Homogeneously Dispersed Zerovalent Iron Nanoparticles Supported on Hydrochar-Derived Porous Carbon: Simple, *in Situ* Synthesis and Use for Dechlorination of PCBs

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Supporting Information

ABSTRACT: Herein, we have developed a simple and effective strategy for *in situ* preparation of nanoscale zerovalent iron (NZVI) supported on porous carbon (PC) using renewable hydrochar as the carbon precursor. Physicochemical properties of the resultant NZVI/PC composites were characterized by XRD, SEM-EDS, TEM, and BET, and the effectiveness of these composites was evaluated for the remediation of PCB-contaminated water. Results showed that the iron ions were uniformly dispersed within the hydrochar matrix and serve as an activation agent for the hydrochar during a subsequent pyrolysis process. The iron is reduced *in situ* to NZVI with diameters of 8.5–10 nm, without requiring an additional reducing agent. At temperatures of 600–800 °C, the well-dispersed NZVI catalyzes the transformation from amorphous carbon to graphitic carbon. The NZVI/PC composite prepared at 800 °C exhibited high efficiency for adsorption and dechlorination of PCBs in aqueous solution. This is attributed to the composites' high surface area, uniformly dispersed nanoscale iron, high degrees of graphitic porous carbon, and substantial amount of mesopores. The present study offers a simple and sustainable approach for the preparation of prospective NZVI/PC with high stability and reactivity from renewable resources.

KEYWORDS: Hydrochar, Nano metal, Carbon material, Biomass, Adsorption

INTRODUCTION

Reactive zerovalent metals such as iron and magnesium are known to efficiently dechlorinate carcinogenic polychlorinated biphenyls (PCBs) in groundwater.^{1,2} Because the dechlorination reaction initiated by ZVI is surface-mediated, nanoscale iron with high surface area is desirable to increase dechlorination efficiency. In addition, the availability of PCBs for adsorption onto the surface of ZVI is limited owing to their extremely low concentration. Therefore, ZVI supported on porous carbon is of great interest due to the strong adsorption of PCBs on carbonaceous materials. Several papers have described PCB removal from aqueous solution using NZVI/PC composites and have shown high removal efficiency due to simultaneous adsorption and dechlorination.^{3–6}

Because of its high adsorption capacity, porous carbon has been widely used as a support of Fe for various other applications, including Fenton reactions and Fischer–Tropsch synthesis.^{7,8} The conventional preparation of NZVI/PC composites is a complicated and time-consuming process, generally involving concentrated acid oxidation of commercial PC, impregnation and chemical reduction of iron salts, and final thermal treatment in a reducing atmosphere. Besides using toxic concentrated acids and costly reducing agents (H₂ or NaBH₄),

conventional NZVI/PC preparation also suffer from the poor dispersion and mechanical stability of NZVI in the resultant NZVI/PC, which must be addressed to enable large-scale application. Therefore, it is important to seek a low-cost, simple method for preparing high-performance NZVI/PC composites.

Hydrochar, produced from hydrothermal carbonization (HTC) of biomass, has gained considerable attention due to its unique properties.^{9,10} Several papers have appeared regarding value-added application of hydrochars as renewable carbon materials.^{11,12} For instance, hydrochar was employed as a bioadsorbent for heavy metal removal from aqueous solution and exhibited high adsorption capacity compared to that of its parent biomass.¹¹ In addition, hydrochar has served as a support for nano Pt/Pd particles used as electrocatalysts in the oxidation of methanol and ethanol.^{13,14} These hydrochar applications not only lower the cost of carbon materials but also provide environmental benefits, as they are produced from renewable biomass resources.¹⁵

Here, we have developed a new strategy to prepare low-cost and highly reactive NZVI/PC. In this preparation approach,

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renewable hydrochar is used as the carbon source for porous carbon, and no additional reducing agent is required; both of these factors contribute to lower preparation costs. The hydrochar is then activated, and NZVI particles are formed *in situ* in a simultaneous single step, which also increases the composite's mechanical stability and reactivity. Furthermore, these materials have enhanced reactivity due to the Fe-catalyzed formation of graphitic structures within the composites.

