adsorbent. Comparative evaluation of the adsorbents (HNT, BC, and BC-Alg) was also conducted to screen the adsorbents and understand the synergistic effect. This experiment allows better understanding of selectivity, binding strength, sequences of sorption performance, and sorption affinity of heavy-metal ions toward the mesoporous biopolymer composites.

2. RESULTS AND DISCUSSION

2.1. Properties of the HNT-BC@Alg. Physiochemical Properties of the HNT-BC@Alg. HNT-BC@Alg were synthesized using calcium ions as a cross-linker of alginate biopolymer. Alkali earth metals mainly reacted with the GC block of the alginate polymer through ionic interaction. Thus, amorphous polymer networks were produced by cross-linking of alginate biopolymer with calcium ions. The X-ray diffraction (XRD) pattern of HNT-BC@Alg beads (before and after adsorption of heavy metals) was identified using powder XRD, which is presented in Figure 1a. The HNT-BC@Alg had similar XRD patterns before and after adsorption, indicating resistance against structural and chemical transformation during adsorption processes. The XRD pattern (Figure 1a) indicated the successful incorporation of HNT and BC inside the cross-link alginate polymer. Aluminum silicate hydroxide/kaolinite (Al₂Si₂O₅(OH)₄) and quartz (SiO₂) were identified in HNT-BC@Alg. In contrast, aluminum silicate hydroxide/kaolinite (Al₂Si₂O₅(OH)₄), quartz (SiO₂), and calcite (CaCO₃) were identified after adsorption of heavy metals, confirming no precipitation taken place during the adsorption process. The d-spacing values of HNT-BC@Alg are 0.12 nm (lower) and 0.84 nm (higher), whereas crystalline sizes are 5.84 nm (lower) and 91.56 nm (higher). The average crystalline size and d-spacing value of the HNT-BC@Alg were calculated as 54.51 and 0.32 nm, respectively. The range of crystalline size of the HNT-BC@Alg is higher due to its versatile counterparts (BC, HNT, and alginate biopolymer).

Table 1 and Figure 1b–d summarize the surface area, porosity, pore area, and pore volume of the polymer beads. The reduction of the external surface area, micropore surface area, and pore volume were observed after the adsorption of heavy-metal ions (Figure 1). The mesoporous structure of the adsorbent is critical for fast and effective adsorption. Mesoporous polymer beads are accessible to ion diffusion, resulting in faster diffusion and metal exchange at a suitable pH. In the rigid xerogels, the Ca₂⁺–alginate junction zones (Ca₂⁺-bound GC blocks having egg-box structure) are resistant to rearrangement and consequently repel interaction among heavy-metal ions because of the limited porosity and poor internal orientation. Post-adsorption BET surface area decreased from 16.00 to 7.11 m²/g, while the Langmuir surface area reduced from 38.71 to 15.71 m²/g. Similarly, the micropore and external surface area decreased from 2.90 and 13.10 to 2.23 and 4.87 m²/g, respectively (Table 1). The pore volume of the adsorbents also decreased from 0.004 to 0.001 cm³/g after adsorption of heavy metals (Table 1). This reduction of surface area and pore volume of the HNT-BC@Alg demonstrated that heavy-metal ions adsorbed not only on the external surface area but also within the adsorbents’ micropore. The range of pore diameter is 2–18 nm. The Barrett–Joyner–Halenda (BJH) pore diameter (average) of the HNT-BC@Alg is approximately 7.19–7.56 nm (in diameter), whereas the Dollimore–Heal (D–H) pore diameter (average) was recorded as 7.93–8.31 nm (in diameter) (Table 1). The porosity of adsorbents indicates the mesoporous structure (7.19–7.56 nm in diameter) of the adsorbent, which allows internal and external diffusion of heavy metals. The size of the studied heavy metals is below 0.2 nm (Table S1). The reductions of pore area and pore volume are higher at a lower pore diameter (near after 2 nm).
Consequently, the reductions of pore area and pore volume of the HNT-BC@Alg after adsorption of heavy-metal ions decreased with increasing size of the mesopore. Thus, a lower range of mesoporous surface is more suitable for adsorption of heavy-metal ions. The mesoporous structure of HNT-BC@Alg also allows interaction with internal active sites of the polymer beads.

Air-dried alginate beads usually have rigid morphology and a stiff nonporous structure compared with nanocomposite polymer beads (Figure S2). An earlier study demonstrated the surface area (m$^2$/g), porosity (nm), pore volume (cm$^3$/g) of polyacrylamide hydrogel, biochar incorporated polyacrylamide hydrogel, and three-dimensional (3D) MnO$_2$ modified biochar-based porous polyacrylamide hydrogel are 0.31, 1.62, 31.17; 1.58, 6.27, 7.32; and 0.0001, 0.003, 0.07, respectively. This study demonstrated that polyacrylamide hydrogel has low active sites, whereas biochar- and metal oxide-modified polyacrylamide hydrogels have high and suitable surface properties and active sites. Freeze-dried beads demonstrate better performance for adsorption of contaminants than air-dried beads for inducing porous structure and generating high surface area.

