Multiscale visualization of the structural and characteristic changes of sewage sludge biochar oriented towards potential agronomic and environmental implication

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Sewage sludge biochars were obtained at different pyrolysis temperatures from 300 °C to 900 °C and their macro- and microscale properties were analyzed. The biochar’s plant-available nutrients and humus-like substances in the water-extractable phase and fixed nutrients in the solid fraction were evaluated for their potential agronomic implications. FT-IR, Raman, XRD, XPS, and SEM techniques were used to investigate the chemical structure, functional groups, and microcrystal structure on the surface of the biochar. The results revealed minor chemical changes and dramatic mass loss in the biochar obtained at 300–500 °C, whereas significant chemical changes in the biochar were obtained at 600–900 °C. The concentrations of plant-available nutrients as well as fulvic- and humic-acid-like materials decreased in the biochar samples obtained at higher temperatures. These results implied that the biochar samples pyrolyzed at 300–500 °C could be a direct nutrient source and used to neutralize alkaline soil. The surface area and porosity of the biochar samples increased with temperature, which increased their adsorption capacity. Rearrangement occurred at higher temperature 600–900 °C, resulting in the biochar becoming increasingly polyaromatic and its graphite-like carbon becoming organized.

Biotreatment of municipal and industrial wastewaters unavoidably leads to significant quantities of sludge. For sewage sludge treatment, pyrolysis is a promising pathway1–3. Pyrolysis of sewage sludge is the thermal degradation of sludge in the absence of air or in an oxygen-deficient atmosphere, transforming the sludge organic matter into biogas, bio-oil, and carbonaceous biochar residue. When compared with raw sludge, sludge biochar has minimum pathogens and odor, and is capable of concentrating heavy metals4 (except mercury and cadmium). Studies comparing sludge biochar with raw sludge revealed that the soil properties were improved after applying sludge biochar to the soil as amendment5–7. Therefore, there has been increasing interest in the use of sludge biochar for soil beneficiation and carbon sequestration in a long-lasting solid form. The agronomic performance and effectiveness of biochar, such as available nutrients, is essentially depend on its characteristics, and the physical and chemical properties of sludge biochars are strongly influenced by the pyrolysis conditions, predominantly by the highest treatment temperature (HTT).

During the pyrolysis process, biochar undergoes various physical, chemical, and molecular changes. Some of the documented changes include those in the yield, volatile contents, pH, electrical conductivity (EC), hardness, bulk density, and element composition that are related to macro-nutrient benefits for agro-application1,8,9. Whereas, the other part of studies have focused on the behavior of heavy metals during low-temperature pyrolysis of sewage sludge at 500 °C10, 300–700 °C11, 300–500 °C11, and 400–450 °C12, which are related to the toxicity for agro-application. These two parts of researches were rarely put together and balanced the pros and cons of sludge biochar simultaneously. Furthermore, concentrations of heavy metals might decrease at higher temperature13. Therefore, it arouses the research demand on higher temperature scenario and the systematic
The yield of biochar dropped from 64.28 to 46.66 wt% of the dry mass when the pyrolysis temperature was increased from 300°C to 900°C. However, only an additional 4.44 wt% yield was reduced when the temperature was increased from 700°C to 900°C. The decrease in the biochar yield with the increasing pyrolysis temperature could possibly be related to the cracking and volatilization process, which was also reported for sludge biochar pyrolyzed at different temperatures of 450°C, 650°C, and 850°C. The heating value of the biochar dropped linearly from 11054.3 to 6635.6 kJ kg⁻¹ when the pyrolysis temperature was increased from 300°C to 600°C, and then almost remained constant with the temperature increasing from 600°C to 900°C.

An increase in the pyrolysis temperature from 300°C to 900°C led to an increase in the fixed carbon (FC) content from 15.75 to 21.25 wt%, and an increase in the ratio of FC to carbon from 42.4 to 84.2. The FC content represented the efficiency of the pyrolytic conversion of ash-free organic matter in the sludge to a relatively pure, ash-free carbon. The highest ash content and lowest volatile matter content were found in biochar sample of 900°C, which was mostly due to volatilization accompanied by the accumulation of inorganic oxides such as Si, Al, and Fe.