In this article, we report the first low-cost preparation approach for NZVI/PC composites, using simple iron ion adsorption onto hydrochar, followed by self-reduction. The NZVI/PC composites were systematically characterized by multiple morphological and structural methods and were used to demonstrate adsorption and dechlorination of PCBs from aqueous solution. Also, based upon the composites' characterization, a formation mechanism is proposed.

■ EXPERIMENTAL SECTION

Preparation of NZVI/PC. Analytical grade iron(III) nitrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] and chromatographic grade acetone and *n*-hexane were used in the present study. Aroclor 1242 were purchased from Sigma-Aldrich.

In the present study, pinewood sawdust-derived hydrochar was adopted as a representative hydrochar. Detailed preparation procedures can be found elsewhere.¹⁶ Briefly, around 10 g of sawdust was loaded with 100 mL of deionized water into a 500 mL autoclave, and the reactor was heated to 200 °C. After maintaining at 200 °C for 20 min, the reactor was cooled to room temperature. The hydrochar was recovered as a solid residue by vacuum filtration and then washed using deionized water. The hydrochar was dried at 105 °C for 24 h and stored in a desiccator before use. Properties of this hydrochar are presented in Table 1. About 2 g of hydrochar, with diameter less than

Table 1. Properties of the Hydrochar Used in the Present Study

sawdust derived hydrochar (PH)	
elemental analysis (daf, wt %)	
C	58.64
H	3.22
N	0.13
S	0.02
O ^a	37.99
proximate analysis (db, wt %)	
volatile matter	56.32
fixed carbon	39.20
ash	0.68
moisture	3.86

^aBy difference.

100 mesh, was immersed into 10 mL of 0.5 mol/L iron(III) nitrate aqueous solution. The resulting mixture was ultrasonicated for 40 min at room temperature, followed by separation through vacuum filtration. The resultant solid residue (Fe-hydrochar) was dried at 105 °C for 24 h prior to thermal treatment.

Thermal experiments were conducted in a horizontal fixed-bed tubular quartz reactor (60 mm i.d., 1000 mm long). In each run, the sample was charged into an aluminum boat that was placed in the quartz tube. After nitrogen gas (flow rate 20 mL/min) was introduced into the system, the furnace was heated to the desired temperature at a heating rate of 5 °C/min and held at the final temperature for 40 min. The sample was then cooled to room temperature while still under N₂ flow inside the reactor. The resultant solid product was then removed, washed several times with deionized water and ethanol, dried, and stored for further analysis. The composites (washed solid products) were designated as "FHC-xxx", where "xxx" indicates the temperature

of the thermal treatment in °C. For comparison, the hydrochar was also treated at 800 °C without iron(III) nitrate impregnation; this product was labeled as HC-800.

Characterization Methods. The crystal properties of the composites were determined by X-ray diffraction (XRD) using a Bruker Advance D8 diffractometer (Germany). Graphite monochromatic copper radiation (CuK α) at 40 kV and 30 mA was applied over the 2θ range 10–80°. Raman spectra were obtained with a LabRAM HR800 from JY Horiba (Japan). The BET surface area was obtained from nitrogen adsorption isotherms at –196 °C using an ASAP 2010 analyzer (Micromeritics, USA). Prior to the N₂ sorption analysis, the sample was degassed at 150 °C for 8 h. The surface morphology was examined by scanning electron microscopy (SEM) using a JSM 6010LA instrument (Japan) equipped with energy dispersive diffraction. TEM images were obtained using a JEM-2100 instrument (JEOL, Japan) under 80 kV acceleration voltages. The metal content of the composites was determined by digestion in concentrated HNO₃ with 30% H₂O₂, followed by analysis using inductively coupled plasma optical emission spectroscopy (ICP-OES) PerkinElmer 3000DV (USA).¹⁷ As for temperature-programmed decomposition (TPD) analysis, around 2 g of hydrochar was used, and it was conducted in a fixed-bed tubular quartz reactor, using temperature ranging from 200 to 900 °C with a heating rate of 5 °C/min and a nitrogen gas flow rate of 20 mL/min.

Reactivity of the Composite. The FHC-600 and FHC-800 were selected as representative materials to evaluate the reactivity of the produced composites for removal of PCBs from aqueous solutions.

