



# Reed biochar supported hydroxyapatite nanocomposite: Characterization and reactivity for methylene blue removal from aqueous media

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## ABSTRACT

Adsorption ability of nanoscale hydroxyapatite (HAP) is compromised by aggregation of HAP particles. In this study, reed derived biochar (BC) was used as a supporting material to stabilize HAP to enhance the Methylene blue (MB) elimination from aqueous media, while the BC-supported HAP (BC-HAP) was synthesized by precipitating the nanoscale HAP on BC surfaces. Characteristics of BC-HAP and its roles in MB adsorption were systematically investigated in the lab. Results showed that HAP was well dispersed on the BC, and aggregation was dramatically reduced. The BC-HAP composite exhibited much higher surface area, pore volume, and superior adsorption ability than virgin BC or HAP, which was ascribed to the enhancement of colloidal stability and surface area, as well as reactivity of BC-HAP. MB adsorption amount was raised with an increasing in solution pH and temperature, while decreased with increasing ionic strength. Meanwhile, the addition of humic acid could improve MB adsorption by BC-HAP, and the equilibrium adsorption data and adsorption kinetics followed the Freundlich isotherm model and the Elovich kinetic model, respectively. Adsorption mechanisms of MB on BC-HAP might be governed by electrostatic attraction, hydrogen-bonding, Lewis acid-base interaction, and  $\pi$ - $\pi$  dispersion interaction. Therefore, the BC-HAP nanocomposite could be an effective and promising adsorbent for MB removal from aqueous media owing to its high efficiency and excellent reusability.

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## 1. Introduction

Dye contaminants in wastewater, such as Methylene blue (MB), jeopardize ecosystems and human beings [1]. MB is a representative phenothiazine-type cationic dye commonly used in dyeing, printing, and leather industries [2,3]. However, due to the mutagenic/carcinogenic effects and non-biodegradability, MB is toxic to human beings and animals, particularly aquatic biota [4], requiring effective removal of MB from the industrial effluents or polluted water.

Several methods have been employed to remove MB from colored effluents (such as solvent extraction, degradation, membrane filtration, coagulation/flocculation, and adsorption), where the adsorption technique is the most feasible one, owing to its procedural simplicity, ease of industrial application, high efficiency, and availability of adsorbent

materials [5,6]. The use of nanoscale hydroxyapatite (HAP) for adsorption removal of dyes present in aqueous effluents has attracted great attention recently [7]. For instance, the removal of reactive blue 204 [8], methylene blue [9] and reactive blue 19 [10] by nanoscale HAP have been reported in the literature. Nanoscale HAP is an environmental benign functional material due to its nontoxicity, biocompatibility, and biodegradability [9]. However, technical challenges persist, limiting the wide application of HAP nanoparticles. Due to the nano-size effects such as relatively large surface area and good reactivity, HAP nanoparticles are unstable in aqueous solution and tend to aggregate rapidly. This causes the formation of much bigger (micrometers to millimeters range) particles/flocs, thereby losing its aqueous dispersibility and chemical reactivity, which then may reduce its adsorption ability towards contaminants [10,11]. Moreover, the application of large quantities of HAP is limited by both the material cost and the secondary contamination, such as eutrophication [12].

To overcome these problems when using nanoscale HAP for toxic dyes removal, efforts have been made to improve the colloidal stability and adsorption efficiency by modifying HAP with stabilization

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techniques [11]. For instance, Liu and Zhao [13,14] reported that sodium carboxymethyl cellulose stabilized iron phosphate and chlorapatite (Cl-substituted HAP) nanoparticles could effectively immobilize Cu(II) and Pb(II) in soil and decrease phosphate leaching into the environment. Wan et al. [15,16] prepared sodium dodecyl sulfate and rhamnolipid stabilized nano-chlorapatite, and they investigated the immobilization efficiency of Pb(II) in contaminated sediment. Contrarily, coupling nanoscale HAP with a support material, such as transition metals-supported HAP [17], clay-supported HAP [18], or Fe<sub>3</sub>O<sub>4</sub>-supported HAP [19], would prevent its aggregation, combining the advantages of the support material and HAP, thereby enhancing adsorption/degradation/immobilization efficiency towards contaminants. However, a good support material also should be inexpensive, eco-friendly, and able to alleviate negative effects caused by bare nanoscale HAP treatment.

Biochar (BC) is one of the most promising support materials for nanomaterials due to its great specific surface, rich functional groups, high porosity, and stability, as well as the cost-effective and environmentally friendly nature [20]. Previous studies have demonstrated the ability of BC as a support material for nanoscale zero-valent iron (nZVI) [21–24], carbon nanotube and graphene oxide [25], iron phosphate nanoparticles [26], and reduced graphene oxide [27]. Recently, BC-supported HAP has been successfully applied for the remediation of lead-contaminated soil [28,29]. However, to our best knowledge, there is no study relating the application of biochar-supported nanoscale HAP in removing contaminants from aqueous media until now.