For instance, the XRF results revealed that the ash composition of the biochar samples comprised 19.1%–22.7% Si. Comparison of the Si, Al, Ca, and Fe contents of the ash composition (Table 2) indicated the increase in the inorganic components with the increasing pyrolysis temperature. One of the main characteristics of sewage sludge is the presence of high amounts of inorganic ash, when compared with other materials such as wood biochar or lignocellulosic char obtained from agricultural waste. The increase in the amount of inorganic ash in the biochar could increase its mineral composition and capacity to adsorb polar molecules.

Carbon, hydrogen, oxygen, nitrogen, and sulfur. The variations in the results of the elemental analyses of the sludge biochar samples with temperature are shown in Table 1. The biochar samples showed the pattern of depleted content of some elements. In samples of 300–900°C, the carbon content decreased from 37.15 to 25.23 wt% of dry mass, the hydrogen content decreased from 4.35 to 0.64 wt%, the nitrogen content decreased from 6.17 to 1.24 wt%, the sulfur content decreased from 1.54 to 0.55 wt%, and the oxygen content decreased from 31.37 to 1.16 wt%. Particularly, when compared with the original dried sludge, more than 67.5% of hydrogen was removed.
in sample at 500 °C, and more than 80.0% of hydrogen was lost in samples pyrolyzed at over 700 °C. Moreover, the H/C and O/C atomic ratios of the biochar samples demonstrated a decreasing trend with increasing pyrolysis temperature. Lower pyrolysis temperatures (samples at 300–500 °C) resulted in a higher H/C ratio (1.41–0.67) and O/C ratio (0.27–0.15), whereas higher temperatures (samples at 600–900 °C) presented lower H/C ratios (0.51–0.30) and O/C ratios (0.15–0.03). When compared with the biochar samples pyrolyzed at lower temperatures, those obtained at higher temperatures were less polar and had greater aromaticity and carbonization.

**Nutrients and trace metals of biochar samples in solid form.** Table 3 showed the total contents of trace metals in raw sludge and sludge biochar samples measured by wet acid-extraction method followed by ICP in accordance with EPA method 3050B. The contents of majority of trace metals, such as Al, Fe, and Zn in the final residue were greater than those in their feedstock sludge, which showed that pyrolysis process condensed and retained these trace metals in the final residue. Furthermore, the enrichment effect became more evidently with pyrolysis temperature rising.

For comparison purposes, we also determined the total amounts of heavy metals in solid form using XRF technique. The results showed that all heavy metals have their total concentration increasing with temperature (Supplemental information: Table S1). Thus, we can find a bit difference between two dataset. It should be noticed firstly that, to gain insight into the precision of the heavy metal analyses found a bit difference between two dataset. It should be noticed firstly that, to gain insight into the precision of the heavy metal analyses found a bit difference between two dataset. It should be noticed firstly that, to gain insight into the precision of the heavy metal analyses.

**Water-extractable fractions of the biochar samples.** The agronomic availability of biochars primarily depends on the initial water-extractable nutrient contents (Table 4). Although dissolved organic matter (DOM) represents a small proportion of organic matter residue in the biochar, it is significant in the soil amendment/ecosystem owing to its mobility and reactivity. The DOC and DN indicate the DOM contents. In the present study, the DOC contents decreased rapidly from 24.23 mg g⁻¹ in sample at 300 °C to 2.66 mg g⁻¹ in sample at 400 °C, and then reduced to almost zero in samples of 600–900 °C. This was due to secondary reactions, which resulted in low molecular weight acids and neutral compounds, which were dominant in the biochars at higher temperatures. The DN and NH₄⁺-N have important agronomic uses because they are the main sources of nitrogen available for plant uptake. Their contents in sample at 300 °C were 6.19 and 4.39 mg g⁻¹, respectively, which decreased to 0.57 and 2.15 mg g⁻¹, respectively, in sample at 400 °C, and then reached almost zero or below the detection limit in samples of 500–900 °C. Reported that the available nitrogen content in the form of DN and NH₄⁺-N was higher in the sludge biochar samples produced at lower pyrolysis temperatures (<400 °C).

The contents of water-extractable K, Na, P, and Mg reduced rapidly with the increasing pyrolysis temperature, and when compared with the raw sludge, almost 90% of the water-extractable K, Na, and P contents and 30% of Mg content were lost in sample at 400 °C. Similarly, the water-extractable Ca content in the biochar samples also presented a downward trend, when compared with the raw sludge.