Serum bottles (50 mL) capped with Viton stops and sealed with aluminum caps were employed for adsorption and dechlorination experiments. Two grams of composite was added to 25 mL of 10 mg/L PCBs aqueous solution, and the mixture was agitated on a platform shaker at 250 rpm at room temperature. At preset intervals, 0.5 mL aqueous samples were removed with a glass syringe and added to 2.5 mL glass vessels filled with 1 mL of *n*-hexane. (The initial sampling interval was 2 h, up to 24 h, then was increased to 48 h.) The aqueous samples were extracted with hexane on a platform shaker at 250 rpm and 25 °C for 24 h followed by centrifugation for 20 min. The hexane layer was analyzed for PCBs and their dechlorinated products by GC-MS (Agilent 7890A/5975C, USA) using an HP-5 column (5% phenyl methyl siloxane, 30 m $\times$ 250 μm $\times$ 0.25 μm). The injected volume was 1 μL , with a split ratio of 30:1. The oven program was 1 min isothermal at 100 °C, followed by a heating rate of 2 °C/min to 210 °C, and a final hold of 1 min. The control experiment for PCB aqueous extraction by hexane without composite was performed, and the recovery efficiency was around 96.30%, which was within the acceptable range.

After 6 days, the solid/liquid mixture was separated by vacuum filtration, and the recovered composite was extracted with 20 mL of acetone/*n*-hexane (v/v = 1) using Soxhlet extraction equipment. The extracts were analyzed for residual PCBs and dechlorinated products by the GC-MS method described above.

■ RESULTS AND DISCUSSION

As shown in Figure 1, there is no peak in the XRD pattern of the composite obtained at 300 °C, implying that no crystal phase was formed under these experimental conditions.^{18,19} For the composite FHC-400, two peaks at 35.40° and 62.35° appeared, indicating the presence of the spinel structure Fe₂O₃.²⁰ Because of the similarity of XRD patterns of γ -Fe₂O₃ and Fe₃O₄, Raman analysis was conducted to identify the difference. As shown in Figure S1, the formation of Fe₂O₃ was confirmed by the appearance of characteristic peaks at 257 and 480 cm^{–1}, and no characteristic peak of Fe₃O₄ was observed.^{21–23} These two peaks were enhanced with increasing temperature from 400 to 600 °C, and other Fe₂O₃ peaks (30.04°, 43.42°, and 57.31°) were also observed within this temperature range. With further temperature increases, the peaks of Fe₂O₃ became weaker and disappeared almost completely in the XRD pattern of FHC-800.

Figure 1. XRD patterns of FHC composites and HC-800.

The characteristic peaks $2\theta = 44.57^\circ$ and 64.94° of ZVI appeared at treatment temperatures above 500°C ; these two peaks correspond to the (110) and (200) plane reflections of the ZVI with a body centered cubic (bcc) structure.²⁴ The calculated ZVI particle sizes using Scherrer's equation were 8.0, 8.5, and 8.9 nm in FHC-600, FHC-700, and FHC-800, respectively.²⁴ The increase of the NZVI particle size with temperature is believed to result from enhanced aggregation from 600 to 800°C . In addition, the peaks at $2\theta = 25.98$ and 43.73° , which correspond to the (002) and (100) plane diffraction peaks of graphite, were clearly observed in the XRD spectra of FHC-700 and FHC-800. The interlayer spacing of the (002) plane was 0.342 nm, and the calculated graphitization degree parameter g was 0.233 and 0.236 for FHC-700 and FHC-800, respectively, implying that substantial amounts of well-developed graphitic structure were present in these samples.²⁵ As a comparison, no reflection of crystal metal phase or graphitic structure was observed in the XRD pattern of HC-800. The deviation of the baseline at small angles ($<30^\circ$) in the XRD pattern originated from the amorphous carbonaceous structure of HC-800.²⁶ All of the above observations indicate clearly that the transformation of carbon from amorphous phase to graphitic structure was catalyzed by *in situ* formation of NZVI, which is highly dependent on temperature.

