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Mössbauer Spectroscopy Studies of Biochar Modified by Iron

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Modified biochar is an environmentally friendly, regenerable adsorbent used to remove potentially toxic elements from water. Biochar modified with iron exhibits a higher adsorption capacity for As. X-ray diffraction, Mössbauer spectroscopy, and transmission electron microscopy were used as complementary methods to identify the phases formed after the pyrolysis of honeycomb biomass and the impregnation of biochar with $Fe(NO_3)_3$. In addition to inorganic compounds, the modified biochar contains several iron-containing phases and can be classified as magnetic carbon.

topics: biochar, adsorption, X-ray diffraction (XRD), Mössbauer spectroscopy

1. Introduction

Water pollution is a serious global problem. Consequently, methods such as ozonation, biodegradation, electrochemical oxidation, and adsorption are used to eliminate potentially toxic organic (e.g., pharmaceuticals, personal hygiene products, reactive dyes) and inorganic (e.g., heavy metals) species. One of the environmentally friendly, regenerable adsorbents used to remove toxic elements from water is biochar (BC), which features a large specific surface area, a stable structure, and a high cation-exchange capacity. However, in its pristine state, BC exhibits insufficient adsorption ability. Therefore, various strategies are being developed to modify BC to enhance its adsorption capacity for removing potentially toxic pollutants. A detailed review of various modification techniques using different BC feedstocks and pyrolysis temperatures to prepare functionalized BC, along with their impact on aquatic systems, is presented in paper [1].

In the present study, attention is focused on BC modification by iron. The goal is not only to improve separation efficiency for reuse and BC recycling, but also to increase the decontamination capability of biochar through interaction/chemical affinity between the contaminants and the loaded Fe. By precipitation, ball milling, thermal reduction, and co-pyrolysis, iron-activated biochar can be synthesized using various iron oxides, zero-valent iron nanoparticles (nZVI), or iron sulfide [2]. Hematite and goethite are the most commonly applied Fe oxides to increase the adsorption efficiency of biochar for heavy metals, such as Hg, As, Cr, Cu, Pb, and Cd [3]. Coating the biochar surface with nZVI and FeOx results in desirable modifications to the surface morphology, functional groups, and elemental composition, increasing the material's efficiency in the sorption of potentially toxic elements [4].

Biochar is a carbon-rich material produced from various organic waste materials, such as municipal sewage sludge and agricultural waste. In this work, biochar was prepared from beekeeping waste, then pyrolyzed and impregnated to obtain a biochar-iron composite. The main goal of the present study was to identify the phases created after the above treatments using X-ray diffractometry (XRD), Mössbauer spectroscopy (MS), and transmission electron microscopy (TEM).

2. Experiment

The honeycomb biomass was dried and homogenized, then extracted with hexane to remove any residual beeswax. Such prepared feedstock was pyrolyzed in a CO_2 atmosphere at 820°C for 5 h in a quartz tube furnace. The synthesized biochar, designated BC_CO_2, served as a matrix for the incorporation of iron species. An 8 g portion of BC_CO_2 was impregnated in 200 ml of a 24% $Fe(NO_3)_3 \cdot 9H_2O$ solution using an ultrasonic bath for 15 min. Subsequently, the carbon suspension was evaporated to nearly dry weight. The obtained material was divided into two equal portions; one was heat-treated at 200°C (sample BC_Fe_200), and the other at 700°C (sample BC_Fe_700) in an N_2 atmosphere for 2 h. To determine the elemental composition of the prepared materials, energy-dispersive X-ray spectroscopy (EDX) was employed; the results are listed in Table I.

The phase composition and structure of the samples were investigated by X-ray diffraction with an Empyrean PANalytical diffractometer using Cu K_α radiation. X'Pert HighScore Plus computer program, equipped with the ICDD PDF+ database, was used for phase analysis. The ^{57}Fe Mössbauer spectra were registered at room temperature using a POLON spectrometer working in transmission geometry and constant acceleration mode. The source ^{57}Co in a Rh matrix was used. The materials' morphology was investigated using a Titan G2-Cubed transmission electron microscope (FEI Company) operating at 60–300 kV. Phase identification was performed by analyzing the fast Fourier transform of high-resolution TEM images.