**Table 3 | Total contents of nutrients and trace metals in raw sludge and sludge biochar samples by acid-extraction method**

| Items (mg g⁻¹) Sludge | 300 Raised (%) | 400 Raised (%) | 500 Raised (%) | 600 Raised (%) | 700 Raised (%) | 800 Raised (%) | 900 Raised (%) |
|-----------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| P                     | 7.74           | 10.43          | 11.56          | 11.63          | 11.48          | 18.23          | 135.5          | 20.01          | 158.5          | 18.98          | 145.2          | 19.48          | 151.6          |
| K                     | 2.05           | 2.25           | 9.7            | 2.48           | 2.75           | 34.1           | 3.83           | 38.0           | 2.91           | 41.9           | 3.43           | 67.3           | 3.35           | 63.4           |
| Na                    | 3.49           | 3.50           | 0.3            | 4.25           | 21.8           | 25.5           | 7.40           | 112.0          | 8.11           | 132.4          | 6.70           | 92.0           | 6.41           | 83.7           |
| Ca                    | 5.00           | 5.33           | 6.6            | 5.59           | 11.8           | 6.00           | 20.0           | 6.45           | 29.0           | 7.80           | 56.0           | 8.55           | 71.0           | 9.14           | 82.8           |
| Mg                    | 1.25           | 1.35           | 8.0            | 1.42           | 13.6           | 1.68           | 34.4           | 2.24           | 79.2           | 2.56           | 104.8          | 2.85           | 128.0          | 3.19           | 155.2          |
| Fe                    | 1.60           | 1.77           | 6.6            | 5.59           | 11.8           | 6.00           | 20.0           | 6.45           | 29.0           | 7.80           | 56.0           | 8.55           | 71.0           | 9.14           | 82.8           |
| Zn                    | 0.81           | 0.51           | 12.3           | 1.11           | 37.0           | 1.58           | 95.1           | 1.72           | 112.3          | 1.78           | 119.8          | 1.70           | 109.9          | 1.73           | 113.6          |
| Mn                    | 0.27           | 0.28           | 37.0           | 0.3            | 11.1           | 0.42           | 55.6           | 0.48           | 77.8           | 0.57           | 111.1          | 0.20           | 25.9           | 0.11           | 59.2           |
| Cu                    | 0.11           | 0.09           | –18.2          | 0.09           | –18.2          | 0.18           | 63.6           | 0.14           | 27.3           | 0.16           | 45.5           | 0.09           | –18.2          | 0.09           | –18.2          |

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Table 4 | Contents of water-extractable compounds in raw sludge and sludge biochar samples

| Items (mg g⁻¹) | Temperature (°C) | 300 | 400 | 500 | 600 | 700 | 800 | 900 |
|---------------|-----------------|-----|-----|-----|-----|-----|-----|-----|
| DOC           |                 | 31.24 | 24.23 | 2.66 | 0.32 | 0.16 | 0.15 | 0.08 | 0.03 |
| DN            |                 | 8.90  | 6.19  | 0.57 | 0.07 | 0.06 | 0.06 | 0.03 | 0.02 |
| NH₄⁻-N        |                 | 5.57  | 4.39  | 2.15 | BD   | BD   | BD   | BD   | BD   |
| P             |                 | 1.39  | 1.00  | 0.21 | BD   | BD   | BD   | BD   | BD   |
| K             |                 | 1.36  | 0.73  | 0.15 | 0.17 | 0.15 | 0.11 | 0.16 | 0.26 |
| Na            |                 | 1.62  | 0.25  | 0.20 | 0.18 | 0.18 | 0.18 | 0.18 | 0.17 |
| Ca            |                 | 0.51  | 0.49  | 0.47 | 0.19 | 0.87 | 1.28 | 1.41 | 0.50 |
| Mg            |                 | 0.60  | 0.53  | 0.21 | 0.18 | BD   | BD   | BD   | BD   |
| Al            |                 | BD    | BD    | BD   | BD   | BD   | BD   | BD   | BD   |
| Fe            |                 | BD    | BD    | BD   | BD   | BD   | BD   | BD   | BD   |
| Zn            |                 | BD    | BD    | BD   | BD   | BD   | BD   | BD   | BD   |
| Mn            |                 | BD    | BD    | BD   | BD   | BD   | BD   | BD   | BD   |
| Cu            |                 | BD    | BD    | BD   | BD   | BD   | BD   | BD   | BD   |

