Supporting Information

Augmenting manure solid as scaffolding for phosphorus release/retention via *in-situ* iron-phosphate complexes procured with Fe-biochar + $FeCl_3$ treatment

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Including 17 pages; material method section, and 11 figures

Chemicals used in this study

Analytical grades of chemicals and reagents used in this study were purchased either from Fisher Scientific (Pittsburgh, PA) or Sigma-Aldrich (St. Louis, MO). Several chemicals, such as hydrochloric acid, ascorbic acid, ferric chloride hexahydrate, potassium antimony tartrate, ammonium molybdate, ammonium nitrate, sodium citrate dihydrate, sodium nitroprusside, trisodium citrate, sodium bicarbonate, sodium dithionite, and sodium tribasic P^{-}, were used in this study. The study employed 18.2 MΩ Milli-Q water for all the experiments conducted here.

Conductometric curve

The manure solids derived after freeze-drying and solid-liquid separation were evaluated for conductometric curve analysis. Briefly, 0.1 g of manure solids (FDSM, MSWF, MSCB, and MSIB) were added with 10 mL of deionized water, followed by the addition of 0 to 30 mL 0.15 M sodium chloride (NaCl). The resulting solution mixture was shaken for 24 h afterward; filtration was done using 0.45 μm membrane filter paper. The manure solids collected on the filter paper were dried and stored at 4 ºC until further characterization. The liquids were stored in 50 mL vials, and the solution pH was recorded for each sample using a pH meter (AB15 Plus, Fisher Scientific). Further, zeta potential and conductivity were documented using a Malvern MANO-593-10 Zetasizer (Malvern Instruments Ltd., Malvern, Worcestershire, UK) at 25 ºC for each liquid sample. The ionic strength of individual samples was calculated using the following equation,

$$I = 1.6 \times 10^{-5} \times C \qquad \text{Eq.……(i)}$$

where I and C are the ionic strength (mol L^{-1}) and conductivity (µS cm^{-1}) at 25 ºC, and 1.6×10^{-5} is an empirical conversion factor for conductivity to ionic strength.

pH metric curve

The pH metric titration curve for different manure solids was conducted to compare acidic properties and determine exchange acidity and metal-ion binding properties. Four manure solids (FDSM, MSWF, MSCB, and MSIB) of 0.1 g each were taken individually and added to 10 mL of 0.05 M NaCl solution. The NaCl solution maintains the stability of the manure solid suspension and increases the ionic strength. Further, 0 to 5 mL 0.1 M HCl/ 0.1 M KOH was added to each vial, and the solution mixture was shaken for 24 h to reach the targeted pH values 2 to 12. The solution was filtered using 0.45 μm membrane filter paper. The manure solids collected on the filter papers were dried overnight at 105 ºC and stored at 4 ºC until further characterization. The liquids were stored in 50 mL vials, and the solution pH was recorded for each sample using a pH meter (AB15 Plus, Fisher Scientific). Zeta potential and conductivity were documented for each liquid sample using a Malvern MANO-593-10 Zetasizer (Malvern Instruments Ltd., Malvern, Worcestershire, UK) at 25 ºC. As mentioned above, the ionic strength of individual samples was determined using Eq. 1.

Mehlich-III extraction

The Mehlich-III (henceforth denoted as 'M-III') solution is commonly employed for P extraction [5]. The M-III extracting solution was used to break the cation and ligand bridging in the manure solids derived after different treatments. The 0.1 g manure solids (FDSM, MSWF, MSCB, and MSIB) were taken individually and added to 10 mL of 0.05 M NaCl solution. The NaCl solution maintains the stability of the manure solid suspension and increases the ionic strength. Further, 0 to 12 mL M-III solution was added to each vial, and the solution mixture was shaken for 24 h. The solution was filtered using 0.45 μm membrane filter paper. The manure solids collected on the filter papers were dried overnight at 105 ºC and stored at 4 ºC until further characterization.