**Improved Thermal Stability of the HNT-BC@Alg Than the Bare Alginate Beads.** Thermogravimetric analysis of the materials could envisage the stability of the materials and confirm their compositional structure. The thermogravimetric analysis (TGA) profile and derivative weight loss of BC, HNT, bare alginate beads (alg), and HNT-BC@Alg are presented in Figure 2a,b. The stability, usability, and formability of the HNT-BC@Alg improved after incorporation of BC and HNT. Trends of the thermal stability of partition materials were identified as HNT > BC > HNT-BC@Alg > alg. Bare alginate beads are vulnerable to decompose at two foremost heating temperatures (225 and 290 °C); the thermal decomposition and weight loss of alginate polymer reduce after incorporating HNT and BC. It is visibly identifiable that HNT-BC@Alg has higher thermal stability than bare alginate beads because of containing BC and HNT inside the composites (Figure 2). Among all materials, HNT shows higher thermal stability up to 400 °C, whereas the weight percentage of BC gradually reduced with increasing temperature because of the degradation of amorphous carbon. The reduction of the weight percentage of polymer beads occurs because of eliminating various volatiles (stem, CO$_2$, CO, and hydrocarbons).

**Internal and External Morphologies of HNT-BC@Alg.** The scanning electron microscopy (SEM) image of HNT (tubular nano-size), BC (<10 μm), bare alginate beads, and a digital photograph of HNT-BC@Alg were presented (Figure S2). SEM images of surface morphology and cross-sectional image of HNT-BC@Alg demonstrated the successful loading of HNT and BC into the polymeric architecture. The digital photograph of HNT-BC@Alg revealed the functionalized biopolymer beads are black in color because of the incorporation of black pyrogenic carbon inside the polymer matrix. The transparency of alginate gel was reduced due to the incorporation of black pyrogenic carbon inside the polymer matrix. The mesoporous channel over the beads because of the porous 3D nano-size), BC (<10 μm) matrix. The transparency of alginate gel was reduced due to higher thermal stability than bare alginate beads due to supercritical drying with air or carbon dioxide (Figure S2d). The hydrogel network of sodium alginate (hydrogel) collapsed under air-dried conditions, resulting in low porosity and surface area, which is unfavorable for the adsorption of heavy-metal ions. However, incorporating BC and HNT helps to open the mesoporous channel over the beads because of the porous 3D polymer hydrogel network, enabling heavy metals to interact with internal BC and HNT.

The particle size of the ball-milled biochars was smaller enough (<10 μm) to interact with heavy metals due to higher exposure of active sites in comparison to regular-shapes.

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**Figure 3.** SEM image of the adsorbents (HNT-BC@Alg): (a–c) SEM image of HNT-BC@Alg beads under lower to higher magnification; (d–f) cross-sectional SEM image of HNT-BC@Alg under lower to higher magnification.
biochars and commercially available activated carbon (1–4 mm). Smaller (nano/microsize particles) carbonaceous materials are promising candidates as filling materials of hydrogel to enhance the selectivity of polymer beads toward target organic and inorganic contaminants. However, the selectivity of biochar toward heavy metals depends on the feedstock sources and pyrolysis temperature. Low higher heating temperature (HHT) and high inorganic content of biochars are suitable for heavy-metal adsorption, whereas a high HHT is suitable for adsorption of organic contaminants. However, heavy-metal selectivity depends on the nature of the active sites of biochars. Sugarcane-derived biochar was synthesized at a low HTT to induce hydrophilic functional groups rather than hydrophobic ones. Hydrophilic functional groups of biochar and HNT could adsorb heavy-metal ions through hydrophilic interaction (e.g., ion-exchange interaction and electrostatic interaction). Those beneficial properties are desirable for effective and selective adsorbents. A highly porous bead was observed, allowing transporting heavy-metal-containing solution inside the polymer beads enabling adsorption of heavy-metal ions inside the polymer beads. A higher-magnified image confirmed the distribution of BC and HNT inside the outer and inner layers of the polymer beads, confirming the successful synthesis of adsorbent (Figure 3).

2.2. Screening of Adsorbents for the Removal of Heavy Metals. A set of adsorbents, including BC, HNT, BC@Alg, and HNT-BC@Alg, were used to evaluate the comparative and selective adsorption performance of the heavy-metal ions (Figure 4). BC@Alg and HNT-BC@Alg have higher sorption amounts than the raw BC and HNT. The sequence of the affinity of heavy metals is Pb > Cu > Cd > Ni for HNT, BC, and BC@Alg, whereas the sequence of adsorption capacity of the heavy metals onto the adsorbents is HNT < BC < BC@Alg < HNT-BC@Alg (Figure 4). Cd and Ni adsorption performance in BC and HNT is comparatively lower than that of Pb and Cu. The application of the BC and HNT is limited concerning removing Cd and Ni due to low selectivity. The selectivity of heavy metals could be improved by polymerization of BC and HNT with alginate biopolymer to introduce hydroxyl and carboxyl active sites. Moreover, porous architecture and the mesoporous surface of the HNT-BC@Alg favor the adsorption of heavy-metal ions. Thus, incorporating BC and HNT into the alginate beads improves the selectivity of Cd and Ni because of the synergistic effect. HNT-BC@Alg could improve the adsorption capacity of Cd and Ni because of higher affinity toward the available active sites. The synergistic impact most likely promoted higher adsorption of the HNT-BC@Alg than that of BC, HNT, and BC@Alg (Figure 4).

2.3. Sorption Isotherm of Heavy Metals. Nonlinear isotherm model fitting for sorption of mixed metal solution (Cd\(^{2+}\), Cu\(^{2+}\), Ni\(^{2+}\), Pb\(^{2+}\)) is presented in Figure 5. The nonlinear Langmuir isotherm model fittings (R\(^2\)) were 0.98, 0.97, 0.99, and 0.99, respectively, and the Freundlich isotherm model fittings (R\(^2\)) were 0.93, 0.98, 0.87, and 0.99, respectively, for Cd\(^{2+}\), Cu\(^{2+}\), Ni\(^{2+}\), and Pb\(^{2+}\) (Figure 5). The Langmuir isotherm model postulates monolayer formation of molecules over the active sites of the uniform adsorbents. In contrast, the Freundlich isotherm model postulates bilayer or multilayer formation of molecules over the adsorbent’s active sites.