BD: below the detect limit.

detect protein- or humus-like organic matters, a limited number of studies had used this technique to analyze biochar with respect to temperature. The EEM spectra, normalized to the DOC content for the primary sludge and sludge biochar samples, are presented in Fig. 1. An EEM spectrum could be divided into four excitation-emission regions: Region I (Ex < 250 nm; Em < 380 nm), protein-like organic compounds; Region II (Ex < 250 nm; Em > 380 nm), fulvic-acid-like materials; Region III (Ex > 250 nm; Em < 380 nm), soluble microbial byproduct-like materials; and Region IV (Ex > 250 nm; Em > 380 nm), humic-acid-like materials.

In the contour of raw sludge itself, organic compounds were found to be composed of aromatic proteins (Region I) and soluble microbial byproduct-like materials (Region III). The volumes of fulvic-acid-like materials (Region II) and humic-acid-like materials (Region IV) were low. The scope and intensity of the fluorescence area were the highest for the biochar sample at 300 °C, followed by samples at 300–500 °C, and eventually became undetectable at higher temperatures (700–900 °C). These results suggested that the sludge biochar produced at lower temperatures (300–500 °C) had more fulvic- and humic-acid-like materials.

The pH and EC values of the biochar samples are listed in Table 1. The pH values of the biochar samples at 300–800 °C ranged from 6.2 to 11.9, and then decreased to 9.4 for sample at 900 °C. The EC values correspond to the concentration of total dissolved salts and could be used to describe the variation in the organic and inorganic ions. The EC value of the primary sludge was 4.70 ds m⁻¹, which decreased to 0.3–0.4 ds m⁻¹ with the increasing pyrolysis temperature. However, regardless of the trend of the pH and EC results, sample at 700 °C increased with the increasing pyrolysis temperature from 4.88 m² g⁻¹ to 34.12 m² g⁻¹. The BET surface area of the biochar increased substantially up to 34.12 m² g⁻¹.

**XRD spectra.** The XRD spectra of the biochar samples are shown in Fig. S2 (Supplemental information: Fig. S2). The analysis of the XRD patterns revealed the presence of several mineral phases. Quartz, with a characteristic peak at 2θ = 26.6°, was the most recognizable crystallographic structure at all temperatures. The sharpness of the peak increased with the increasing temperature, possibly owing to the ultrastructural changes in the sludge biochar. Calcite (CaCO₃) and dolomite [CaMg(CO₃)₂] were detected in the biochar samples at 300–800 °C, while carbonates underwent decomposition and were not present at higher temperatures (>800 °C). Some amount of Ca, which was present as CaCO₃ in samples heated at 700 °C, decomposed to CaO during high-temperature pyrolysis. This was also a reason for the higher pH values of the samples pyrolyzed at 700–800 °C, and the samples’ basicity was mainly linked to the presence of Ca.

**BET surface area and SEM morphology.** The BET surface areas of the raw sludge and biochar samples are listed in Table 1. The BET surface area of the as-received sludge was considerably low (2.88 m² g⁻¹). However, the surface area of the sludge biochar linearly increased with the increasing pyrolysis temperature from 4.88 m² g⁻¹ at 300 °C to 19.11 m² g⁻¹ at 800 °C. At 900 °C, the BET surface area of the biochar increased substantially up to 34.12 m² g⁻¹.

The SEM general morphology (Supplemental information: Fig. S3) of the biochar samples also exhibited an increased surface area with the increasing pyrolysis temperatures. The SEM images of the as-received sludge indicated plate-like layer construction and poor structure that was smoothly compacted (Fig. S3a). However, as shown in Fig. S3b, a crack appeared and tar agglomerates seemed to cover the surface of the biochar particle. Furthermore, in the biochar samples, the dense and tightly packed microstructure disintegrated, gradually forming fragments (Fig. S3c–e), and a characteristic hollow was observed (Fig. S3f–h). On the one hand, lower temperature entailed condensation of organic volatiles, which could lead to pore clogging and reduction in the total surface area. On the other hand, at higher temperature, volatilization was more subtle, making the biochar more porous and creating voids within the biochar matrix.
FT-IR and XPS spectra. Fig. S4 (Supplemental information: Fig. S4) presented the FT-IR spectra of the dried raw sludge and biochar samples. The absorption bands and peaks provided evidence of the presence of some surface functional groups. In general, the organic functional groups found in the biochar spectra decreased or even disappeared as a result of pyrolysis.