The liquids were stored in 50 mL vials, and the solution pH was recorded for each sample using a pH meter (AB15 Plus, Fisher Scientific). Zeta potential and conductivity were documented for each liquid sample using a Malvern MANO-593-10 Zetasizer (Malvern Instruments Ltd., Malvern, Worcestershire, UK) at 25 ºC. As mentioned above, the ionic strength of individual samples was determined using Eq. 1.

Another M-III extraction was also done without any dispersing medium, where 0.1 g of manure solids (FDSM, MSWF, MSCB, and MSIB) were taken individually and added to 20 mL of M-III solution. The solution mixture was shaken for 24 h. The solution was filtered using 0.45 μm membrane filter paper. With manure liquid, manure solids collected on the filter papers were dried overnight at 105 ºC and stored at 4 ºC until further analysis.

Olsen extraction

Olsen extracting solution (0.5 M $NaHCO_3$) has been used for calcareous, alkaline, or neutral soils containing Ca-P^- to extract P^-. This extracting solution decreases the Ca concentration in the solution by causing precipitation of Ca as $CaCO_3$, which promotes P concentration in the solution [6,7]. Different manure solids and freeze-dried swine manure were employed for P extraction using an extracting solution at a nearly constant pH of 8.5 using 5 M NaOH. In short, 0.1 g of freeze-dried swine manure/manure solids (FDSM, MSWF, MSCB, and MSIB) were taken into 50 mL centrifuged tubes, and 20 mL of previously prepared Olsen extracting solution was added. The resulting solution was shaken for 24 h using a reciprocal shaker [8]. The solution was filtered using 0.45 μm membrane filter paper, and the resulting solution was stored at 4 ºC until inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis was done, considering USEPA method 200.7 [9].

Citrate-bicarbonate-dithionite (CBD) extraction

In our study, we adopted the measurement of CBD extraction of soils to characterize the organically bound metal oxides associated with P from different manure solids/ freeze-dried manure [10]. Briefly, 0.1 g of FDSM, MSWF, MSCB, and MSIB were weighed into 50 mL centrifuge tubes. Then, 40 mL of 0.3 M trisodium citrate ($Na_3C_6H_5O_7$) and 5 mL of 1 M sodium bicarbonate ($NaHCO_3$) solution were added. The $Na_3C_6H_5O_7$ acts as a metal ion complexing agent, and $NaHCO_3$ acts as a buffer to maintain the solution pH (7.3). This solution pH prevents the hydrolysis of organic matter, its protonation, and adsorption to the sediment particles. The temperature was brought to 60 ºC in a water bath, and 1 g sodium dithionite ($Na_2S_2O_4$) was added to each vial separately. The mixture was stirred constantly for an initial 5 minutes and left overnight. The following day, the mixture was filtered using 0.45 μm membrane filter paper, and the resulting solution was stored at 4 ºC until inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis was done considering USEPA method 200.7 [9].

Fourier-transformed infrared spectra (FTIR) analysis

Fourier-transform infrared spectra (FTIR) of manure solids (FDSM, MSWF, MSCB, and MSIB) were done using an FTIR spectrophotometer (Nicolet Magma-IR 560 Spectrophotometer). The samples were dried at 105 ºC before the FTIR analysis. Before the dried samples were arranged next to the chamber, a background scan was done to eliminate the effect of any impurities or moisture. To keep a low signal-to-noise ratio for each sample, 64 scans were performed in the infrared region between 4000 and 500 cm^{-1}.

X-ray diffraction (XRD) analysis

The primary inorganic mineral phase in the manure solid (MSIB), which was produced due to chemical treatments (before and after Olsen extraction), was assessed by XRD analysis. The XRD spectra were recorded using a scintillation detector, a diffracted-beam monochromator, and a Cu-x ray tube running at 45 kV and 30 mA. With two theta values ranging from 5 to 70 degrees, the samples were scanned with a step size of 0.05 degrees and a dwell time of seven seconds per step. The samples were side-loaded into the holder and crushed with a mortar and pestle before the XRD analysis to reduce the preferred orientation. All the XRD analyses were carried out using the Jade software (Livermore, California, version 9.5). The International Centre for Diffraction Data (ICDD) and the Inorganic Crystal Structure Database (ICSD) were utilized to determine the crystalline phase.

