Synthesis, characterization, and dye sorption ability of carbon nanotube–biochar nanocomposites

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Abstract

Innovative technologies incorporating engineered nanoparticles into biochar production systems could improve the functions of biochar for many applications including soil fertility enhancement, carbon sequestration and wastewater treatment. In this study, hybrid multi-walled carbon nanotube (CNT)-coated biochars were synthesized by dip-coating biomass in varying concentrations of carboxyl-functionalized CNT solutions (0.01% and 1% by weight) prior to slow pyrolysis. Untreated hickory and bagasse biochars (HC and BC, respectively) and CNT–biochar composites (HC–CNT and BC–CNT, respectively) were characterized, and the methylene blue (MB) sorption ability of the resulting chars was evaluated in batch sorption experiments. The addition of CNTs significantly enhanced the physiochemical properties of the biochars with HC–CNT-1% and BC–CNT-1% exhibiting the greatest thermal stabilities, surface areas (351 and 390 m² g⁻¹, respectively), and pore volumes (0.14 and 0.22 cc g⁻¹, respectively). Sorption kinetic and isotherm data showed that, among the biochars examined, BC–CNT-1% had the highest MB sorption capacity (6.2 mg g⁻¹). While increased pH (up to ~7), promoted the uptake of MB by all the biochars, whether coated or not, increasing ionic strength decreased the uptake of MB by all biochars tested. These findings suggest that electrostatic attraction was the dominant mechanisms for the sorption of MB onto the chars, though diffusion controlled its rate. Hybridized CNT–biochar nanocomposite can thus be considered a promising, inexpensive sorbent material for removing dyes and organic pollutants from aqueous systems.

1. Introduction

The use and release of organic dyes in many industrial products are a threat to water systems [1]. The complex aromatic structure of dyes makes them of low biodegradability and stable toward light and chemical treatments [2]. Methylene blue (3,7-bis(dimethylamino)-phenothiazin-5-iium chloride) is a cationic dye found in many industrial effluents that may induce aesthetic, and more importantly health problems such as cancers, reproductive and neurological disorders in humans and aquatic organisms [3]. A number of treatment techniques including ionic exchange, adsorption, coagulation, membrane filtration and photo-catalysis have been extensively tested for the removal of dyes from wastewater [4–8]. Among these methods, adsorption is known to be a more economical and simple treatment approach [2]. Thus, research on low-cost, high-capacity adsorbents for organic dyes is increasing [9].

Biochar is a low-cost, porous, carbon-rich product derived from the thermal degradation of organic matter (particularly waste biomass) in an oxygen-limited environment [10]. The benefits of employing eco-friendly biochars, including activated biochars, in wastewater treatment technologies have already been established [11–17]. In addition, a recent study showed that ENPs may bind to biochar surfaces (particularly after modification) to a greater extent than to commercial activated carbons [18]. Thus, marrying existing biochar technology with emerging nanotechnology to create hybrid nanomaterial–biochar composites, has great potential to...
create a new class of environmentally-friendly and cost-effective sorbents to treat a wide array of contaminants [19–24]. Carbon nanotubes (CNTs) are cylindrical tubes of graphene material that exhibit exceptional properties such as ultra-low weight, high mechanical strength, and thermal and chemical stability [25]. The potential use of CNTs as adsorbents has generated much interest [26–29] because the hollow, layered structure of CNTs endows them with characteristically high specific surface areas and correspondingly high sorption capacities for various contaminants [26,30]. Moreover, chemically functionalized CNT surfaces, grafted with specific functional groups (carboxyl, hydroxyl, amine, fluorine) provide high-affinity sorption sites for increased binding of target pollutants such as dyes via electrostatic attractions or π–π electron bonding [9,31,32]. Despite these sorptive properties, practical application of CNTs remains limited by its poor solubility, and rapid aggregation in its native state [33]. Several research efforts have been made to overcome these limitations, by loading CNTs on sorptive supports using sol gel [34], crosslinking agents [35], and carbon vapor deposition (CVD) growth techniques [25,36]. However, the high cost and formation of by-products with many of these methods has made it necessary to consider other supports. Thus, biochar is examined here as such a potential, low-cost support for CNTs.