The broad band at 3400 cm\(^{-1}\) was assigned to hydroxyl (-OH) stretching, and the peak intensity decreased rapidly at samples 300–500 °C, suggesting an ignition loss of -OH\(^1\). The peaks at 2925 and 2855 cm\(^{-1}\) corresponded to the aliphatic CH\(_3\) asymmetric and symmetric stretching vibration, respectively, which had been assigned to the fats and lipids of the sewage sludge\(^2\). These peak intensities decreased owing to the continuous decrease in the labile aliphatic compounds as well as demethylation and dehydration. The loss of -OH and aliphatic groups as well as a concurrent development of fused-ring structures gave rise to pore formation. These results were consistent with the SEM findings. The peaks at 1650 cm\(^{-1}\) were assigned to the amide I bands of protein origin. These bands gradually broadened and shifted towards lower wavenumbers as a result of pyrolysis. The decomposition of protein mainly occurred at 300–400 °C\(^3\), which could be explained by a decrease in the amide groups and simultaneous increase in the amino acid functionalities. The band at 1430 cm\(^{-1}\) became invisible, and this wavenumber had been assigned to the stretching of C in the heteroaromatic structures\(^3\). The sharp peak at 1030 cm\(^{-1}\) was assigned to C-O stretching of polysaccharides or polysaccharide-like substances. This peak decreased at higher pyrolysis temperature and appeared as a shoulder for the amine I bands of protein origin. These bands gradually broadened and shifted towards lower wavenumbers as a result of pyrolysis.

Raman spectra. Raman spectrum was also used to further analyze the structure of the carbon materials, and the results of the Raman spectra in the region from 0 to 2000 cm\(^{-1}\) are shown in Fig. S5 (Supplemental information: Fig. S5). All of the curves exhibited two relatively broad Raman bands at Raman shifts at 1350 and 1580 cm\(^{-1}\), which corresponded to the D-band and G-band, respectively. The D-band could be labeled as the amorphous or disordered graphite, while the G-band could be regarded to indicate the presence of graphitic crystallites. The graphic degree of carbons was confirmed by the value of I\(_D\)/I\(_G\). The I\(_D\)/I\(_G\) ratios calculated by the Gaussian function of each sample were 8.3, 7.5, 5.7, 4.9, 4.2, 3.8, and 6.4, and the values were found to decrease gradually with increasing pyrolysis temperature. Kwiecinska\(^4\) demonstrated that the I\(_D\)/I\(_G\) results (3.1–0.0) decreased from greenschist facies to granulite facies graphite, indicating the increase in crystallographic order. Rhim\(^5\) reported an increase in the I\(_D\)/I\(_G\) ratio (0.0–2.6) with the increasing pyrolysis temperature from 300 °C to 650 °C, and the
subsequent decrease in the ratio (2.6–0.0) with the increasing temperature from 650 °C to 2000 °C by using microcrystalline cellulose as the carbonaceous sample. McDonald-Wharry\textsuperscript{46} obtained the I\textsubscript{sp}/I\textsubscript{G} ratio by using graphites and regular fullerenes, and found that an increase in the I\textsubscript{sp}/I\textsubscript{G} ratio (0.55–1.20) indicated a conversion of amorphous carbon to graphene-like domains. These variations in the I\textsubscript{sp}/I\textsubscript{G} ratios were mainly owing to the properties and carbon purity of the selected carbonaceous material. In fact, in the present study, trace oxygen concentration still remained even at high temperatures. These residual oxygen atoms were involved in the cross-linking of the carbon microstructure, yielding a non-graphitizing hard carbon\textsuperscript{35}. However, the Raman spectra displayed characteristics that can be attributed to the carbonaceous materials with the least amount of structure order. In general, the growth and organization of aromatic clusters as well as carbon microstructure in the biochar samples became ordered and condensed at higher pyrolysis temperature.