The surface morphology of MSIB, before and after Olsen extraction, was analyzed using a scanning electron microscope (FEI QUANTA FEG 250 SEM) coupled with an energy-dispersive X-ray spectrometer (Oxford Aztec EDS). EDS was performed using a 10 kV beam of about 1 nA.

Raman spectroscopy analysis

The manure solids (FDSM, MSWF, MSCB, and MSIB) used for conductometric curve analysis were further tested using a DXR3 Raman Microscope (Thermo Scientific™, USA). The samples were initially probed with Melles Griot 543 series Ar ion laser operating at 532 nm.

References

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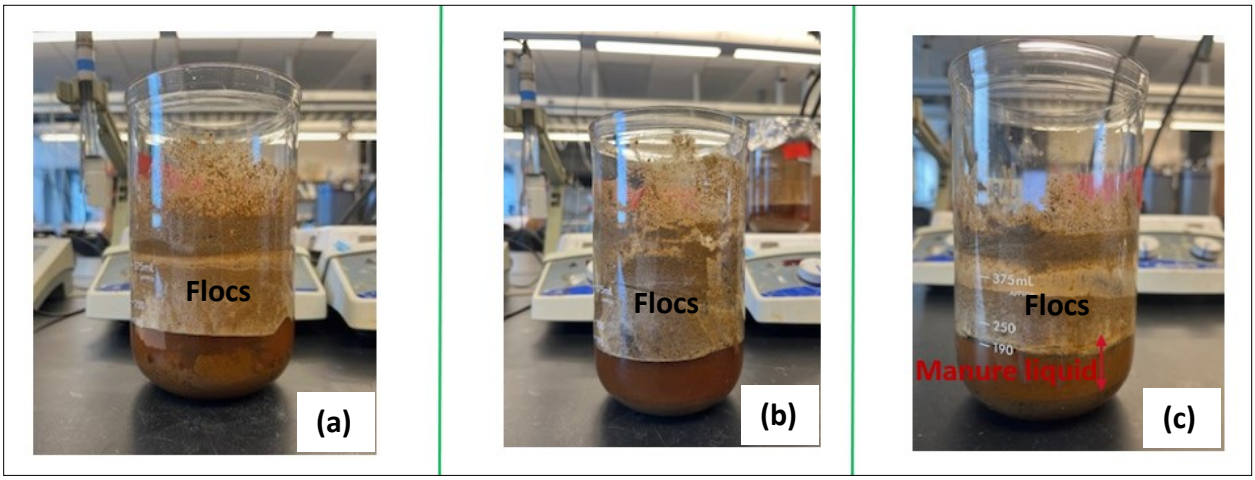


Fig. S1. Influence of different treatments on solid-liquid separation: (a) 0.15 M $FeCl_3$ (without biochar), (b) 0.15 M $FeCl_3$ and CB (c) 0.15 M $FeCl_3$ and IB.