The experimental data fit more accurately with the Langmuir isotherm model than with the Freundlich isotherm model, demonstrated monolayer formation of heavy metals over the active sites of HNT-BC@Alg (Figure 5). The maximum adsorption capacities of Ni, Cd, Cu, and Pb were 2.85 ± 0.08, 6.96 ± 0.31, 16.87 ± 1.50, and 26.49 ± 2.04 mg/g, respectively (Table S1). The Langmuir constant (K\(_L\)) is related to the affinity between adsorbent and adsorbate. The calculated K\(_L\) values of different heavy metals are quite different from each other. The K\(_L\) values of Ni, Cd, Cu, and Pb are 0.18, 0.18, 0.19, and 1.11 L/mg, respectively (Table S2). Thus, the sequence of the affinity of heavy metals toward the adsorbents is Pb > Cu > Cd > Ni. The trends of adsorption capacity and K\(_L\) are quite similar. The dimensionless constant (1/n) and Freundlich constant values show similar trends to the K\(_L\) values (sorption affinity) and the adsorption capacity of the heavy-metal ions (Table S1). The dimensionless constant (1/n) values range from 0.33 to 0.48 for all of the heavy metals under study (Table S2). The 1/n values vary with the degree of heterogeneity of the adsorbing sites, reflecting the magnitude of the sorption force.

The sequence and selectivity of heavy-metal-ion adsorption are influenced by the functional group or surface chemistry of the adsorbents. The sequence of adsorption capacity and affinity toward the adsorbents is Ni < Cd < Cu < Pb. Similar trends (Pb\(^{2+}\) > Cu\(^{2+}\) > Cd\(^{2+}\)) for the adsorption of heavy metals onto calcium alginate thin films were also reported. The difference among the sorption performance of different metals is attributed to the binding strength and affinity of individual metals toward the active sites of beads.

Heavy metals are classified into three categories: class A (oxygen seeking); class B (nitrogen/sulfur seeking), and borderline (or intermediate) metal ions. Their bonding affinity can be predicted by their ionic charge of metals (z), the radius of the metal ions (r), and the electronegativity of the metals (\(\chi_m\)). Ionic charge density is relevant to electrostatic bonding strength, while valence orbital energy is relevant to covalent bonding strength. The radius of the divalent cations are 0.15, 0.14, 0.14, and 0.16 nm, and the electronegativities are 1.68, 1.90, 2.33, and 1.91 (Pauling scale) for Cd, Cu, Pb, and Ni, respectively (Table S2). Thus, the trends of constant hydrolysis values are Cd > Ni > Pb > Cu. The lower hydrolysis constant of heavy metals (Pb and Cu) may lead to the high affinity with the adsorbents and enhance rapid and selective adsorption. As a result, Pb and Cu adsorbed higher than Cd and Ni. The sequence of electrostatic binding strength is Cd > Cu > Pb > Ni, whereas the sequence of the...
covalent binding strength is Pb > Ni > Cu > Cd. However, the sequences of sorption in this study followed neither sequence of electrostatic binding strength nor the sequence of the covalent binding strength, demonstrating other sorption mechanisms (e.g., physical sorption) also play a significant role in the adsorption of heavy-metal ions.

The sequences of electrostatic binding strength and covalent binding strength also follow the hard and soft acid and base theory.52 The hardness of heavy metal depends on the proton binding strength. Hard and soft acids prefer to bind hard bases and weak bases, respectively.53,54 In this study, Pb, Cu, and Ni are intermediate acids (borderline class), whereas Cd is a soft acid. Intermediate acids have weak interaction with hard bases and soft bases, whereas soft acids have strong interaction with only soft bases.55 Thus, Cu and Pb (intermediate acid) have higher affinity than Cd (soft acid) toward hard carboxyl and hydroxyl bases of the polymer beads. However, given that the sequence of electrostatic binding strength is Cd > Cu > Pb > Ni, Ni has lower sorption affinity toward the active sites of adsorbents. Thus, the adsorption of the divalent cations is mainly influenced by carboxyl groups and hydroxyl groups. However, because of variation in the formation of G-block and M-block of alginate polymer beads, not all carboxyl groups may act as active sites for binding heavy metals. Usually, soft acids prefer to bind with the M-block of the polymer, whereas hard and intermediate acids prefer to bind with a strong acid. Pb and Cu could bind with hydroxyl and carboxyl groups together in the G-block and M-block of the polymer. A weak acid (Cd^{2+}) may prefer to be adsorbed with carboxyl and hydroxyl groups from the M-block of the polymers. The adsorption of borderline acids is less affected by solution pH and cation exchange capacity with proton in the adsorption medium due to high affinity toward the hard bases. As Cd is a soft acid, which has low affinity toward the hard bases, thus, the sorption of Cd is strongly influenced by the solution pH.

