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Remediation and Restoration

Functionalized Biochar/Clay Composites for Reducing the Bioavailable Fraction of Arsenic and Cadmium in River Sediment

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Abstract: Biochar has frequently been used for the treatment of heavy metal pollution in water and soil; its effect on contaminated sediments requires further research. To improve the ability of biochar to immobilize heavy metals in sediment, we prepared a functionalized biochar/attapulgite composite by pyrolysis of the clay attapulgite and zinc chloride–pretreated rice straw biomass. Compared with the original biochar, the biochar/attapulgite composite had a large increase in specific surface area, pore volume, oxygen-containing functional groups, and cation exchange capacity. Biochar effectively improved the dispersibility of attapulgite as a matrix. The results showed that the biochar/attapulgite composite effectively reduced the bioavailable fraction of arsenic (As) and cadmium (Cd) in river sediment, which was a great improvement compared with the raw biochar. After the sediment was treated with different biochar/attapulgite composites, the concentrations of As and Cd in the overlying water and the porewater, and the content of acid-extractable and toxicity characteristic leaching procedure (TCLP)-extractable As and Cd in the solid phase of the sediment decreased significantly. Both zinc chloride activation and attapulgite improved As and Cd immobilization in sediment when we used the biochar/attapulgite composite. The results suggest that biochar/attapulgite composite can be used as an efficient in situ sorbent amendment to improve the heavy metal immobilization ability of the sediment. *Environ Toxicol Chem* 2019;38:2337–2347. © 2019 SETAC

Keywords: Bioavailability; Heavy metals; Sediment toxicity; Sediment chemistry; Environmental chemistry

INTRODUCTION

Heavy metals are pollutants with acute toxicity, persistence, nonbiodegradability, and bioaccumulation characteristics (Fan et al. 2008). Studies have shown that heavy metals entering the water system are mainly concentrated in suspended solids and sediment, and that the concentration of most metals in the sediment is several orders of magnitude higher than the concentration in the water. Sediment is an important reservoir and destination for heavy metals in water, and it is also the main living place and food source of benthic organisms (Yu et al. 2001). The heavy metals in sediment may accumulate in benthic organisms, inhibiting their growth and reproduction, and they can also be enriched in shellfish, fish, and mammals through food chain biomagnification, finally entering the human body (Mao et al. 2013). At the same time, heavy metals in sediment can be rereleased into the water body by dissolution, desorption, and biodegradation, causing secondary pollution (Yu et al. 2001; Mao et al. 2013). Thus the problem of heavy metal pollution in sediment needs to be addressed.

Biochar has great potential for adsorption of heavy metals because the raw materials are widely available, it is low cost, and it has favorable physical/chemical characteristics (Tan et al. 2015). A great number of studies have addressed the application of biochar for treatment of heavy metal pollution in water and soil (Beesley et al. 2011; Lehmann et al. 2011; Ahmad et al. 2014; Liu et al. 2015; Ding et al. 2016; Huang et al. 2018; Shi et al. 2018). Biochar can also be used as an effective carbonaceous material for in situ remediation of contaminated sediment by adsorbing heavy metals, preventing the release of heavy metals from sediments into water bodies,

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and reducing their bioavailability (Ghosh et al. 2011; Yan et al. 2016; Bekris et al. 2017; Lin et al. 2018). However, the functionality of biochar depends on its physical and chemical properties, which are greatly influenced by the raw materials used, pyrolysis techniques, and pyrolysis conditions (Tan et al. 2015; Bakshi et al. 2018; Cai et al. 2018). A number of researchers have recently attempted to synthesize biochar composites to improve its properties and expand its application range (Rajapaksha et al. 2016; Tan et al. 2016; Zhu et al. 2018).

Clay minerals have been widely used to develop cost-effective adsorbents for pollutant removal from water (Jiang et al. 2018; Li D et al. 2018; Li H et al. 2019; Zhang et al. 2019). The physicochemical properties of clay minerals (including their layered structure, high specific surface area, and high ion exchange capacity) give them a great potential to immobilize various contaminants such as heavy metals and organic compounds (Yao et al. 2014; Yadav et al. 2019; Zhang et al. 2019). Attapulgite is one of the most studied clays and can potentially be used as a low-cost adsorbent. Attapulgite is a natural fibrous hydrated magnesium silicate crystal with a medium cation exchange capacity (CEC), a large specific surface area, and an active hydroxyl group on its surface (Huang et al. 2012; Mu et al. 2013; Mu and Wang, 2015; Yin et al. 2019). Due to its low cost, abundance in nature, unique structure, and nontoxicity, attapulgite has been widely recognized as a low-cost adsorbent (Li Y et al. 2017; Mu and Wang, 2015). To reduce the cost of biochar adsorbents and increase its adsorption capacity of pollutants, several studies have been conducted to develop effective and simple methods for producing biochar/mineral composites. Among these composite materials, biochar is used as a good porous matrix to support mineral nanoparticles (Yao et al. 2014; Li Y et al. 2017; Liu et al. 2019). At the same time, the higher CEC and specific surface area of clay minerals contribute to the improvement of biochar adsorption capacity. Yao et al. (2014) synthesized montmorillonite- and kaolinite-loaded biochar/clay mineral composites, which had nearly 5 times more adsorption capacity for methylene blue than raw biochar. Y. Li et al. (2017) prepared biochar/clay mineral composites using natural attapulgite, which significantly improved the adsorption of norfloxacin compared with the original biochar. S. Wang et al. (2015) synthesized manganese oxide–modified and birnessite-modified biochars for arsenate and lead sorption, and the results suggested that the sorption capacities of the 2 modified biochars were significantly higher than that of the unmodified biochar. Among the many biochar-based mineral composites recently developed, few have been used for removing contaminants from sediment. Furthermore, previous studies have reported that the introduction of a mineral into biochar may block the pores of the biochar, decreasing its specific surface area (Wang S et al. 2015; Yu et al. 2015).