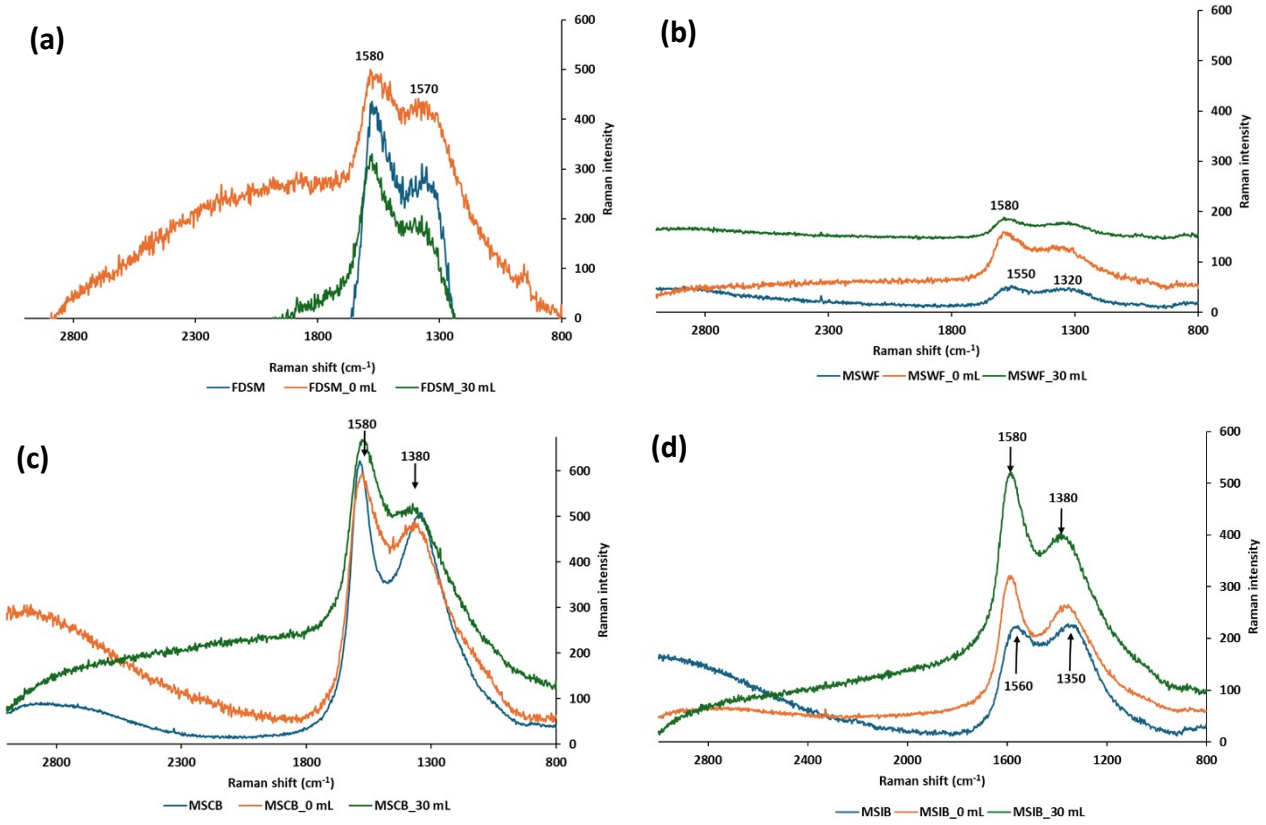


Fig. S2. Raman spectra of manure solids (a) FDSM, (b) MSWF, (c) MSCB, and (d) MSIB, before and after conductometric curve analysis of 0 mL and 30 mL of 0.15M NaCl solution. (FDSM- freeze-dried swine manure, MSWF- manure solid with $FeCl_3$, MSCB- manure solid with control biochar, MSIB- manure solid with iron biochar).

(a)