The overarching objective of this study was to develop a simple method to synthesize hybrid CNT–biochar nanocomposite material and test its potential applications. Our specific objectives were to: (1) characterize the CNT–biochar nanocomposite, (2) determine the effects of CNT hybridization on the physiochemical properties of the biochars, (3) examine the influence of pH, contact time, and ionic strength conditions on the sorption of MB on the CNT–biochar nanocomposites, and (4) elucidate and understand the interaction mechanisms governing the sorption of MB on the CNT–biochar nanocomposite.

2. Materials and methods
2.1. Materials
Carboxylic acid-functionalized multi-walled CNTs with diameters ranging 10–20 nm were purchased from the Sinonano Company (PR China). Hickory chips and sugarcane bagasse biomass were obtained from the North Florida Research and Education Center of the University of Florida. The biomass feedstocks were dried and milled to 500 μm size fraction. Methylene blue (C16H18ClN3S, molecular weight, 319.86 g) and other chemicals employed in this study were of analytical grade and obtained from Fisher Scientific, Georgia.

2.2. Preparation of CNT–biochar nanocomposite
CNT suspensions were prepared by adding either 20 mg (0.01% by weight) or 2 g (1% by weight) of CNT powder to 200 ml of deionized (DI) water. The CNT suspensions were sonicated in an ultrasonic homogenizer (Model 300 V/T, Biologic, Inc.) with an output frequency of 20 kHz for 1 h at pulse intervals of 12 min. The resulting suspensions were designated as CNT-0.01% and CNT-1%, respectively, and used for the preparation of CNT–biochar nanocomposite.

Milled hickory chips and sugarcane bagasse biomass (feedstocks) were converted to CNT–biochar nanocomposite following a dip-coating procedure [19,37]. Specifically, 10 g of each feedstock were placed in 100 ml of the CNT suspensions and stirred for 1 h using a magnetic stirrer at 500 rpm, after which, each of the dip-coated CNT treated feedstocks was removed and oven-dried at 105 °C. Next, each of the dried CNT-treated feedstocks was placed in a quartz tube inside a tubular furnace (MTI, Richmond, CA) and pyrolyzed at 600 °C for 1 h at 10 °C/min in a flowing N2 environment. In addition, each of the untreated feedstocks was also converted into the corresponding untreated biochar using the same pyrolysis conditions. The resulting biochars produced were designated as hickory chips (HC), CNT-modified hickory chips (HC–CNT-0.01% and HC–CNT-1%), sugarcane bagasse (BC), and CNT-modified sugarcane bagasse (BC–CNT-0.01% and BC–CNT-1%). All biochars were rinsed with distilled, de-ionized water several times, oven dried, and sealed in glass containers for subsequent testing.

2.3. Characterization
Elemental carbon, hydrogen, nitrogen and oxygen content (C, H, N, and O); zeta potential, pH, and surface areas of the sorbents were determined using previously reported methods [11,24]. Because all the sorbents were made at 600 °C, the volatile matter content was not determined. Thermogravimetric analysis (TGA) was performed in a stream of air at a heating rate of 10 °C/min with a Mettler TGA/DSC1 analyzer (Columbus, OH) to test the thermal stability of the samples. The morphology of CNT-modified biochar composites was examined by transmission electron microscopy (JEOL 2010F TEM). Physiochemical features of the samples were investigated by Raman spectroscopy (Renishaw Bio Raman).

2.4. Sorption of methylene blue
An initial evaluation of the sorption ability of the chars was conducted using MB solution in batch sorption experiments. About 25 mg of each test biochar was mixed in 50 ml digestion vessels (Environmental Express) with 12.5 ml of 20 mg L−1 MB solution at room temperature (22 ± 0.5 °C). The sample solutions and their corresponding blanks and experimental controls (without either sorbent or sorbate) were agitated for 24 h on a reciprocating shaker, then filtered through 0.22 μm pore size nylon membrane (GE cellulose nylon membranes). Measurements of MB concentrations in the filtrates were determined using a Thermo Scientific EVO 60 UV–VIS spectrophotometer at a wavelength of 665 nm. Sorbed amounts of MB on test biochars were calculated as the difference between the initial and final aqueous MB solution concentrations. Sorption experiments were conducted in duplicate and the average values are reported here.