To further improve the properties and performance of the biochar/mineral composites, the biochar can be activated and modified by physical and chemical methods (Rajapaksha et al. 2016; Tan et al. 2016; Sizmur et al. 2017). In the chemical activation method, certain acids, bases, and oxidants are used to activate the biochar, and the physicochemical properties of the biochar obtained are significantly improved (Tan et al. 2017). Therefore, to improve the ability of biochar to immobilize heavy metals in sediments, the present study synthesized biochar/attapulgite composites using a one-pot method involving slow pyrolysis of the attapulgite and zinc chloride ($ZnCl_2$)-pretreated rice straw biomass. The physicochemical properties of the composites were analyzed. The effects of biochar/attapulgite composites on heavy metal immobilization in arsenic (As)- and cadmium (Cd)-contaminated sediment were investigated.

MATERIALS AND METHODS

Sediment collection

Sediment was obtained from the top 20 cm at the Changsha section of the Xiangjiang River in China. The impurities in the sediment were removed and the fine sediment obtained was well blended to create a homogeneous sediment mixture. Sediment samples were transported to the laboratory, naturally air-dried, and then stored in sealed sample bags. The characteristics of the sediment used in the present study are shown in the Supplemental Data, Table S1.

Preparation of biochar/attapulgite composites

The one-pot method with slow pyrolysis of the attapulgite and $ZnCl_2$-pretreated rice straw biomass was used to prepare biochar-based attapulgite composites. First, 2.5 g of attapulgite and 5.0 g of rice straw biomass powder were added to 100 mL of deionized water, and then 2.5 and 5.0 g of anhydrous $ZnCl_2$ were added separately. The suspension was stirred, ultrasonically dispersed, and then immersed for 24 h. Subsequently, the mixture was dried at 80 °C, and then pyrolyzed at 450 °C for 1 h in an N_2 atmosphere using a tube furnace (SK-1200 °C, Tianjin Zhonghuan Test Electrical Furnace). After pyrolysis, the electric furnace was naturally cooled to room temperature, and the prepared composite material was taken out and washed several times with a 1.2-mol/L hydrochloric acid solution to remove residual organic matter and other impurities; then the product was washed several times with deionized water until the pH was approximately 7. Finally, the product was dried at 105 °C. The samples treated with 2.5 and 5.0 g of $ZnCl_2$ (termed attapulgite/biochar1 and attapulgite/biochar2, respectively) were placed in a sealed bag and stored in a desiccator until use. For the preparation of $ZnCl_2$-activated biochar, 5.0 g of rice straw biomass powder and different amounts of $ZnCl_2$ were used and synthesized following the same steps. The activated biochars obtained and treated with 2.5 and 5.0 g of $ZnCl_2$ were termed biochar-ZC1 and biochar-ZC2, respectively. The original biochar without the attapulgite and $ZnCl_2$ treatment was prepared using rice straw biomass under the same pyrolysis conditions.

Characterization methods

The surface crystal structure of the biochar/attapulgite composite was measured by an X-ray diffractometer (XRD; Siemens D500, using Cu Kα radiation). The pore characteristics

of the composites were determined by the N_2 adsorption static volumetric method using a surface area and porosity analyzer (Tristar II 3020; Micromeritics), and the specific surface area was calculated using the Brunauer–Emmett–Teller equation. The structure and surface characteristics of the samples were analyzed by high-resolution transmission electron microscopy (JEM-3010; JEOL) and scanning electron microscopy (Nova NanoSEM 230; FEI). The surface chemistry and chemical states of elements were analyzed by an X-ray photoelectron spectroscope (XPS; ESCALAB 250Xi; Thermo Fisher) under Al-Kα X-ray radiation.

Incubation experiment

Sets of 50-g air-dried sediment samples were placed in 100-mL screw-top bottles, then 60 mL of deionized water was added to each bottle, and the samples were left to stand for 24 h. Subsequently, 1 g of different biochars (2% of dry wt of the sediment) was added to the bottle, which was shaken up and placed in an artificial climate chamber at a temperature of 20 °C for incubation in the dark over a specified number of days. To compare the performance of the different biochars (biochar, biochar-ZC1, biochar-ZC2, attapulgite/biochar1, and attapulgite/biochar2) in sediment, the samples were withdrawn for analysis after 60 d of incubation. To investigate the effect on remediation of different amounts, 2% (1 g), 3% (1.5 g), and 5% (2.5 g) of attapulgite/biochar2 were added to the sediment, and these samples were incubated under the same conditions.

Liquid equilibrium concentration

After incubation for 90 d, the overlying water was taken from each screw-top bottle and filtered through a 0.45-μm filter. Then the As and Cd concentrations in the overlying water (C_{OW}) was analyzed by inductively coupled plasma–optical emission spectroscopy (ICP–OES; Optima 5300DV device; PerkinElmer). After the overlying water was completely removed, some of the remaining sediment was transferred into centrifuge tubes and centrifuged at 4000 rpm for 15 min. The porewater was obtained from the supernatant of the centrifuge tube and filtered through a 0.45-μm filter. The As and Cd concentration of porewater (C_{PW}) was determined by ICP–OES. All residual sediment samples were freeze-dried for 48 h, then ground to pass through a 100-mesh sieve, and reserved at 4 °C for subsequent analysis.

Community Bureau of Reference sequential extraction

Community Bureau of Reference sequential extraction was conducted to determine 4 different fractions of As and Cd in sediment by the procedure described in a previous study (Jiang et al. 2012). The extraction procedure was conducted by adding 0.5 g of freeze-dried and sifted sediment sample into a 50-mL centrifuge tube. Then 4 sequential steps were applied for metal extraction: 0.11 mol/L CH_3COOH for the acid-soluble fraction, 0.5 mol/L $NH_2OH{\cdot}HCl$ and 0.05 mol/L HNO_3 for the reducible fraction, 8.8 mol/L H_2O_2 followed by 1.0 mol/L CH_3COONH_4 (adjusted to pH 2 with HNO_3) for the oxidizable fraction, and the 3-acid digestion method (HNO_3, HF, and $HClO_4$) for the residual fraction of the metals.