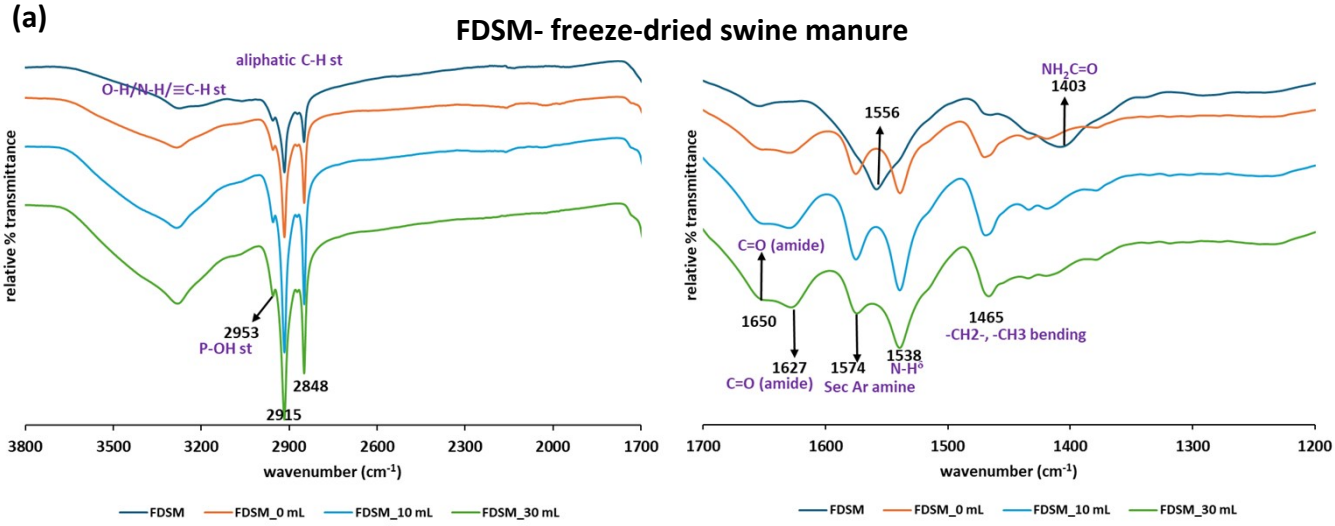
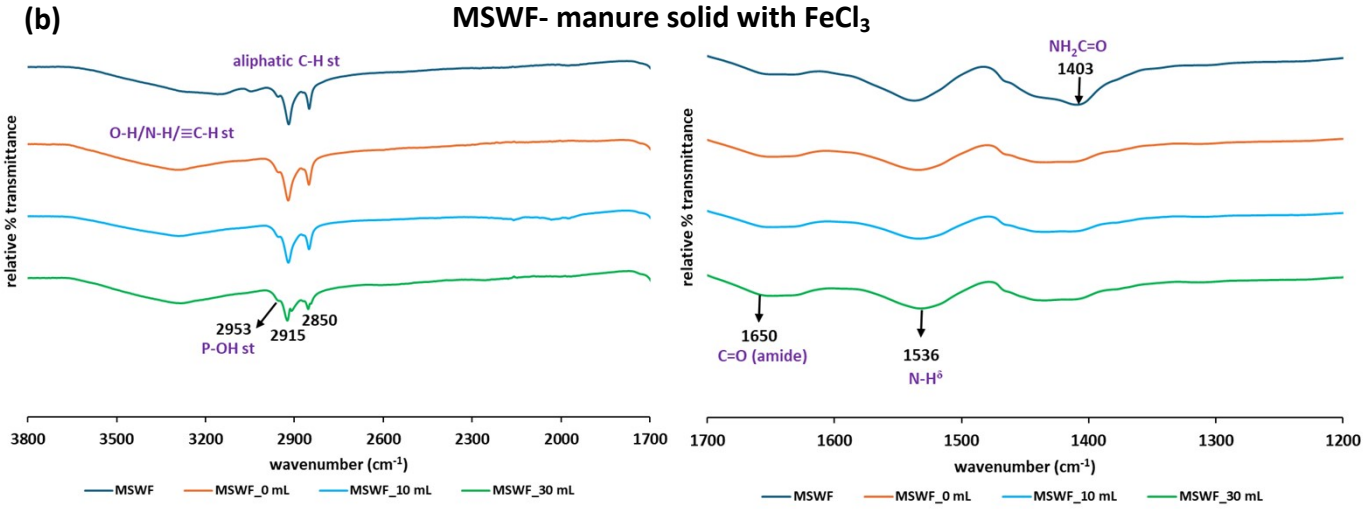
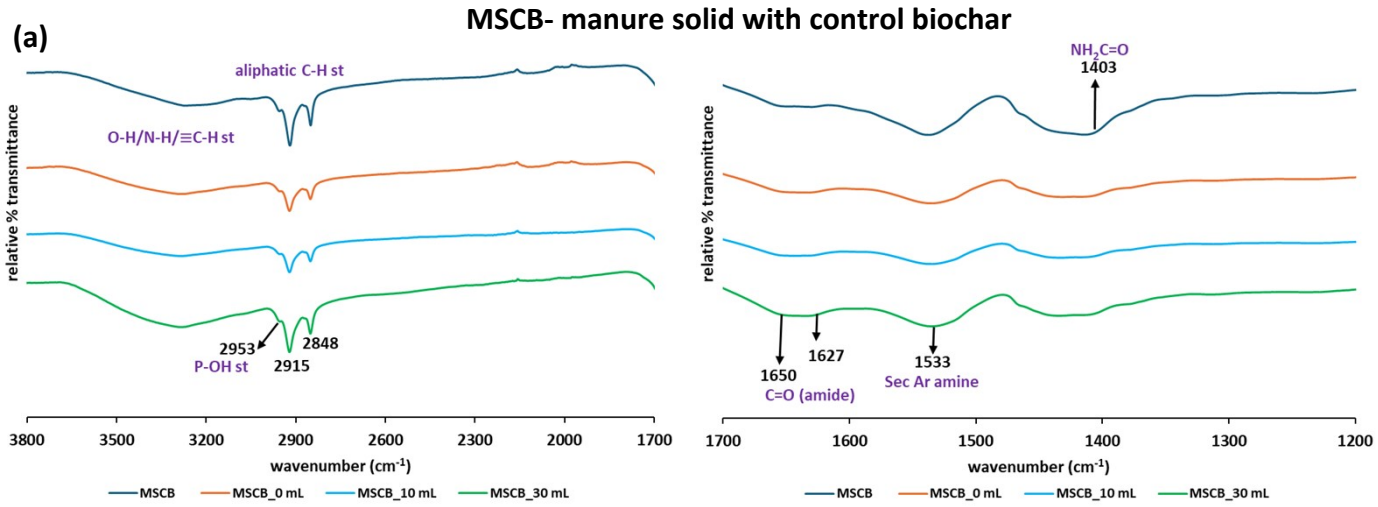