Following the initial evaluation experiments, sorption kinetics and isotherm studies of MB sorption on unmodified biochar (HC and BC) and CNT–biochar nanocomposites (HC–CNT-1% and BC–CNT-1%) were conducted. To examine sorption kinetics, 25 mg of each sorbent was mixed with 12.5 ml of 20 mg L−1 MB solution in 50 ml digestion vessels at room temperature. The sample solutions and their corresponding controls were withdrawn from the agitator at time intervals of about 2 h up to 24 h and filtered through 0.22 μm pore size nylon membranes for measurements. The pH of the filtered sample solutions were noted prior to and after sorption experiments. Sorption isotherms were obtained by adding 25 mg of each biochar to 12.5 ml MB solutions of varying concentrations (5–80 mg L−1). Sorption kinetics and isotherm experiments were performed in triplicate and the average results are presented with standard deviations.

2.5. Effect of pH and ionic strength
The effect of pH on MB sorption by the CNT-modified and unmodified biochar sorbents was evaluated by adding 25 mg of each biochar to 12.5 ml of 20 mg L−1 MB solutions in 50 ml digestion vessels with pH condition ranging (2–10, adjusted by adding aqueous solutions of either 0.1 M NaOH or 0.1 M HCl. To study the effect of ionic strength, pre-determined amounts of NaCl were
added to obtain 0.01 M, 0.05 M, 0.1 M, and 0.5 M ionic strength solutions. The sample mixtures and their corresponding blanks were agitated for 24 h, and then filtered and treated as described above. Sorption experiments at different pH or ionic strength were conducted in triplicate.

3. Results and discussion

3.1. Biochar properties

The properties of both hickory (HC) and bagasse biochars (BC) were generally improved by the addition of 1% CNTs (Table 1). In particular, the surface areas of HC–CNT-1% and BC–CNT-1% were about 3 and 40 times greater than their unmodified control biochars (HC and BC), surface areas, respectively, suggesting more CNTs were anchored to BC than to HC. In addition, the pore volume of the sorbents also increased with the addition of the CNTs (Table 1), suggesting the CNT pretreatment could potentially increase the porosity of the biochars. Results of the zeta potential measurements showed that the surfaces of the hybrid biochar sorbents also became increasingly negatively charged with increasing amounts of CNTs added, probably because the CNTs (zeta potential \(\pm 46.3 \text{ mV}\)) used in this work are negatively charged.

TGA profiles of HC and BC samples exhibited a slightly higher thermal stability with increasing introduction of CNTs (Fig. 1a and b), though, the difference in stability was more obvious for BC–CNT nanocomposites. The thermal degradation of pyrolyzed carbon materials, typically show loss of moisture (50–100 °C), followed by the disappearance of transformation carbon (e.g., aromatic C–C groups) from 100 to 350 °C, and finally, the formation of graphitic chars beyond 350 °C [19,38]. Weight losses in both CNT-modified and unmodified biochars were insignificant until 350 °C, thereafter, comparatively greater weight losses (~80%) were observed in the unmodified chars from about 350–500 °C than CNT-modified chars (~70%). The thermal decomposition behavior of the CNT-1% biochars, particularly, BC–CNT-1% closely resembled the CNT thermal curve, degrading at about 400 °C.

Features of the Raman spectra (Fig. 2a and b) include the disorder mode D-band (~1350 cm\(^{-1}\)) induced by sp\(^3\) hybridization and the tangential mode G-band, representing crystalline graphitic/sp\(^2\) carbon stretching vibrations (1500–1600 cm\(^{-1}\)) [31,39]. Generally, the D-band originates from defects and functionalities (e.g., –OH, –C=O, –COOH, and –F) within CNT walls [40], and increased \(I_D/I_G\) indicates higher defect concentration (increased functional groups) on the sorbents surface [31]. Unmodified HC and BC biochars had lower \(I_D/I_G\) ratios (1.12 and 1.11, respectively), than CNT (1.78) (Table 1). But, after incorporating CNTs onto the biochars, \(I_D/I_G\) ratios of the hybrid HC–CNT and BC–CNT samples increased, indicating increased functionalities on the hybrid sorbents. TEM images of HC–CNT-1% and BC–CNT-1% (Supplementary information, Fig. S1) showed the presence of tubular CNT bundles (diameter, 15–25 nm) on the char surfaces which further demonstrates the incorporation of CNTs in the biochar nanocomposites.