It is worth noting that diffraction peaks corresponding to iron carbides ($2\theta = 37.78^\circ, 42.81^\circ, 45.87^\circ, 48.56^\circ$, and 49.17°) were observed in the composites when the temperature was $\geq 700^\circ\text{C}$. It is known that nanometal-supported porous carbon suffers from low mechanical stability due to weak interactions between the metal and support carbon. One strategy to improve this stability is to form metal–carbon compounds.²⁷ In the present study, the formation of iron carbide indicates high mechanical stability of the composites.²⁷

The analysis results of BET surface areas, total pore volumes, and average pore sizes of the composites are summarized in Table 2. Figure 2 shows N_2 adsorption–desorption isotherms of HC-800, FHC-600, FHC-700, and FHC-800. In comparison with HC-800 and FHC-400, the BET surface areas of NZVI/

Table 2. Detailed Properties of the Composites Obtained from Different Thermal Treatments^a

sample	S_{BET} (m^2/g)	pore volume (cm^3/g)	average pore size (nm)	metal content (wt %)
FHC-400	32	0.04	1.24	24.32
FHC-500	423	0.23	1.67	13.59
FHC-600	459	0.26	1.72	12.45
FHC-700	416	0.28	1.84	15.36
FHC-800	472	0.22	1.79	8.22
HC800	20	0.04	1.43	ND

^aND: not detected.

Figure 2. N_2 adsorption/desorption isotherms of FHC-600, 700, 800, and HC-800.

PC composites were significantly increased by the addition of iron(III) nitrate. This indicates that iron(III) nitrate served as an activation agent during hydrochar thermal treatment within the temperature range of 500 – 800°C . The slight decrease of pore volume and surface area of NZVI/PC composites as the temperature increased from 600 to 800°C is ascribed to the partial collapse and combination of pores caused by high temperature. As can be seen in Figure 2, FHC-600, FHC-700, and FHC-800 exhibited a type IV nitrogen adsorption/desorption isotherm according to the IUPAC classification. The hysteresis loop at higher relative pressure ($P/P_0 = 0.20$ – 0.95) between adsorption and desorption isotherms indicates the presence of mesopores, especially for the FHC-800 composite.²⁸ The formation of mesopores is attributed in part to carbon removal by *in situ* formed NZVI; the same catalytic reaction has been observed in an aerogel carbonization process.^{25,29} Furthermore, the upward tendency at high relative pressure ($P/P_0 = 0.95$ – 1.00) results from the adsorption of the macropores and accumulation of carbon particles. In addition, the hysteresis loop of H3 showed nonlimiting adsorption at high relative pressure, suggesting the slit-shaped porous nature of the FHC composite.²⁸

Figure 3 shows SEM images of HC-800 and FHC-800. As shown in Figure 3a, HC-800 has relatively smooth surfaces, with no clear porous structure. In contrast, pores of different sizes and shapes can be observed clearly on the irregular external surfaces of FHC-800 (Figure 3b). Figure 3c shows a two-dimensional X-ray mapping of FHC-800 in a selected region to investigate the distribution of C, Fe, and O elements in the PC matrix. All three elements were nearly uniformly dispersed throughout the PC matrix.

The TEM images of FHC-800 (shown in Figure 4) provide evidence of the well-dispersed morphology of iron particles.

Figure 3. SEM images of (a) HC-800, (b) FHC-800, and (c) corresponding mapping of elemental Fe, C, and O in FHC-800.

Figure 4. TEM micrographs of FHC-800 at different viewing angles and magnifications.

According to calculations using Scherrer's equation, these particles have a mean size of 8.9 nm. In addition, the TEM images FHC-800 further reveal the pore structure of FHC-800 and clearly show two types of carbon phases within the porous carbon: crystalline graphitic carbon (around nano Fe regions) and amorphous carbon (Figure 4). Compared to FHC-600, the graphitic structure was significantly increased in FHC-800, confirming that high temperature is vital for Fe catalytic transformation from amorphous carbon to graphitic carbon. The well-distributed NZVI within the highly graphitic structure of PC suggests the high reactivity of the ZVI.³⁰

Figure 5 shows the TPD curves for the four main gas products evolved during the thermal treatment of hydrochar and Fe-hydrochar. The majority of the gas product was H₂ and CO for both hydrochar and Fe-hydrochar. The formation of CO and CO₂ indicates that substantial amounts of oxygen-containing functional groups were present in the hydrochar. Methane (CH₄) likely originates from the decomposition of methyl groups attached to aromatic units of the hydrochar. For hydrochar, gas yields significantly increased at temperatures above 600 °C, except CH₄, which reached its maximum yield at 600 °C and then decreased at higher temperatures. In the case of Fe-hydrochar, iron(III) nitrate addition significantly changed the gas evolution behavior during thermal treatment. The Fe-hydrochars gave increased gas yields overall and especially