3. Results and discussion

Independent studies using Raman spectroscopy have shown that the carbon in the prepared material is amorphous. The results of XRD measurements for BC_CO_2, BC_Fe_200, and BC_Fe_700 samples are presented in Fig. 1. The diffraction lines registered for the pristine biochar (Fig. 1a) originate from a number of crystalline inorganic compounds embedded in amorphous carbon matrix, i.e., K_2SO_4 ($\sim 7\%$), $K_{0.21}Ca_{2.58}Mg_{0.21}(PO_4)_2$ ($\sim 24\%$), SiO_2 ($\sim 30\%$), $K_2Mg_2(SO_4)_3$ ($\sim 19\%$), and $K_2CaP_2O_7$ ($\sim 20\%$). The XRD pattern of BC_Fe_200 (Fig. 1b) does not show any crystalline phases of iron, while the visible peak near $2\Theta = 27°$ comes from the SiO_2 compound. Finally, the pattern for the BC_Fe_700 sample (Fig. 1c) exhibits diffraction lines from non-stoichiometric Fe_3O_4 ($\sim 79\%$), metallic Fe ($\sim 15\%$), and SiO_2 ($\sim 15\%$). The identified iron-containing crystallites have average sizes of 27 nm (Fe_3O_4) and ~ 202 nm (metallic iron). It can be noted that there is a significant increase in Si content after heating the sample at 700°C (see EDX results in Table I). During the thermal processing of the composite at 700°C, the carbon matrix undergoes catalytic decomposition facilitated by iron species, resulting in a reduction of carbon content [5]. In contrast, silica most likely remains unchanged due to strong Si–O–Si bonds [6], leading to its densification within the composite structure mainly on the grain surface, to which EDX analysis is sensitive. Consequently, the Si content determined for the BC_Fe_700 material is the highest.

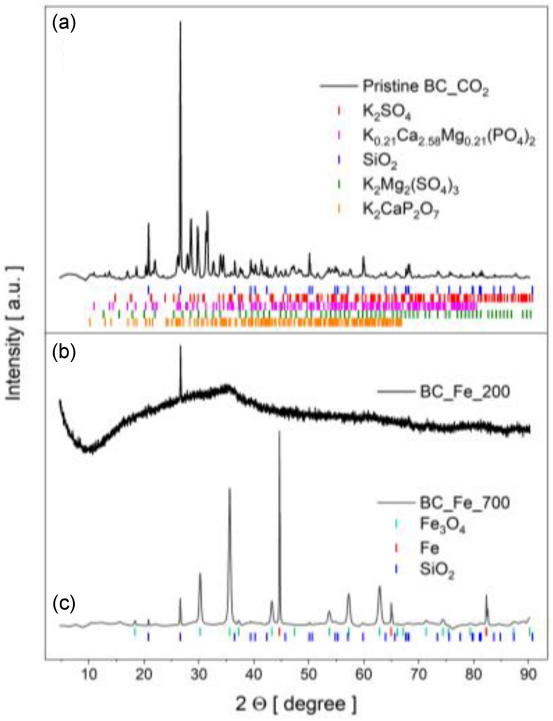

Fig. 1. XRD patterns for pristine biochar (a) as well as for iron-modified biochar: (b) BC_Fe_200 and (c) BC_Fe_700.

TABLE I

Elemental composition of the samples from EDX analysis (values are in wt%).