2.4. Sorption Kinetic of Heavy Metals. Sorption is a two-way process, where adsorption and desorption occur simultaneously. The adsorption kinetics can be generally classified into three stages: (1) the adsorbate diffuses into the external surface of the adsorbent; (2) the adsorbate can diffuse over and around the pore of the adsorbents; and (3) the adsorbate can diffuse inside the pores of the adsorbents.56,57 It is difficult to distinguish these three stages. However, two identical steps have been confirmed from the kinetics of heavy-metal sorption (Figure 6). The initial rapid adsorption is due to the rapid sorption of divalent cations over the adsorbents’ high binding sites and pore filling, where slow adsorption indicates sorption onto residual binding sites and diffusion of
heavy metals. However, the equilibrium time also depends on the sorbate concentration, adsorbent dose, and particle size. The adsorption of Pb and Cu is significantly higher than the adsorption of Cd and Ni because of the high sorption affinity of hard acid with the available active sites onto the polymer beads (HNT-BC@Alg). The sorption of Pb and Cu reached equilibrium within 3 h, but this takes longer for Cd and Ni (~5 h) because of slight desorption after 2 h of contact time.

Adsorption of heavy metals onto HNT-BC@Alg followed both pseudo-first-order and pseudo-second-order kinetics models, which demonstrated that physisorption and chemisorption are involved in the adsorption of heavy-metal ions. Physisorption occurs because of pore filling and surface adsorption of heavy metals, while chemisorption occurs because of electrostatic interaction, ion exchange, and coordination bonding. The average pore size of the HNT-BC@Alg is approximately 7.19 to 7.56 nm (Table 1), whereas the diameter of the heavy-metal ions is less than 0.2 nm, enabling the pore filling sorption mechanism. Thus, heavy-metal ions could get into the pore network of the adsorbents and promote pore-dependent adsorption.

Additionally, the pore volume and surface area of the HNT-BC@Alg could promote physically active sites for sorption. The surface area, porosity, and pore volume of the HNT-BC@Alg decreased after adsorption, confirming the physical adsorption mechanism for heavy-metal ions (Table 1). Moreover, a substantial amount of heavy metal is adsorbed even under highly acidic conditions, indicating that charge-dependent sorption of heavy metals is not the only sorption mechanism. Additionally, the adsorption of heavy metals increased with decreasing acidity of the solution, which confirms the occurrence of chemisorption. Recent studies demonstrated that the adsorption of divalent metal ions onto the alginate surface could be due to ion-exchange reaction with the release of calcium ions from the alginate beads.\(^{49,58,59}\) Mohammad et al. also found that adsorption of heavy-metal ions onto alginate thin film is strongly governed by ion exchange, diffusion, and coordination binding, resulting in sorption kinetics followed by the pseudo-second-order kinetic model.\(^{59}\) Carboxyl groups of alginate beads create sites for covalent bonding between carboxyl groups and metal ions.\(^{59}\)

2.5. Influence of Solution pH and Ionic Strength (Competitive Sorption) on Adsorption. The solution pH played a significant role in the adsorption of heavy metals. The effect of solution pH on the adsorption capacity of heavy metals is presented in Figure 7a. Calcium alginate polymer has two individual types of active sites: (1) carboxylic groups from the G-block of alginate polymer could participate in the egg-box structure and are less suitable to metal-ion sorption; (2) carboxyl groups from M-block are easily accessible to the sorption process. Moreover, hydroxyl groups from both G blocks and M blocks of alginate polymer could act as active sites for the adsorption of heavy-metal ions.

The adsorption capacity increased with the increase of solution pH up to 8.5 as the point of zero charges of the adsorbents was identified as 5.15 (Figure S3). At pH above pH\(_{PZC}\), the adsorbents are negatively charged, which is suitable for the adsorption of divalent heavy-metal ions.\(^{60,61}\) However, even below pH\(_{PZC}\) a few active sites (e.g., carboxyl groups) could adsorb heavy metals through electrostatic interaction and coordination formation because of the lower acid dissociation constant values.\(^{62,63}\) At a very low solution pH (approximately 1.5), the adsorption capacities for Pb, Cu, Ni, and Cd are approximately 4.0, 1.4, 0.8, and 0.4 mg/g, respectively, which indicates that ion exchanges are not the only adsorption mechanism. However, the adsorption capacity is comparatively high at pH 5–8.5 compared with lower solution pH. Usually, soft acids prefer to bind with soft bases, whereas hard acids prefer to bind with hard bases. Moreover, intermediate acids prefer to adsorb with both hard and soft bases. Thus, intermediate acids (Pb, Cu, Ni) like to be adsorbed with carboxyl and hydroxyl groups of the polymers, which is easily influenced by solution pH. Pb and Cu could bind with hydroxyl and carboxyl groups together in the polymer’s G-block and M-block. Thus, Pb and Cu (intermediate acid) show greater affinity toward hard bases than Cd. Consequently, the adsorption of Pb and Cu are less affected by solution pH and cation exchange capacity. It has been reported that the pK\(_a\) values of carboxylic groups (hard acid) are ranging from 1.7 to 4.7.\(^{64}\) Thus, carboxylic groups are negatively charged above pH 4.7 and are suitable for the adsorption of divalent cations. At solution pH below the point, the carboxyl groups are protonated, resulting in competition between H\(^+\).
and $M^{2+}$ (divalent metal) species in the solution. Thus, the effect of pH on the sorption of heavy metals depends on the affinity among functional groups and the sorbates.