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>Zeta potential (mV)</th>
<th>BET N(_2) surface area (m(^2) g(^{-1}))</th>
<th>Pore volume (cc g(^{-1}))</th>
<th>C %</th>
<th>H %</th>
<th>N %</th>
<th>O %</th>
<th>Raman intensity (disorder/order ratio) (I_D/I_G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC</td>
<td>7.3</td>
<td>-28.8</td>
<td>289</td>
<td>0.001</td>
<td>81.8</td>
<td>2.2</td>
<td>0.7</td>
<td>15.3</td>
<td>1.11</td>
</tr>
<tr>
<td>HC–CNT-0.01%</td>
<td>7.4</td>
<td>-33.2</td>
<td>257</td>
<td>0.003</td>
<td>84.1</td>
<td>2.5</td>
<td>0.4</td>
<td>13</td>
<td>1.14</td>
</tr>
<tr>
<td>HC–CNT-1%</td>
<td>7.5</td>
<td>-41.4</td>
<td>352</td>
<td>0.138</td>
<td>80.3</td>
<td>2.1</td>
<td>0.2</td>
<td>17.4</td>
<td>1.30</td>
</tr>
<tr>
<td>BC</td>
<td>6.9</td>
<td>-32.7</td>
<td>9</td>
<td>0.000</td>
<td>76.4</td>
<td>2.9</td>
<td>0.8</td>
<td>19.9</td>
<td>1.12</td>
</tr>
<tr>
<td>BC–CNT-0.01%</td>
<td>7.0</td>
<td>-34.1</td>
<td>120</td>
<td>0.008</td>
<td>79.3</td>
<td>2.2</td>
<td>0.8</td>
<td>17.7</td>
<td>1.15</td>
</tr>
<tr>
<td>BC–CNT-1%</td>
<td>7.3</td>
<td>-44.6</td>
<td>390</td>
<td>0.220</td>
<td>85.7</td>
<td>1.7</td>
<td>0.7</td>
<td>11.9</td>
<td>1.28</td>
</tr>
</tbody>
</table>

3.2. Methylene blue removal efficiency of biochars

Though MB was sorbed by both CNT-modified and unmodified biochars, MB removal efficiencies increased with increasing CNT additions (Fig. 3). The highest removal of MB by the sorbents was observed for HC–CNT-1% (47% removal) and BC–CNT-1% (64% removal). The removal of MB by the biochars modified with 0.01% CNTs, however, was similar to or even slightly lower than that by the unmodified one (Fig. 3). These findings are consistent with characterization results which showed the most improvements in specific surface area/pore volume and surface chemistry properties (e.g., zeta potential and Raman functionality) of biochars with additions of 1% CNT. Several mechanisms have been proposed for the interaction of organic contaminants with pristine and functionalized CNT including hydrophobic interaction, hydrogen bonding, electrostatic attractions and \(\pi-\pi\) interactions between
graphitic surfaces of CNT and organic molecules containing C@C bonds [2,30,41]. To elucidate the sorption interaction between the hybrid-CNT-sorbents and MB, further testing under varied conditions was conducted using the HC–CNT-1% and BC–CNT-1%.

3.3. Sorption kinetics

Sorption versus time profiles for the sorbents showed different sorption behaviors for the biochars (Fig. 4a–d). For instance, pseudo-equilibrium times for MB sorption were reached in the order of BC–CNT-1% < HC < BC < HC–CNT-1%. The sorption kinetic data were simulated with the pseudo-first order, pseudo-second order, and Elovich models. The CNT–biochar nanocomposites exhibited much better correlation of the experimental data with first and second order models ($R^2 > 0.75$) than HC and BC ($R^2 < 0.59$, Table 2). The first ($k_1$) and second order ($k_2$) sorption rate constants were higher for HC (1.08 and 1.90 h⁻¹) and BC (18.94 and 19.44 h⁻¹) than for their respective CNT-modified chars (HC–CNT-1% (0.97 and 0.67 h⁻¹) and BC–CNT-1% (13.08 and 5.16 h⁻¹)), suggesting faster initial uptake of MB on the unmodified biochars. This could be attributed to the fact that the CNT–biochar nanocomposites have larger porosities (pore volume), which could increase the diffusive interaction time to delay the initial MB sorption. Intraparticle diffusion kinetic plots were linear and well-correlated with MB sorption ($R^2 > 0.75$) for all sorbents (Supplementary information, Fig. S2), confirming the importance of the diffusive interaction between the MB and the sorbents.