Toxicity characteristic leaching procedure

The toxicity characteristic leaching procedure (TCLP) was carried out to determine the mobility of As and Cd in the sediment based on US Environmental Protection Agency method 1311 (1992). Briefly, 2 g sediment was mixed with 40 mL extraction fluid (CH_3COOH, pH = 4.93 ± 0.05) in a 50-mL centrifuge tube. The tube was shaken at 190 rpm for 18 h at 25 °C, and then centrifuged at 4000 rpm for 15 min. The supernatant was filtered, and the heavy metal concentration was determined by ICP–OES.

Statistical analysis

Differences among treatments were assessed by analysis of variance using SPSS Ver. 18. The results shown in the figures represent the averages of 3 independent replicate treatments, and the data are presented as means ± standard deviations.

RESULTS AND DISCUSSION

Characterization of biochar/attapulgite composites

The pore characteristics of the biochar/attapulgite composite are shown in the Supplemental Data, Table S2. Both the original biochar and the original attapulgite had relatively small specific surface areas and pore volumes. The composites had large increases in specific surface area and pore volume compared with the 2 original materials, and the pore size was remarkable reduced. This was mainly because during synthesis of the composite, the $ZnCl_2$ activator reacted with the surface and pores of the biochar and attapulgite composites to create new micropores and mesopores (Sevilla and Fuertes, 2006). During the activation process, $ZnCl_2$ acted as a dehydrating agent, and $ZnCl_2$ catalyzed dehydration during the pyrolysis stage, so that hydrogen and oxygen atoms in the material were released in the form of water to form a porous structure. At the same time, $ZnCl_2$ acted as a framework to provide support for the new pore structure of the material during heating (Du et al. 2016). In addition, the degree of improvement in the composite pore characteristics was related to the amount of $ZnCl_2$ activator added. The specific surface area of attapulgite/biochar2 was much higher than that of attapulgite/biochar1, mainly because sufficient activator allowed more complete activation of the composite (Li Z et al. 2018; Wang M et al. 2018).

The scanning electron micrograph and energy-dispersive X-ray (EDX) mapping of the biochar/attapulgite composites is shown in Figure 1. It can be seen that a large number of particles adhered to the surface of the composite, indicating that the attapulgite particles had combined with the biochar, which was

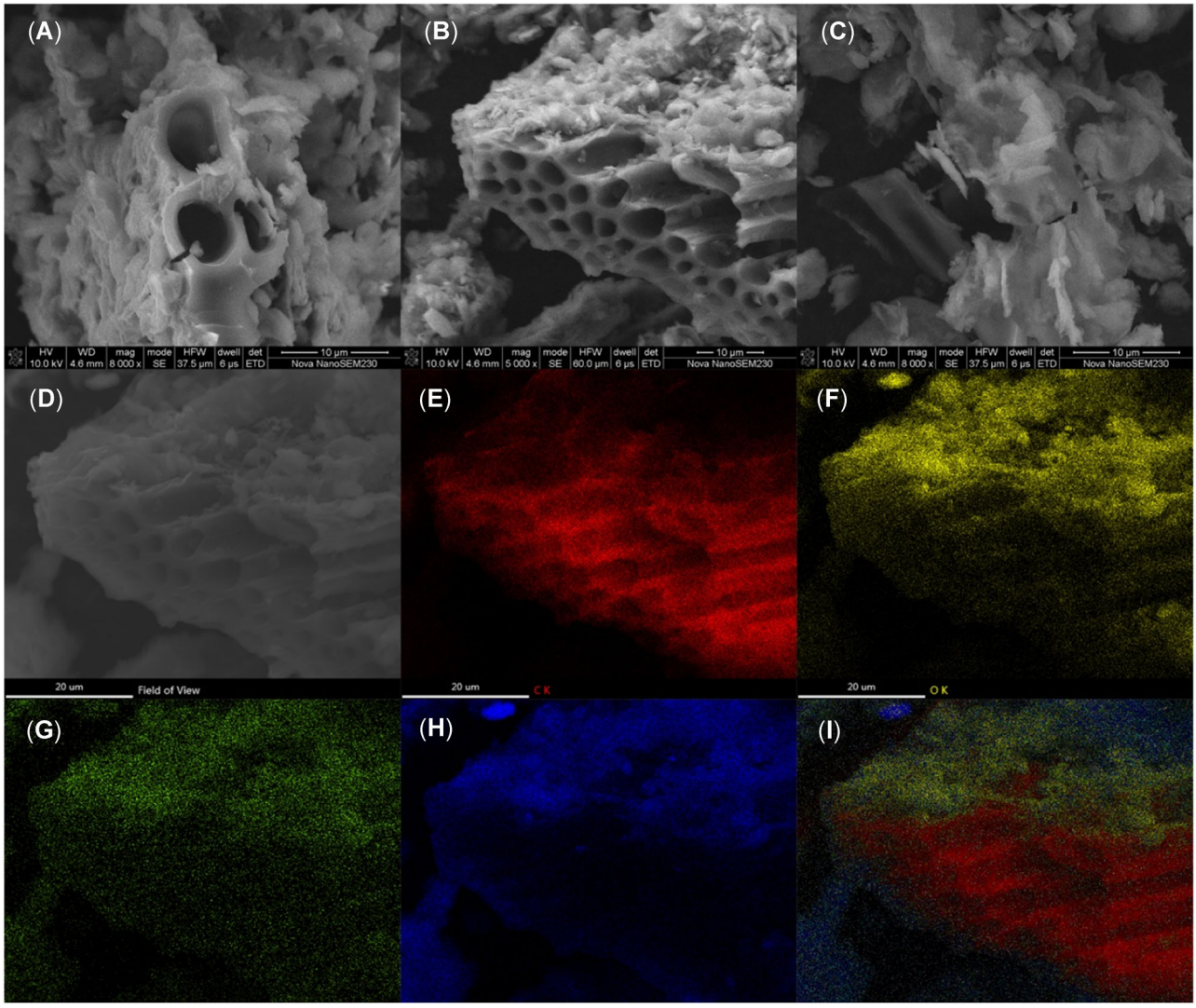

FIGURE 1: Scanning electron microscopy (SEM) photograph and energy-dispersive X-ray (EDX) mapping of biochar/attapulgite composites: (**A–C**) SEM photograph, (**D**) field of view, (**E**) carbon, (**F**) oxygen, (**G**) magnesium, (**H**) silicon, and (**I**) cascading image.