The electronegativity, electronic configuration, ionization energy, and acidity of Pb, Ni, Cu, and Cd are highlighted in Table S2. Pb$^{2+}$ has the lowest ionization energy for the first, second, and third electrons from the electron configuration (Xe) 4f$^4$ 5d$^{10}$ 6s$^2$ 6p$^5$. Given that the electron in the sixth shell is comparatively easy to exchange with existing functional groups, enthalpy associated with the ion-exchange reaction is low. This explanation also validates the results shown with Cu$^{2+}$ and Cd$^{2+}$. However, the adsorption of heavy metals (particularly for Cd and Pb) is slightly reduced when the solution pH increased from 9.0 to 11.5 because of the reduction of neutral and/or negative charge of heavy-metal ions with increasing solution pH. These two metals (Cd and Pb) showed lower adsorption capacity compared with Ni and Cu at a low solution pH, indicating higher pH-dependent sorption for Cd and Pb. Moreover, Do et al. reported that hydrogen bonding could occur for the sorption of heavy metals alongside ion-exchange interaction.

The influence of background electrolytes and organic molecules on the adsorption of heavy metals was conducted in an environmentally relevant concentration. Background electrolytes could influence competition within the heavy metals, influence electric double-layer thickness, and subsequently interface the sorption potential of the adsorbents. The removal percentage of the studied heavy metals with and without electrolytes and organic molecules is presented in Figure 7b. In the absence of any electrolytes, the trends of the removal percentage of heavy metals were recorded as Pb (99.05%) > Cu (95.01%) > Cd (92.5%) > Ni (80.85%). The removal percentage of Pb and Cu is quite similar even in the presence and absence of background electrolytes and charged organic molecules, demonstrated superior affinity of Pb and Cu toward the HNT-BC@Alg. The removal percentages of Cd and Ni slightly reduced in the presence of 0.01 CaCl$_2$ electrolytes competing between Ca with Cd and Ni sorption. Moreover, the organic molecules have an insignificant influence on the adsorption of heavy metals toward the adsorbents. The effect of electrolytes on the separation of heavy metals is negligible, demonstrating a higher affinity of heavy metals toward adsorbing heavy metals.
2.6. Effect of Adsorbent Dose on the Adsorption Capacity and Removal Percentage of Heavy Metals. The effect of the adsorbent dose was tested to identify adsorption capacity and removal percentage from multicomponent (Pb, Cu, Cd, and Ni) heavy-metal solution. The adsorption capacity of heavy metals decreased, whereas the removal percentage increased with increasing adsorbent dose (Figure 8). The trends of removal percentage and adsorption capacity were Pb > Cu > Cd > Ni. Cu and Pb could be removed up to 95% from 20 mg/L of Pb, Cu, Cd, and Ni, where the adsorbent dose was 20 g/L (Figure 8). A sharp decrease in the adsorption amount of heavy-metal ions was observed where the adsorbent dose increased from 1 to 4 g/L. The decreasing adsorption amount slowed down when increasing adsorption dose from 4 to 20 g/L. (Figure 8). Additionally, the removal percentage had a sharp increase up to 5 g/L (adsorbent dose). Later, the increasing rate of removal percentage reduced when increasing the adsorbent dose up to 20 g/L (Figure 8). This phenomenon occurs because of the presence of unsaturated/saturated active sites over the adsorbent surface. However, the removal percentage was low for Ni and Cd because of their low affinity with existing functional groups and competition with borderline acid.

2.7. Proposed Adsorption Mechanism. Transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS) elemental mapping, and Fourier transform infrared (FTIR) were performed to understand sorption characteristics and the sorption mechanism of heavy-metal ions onto the HNT-BC@Alg. The mass and atomic percentage of HNT-BC@Alg (pre-sorption and post-sorption) confirm the adsorption of aqueous heavy-metal ions (below 0.5% of the total atomic mass of the adsorbents) (Figure 9). The relative carbon and oxygen content were reduced after the adsorption of the heavy metals. The atomic and mass percentages of lead and copper were higher than the nickel and lead content, consistent with the experimental trends. Comparatively, higher contents of lead and copper support the sorption selectivity study.

The EDS elemental mapping of the HNT-BC@Alg after sorption is presented in Figure 10. The elemental mapping confirmed that active sites come from BC and HNT can sorb heavy-metal ions. The mesoporous structure of HNT-BC@Alg allows heavy-metal ions to sorb inside the active sites of polymer beads. The elemental association and distribution of heavy-metal ions with the elemental composition of the adsorbents were also observed with SEM-EDS elemental mapping, which is consistent with the TEM-EDS mapping, supporting the explained sorption interface mechanism (Figure S4). The elemental mapping of Figure 10a demonstrates that carbon has a limited association with O, Si, Al, and Ca. Alternatively, C, Ca, and O are consistently distributed over selected areas, indicating a uniform polymer network generated through the cross-linking process (Figure 10). The calcium added during the polymerization process replaced sodium ions from the alginate polymer networks during the cross-linking process. The elemental C, H, and O are derived from the
alginate biopolymer and biochar. Inorganic elements, including Si, Al, O, and other impurities (e.g., Fe), are derived from HNT and BC. The EDS mapping demonstrated that heavy metals are co-distributed with Si, Al, C, and O (Figure 10). The association and dissociation of elements both from the adsorbent and adsorbates confirm that the influence of additional active sites (derived from BC and HNT) could participate in the adsorption of heavy-metal ions. The impregnated HNT and BC could perform adsorption of heavy metals apart from enhancing surface area, active sites, and porosity of the HNT-BC@Alg. HNT can adsorb heavy metals through ion-exchange reaction, electrostatic interaction, and interparticle diffusion because of the presence of abundant active sites on the outer surface and Al–O-containing functional groups inside the lumen. HNT-BC@Alg can adsorb heavy metals through ion-exchange reaction, electrostatic interaction, and surface complexation, depending on feedstock sources and pyrolysis temperature.42,72,73 BC has an abundance of oxygen-containing functional groups, and HNT has Si–O-containing active sites on the outer surface and Al–O-containing active sites inside the lumen that could participate in adsorbing heavy-metal ions.32,61,74–76 Sugarcane bagasse as feedstock material was selected to synthesize ball-milled BC, which contains silicon (primary inorganic phase) and could support co-precipitation of heavy-metal ions.