Figure 5. Gas evolution from (a) hydrochar and (b) Fe-hydrochar at different temperatures.

showed higher gas evolution at lower treatment temperatures. In addition, yields of H₂ and CO first increased from 200 to 400 °C, then decreased within the temperature range of 400 to 700 °C, and again increased at temperatures above 700 °C. The highest yields of H₂ and CO were achieved at a treatment temperature of 900 °C, while the yields of CH₄ were relatively constant over the entire temperature range of 200 to 900 °C.

On the basis of these chemical characterization results and information regarding textural structure, a formation mechanism of NZVI/PC composites can be proposed.^{31–33} The ultrasonic treatment and unique surface properties of the hydrochar results in well-dispersed iron ions within the hydrochar matrix by means of physical adsorption and coordination (confirmed by Figure S2). During the thermal process, the iron ions are first hydrolyzed to iron(III) hydroxide. With further heating, the iron(III) hydroxide is dehydrated and transformed into iron(III) oxide, which is then reduced to ZVI mainly by H₂, CO, and amorphous carbon at temperatures higher than 600 °C.³⁴ The reductions of iron(III) oxide by H₂, CO, and amorphous carbon are supported by the decreased yield of H₂ and CO from Fe-hydrochar treated at 500 °C and significantly increased CO₂ yield compared to that from hydrochar, respectively. The enhanced gas formation from Fe-hydrochar creates large numbers of pores within the derived composite. In addition, reduction of iron(III) oxide by amorphous carbon contributes to the increase of surface area and formation of mesopore structures.³⁵ Subsequently, the *in situ* formed NZVI induces the transformation from amorphous carbon to a more graphitic structure at temperatures above 600 °C. The formation mechanism of NZVI/PC composite can be mainly described in the following equations:

Hydrochar activation/NZVI formation:

(1) Hydrolysis of Fe³⁺

(2) Dehydration of Fe(OH)₃

(3) Reduction of iron oxide ($T \geq 500$ °C)

NZVI catalyzing ($T \geq 600^\circ\text{C}$)

In the present study, the uniform dispersion of NZVI was achieved by well-dispersed metal ions within the hydrochar matrix. During thermal treatment, these well-dispersed ions are self-reduced to NZVI by hydrochar-derived H_2 , CO, and amorphous carbon. Thus, the NZVI is formed *in situ* and is supported on the hydrochar-derived porous carbon. The preparation approach in the present study well overcomes the drawbacks of conventional preparation of NZVI/PC such as poor dispersion of NZVI and high cost.

Waste PCBs typically occur in the environment as mixtures of different chlorine-substituted PCBs. In this study, Aroclor 1242 (di-, tri-, tetra-, and penta-chlorinated PCBs) was adopted as a representative PCB sample. Individual chlorinated PCBs, selected to represent different classes of compounds, were chosen for analysis. For example, 2,3- and 2,6'-dichloro-1,1'-biphenyl represented dichlorinated biphenyls (2CB); 2,5,5'- and 2,3,4-trichloro-1,1'-biphenyl represented trichlorinated biphenyls (3CB); 2,3,4,6'- and 2,4,4',6-tetrachloro-1,1'-biphenyl represented tetra-chlorinated biphenyls (4CB); 2,3,4,4',5'- and 2,3',4',5,6'-penta-1,1'-biphenyl represented penta-chlorinated biphenyls (5CB). Figure 6 shows the removal rates of different

Figure 6. Removal rates of PCBs by FHC-600 and FHC-800 as a function of time at room temperature (PCBs concentration 10 mg/L; dose 80 g/L).

chlorine-substituted PCBs in aqueous solution when treated with FHC-600 and FHC-800. More than 91% of PCBs were removed within 12 h by both FHC-600 and FHC-800. Initial rates of removal were higher with FHC-800 compared to that with FHC-600. This is attributed to the greater presence of mesopores in FHC-800, which provide transport pathways for microporous adsorption, and the slit-shaped porous shapes, which are easily accessed and filled efficiently.^{36–38} Pseudo-first-order (eq 7) and pseudo-second-order (eq 8) equations

were employed to investigate the PCBs' removal behavior with FHC-600 and FHC-800.