FDSM- freeze-dried swine manure
aliphatic C-H st
O-H/N-H/≡C-H st
relative % transmittance
2953
P-OH st
2848
2915
3800
3500
3200
2900
2600
2300
2000
1700
wavenumber (cm-1)
FDSM
FDSM_0 mL
FDSM_10 mL
FDSM_30 mL
NH2C=O
1403
1556
C=O (amide)
1650
1627
C=O (amide)
1574
Sec Ar amine
1538
N-H
1465
-CH2-, -CH3 bending
1700
1600
1500
1400
1300
1200
wavenumber (cm-1)
FDSM
FDSM_0 mL
FDSM_10 mL
FDSM_30 mL

Fig. S3. Fourier transform infrared spectra of freeze-dried swine manure (FDSM) and manure solid (MSWF) before and after conductometric curve analysis of 0 mL, 10 mL, and 30 mL of 0.15M NaCl solution. (FDSM- freeze-dried swine manure, MSWF- manure solid with $FeCl_3$).




(a)
MSCB- manure solid with control biochar
aliphatic C-H st
O-H/N-H/≡C-H st
relative % transmittance
2953
P-OH st
2915
2848
3800
3500
3200
2900
2600
2300
2000
1700
wavenumber (cm-1)
MSCB
MSCB_0 mL
MSCB_10 mL
MSCB_30 mL
NH2C=O
1403
1650
C=O (amide)
1627
1533
Sec Ar amine
1700
1600
1500
1400
1300
1200