The FTIR spectra of the BC, HNT, and HNT-BC@Alg beads are presented in Figure 11. The abundance of oxygen-containing functional groups promotes coordination bonding, hydrogen bonding, and complexation reaction for immobilizing heavy metals.84–86 Alginate is an anionic polysaccharide with an abundance of hydroxyl and carboxyl functional groups over the backbone chain of hydrophilic molecular structure.34,39 The band at 2915 cm−1 was assigned to C–H stretching because of the incorporation of alginate polymer. The peaks at 3360–3395 cm−1 correspond to hydroxyl functional groups derived from BC and calcium alginate polymers, suggesting the presence of a phenolic group (Figure 11). The intensity of OH− groups of biochar increased after polymerization processes—the peaks of broad OH− stretching resulting from low affinity between O and H. However, the intensity of OH− groups reduced after adsorption of heavy-metal ions; electrostatic interaction plays a significant role in the adsorption of heavy-metal ions. COO− asymmetric and symmetric stretching vibrations were observed at 1604 and 1419 cm−1 wavelengths, respectively. The appearance of COO−containing functional groups (1419 cm−1) occurs because of the formation of calcium alginate during the cross-linking process. However, after the adsorption of heavy-metal ions, the intensity of COO−containing functional groups reduced. Moreover, COO− vibration shifted toward a higher wavelength after the adsorption of heavy-metal ions, proving the interaction between functional groups of sodium alginate and heavy-metal ions. A new peak appears near the COO− symmetric vibration at 1380 cm−1, resulting from the interaction among the functional groups and heavy-metal ions. The peaks at 3634 and 3691 cm−1 are assigned to the stretching vibrations of Al–OH groups, and the peaks at 1091 and 1025 cm−1 are assigned to the stretching of Si–O–Si and Si–O–Al peaks were also observed in 786 and 744 cm−1, respectively (Figure 11). The silicon- and aluminum-containing functional groups come from HNT because HNT is a 1:1 kaolin group of clay minerals and composed of tetrahedral (Si–O) sheets and octahedral (Al–OH) sheets. Thus, HNT could induce Si- and Al-based active sites inside the polymer network. HNT can perform electrostatic interaction with cationic ions because of their externally negatively charged surface that is induced from Si–O-containing functional groups of HNT.45,82,83 Moreover, HNT has external and internal diameters of approximately 30–190 and 10–100 nm, respectively; those pores may also perform as active sites for loading heavy-metal ions through physical adsorption.84,85 Sugarcane bagasse-derived biochar shows peaks at 2919, 2888, 1700, 1612, 1052, 898, and 786 cm−1, corresponding to the bending vibration of −C−(CH3), C−(CH2), C=O, C≡C, COOH−, Si–O–Si, and Si–OH− (Figure 11). Usually, the bends at 2919 and 2888 cm−1 (CH2 and CH3 bend) disappear and transfer into aromatic C–H bending during the feedstock pyrolysis at a high heating temperature (HHT).86 Thus, the biochar is pyrolyzed with a low HHT to have oxygen-containing functional groups and...
aliphatic carbon to adsorb heavy-metal ions onto deprotonated active sites.

3. CONCLUSIONS

Mesoporous HNT-BC@Alg beads as adsorbent were prepared using single-route polymerization and freeze-drying process for competitive separation of soluble heavy-metal ions. The synergistic effects of alginate biopolymer, BC, and HNT could enhance heavy-metal sorption onto the adsorbent. The competitive adsorption study indicates that HNT-BC@Alg beads have higher sorption performance than the BC, HNT, and BC@Alg beads. HNT-BC@Alg beads overcome the limitations of bare alginate beads by generating mesoporous surface structure, which enables infiltration and interacts with internal active sites to immobilize heavy metals. The maximum adsorption capacities of Ni, Cd, Cu, and Pb are 2.85 ± 0.08, 6.96 ± 0.31, 16.87 ± 1.50, and 26.49 ± 2.04 mg/g, respectively. The sequence of the affinity of heavy metals is Pb > Cu > Cd > Ni. Thus, the removal percentage and sequence of selectivity were recorded as Pb (99.97−99.05%) > Cu (95.01−90.53%) > Cd (92.5−55.25%) > Ni (80.85−50.6%), even in the presence of background electrolytes and organic pollutant from environmentally relevant concentration. Increasing the solution pH also increased the adsorption capacity of heavy-metal ions due to the deprotonation of active sites of the adsorbents. Pb and Cu have greater affinity with the HNT-BC@Alg beads, which is less affected by the solution pH. The selectivity of Cd and Ni was improved from the incorporation of HNT and BC into alginate polymer beads. The experimental result of adsorbents and post-characterization confirmed that ion exchanges, electrostatic interaction, and physical sorption, including pore filling, were performed in the adsorption processes. The laboratory-scale experimental results justify that HNT-BC@Alg have higher removal percentage and selectivity at a wider range of adsorbate concentrations (20 mg/L to 200 μg/L). Thus, HNT-BC@Alg has the potential to be utilized at both point and nonpoint sources of heavy metals contaminated water for practical application. However, complete removal of mixed heavy-metal ions from the multicomponent system remains a challenging task.