Element	BC_CO_2	BC_Fe_200	BC_Fe_700
C	66.85 ± 2.20	22.02 ± 2.81	16.38 ± 1.37
O	13.78 ± 0.66	28.83 ± 0.70	25.41 ± 4.03
Fe	0.13 ± 0.03	44.26 ± 1.54	49.25 ± 5.36
N	3.81 ± 0.06	2.14 ± 0.20	1.91 ± 0.45
K	5.47 ± 0.47	1.12 ± 0.15	1.73 ± 0.48
P	3.83 ± 0.64	1.47 ± 0.27	1.49 ± 0.29
Ca	1.29 ± 0.38	0.92 ± 0.07	1.3 ± 0.17
Mg	1.49 ± 0.34	0.66 ± 0.05	0.67 ± 0.21
Si	0.37 ± 0.13	0.35 ± 0.07	2.11 ± 1.13

TABLE II

Hyperfine interaction parameters derived from numerical elaboration of MS spectra: δ — isomer shift, Δ — quadrupole splitting (shift), B_{hf} — hyperfine magnetic field, Γ — half-width at half maximum of the spectral line, C — component. Uncertainty is ±0.01 mm/s for δ and Δ, ±0.02 mm/s for Γ, and ±0.1 T for B_{hf}.

Sample	δ [mm/s]	Δ [mm/s]	B_{hf} [T]	Γ [mm/s]	C
BC_Fe_200	0.35	0.61	–	0.19	doublet 1
	0.35	1.11	–	0.23	doublet 2
BC_Fe_700	0.69	–	–	0.23	singlet
	0.62	1.36	–	0.44	doublet
	0.01	0.00	33.1	0.13	α–Fe
	0.30	0.02	49.4	0.29	sextet A
	0.87	0.08	47.2	0.30	sextet B

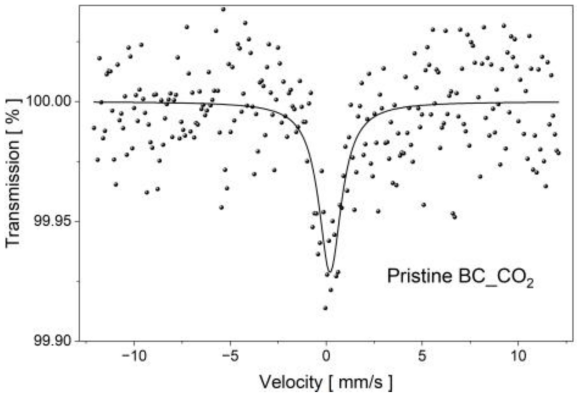

Fig. 2. Mössbauer spectrum of pristine biochar.

As the EDX analysis showed, the BC_CO_2 pristine sample contained 0.13(3) wt% of Fe. Therefore, the MS spectrum (Fig. 2), which showed poor statistics, only confirmed the presence of negligible iron in biochar.

The singlet with isomer shift $\delta = 0.31 \pm 0.08$ mm/s and spectral line width $\Gamma = 0.72 \pm 0.12$ mm/s may indicate the presence of very small superparamagnetic iron or iron oxide particles in a carbon matrix.

As mentioned, the XRD pattern of BC_Fe_200 did not show any crystalline phases of iron; however, MS shows two paramagnetic doublets (Fig. 3a) with hyperfine interaction parameters characteristic of akaganeite β-FeOOH [7]. Finally, for the BC_Fe_700 composite, the Mössbauer spectrum reveals complex hyperfine structure with five components (Fig. 3b). Two of them — metallic iron (α-Fe sextet) and non-stoichiometric magnetite (sextet A and sextet B) — were identified in the XRD pattern. The remaining components, singlet and doublet, may originate from iron oxides with small particle sizes. The hyperfine interaction parameters for all identified phases are listed in Table II.