also reflected in the EDX mapping analysis. Attapulgite is a hydrated magnesium silicate crystal with a fiber form, and its chemical composition is $Mg_5Si_8O_{20}(OH)_2(OH_2)_4{\cdot}4H_2O$ (Li Y et al. 2017; Yin et al. 2017). The EDX mapping spectrum results showed that the composite contained a large amount of well-dispersed silicon and magnesium, which are the typical elements of attapulgite. These results indicate that the attapulgite particles were evenly loaded onto the carbonaceous framework and that the biochar/attapulgite composite was successfully synthesized. At the same time, as the $ZnCl_2$ activator was added during preparation, the pores in the skeleton of the biochar/attapulgite composite were opened. Transmission electron microscopy images of the biochar/attapulgite composite are shown in Figure 2. The original attapulgite had a layered crystal structure in the form of fibers (Figure 2). Figure 2A shows that the biochar exhibited an amorphous carbon structure and that the crystal structure of the attapulgite was dispersed on the biochar matrix, indicating that biochar as a matrix can effectively improve attapulgite dispersibility. The XRD pattern of the biochar/attapulgite composite is shown in Figure 2D. The diffraction peaks of the composite ($2\theta = 8.3°$, 16.4 °, 19.9 °, 20.8 °, 28.8 °, 34.6 °, 34.9 °, and 35.4 °) matched well with the crystal structure of attapulgite (the standard reference PDF no. 31-0783; Pan et al. 2017), suggesting that attapulgite was successfully introduced into the composite. Other peaks closely matched that of standard quartz (PDF no. 46-1045), which was derived from the biochar minerals (Zhang et al. 2015).

To determine the surface properties of the original biochar and attapulgite/biochar2, curve-fitting procedures on the O 1s and C 1s peaks of the samples were conducted. The XPS O 1s spectra of the original biochar (Figure 3A) can be deconvoluted into 3 individual component peaks: 531.3 eV (C=O groups), 532.4 eV (C–O and O=C–O groups), and 533.2 eV (C–O–C groups; Meng et al. 2019). Compared with the original biochar, attapulgite/biochar2 (Figure 3B) had similar peaks at 532.1 eV (C–O and O=C–O groups) and 533.5 eV (C–O–C groups), and a new peak appeared at 534.8 eV corresponding to carboxyl–COOH (Meng et al. 2019; Yuan and Dai, 2015). The C 1s

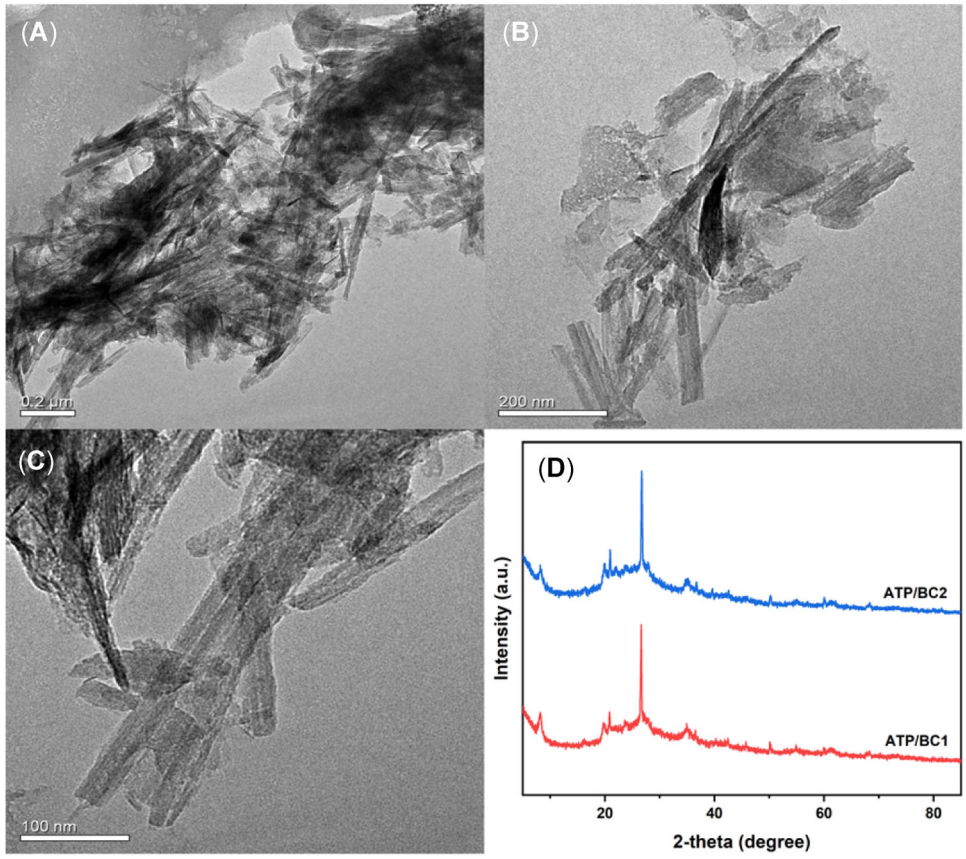

FIGURE 2: (**A**–**C**) Transmission electron microscopy (TEM) photograph and (**D**) X-ray diffractometer (XRD) spectrogram of attapulgite/biochar (ATP/BC) composites.

spectra of the original biochar (Figure 3C) was deconvoluted into 3 peaks at 284.8, 286.0, and 288.3 eV, which were assigned to C=C, C–O, and O–C=O, respectively (Li L et al. 2019). Peaks at 284.6, 285.1, and 286.2 eV appeared in the C 1s spectra of attapulgite/biochar2 and were assigned to C=C, C–C, and C–O, respectively (Li L et al. 2019; Figure 3D). Thus the biochar/attapulgite composite had more oxygen-containing functional groups than the original biochar, which might be beneficial to the adsorption of heavy metals (Shi et al. 2018; Xue et al. 2018).