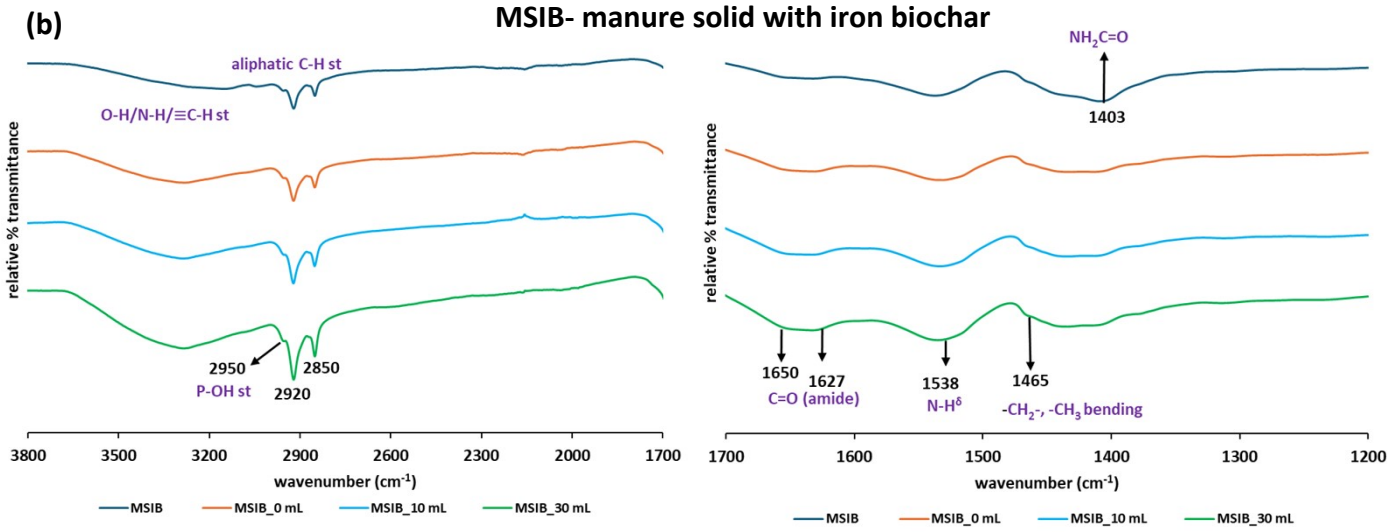
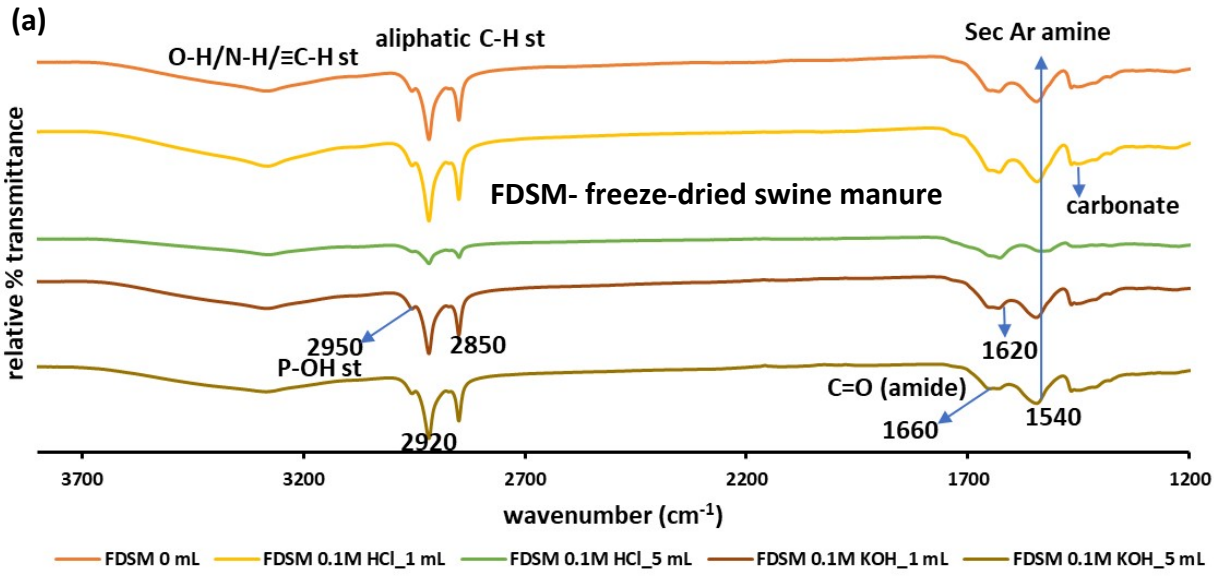