Discussion

Analysis of the acid-extractable and water-extractable fractions of the sludge biochar was conducted to evaluate the sludge biochar characteristics as well as visualize the microstructure of the solid form to describe the development on the surface of the sludge biochar. The pyrolysis process induced a significant change in the sludge-derived biochar carbon microstructure, and influenced the changes in the apparent characteristics of the biochar samples. As the sludge biochar samples exhibited widely varying properties, the present findings could help to select suitable biochar for different applications. The observed diversity of the biochar properties necessitates careful definition of the purpose of the agricultural applications of the biochar, such as pH amelioration, nutrient retention, or sequestration of soil organic matter, before selecting appropriate biochar. The multiple properties were classified and the purposes were summarized at Fig. 2.

(1) Some molecular arrangements and functional groups presented during the pyrolysis process were mainly composed of carboxyl groups, lactones, and phenols, all of which enhanced the capacity of the biochar to chemisorb nutrients, minerals, and DOM, in association with the surface oxidation capacity of the biochar\textsuperscript{28–30}. The biochars obtained at higher temperatures, which developed a significant surface area, may improve the retention of nonpolar pollutants in soils or decrease the bioavailability of heavy metals to alleviate plant damage. The soils benefit more from biochars with high surface area, which are more efficient in increasing the water-holding capacity\textsuperscript{31} and reducing denitrification. Furthermore, owing to their high aromatization and recalcitrance, biochars could be stored in the field environment and could be helpful in effectuating C sequestration in soil.

(2) The concentration of water-extractable nitrogen, phosphorus, and potassium, particularly in its available form for plant uptake, was found to decrease with the temperature. Considering the biochars’ yield, the results regarding the available form of nutrient elements and trace metals, as well as the presence of fulvic- and humic-acid-like compounds, lower temperature (300–500 °C) could be deduced as suitable for biochar production. The mineral contents of biochar could play an important role in agronomic response even on a fertile soil. Hence, attention is needed when biochar, with very low nutrient content, is applied to agricultural soils, and supplementation with fertilizers may be required for adequate plant nutrition.

Methods

Preparation of sludge biochar. Dewatered sewage sludge was collected from a local municipal wastewater treatment plant in Shanghai, China. The plant treats 75,000 m\textsuperscript{3} of wastewater (93% domestic and 7% industrial sewage) by using an anoxia–anaerobic–aerobic process. The sludge was dewatered by centrifugation with the addition of 2–5 wt% polyacrylamide as the flocculating agent. The dewatered sludge was incubated at 105 °C in an oven to remove the residual water prior to pyrolysis. The primary properties of the as-received dried sludge are listed in Table 1.

Methods

Proximate analysis. The yield of biochar was determined as the ratio of the weight of the produced biochar to the dry weight of the sewage sludge subjected to pyrolysis. The heating values were estimated using an oxygen bomb calorimeter (XRY-1A, Shanghai, China). The ash content was determined by dry combustion in a muffle furnace at 550 ± 10 °C, and the volatile matter content was determined at 900 ± 10 °C under air-free conditions. The fixed carbon (FC) content was estimated as follows: FC (%) = 100% – ash (%) – volatile matter (%).

The pH, EC, concentrations of available nutrients and heavy metals in the water-extracted fraction. Water leaching tests were performed by shaking the samples with deionized water (1:10, w/v) at 200 rpm for 4 h in a horizontal shaker kept at room temperature. Thereafter, the pH of the supernatant was determined by using a pH electrode (pHS-2F, Shanghai, China), and the EC was ascertained by using an EC meter (DDS-307A, Shanghai, China). The filtrate of each biochar sample was passed through a 0.45 μm polytetrafluoroethylene filter and the aqueous extracted fraction was analyzed. A total organic carbon analyzer (TOC-VCPH, Shimadzu, Japan) was used to measure the dissolved organic carbon (DOC) and dissolved nitrogen (DN). The ammonium nitrogen (NH\textsubscript{4}\textsuperscript{+}–N) concentration was determined using a Kylytec 8400 analyzer (Foss, Sweden). The dissolved phosphorous content was determined according to molybdate-antimony-scandium spectrophotometry method at the wavelength of 650 nm (UV-1800 spectrophotometer, Shimadzu, Japan). The concentrations of K\textsuperscript{+} and Na\textsuperscript{+} were measured by employing an atomic absorption spectrometer (AAnalyst 400, Perkin Elmer, USA). The Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, and heavy metal contents were analyzed using inductive coupled plasma atomic emission spectroscopy analysis (Agilent 7250ES, Varian, USA) in scan mode. A detailed account of the EEM analysis has been presented elsewhere\textsuperscript{38,39}.