The pseudo-second order model, which predominantly describes chemisorption processes and interaction of functional groups on sorbents with contaminants [42], was the best fit for BC–CNT-1% sorption kinetics data ($R^2 = 0.96$). This suggests stronger affiliations of MB to the —COOH functionality on BC–CNT-1% than present for the unmodified biochars. The Elovich model, which also evaluates chemisorption mechanisms [43], did very well modeling MB sorption by HC–CNT-1% ($R^2 = 0.98$) and may also due to the involvement of carboxyl groups in MB sorption.

3.4. Sorption isotherms

Equilibrium isotherms of HC, BC, HC–CNT-1%, and BC–CNT-1% (Fig. 5a–d) showed increasing uptake of MB with increasing concentrations of aqueous MB until apparent maximum sorption capacity was reached. Sorption capacities of HC–CNT-1% and BC–CNT-1%, indicated via Langmuir modeling (2.4 and 5.5 mg g⁻¹, respectively), were almost twice those of their respective unmodified biochar, (1.3 and 2.2 mg g⁻¹, respectively). Similar sorption capacities were reported for some carbonaceous waste materials but the observed values are much lower than those of some other hybrid CNT materials (Supplementary information, Table S1), suggesting further investigations are still needed to optimize the synthesis of the CNT–biochar nanocomposites to improve their sorption capacities to MB.

While both Langmuir and Freundlich models reproduced the sorption isotherm data reasonably well, the Langmuir–Freundlich (L–F) model fit both unmodified and CNT-modified biochars ($R^2 > 0.90$) best (Table 2 and Fig. 5), indicating the sorption of MB on the biochar base sorbents could be controlled multiple mechanisms. In the literature, the L–F model is often used to describe the sorption of chemicals by heterogeneous materials, including biochars, through multiple processes [12,44]. In this work, the sorption of MB on the CNT–biochar nanocomposites could be controlled by two processes: (1) MB sorbed onto high affinity binding sites within CNT and (2) MB sorbs to biochar itself as the CNT sites become filled.

3.5. Effect of pH

Solution pH can influence both the surface charge of a sorbent as well as the degree of ionization and conformation of a sorbate (such as MB) [9,45,46]. With increasing pH, there was an increase in MB sorption by all the biochars, until pH of 7, above which, no significant pH dependence was observed (Fig. 6a). Similar trends have been reported in the literature for MB sorption on other sorbents [1,46]. All the biochars used in this study were predominantly negatively charged in DI water (Table 1), which...
Fig. 4. Sorption kinetics plots of biochar based sorbents: (a) HC, (b) HC–CNT-1%, (c) BC, and (d) BC–CNT-1%.

Table 2
Summary of models and best-fit parameters of the sorption kinetics and isotherms.