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (7)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

where q_t and q_e (mg/g) are the amount of adsorbed PCBs at time t (h) and time of equilibrium k_1 (1/h) and k_2 (g/mgh) are the rate constants for pseudo-first-order and pseudo-second-order adsorption kinetics, respectively.

Table 3 shows the parameters derived from application of pseudo-first-order and pseudo-second-order kinetics for PCB removal (PCB removal rate is taken as the average removal rate of the representative compounds 2CB, 3CB, 4CB, and 5CB). PCB removal by FHC-600 and FHC-800 are satisfactorily described by the pseudo-second-order equation as a result of synergistic combination of the PCBs' adsorption and dechlorination. The kinetic constants calculated from the pseudo-second-order equation are consistent with the fast removal of PCBs from aqueous solution by the composites FHC-600 and FHC-800. However, due to higher dechlorination rates, the pseudo-first-order fitting was slightly better for FHC-800 than FHC-600 (R^2 was 0.98 and 0.96 for FHC-800 and FHC-600, respectively).

Figure 7 shows the dechlorination rates of the representative compounds of different-chlorinated PCBs. As can be seen,

Figure 7. Dechlorination rates of different substituted PCBs by FHC-600 and FHC-800 at room temperature (dose 80 g/L; reaction time 6 days).

trichlorinated biphenyls have the highest dechlorination rates of about 78% and 86% when using FHC-600 and FHC-800, respectively, for 6 days at room temperature. Accounting for the inevitable transformation of highly chlorinated PCBs to these less highly chlorinated representative compounds, it can be concluded that the actual dechlorination rates of PCBs was higher than the dechlorination rates observed here. In addition,

Table 3. Pseudo-first-order and Pseudo-second-order Kinetic Parameters for PCB Removal by FHC-600 and FHC-800

equations	pseudo-first-order			pseudo-second-order		
parameters	k_1 (h)	q_e (mg/g)	R^2	k_2 (g/mgh)	q_e (mg/g)	R^2
FHC-600	0.28	58.79	0.96	6.26×10^{-4}	105.26	0.99
FHC-800	0.33	43.49	0.98	6.26×10^{-4}	105.26	0.99

only small amounts of biphenyl, the completely dechlorinated product, were detected in the aqueous solution, suggesting that the dechlorinated products preferentially adsorbed on the composites rather than diffusing into the aqueous solution.

The reduction of PCBs by NZVI generally involves mass transport of the PCBs from aqueous solution to the NZVI surface area, where surface reduction reactions occur. The efficient room temperature dechlorination of PCBs with FHC-800 and FHC-600 in the present study are ascribed to the higher surface area of NZVI and enhanced contacting between the PCBs and NZVI, due to the highly graphitic nature of PC.³⁴ Because of the crystalline graphitic structure in the FHC-800 matrix, electrons of the NZVI available for electrochemical reduction reactions can readily transport throughout the structure and therefore expand the reactive surface area available for reduction.

CONCLUSIONS

In this study, a simple and effective strategy for preparing NZVI/PC composites was developed using hydrochar and iron(III) nitrate as precursors. The metal ions are dispersed uniformly throughout the hydrochar matrix, and during subsequent thermal treatment, the iron ions are self-reduced to NZVI. In addition, when heated in the temperature range of 600–800 °C, the *in situ* formed NZVI catalyzes the formation of graphitic structures and promotes the formation of mesopore structures. The NZVI/PC composites showed high performance for PCB removal from aqueous solutions. The synergistic adsorption and dechlorination of PCBs with NZVI/PC was well described by pseudo-second-order kinetic equations.

In the present study, renewable hydrochar was used as the precursor of the porous carbon, and no additional reducing agent was required. In addition, activation of the hydrochar and formation/deposition of NZVI were realized simultaneously through a one-step process. This approach offers a simple, low-cost, and green production method for NZVI/PC composites, which have the potential for wide applicability and provide significant environmental and cost benefits.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.6b00306.

Raman spectra of the composites FHC-400, 500, 600, and 700 and SEM images of Fe-hydrochar and corresponding mapping of carbon, iron, and oxygen (PDF)

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Notes

The authors declare no competing financial interest.

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