Heavy metal concentrations in the liquid phase

The concentrations of heavy metals in the overlying water and porewater after treatment with different biochar/attapulgite composites are shown in Figure 4. It can be seen that the concentrations of the heavy metals As and Cd in the overlying water of the sediment were significantly reduced after the sediments were treated with different biochar/attapulgite composites. At the same time, the concentrations of heavy metals in the biochar/attapulgite composite–treated sediments were significantly lower than those in the raw biochar-treated sediments. This finding indicates that the composite was able to effectively increase the adsorption and fixation ability of sediment to heavy metals and reduce the migration of heavy metals to the overlying water in the sediment, an effect that was greatly increased compared with the original biochar. Previous studies have also reported that introducing sorbent amendments into contaminated sediments could increase contaminant binding and reduce the bioavailability of contaminant (Ghosh et al. 2011; Gilmour et al. 2013). The effect of the biochar/attapulgite composite was related to the amount of $ZnCl_2$ activator added during the preparation process, and increased significantly with an increase in the amount of activator. After treatment with 2 composite materials (attapulgite/biochar1 and attapulgite/biochar2), the concentration of As in the overlying water decreased by 79 and 82%, respectively, and the Cd concentration decreased by 36 and 44%, respectively, compared with the original biochar.

At the same time, the concentration of heavy metals in the porewater of the sediment after biochar/attapulgite composite treatment was also significantly reduced (Figure 4). Concentrations of As and Cd in the porewater differed under the action of different materials: original biochar > attapulgite/biochar1 > attapulgite/biochar2. Similar to the overlying water, the biochar/attapulgite composite had a significantly higher ability than the original biochar to treat heavy metals in the sediment, and the treatment effect was significantly improved as the amount of activator was increased during the material preparation process. After treatment with attapulgite/biochar1 and attapulgite/biochar2, the As concentration in the sediment porewater decreased by 68 and 82%, and the Cd concentration

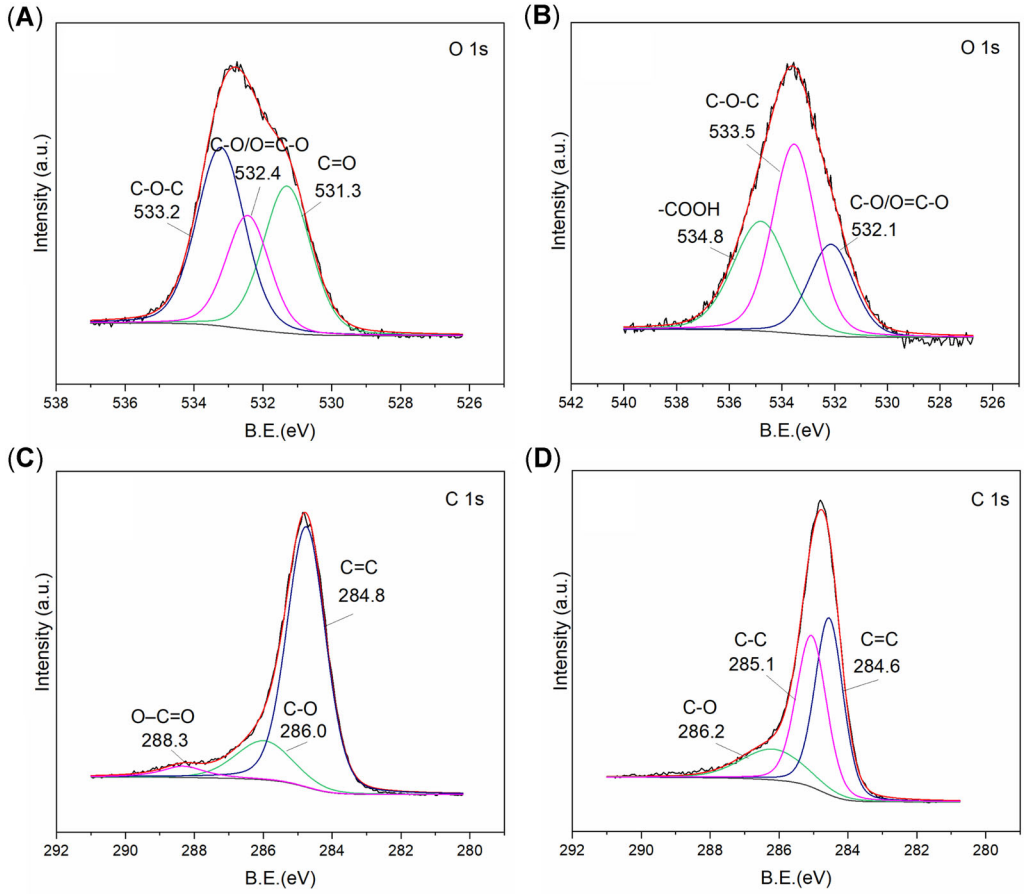

FIGURE 3: X-ray photoelectron spectroscopic high-resolution spectra of original biochar (**A** and **C**) and biochar/attapulgite composites (**B** and **D**). B.E. = binding energy.