<table>
<thead>
<tr>
<th>Sorbents</th>
<th>Model</th>
<th>Parameter 1</th>
<th>Parameter 2</th>
<th>Parameter 3</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC</td>
<td>First order ( q_t = q_e \left(1 - e^{-k_1 t}\right) )</td>
<td>( k_1 = 1.08 )</td>
<td>( q_e = 0.80 )</td>
<td>–</td>
<td>0.464</td>
</tr>
<tr>
<td></td>
<td>Second order ( q_t = k_2 q_e e^{-k_2 t} )</td>
<td>( k_2 = 1.90 )</td>
<td>( q_e = 0.89 )</td>
<td>–</td>
<td>0.588</td>
</tr>
<tr>
<td></td>
<td>Elovich ( q_t = \frac{1}{a + \beta t} )</td>
<td>( a = 10.86 )</td>
<td>( \beta = 8.19 )</td>
<td>–</td>
<td>0.761</td>
</tr>
<tr>
<td></td>
<td>Langmuir ( q_t = \frac{K_s q_e}{1 + K_s C_e} )</td>
<td>( K_s = 1.10 )</td>
<td>( S_{max} = 1.28 )</td>
<td>–</td>
<td>0.930</td>
</tr>
<tr>
<td></td>
<td>Freundlich ( q_t = K_F C_e^{1/n} )</td>
<td>( K_F = 0.62 )</td>
<td>( n = 0.19 )</td>
<td>–</td>
<td>0.748</td>
</tr>
<tr>
<td></td>
<td>Langmuir–Freundlich ( q_t = \frac{S_{max} (K_s C_e)^{1/n}}{1 + (K_s C_e)^{1/n}} )</td>
<td>( K_s = 4.047 )</td>
<td>( S_{max} = 2.40 )</td>
<td>( n = 9.23 )</td>
<td>0.940</td>
</tr>
<tr>
<td>HC–CNT-1%</td>
<td>First order ( q_t = q_e \left(1 - e^{-k_1 t}\right) )</td>
<td>( k_1 = 0.97 )</td>
<td>( q_e = 2.10 )</td>
<td>–</td>
<td>0.759</td>
</tr>
<tr>
<td></td>
<td>Second order ( q_t = k_2 q_e e^{-k_2 t} )</td>
<td>( k_2 = 0.67 )</td>
<td>( q_e = 2.28 )</td>
<td>–</td>
<td>0.869</td>
</tr>
<tr>
<td></td>
<td>Elovich ( q_t = \frac{1}{a + \beta t} )</td>
<td>( a = 22.2 )</td>
<td>( \beta = 3.11 )</td>
<td>–</td>
<td>0.978</td>
</tr>
<tr>
<td></td>
<td>Langmuir ( K_s = 17.19 )</td>
<td>( S_{max} = 2.40 )</td>
<td>–</td>
<td>0.851</td>
<td></td>
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<tr>
<td></td>
<td>Freundlich ( K_F = 1.44 )</td>
<td>( n = 0.14 )</td>
<td>–</td>
<td>0.764</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Langmuir–Freundlich ( K_s = 4.407 )</td>
<td>( S_{max} = 2.40 )</td>
<td>( n = 27.86 )</td>
<td>–</td>
<td>0.987</td>
</tr>
<tr>
<td>BC</td>
<td>First order ( q_t = q_e \left(1 - e^{-k_1 t}\right) )</td>
<td>( k_1 = 18.94 )</td>
<td>( q_e = 1.90 )</td>
<td>–</td>
<td>0.265</td>
</tr>
<tr>
<td></td>
<td>Second order ( q_t = k_2 q_e e^{-k_2 t} )</td>
<td>( k_2 = 19.44 )</td>
<td>( q_e = 1.92 )</td>
<td>–</td>
<td>0.336</td>
</tr>
<tr>
<td></td>
<td>Elovich ( q_t = \frac{1}{a + \beta t} )</td>
<td>( a = 27.107.52 )</td>
<td>( \beta = 7.32 )</td>
<td>–</td>
<td>0.764</td>
</tr>
<tr>
<td></td>
<td>Langmuir ( K = 2.09 )</td>
<td>( S_{max} = 2.20 )</td>
<td>–</td>
<td>0.917</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Freundlich ( K_F = 1.07 )</td>
<td>( n = 0.20 )</td>
<td>–</td>
<td>0.797</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Langmuir–Freundlich ( K = 2.24 )</td>
<td>( S_{max} = 2.20 )</td>
<td>( n = 1.81 )</td>
<td>–</td>
<td>0.920</td>
</tr>
<tr>
<td>BC–CNT-1%</td>
<td>First order ( q_t = q_e \left(1 - e^{-k_1 t}\right) )</td>
<td>( k_1 = 13.08 )</td>
<td>( q_e = 4.30 )</td>
<td>–</td>
<td>0.935</td>
</tr>
<tr>
<td></td>
<td>Second order ( q_t = k_2 q_e e^{-k_2 t} )</td>
<td>( k_2 = 5.16 )</td>
<td>( q_e = 4.37 )</td>
<td>–</td>
<td>0.956</td>
</tr>
<tr>
<td></td>
<td>Elovich ( q_t = \frac{1}{a + \beta t} )</td>
<td>( a = 0.099779.76 )</td>
<td>( \beta = 3.91 )</td>
<td>–</td>
<td>0.799</td>
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<tr>
<td></td>
<td>Langmuir ( K = 4.84 )</td>
<td>( S_{max} = 5.50 )</td>
<td>–</td>
<td>0.961</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Freundlich ( K_F = 3.02 )</td>
<td>( n = 0.18 )</td>
<td>–</td>
<td>0.757</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Langmuir–Freundlich ( K = 5.12 )</td>
<td>( S_{max} = 5.50 )</td>
<td>( n = 1.08 )</td>
<td>–</td>
<td>0.961</td>
</tr>
</tbody>
</table>