This study prepares and uses a type of BC-supported HAP (BC-HAP) nanocomposite (using reed (*Phragmites australis*) derived BC as a supporting material) as a novel adsorption material for MB removal from aqueous media, thus avoiding the negative effect of nanoscale HAP in environmental remediation. The structural characteristics of as-obtained BC-HAP material will be evaluated via various characterized techniques. To further quantitatively investigate its adsorption performance to MB, we focus on the effects of pH, BC-HAP dosage, adsorption time, ionic strength, temperature, and the presence of humic acid on MB adsorption properties. Moreover, adsorption kinetics and isotherms for MB adsorption will be investigated. Finally, the reusability of the adsorbent will be explored.

## 2. Materials and methods

### 2.1. Preparation of BC

Raw feedstocks used for BC production are reed straw biomass, collected from an estuarine wetland in Changsha, China. The reed straw biomass was washed with deionized water, cut to 1–2 cm pieces, dried in an oven at 60 °C for 24 h, and crushed into pieces of ~0.45–1.0 mm. The powdered feedstocks were then placed in a quartz porcelain boat and pyrolyzed in a furnace at 500 °C for 2 h with an atmosphere of N<sub>2</sub> (nitrogen flow rate = 300 cm<sup>3</sup>/min). After cooling, the BC samples were ground to <150 μm (100 mesh sieve), washed with deionized water, dried in an oven at 80 °C for 4 h, and sealed for further use.

### 2.2. Preparation of BC-HAP

All chemicals used were of analytical grade, purchased from Sinopharm Chemical Reagent Company (Shanghai, China). BC-HAP composite samples were prepared using the following procedure. Firstly, NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> was dissolved in deionized water to get a 0.03 mol/L solution. Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O was then dissolved in deionized water to get a 0.05 mol/L solution. Meanwhile, 1 g of fine BC particles was dispersed in the calcium nitrate solution according to a previously reported method [30]; and then phosphate solution was added dropwise into the calcium nitrate solution. The mixture was agitated continuously for 2 h at room temperature. The pH of the mixture was kept at 11 during the reaction. The precipitates were then washed with

deionized water four times. The obtained materials were dried at 80 °C for 72 h. The final product was labeled as BC-HAP with a BC to HAP mass ratio of 1:5. The BC:HAP materials with BC to HAP mass ratios of 1:1 and 1:10 were also prepared through the above process, respectively. Unsupported HAP (without BC) was also synthesized using the same method.

### 2.3. Characterization of the prepared adsorbent

The ash content of BC was determined by heating the samples in a muffle furnace at 750 °C for 4 h [31]. Elemental analysis (C, H, O and N) were recorded on an Elementar Vario EL III element analyzer (Elementar Instruments, Inc., Germany). The pH of BC was determined by a pH meter in water at a 1:5 (w/v) ratio. The Brunauer-Emmett-Teller (BET) specific surface areas of BC and BC-HAP were examined using N<sub>2</sub> adsorption-desorption isotherm analysis at 77 K on a Micromeritics ASAP 2010 surface area/pore size analyzer (Micromeritics, USA). Scanning electron microscopy (SEM, Model S-3000N, Hitachi, Japan) was adopted to investigate the surface morphology of the synthetic materials. Crystal structures of BC and BC-HAP were analyzed using an X-ray diffractometer (XRD, Rigaku D/max-IIIb, Tokyo, Japan). Fourier transform-infrared spectroscopy (FTIR, Nicolet iS5, Thermofisher, USA) was used to identify the functional groups of BC and BC-HAP over a wavenumber range from 500 to 4000 cm<sup>-1</sup>.

### 2.4. Sedimentation curves

To compare the dispersity and colloidal stability of virgin HAP with the BC-supported HAP composite, the sedimentation curves of HAP and BC-HAP were determined using UV scanning [32]. The suspension (1.0 g/L) of each sample was applied and sonicated for 10 min, and then the absorbance was measured continuously for 4 h at 300 nm with a UV detector.

### 2.5. Batch adsorption studies

In a typical adsorption procedure, 50 mg BC-HAP adsorbent and 50 mL of different concentrations of MB solution were placed in a 100 mL flask and agitated at 25 °C and 200 rpm. To investigate the influence of pH, batch adsorption experiments were conducted of 50 mL of MB solution (50 mg/L) with various pH values (3–11, adjusted with 0.1 mol/L NaOH or HCl). The MB adsorption isotherms were obtained using different flasks, which contained the MB (50 mL) solution with initial concentrations of 20, 40, 60, 80, 100, 150, and 200 mg/L in the presence of 50 mg of adsorbent. The mixtures in the flasks were then stirred at 200 rpm at 283 K, 298 K, and 313 K. To explore the adsorption kinetics, the 500 mL of MB solution (20, 50, and 80 mg/L) was added to different flasks and shaken at 200 rpm with 50 mg of adsorption material. The solid and MB solution were separated by centrifugation. The residual concentration of MB was measured on a UV-vis spectroscopy (Shimadzu, UV-2550) at wavelengths of 664 nm. The adsorption for MB was calculated by conducting mass balance between initial and final concentrations. The adsorption capacity ( $q_e$ ) and removal rate (%R, removal percentage of MB) were calculated using the following formulas:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

$$\%R = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

where  $q_e$  (mg/g) is the equilibrium adsorption capacity;  $C_0$  and  $C_e$  (mg/L) are the beginning and remaining concentration at equilibrium, respectively;  $V$  (L) is the solution volume; and  $m$  (g) is the mass of

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