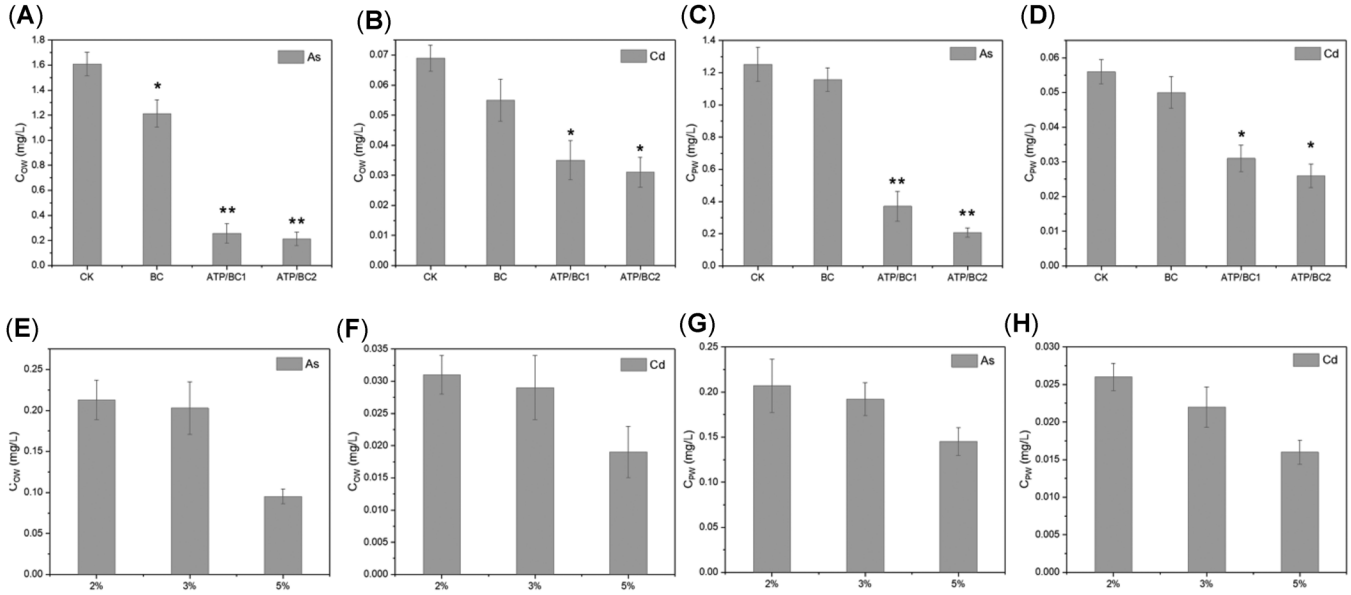

FIGURE 4: Heavy metal concentration in overlying water and porewater of sediment after treatment with different biochars: (**A** and **B**) arsenic (As) and cadmium (Cd) in overlying water, (**C** and **D**) As and Cd in porewater. Effect of addition amount on heavy metal concentration in overlying water and porewater of sediment after treatment with attapulgite/biochar (ATP/BC)2: (**E** and **F**) As and Cd in overlying water, (**G** and **H**) As and Cd in porewater. The results are mean values ± standard deviations ($n = 3$); error bars indicate standard deviations. * Significant at $p < 0.05$ compared with control (CK; untreated sediment); ** Very significant at $p < 0.01$ compared with control (CK; untreated sediment). C_{OW} = concentration in overlying water; C_{PW} = concentration of porewater.

decreased by 38 and 48%, respectively, compared with the original biochar. Thus the biochar/attapulgite composite can be used as an inexpensive and efficient in situ remediation material to improve immobilization of heavy metals in sediment, and to inhibit the transfer of heavy metals to the liquid phase of the sediment.

At the same time, the amount of added composite greatly influenced its effect on the concentration of heavy metals in the overlying water and porewater, as shown in Figure 4, where it can be seen that As and Cd concentrations in both waters decreased with increases in added attapulgite/biochar2, indicating that the higher attapulgite/biochar2 addition improved the processing efficiency of the material. However, such increases will increase the processing cost, so the practical effects and economic benefits should be comprehensively considered in practical applications.

Chemical speciation of heavy metal in sediment

After the sediments were treated with different biochars, they were analyzed by Community Bureau of Reference continuous extraction and speciation of heavy metal in sediment, and the results are shown in Figure 5. It can be seen that the content of acid-extractable As and Cd in the sediment after treatment with different biochars was significantly lower than that of the untreated sediment, a decrease indicating that the biochars could effectively promote the fixed conversion of heavy metals in the sediment (Huang et al. 2017; Liu et al. 2018; Zhang et al. 2018). At the same time, the effect of the biochar/attapulgite composite was significantly improved compared with the original biochar. The order of acid-extractable heavy metals in the different treated sediments was: original biochar > attapulgite/biochar1 > attapulgite/biochar2, which was consistent with the change in heavy metal content in overlying water and porewater. Compared with the original biochar, the acid-extractable As content decreased by 37 and 43%, respectively, and the acid-extractable Cd content decreased by 8 and 11%, respectively. Thus attapulgite addition and $ZnCl_2$ activation effectively improved biochar performance.

The addition of different biochars also had an effect on the reducible fraction of heavy metals in the sediment, and the reducible fractions increased differently. The oxidizable fraction of As and Cd in the sediment accounted for a small proportion of the total content. The oxidizable As content was lower than the detection limit, and the oxidizable Cd in the sediment had different degrees of increase under the action of different biochars. After treatment with different biochars, the ratio of residual As and Cd in the sediment increased compared with the untreated sediment and the original biochar-treated sediment.