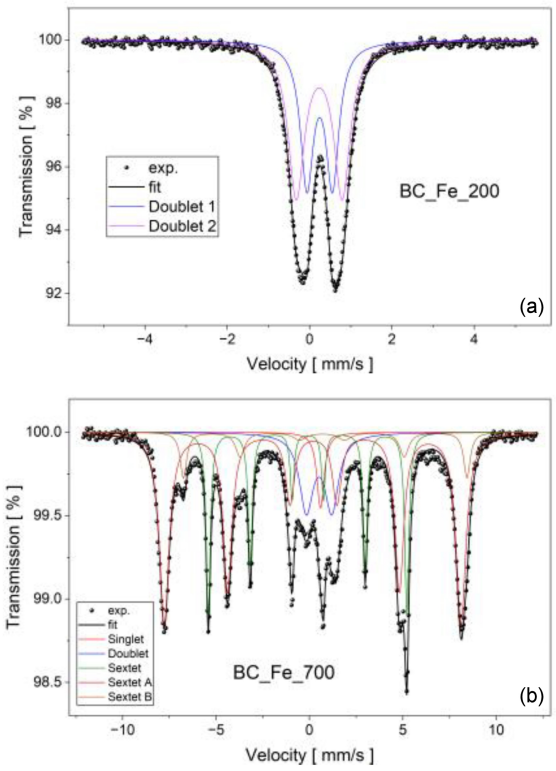

Fig. 3. Mössbauer spectra of (a) BC_Fe_200 and (b) BC_Fe_700 samples.

The results from XRD and Mössbauer spectroscopy are confirmed by phase analysis based on TEM images. One of the inorganic phases — $K_2CaP_2O_7$ — can be seen as small particles in an amorphous carbon matrix (Fig. 4).

TEM studies confirmed the presence of akageneite in modified biochar heat-treated at 200°C (Fig. 5).

Finally, for the BC_Fe_700 sample, the presence of magnetite Fe_3O_4 particles, visible both in the XRD pattern and the MS spectrum, was confirmed

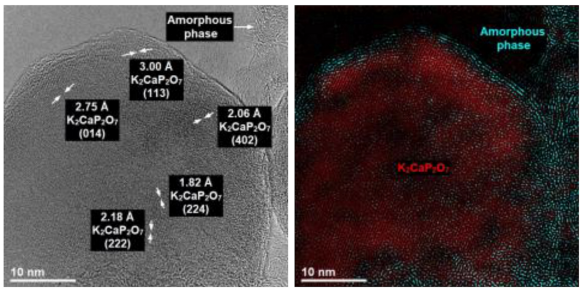

Fig. 4. TEM image of pristine biochar.

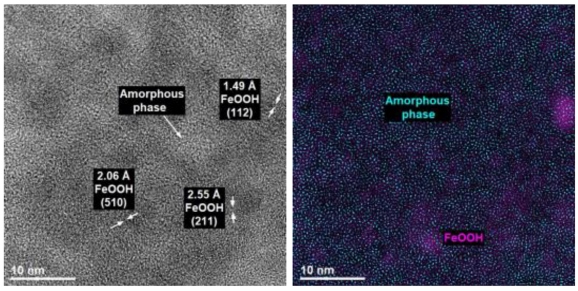

Fig. 5. TEM image of BC_Fe_200 sample.

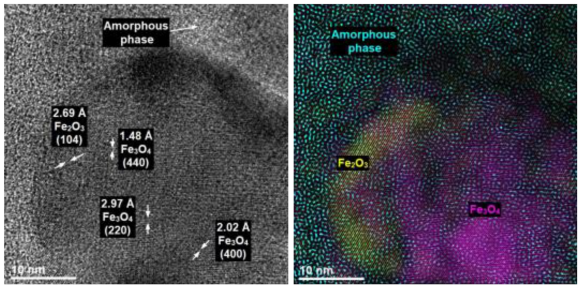

Fig. 6. TEM image of BC_Fe_700 sample.

by TEM analysis (Fig. 6). Moreover, particles of Fe_2O_3 revealed by TEM can be assigned to a doublet component with a large value of quadrupole splitting seen in the MS spectrum in Fig. 3b.

4. Conclusions

The presence of various iron species, i.e., Fe^0 in metallic iron, Fe^{2+} and Fe^{3+} in Fe_3O_4, as well as Fe^{3+} in FeOOH and Fe_2O_3 on the biochar surface, revealed by MS and TEM, is crucial for the sorption properties of hybrid materials. Increasing the composite heat-treatment temperature from 200 to 700°C induces the formation of magnetic iron phases in the biochar matrix. The obtained results provide a basis for further research on the properties of iron-modified biochar to enhance its sorptive capacity for removing potentially toxic elements from wastewater.

References

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