\( q_t \) and \( q_e \) are the amount of sorbate removed at time \( t \) and at equilibrium, respectively (mg g⁻¹), and \( k_1 \) and \( k_2 \) are the first-order and second-order sorption rate constants (h⁻¹), respectively, \( x \) is the initial sorption rate (mg g⁻¹ h⁻¹) and \( \beta \) is the desorption constant (g mg⁻¹). \( K \) and \( K_F \) are the Langmuir bonding term related to interaction energies (L mg⁻¹) and the Freundlich affinity coefficient (mg⁻¹ L² g⁻¹), respectively, \( S_{max} \) is the Langmuir maximum capacity (mg g⁻¹), \( C_e \) is the equilibrium solution concentration (mg L⁻¹) of the sorbate, and \( n \) is the Freundlich linearity constant.
would promote the sorption of positively charged MB (pK<sub>a</sub> 3.8) by electrostatic attraction [45]. In particular, the electrostatic attraction of positively charged MB to the CNT–biochar nanocomposites should increase with increasing pH (below 7) because of the increasing deprotonation of the functional (e.g., carboxyl and hydroxyl) groups of the CNTs within the biochar matrix. On the other

Fig. 5. Sorption isotherms of biochar based sorbents: (a) HC, (b) HC–CNT-1%, (c) BC, and (d) BC–CNT-1%.

Fig. 6. Effects of solution chemistry on methylene sorption on biochar based sorbents: (a) pH effects, (b) ionic strength effects on HC and HC–CNT-1%, and (c) ionic strength effects on BC and BC–CNT-1%.
hand, because MB consists of benzene rings, which can donate π electrons to π-electron acceptors like the functional groups of the CNTs, π–π coupling may be another important mechanism promoting the sorption of MB on the CNT–biochar nanocomposites. In this case, a low pH causes protonation of the carboxyl groups, which should favor the sorption of strong π-donor compounds [14,47,48].

3.6. Effect of ionic strength

The presence of cations such as Na⁺ have been shown previously to reduce the sorption of MB onto fungus [49]. In theory, when electrostatic forces between sorbent surfaces and sorbate ions are attractive, an increase in ionic strength will decrease the sorption capacity of the sorbate due to competition of Na⁺ with positively charged MB for sorption sites [9]. Here, MB sorption onto all the biochar based sorbents decreased somewhat as concentrations of NaCl increased from 0.01 to 0.1 M (Fig. 6b and c), confirming involvement of electrostatic interaction in MB sorption. With 0.5 M of NaCl, however, there was no significant decrease, and even a slight increase in MB sorption by some of the sorbents. This effect has been reported previously and may arise from dimerization or aggregation of dye molecules at very high salt concentrations [9,50] and is independent of MB interactions with the sorbent.

4. Conclusions

Characterization of the sorbents indicated that the physicochemical properties (e.g., surface area, porosity, and thermal stability) of the biochars were enhanced by additions of CNTs. The BC–CNT-1% char had the highest sorption capacity to MB among all the sorbents, likely because it may have anchored more CNTs judging from its better thermal stability, higher surface area, and larger pore volume. The data collected suggests that electrostatic attraction was the dominant mechanism for sorption of MB onto the chars, but chemisorption such as π–π bonding should not be ruled out as a contributing sorption mechanism. Intrapore diffusion was also likely to control the rate at which MB was removed from solution onto the biochar based sorbents.

Though the overall sorption capacity of the CNT-hybridized chars studied were lower than those of some other hybrid sorbents reported in literature, the synthesis procedure employed here is simple, inexpensive, and can be further optimized. The results presented have established the potential of biochar-CNT hybrid sorbents to be used for environmental remediation of dyes and possibly other organic pollutants. In addition to their low cost, they may provide additional environmental benefits, such as carbon sequestration and soil amelioration.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/jcej.2013.09.074.

References