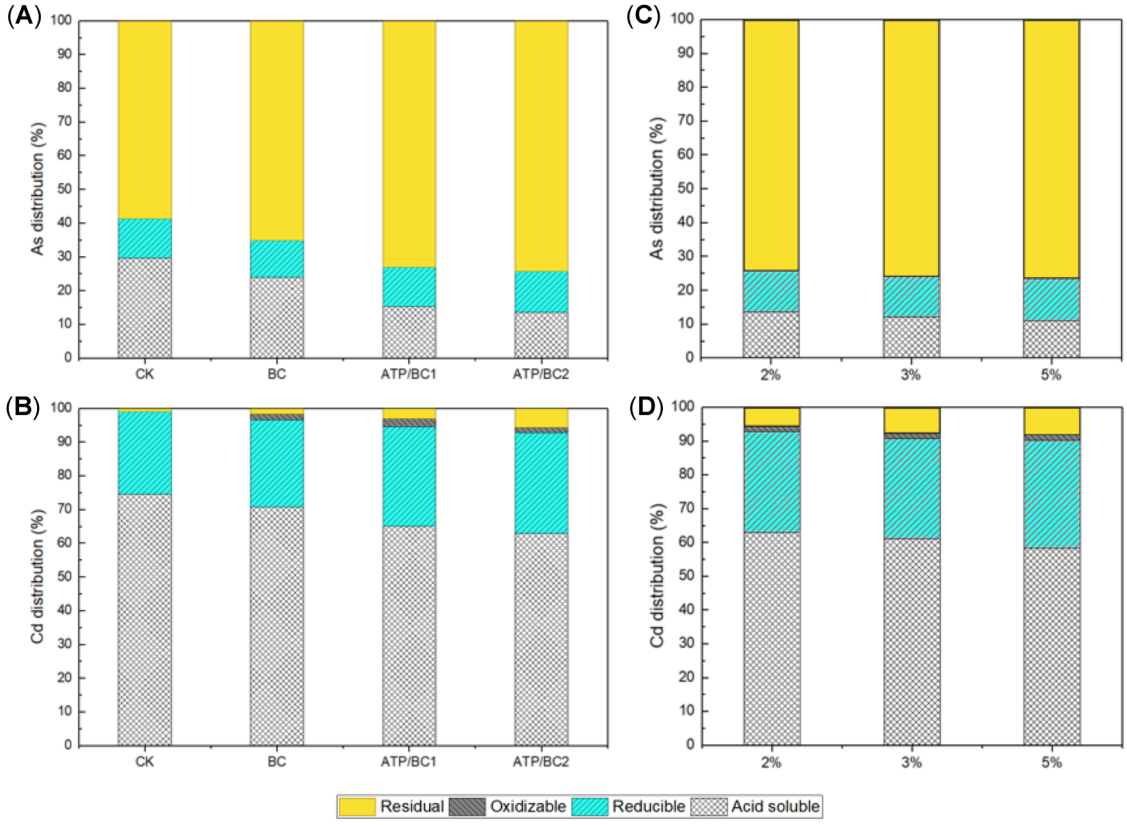

FIGURE 5: Fractions of arsenic (As) and cadmium (Cd) in sediment determined by Community Bureau of Reference sequential extraction after treatment with different biochars: (**A**) fraction of As, (**B**) fraction of Cd. Effect of addition amount on fraction of As and Cd in sediment determined by Community Bureau of Reference sequential extraction after treatment with attapulgite/biochar composites (ATP/BC1 and -2): (**C**) fraction of As, (**D**) fraction of Cd.

At the same time, the amount of composite added greatly influenced the effect, as shown in Figure 5: As and Cd contents in the acid-extractable heavy metals of the sediment decreased with increased addition, and the proportion of the residual As and Cd increased gradually, indicating that the higher amount of composite improved the effect of the biochar to a certain extent.

Metal TCLP leachability

The TCLP method is a commonly used ecological risk assessment tool, and the effectiveness of heavy metal immobilization can be evaluated by determining the TCLP-extractable content in contaminated sediment (Song et al. 2019). The concentrations of heavy metal in the TCLP leaching solution of the sediment after biochar/attapulgite composite treatment were significantly reduced (Figure 6), indicating that the biochar/attapulgite composite could effectively improve the adsorption and fixation capacity of the sediment for heavy metals. The As and Cd concentrations in the TCLP leaching solution of the sediment after treatment with different biochars were as follows: original biochar > attapulgite/biochar1 > attapulgite/biochar2. The effect of the biochar/attapulgite composites was significantly higher than that of the original biochar, and the effect was significantly improved with the addition of activator during the preparation process. After treatment with attapulgite/biochar1 and attapulgite/biochar2, the concentration of As in the TCLP leaching solution decreased by 64 and 68%, respectively, compared with the original biochar. The concentration of Cd in the TCLP leaching solution decreased by 19 and 22%, respectively, compared with the original biochar. At the same time, the amount of attapulgite/biochar2 added greatly influenced its effect (Figure 6): the As and Cd concentrations in the TCLP leaching solution of the sediment decreased with the increase of added attapulgite/biochar2, indicating that the higher addition improved the effect of the composite. The TCLP-extractable Cd in 2, 3, and 5% attapulgite/biochar2-treated sediment was reduced by 21.5, 26.9, and 48.4%, respectively, compared with the untreated sediment, which was more efficient than in a previous study (Huang et al. 2017; Liu et al. 2018).

Immobilization mechanisms of heavy metals in sediment by biochar/attapulgite

The results indicated that the biochar/attapulgite composite could effectively reduce the bioavailable fraction of heavy metals in overlying water, porewater, and the solid phase of the sediment. To determine the specific immobilization mechanisms of heavy metals in sediment, the performance of