Total concentration of nutrient elements and heavy metals. The dried and ground samples were subjected to acid digestion according to USEPA3050B using HF, HClO\textsubscript{4}, HNO\textsubscript{3} and peroxide. The concentration of total phosphorus (TP) was determined using the molybdate-antimony-scandium spectrophotometry method at the wavelength of 650 nm (UV-1800 spectrophotometer, Shimadzu, Japan). The total concentration of K\textsuperscript{+} and Na\textsuperscript{+} were measured by employing an atomic absorption spectrometer (AAnalyst 400, Perkin Elmer, USA), while the other nutrient elements

### Table 5 | XPS Integrated areas (%) of N regions corresponding to their binding energies for raw sludge and sludge biochar samples

| Binding type | Binding energy (eV) | Sludge | 300 | 400 | 500 | 600 | 700 | 800 | 900 |
|-------------|--------------------|--------|-----|-----|-----|-----|-----|-----|-----|
| N-6         | 398.7              | 11.1   | 34.8| 59.0| 57.1| 53.6| 54.9| 44.4| 40.4|
| N-5         | 400.4              | 61.1   | 65.2| 39.8| 36.8| 38.8| 35.7| 43.3| 38.3|
| N-Q         | 401.1              | 27.8   | 0   | 1.2 | 6.1 | 7.6 | 9.4 | 12.3| 21.3|
and metal contents were analyzed using inductive coupled plasma atomic emission spectroscopy (Agilent 720ES, USA). All of the analyses were carried out in triplicate.

**Porosity development.** The biochar surface area was determined using a surface area analyzer (ASAP2020, Micromeritics, USA) based on the nitrogen adsorption principle, and was calculated by employing the Brunauer–Emmet–Teller (BET) equation. SEM (S-3400N, Hitachi, Japan) was used to examine the phase development and microstructure on the surface of the sludge biochar particles. The SEM was operated at 15 kV acceleration voltages, and the samples were gilded with Au and stored in a vacuum desiccator until further analysis.

**Functional groups, microcrystal structure, and chemical structure.** The contents of elemental carbon, hydrogen, nitrogen, and sulfur in the sludge biochar were determined using the element analyzer (Vario EL III, Germany), and the oxygen content was calculated by difference. The X-ray fluorescence (XRF) spectroscopy (S4 Explorer, Bruker-Axs Co., Germany) was used for the quantification of the inorganic constituents of the sludge biochar.

The FT-IR technique was used for qualitative estimation of the functional groups on the surface of the sludge biochar. FT-IR spectroscopy (Nicolet 5700, USA) was performed using the potassium bromide (KBr) pellet method. The spectra for all of the samples were obtained by subtracting the value obtained from the blank sample.

The XRD patterns were recorded using an X-ray diffractometer (Bruker D8 Advance Series 2, Bruker Co., Germany) to monitor the mineral composition and degree of crystallinity on the surface of the sludge and its biochar. A quartz standard slide was run to check for instrument wander and obtain an accurate location of 2θ peaks.

The Raman technique was used to further analyze the graphite-like microstructure evolution of the carbon materials. Raman spectroscopy analysis was conducted using a visible Raman system (LabRam-1B, JY Co., France) with a 15 mW, 632.8 nm He-Ne laser.

The XPS experiments were carried out on an RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg Kα radiation (hv = 1253.6 eV) or Al Kα radiation (hv = 1486.6 eV) to describe the evolution of the nitrogen forms. Any binding energy correction for the biochar samples was made by assigning a binding energy of 284.6 eV to the principal C1s component, and the fitting procedure was based on the FWHM of 1.8 eV.

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Author contributions
J.N.Z. and F.L. designed the experiments, D.Z.C. prepared the experimental materials, J.N.Z. and F.L. performed the experiments and wrote the paper with the help of F.L., H.Z., L.M.S. and P.J.H. All authors reviewed the manuscript.

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