4. EXPERIMENTAL SECTION

4.1. Materials and Chemicals. Sodium alginate (Alg), calcium chloride (CaCl₂), HNT (chemical formula: Al₂Si₂O₅(OH)₄), heavy-metal salts (CdCl₂, CuSO₄, NiCl₂, and Pb(NO₃)₂), and liquid chromatography−mass spectrometry (LC−MS)-grade methanol were purchased from Sigma-Aldrich. All chemicals were used without any further purification. A mixed stock solution of 100 mg/L of Cd, Cu, Ni, and Pb was prepared into Milli-Q water with 1% nitric acid, where each metal has an individual concentration of 100 mg/L. The detailed properties of heavy-metal ions are presented in Table S2. HNT was dried at 80 °C to remove free moisture before use. Raw sugarcane bagasse was collected from the Sunshine Sugar Mill, New South Wales, Australia. It was mechanically sieved (diameter < 2 mm) and dried under sunlight in a glasshouse for 2 weeks before thermal and chemical modifications. The sun-dried sugarcane bagasse was sieved to less than 2 mm and stored in an airtight plastic container before any further modification. All chemical reagents used in the study are highlighted with CAS number and mass fraction percentage (Table S3).

4.2. Preparation of HNT and BC Incorporated Mesoporous HNT-BC@Alg. Preparation of Biochar. The sugarcane bagasse was washed three times with a mixture of 30% Milli-Q water and 70% methanol before being dried at 80 °C for 24 h to reduce organic and inorganic debris and moisture. The dried sugarcane bagasse was placed in a quartz container and pyrolyzed in a muffle furnace at 400 °C for 1 h in the nitrogen environment. The pressure of nitrogen gas is programmed as 200 kPa (30 psi) to ensure nitrogen-controlled environment. Isopropanol and water were used to collect oil, syngas, and other byproducts. The prepared biochar was collected and denoted as BC after cooling. The biochar was washed with deionized water until the pH of the flushed water reached neutral. The washed BC was dried at 80 °C for 24 h under limited oxygen conditions in an oven before ball milling and polymerization.

Preparation of Ball-Milled Biochar (BC). A ball mill (Fritsch pulverisette) was used to reduce the particle size of the BC. BC was mixed with zirconium balls in a zirconium bowl. The weight ratio of the BC and ball was 1:30, where the ball diameter was 9.36 mm, the weight of each ball was 2.75 g, and the rotating speed was 300 rpm (r/min). A zirconium...
bowl (3.5 kg) was used during the ball-milling process. Approximately 15 clockwise and 15 anticlockwise rotations (total 1 h) were programmed with 2 min run time and 2 min break time between runs to allow cooling down of the instrument. The ball-milled BC was sieved to 63 μm and subsequently washed with Milli-Q water. The BC was then freeze-dried at −50 °C for 2 days in vacuum. The ball-milled BC was stored in an airtight container before any further modification.

Preparation of HNT-BC@Alg. An ionic polymerization route was used to synthesize porous polymer beads.41 The key synthesis procedure for the HNT-BC@Alg is presented in Figure 12. Approximately 4 g of sodium alginate was mixed with a mixture of 300 mL of H2O and 100 mL of methanol (1% sodium alginate), which was stirred for 2 days under airtight conditions to obtain a homogeneous mixture. Then, 4 g of BC and 4 g of dried HNT were mixed homogeneously with 1% sodium alginate (Alg) solution for 24 h at 25 °C (Figure 12). The composite solution was further magnetically stirred (450 rpm) at 50 °C for 6 h. The blended mixture was then added dropwise, falling to a 2% CaCl2 solution with vigorous stirring (300 rpm for 12 h) to form functionalized mesoporous beads (HNT-BC@Alg). The product beads were washed with deionized water several times to remove adjacent free sodium alginate and calcium chloride. The beads were then frozen at −20 °C for 48 h. The frozen beads were freeze-dried at −50 °C for 72 h in a freeze drier (α 1–4 LD plus, John Morris). After drying, the samples were stored in an airtight container for the characterization and sorption study.

4.3. Characterization Methods. Multiple characterization techniques were employed to understand the adsorbent properties, sorption characteristics, and interfacial interactions between HNT-BC@Alg and heavy-metal ions. The adsorbent was characterized using different techniques, including scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS), EDS elemental mapping, X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR). The exhausted adsorbents were collected and freeze-dried for 48 h for post-sorption characterization. SEM and EDS analyses (Bruker Nano GmbH, Germany) were conducted to understand the surface morphology and elemental composition of the adsorbents under lower to higher magnification. EDS elemental mapping was conducted at 200 kV to investigate the distribution of adsorbed heavy-metal ions over the adsorbent surface in a transmission electron microscope (JEOL TEM 2100). The FTIR spectra were collected by an FTIR spectrometer (Agilent Technologies Cary 600 series) to understand the interaction of heavy-metal ions with the active sites of the HNT-BC@Alg. Approximately 16 repetitive scans were performed at a resolution of 8 cm−1 from 500 to 4000 cm−1 to detect functional groups and their interaction with adsorbed heavy metals. To identify crystalline structures, HNT-BC@Alg (before and after sorption of heavy metals) were analyzed by XRD at room temperature (25 °C) with cobalt (Co) anode for a 3 h run time. The scan angle covered 5° < 2θ < 100° with a step size of 0.017° and a counting time of 23.622 s. The crystalline size of the materials is calculated by the Scherrer formula.87 A Brunauer–Emmett–Teller (BET) surface area analyzer (Micromeritics Tri-Star II) was used to analyze the surface area, pore size, pore diameter, and pore volume of the adsorbents (both pre-sorption and post-sorption). The thermal stability of the adsorbents was investigated at temperatures from 30 to 800 °C in a nitrogen environment, where the heating rate was selected as 20 K/min. The point of net charge (pHpzc) of the adsorbent was conducted following the immersion technique.88,89 The suspension solution pH was adjusted using 0.1/1.0 M HCl/NaOH. The suspension was rotated for 24 h in an orbital shaker at 120 rpm (r/min) to reach equilibrium pH. The changes of pH (∆pH = initial pH – final pH) were identified and plotted in relation to initial pH to determine the point of net charge of the HNT-BC@Alg.