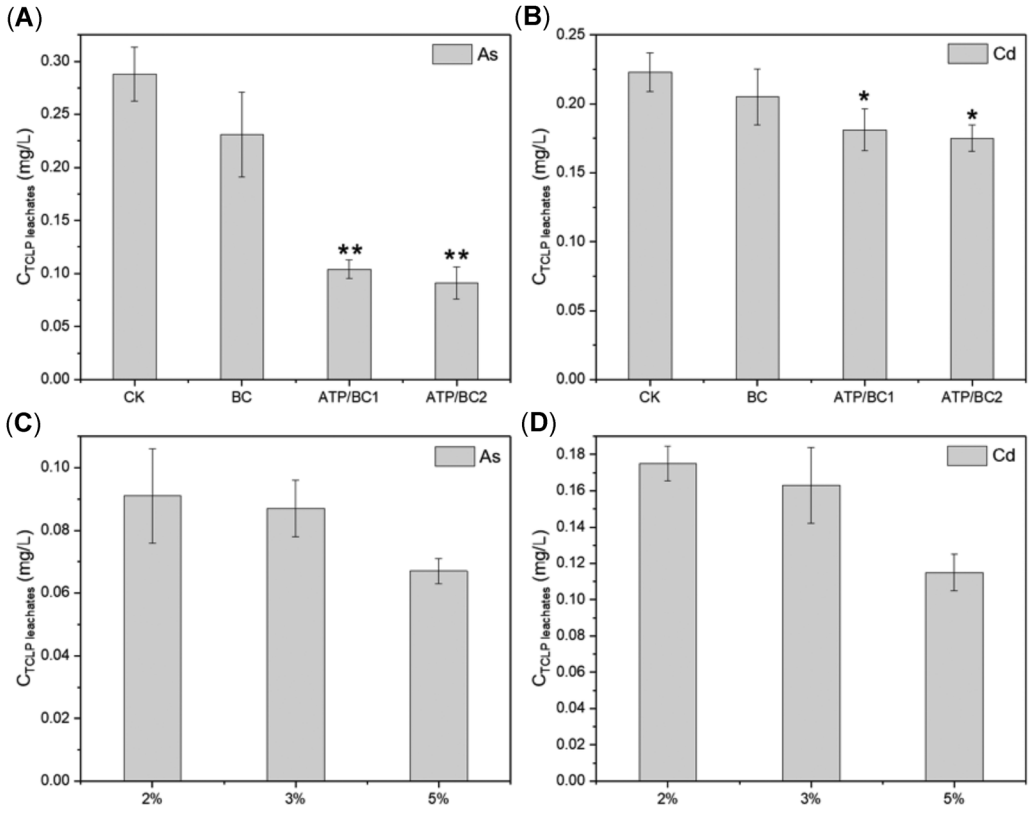

FIGURE 6: Heavy metal concentrations in toxicity characteristic leaching procedure (TCLP) leachates of sediment after treatment with different biochars: (**A**) concentration of As, (**B**) concentration of Cd. Effect of addition amount on heavy metal concentrations in TCLP leachates of sediment after treatment with attapulgite/biochar composites (ATP/BC1 and -2): (**C**) concentration of As, (**D**) concentration of Cd. The results are mean values ± standard deviations ($n = 3$); error bars indicate standard deviations. * Significant at $p < 0.05$ compared with control (CK; untreated sediment); ** Very significant at $p < 0.01$ compared with control (CK; untreated sediment).

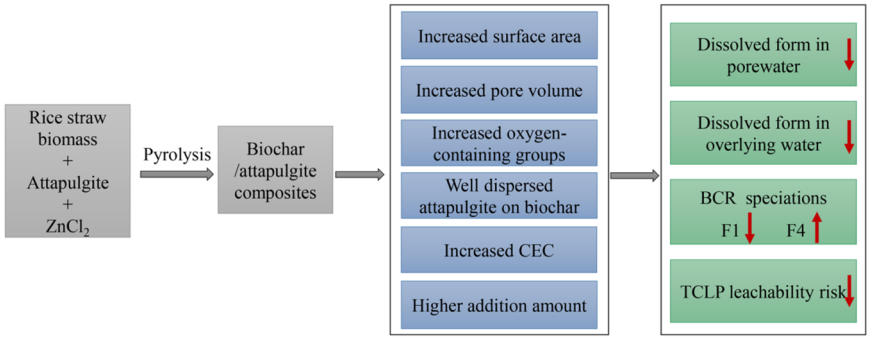

FIGURE 7: Possible immobilization mechanism of heavy metals in sediment by biochar/attapulgite composites. F1 and F4 are the acid-soluble fraction and the residual fraction in the solid phase of the sediment, respectively. CEC = cation exchange capacity; BCR = Community Bureau of Reference; TCLP = toxicity characteristic leaching procedure.

different biochars (original, $ZnCl_2$-activated, and attapulgite and $ZnCl_2$-modified biochars) was compared. As shown in the Supplemental Data, Figure S1, $ZnCl_2$-activated biochar (biochar-ZC1 and biochar-ZC2) was more effective for As and Cd immobilization than the original biochar, which suggested that the activation of biochar was conducive to the enhancement of adsorption. The As and Cd immobilization performance of attapulgite and $ZnCl_2$-modified biochar (attapulgite/biochar1 and attapulgite/biochar2) was the best among the tested biochar materials. This finding further indicated that the incorporation of attapulgite also increased the adsorption ability of biochar, and therefore both $ZnCl_2$ activation and attapulgite were beneficial for As and Cd immobilization.

Furthermore, as seen from the characterization of biochar/attapulgite composites, attapulgite was well dispersed on biochar, which served as an effective material for both As and Cd adsorption (Chen et al. 2011; Yin et al. 2017; Pan et al. 2018; Wang Y et al. 2018). After $ZnCl_2$ activation, the biochar/attapulgite composite had a higher specific surface area and pore volume than the raw biochar (Supplemental Data, Table S2), which could provide more opportunity for metals to interact with the composite (Zhang et al. 2018). In addition, more oxygen-containing functional groups existed in the composite than in the original biochar, suggesting that there were more adsorption sites on the composite for binding of As and Cd by surface complexation (Yin et al. 2017; Pan et al. 2018; Zhang et al. 2018).

The addition of the biochar/attapulgite composite was able to change the properties of sediment so that it could interact with the heavy metals, resulting in heavy metal stabilization (Figure 7). Supplemental Data, Figure S2a, shows that the CEC of biochar-treated sediment significantly increased after addition of different biochars, which favored the stabilization of Cd in sediment by ion exchange (Bache 1976; Atkinson et al. 2010; Singh et al. 2014; Zhang et al. 2014; Song et al. 2017). However, there was little difference between the XRD patterns of untreated sediment and 2% attapulgite/biochar2-treated sediment (Supplemental Data, Figure S2b), suggesting that no precipitation of metals was revealed by XRD in the present study. This suggested that precipitation of metals was not the main immobilization mechanism of heavy metals in sediment, or that precipitation with metals in the composite-amended sediment was below the detection limit of XRD (Zhang et al. 2018).

CONCLUSIONS

The present study successfully prepared biochar/attapulgite composite with improved properties and well-dispersed attapulgite on biochar. The biochar/attapulgite composite effectively reduced the bioavailable fraction of As and Cd in the sediment significantly more than the original biochar, and the effect was improved when more composite was added. We conclude that biochar/attapulgite composite can be used as an efficient in situ remediation material to improve the ability of the sediment to immobilize heavy metals. Future studies should analyze the effect of biochar/attapulgite composite on heavy metal immobilization on a field scale.

Supplemental Data—The Supplemental Data are available on the Wiley Online Library at DOI: 10.1002/etc.4542.

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Data Accessibility—Data, associated metadata, and calculation tools are available from the corresponding author (tanxf@hnu.edu.cn).

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