4.4. Batch Adsorption Experiment. Adsorption isotherm, kinetics, the effect of solution pH, and adsorbent dose studies were conducted at 25 ± 1 °C to understand the sorption mechanism and removal of the divalent cations onto the studied adsorbents. All studies were performed in a 50 mL centrifuge tube containing 20 mL of adsorbate solution, which were equilibrated at 120 ± 2 rpm in an end-over-end shaker prior to sampling for measurement. For the isotherm study, individual initial concentrations (Ci) of Cd, Ni, Cu, and Pb ranging from 0.5 to 80 mg/L were employed, where adsorbent dose (m/v) = 3 g/L, contact time (T) = 12 h, and solution pH = 6.25 ± 0. To investigate sorption kinetics, samples were taken at different intervals (0.08–24 h), where C0 was 20 mg/L for Cd, Ni, Cu, and Pb; m/v was 3 g/L, and solution pH was 6.25 ± 0.1. The effect of pH on divalent cation adsorption was investigated at pH 1.80–11.50, while m/v was 5 g/L, T was 12 h, and C0 was 20 mg/L for heavy-metal ions (Cd, Ni, Cu, Pb). The pH of each sorption medium was adjusted with either 0.1/1 M HCl or 0.1/1 M NaOH. The effect of the adsorbent dose (from 1 to 20 g/L) was investigated to understand the removal percentage and the influence of the doses (where pH was 5.80, C0 was 20 mg/L for heavy-metal ions (Cd, Ni, Cu, Pb)), and T was 12 h). Additionally, the comparison of the adsorbents including BC, HNT, BC-Alg, and HNT-BC@Alg was investigated (where m/v was 5 g/L, T was 12 h, pH was 5.80 ± 0.1, and C0 was 20 mg/L for adsorption of heavy-metal ions (Cd, Ni, Cu, Pb)). The influence of background electrolytes was evaluated for the removal percentage of heavy metals under environmentally relevant conditions (C0 of each metal ion was 200 μg/L, m/v was 20 g/L, and T was set for 12 h) in the presence of electrolytes (0.001/0.01 M Na2SO4 and CaCl2) and charged organic molecules (1/10 mg/L of methylene blue). The heavy-metal ions were analyzed by either inductively coupled plasma mass spectrometry (ICP-MS, PerkinElmer NexION 350) or inductively coupled plasma optical emission spectrometry (ICP-OES, PerkinElmer Ario 200) depending on the concentration. The lowest point of detection for each of Ni, Cu, Cd, and Pb was recorded as 0.08, 0.71, 0.11, and 0.11 μg/L, respectively, in the ICP-MS, whereas 0.005, 0.091, 0.004, and 0.012 mg/L, respectively, in the ICP-OES. The recovery rates of Ni, Cu, Cd, and Pb were recorded as 96.3 ± 0.02, 97.1 ± 0.02, 96.3 ± 0.04, and 97.3 ± 0.03%, respectively. The data were analyzed using OriginPro software and were presented as the mean ± standard deviation. The Langmuir and Freundlich nonlinear isotherm model and the pseudo-first-order and pseudo-second-order nonlinear kinetic models were used to fit experimental results in the OriginPro software (Supporting Information Text S1). The sorption capacity (qe) and removal percentage of heavy metals were calculated using the following eqs E1 and E2.
adsorption capacity, \( q_e = \frac{(C_0 - C_f) V}{m} \) \hspace{1cm} (E1)

removal \( \% = \frac{(C_0 - C_f)}{C_0} \times 100 \) \hspace{1cm} (E2)

where \( q_e \) is the amount of heavy metals adsorbed (mg/g), \( C_0 \) and \( C_f \) are the initial and final concentrations of heavy metals, respectively, \( V \) is the volume of the solution (L), and \( m \) is the mass of adsorbents (g).

**ASSOCIATED CONTENT**

0 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c01642.

- Supporting Information
  - Isotherm and kinetics models (Text S1); isotherm and kinetics model parameters for sorption of heavy-metal ions onto the adsorbent (HNTs-BC@Alg) (Table S1); properties of heavy-metal ions (Table S2); list of reagents used in the study (Table S3); molecular structure of sodium alginate polymer (Figure S1); SEM image of (a) HNTs, (b) ball-milled BC, (c) digital photograph of HNT-BC@Alg, and (d) SEM image of bare calcium alginate beads (alg.) (Figure S2); point of zero charge of HNT-BC@Alg (Figure S3); and SEM-EDS color mapping of HNT-BC@Alg after adsorption of heavy-metal ions: (a) mapping area, elemental distribution of (b) carbon, (c) oxygen, (d) calcium, (e) iron, (f) aluminum, (g) phosphorous, (h) combination of silicon, aluminum, and phosphorus, (i) copper, (j) nickel, (k) cadmium, and (l) lead (Figure S4) (PDF).

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