(b)
MSIB- manure solid with iron biochar
aliphatic C-H st
O-H/N-H/≡C-H st
relative % transmittance
2950
P-OH st
2920
2850
3800
3500
3200
2900
2600
2300
2000
1700
wavenumber (cm-1)
MSIB
MSIB_0 mL
MSIB_10 mL
MSIB_30 mL
NH2C=O
1403
1650
C=O (amide)
1627
1538
N-Hδ
1465
-CH2-, -CH3 bending
1700
1600
1500
1400
1300
1200
wavenumber (cm-1)
MSIB
MSIB_0 mL
MSIB_10 mL
MSIB_30 mL

Fig. S4. Fourier transform infrared spectra of manure solids (MSCB and MSIB) before and after conductometric curve analysis of 0 mL, 10 mL, and 30 mL of 0.15M NaCl solution. (MSCB- manure solid with control biochar, MSIB- manure solid with iron biochar).



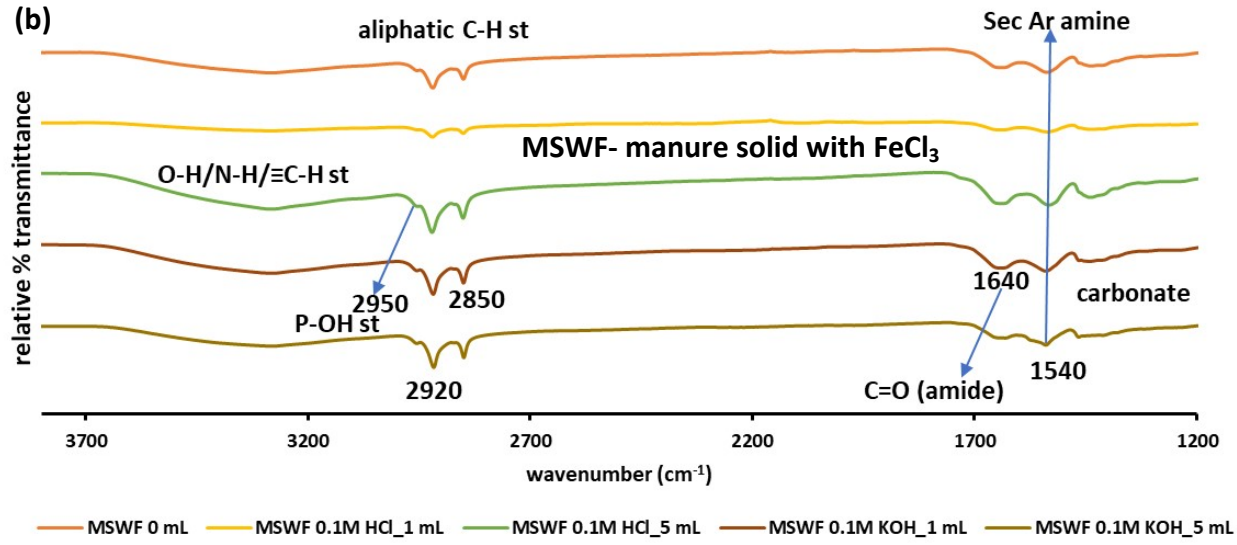


Fig. S5. Fourier transform infrared spectra of freeze-dried swine manure (FDSM) and manure solid (MSWF) after pH metric analysis of 0 mL (without acid or base), 1 mL, and 5 mL of 0.1M HCl and 0.1M KOH solution. (FDSM- freeze-dried swine manure, MSWF- manure solid with $FeCl_3$).

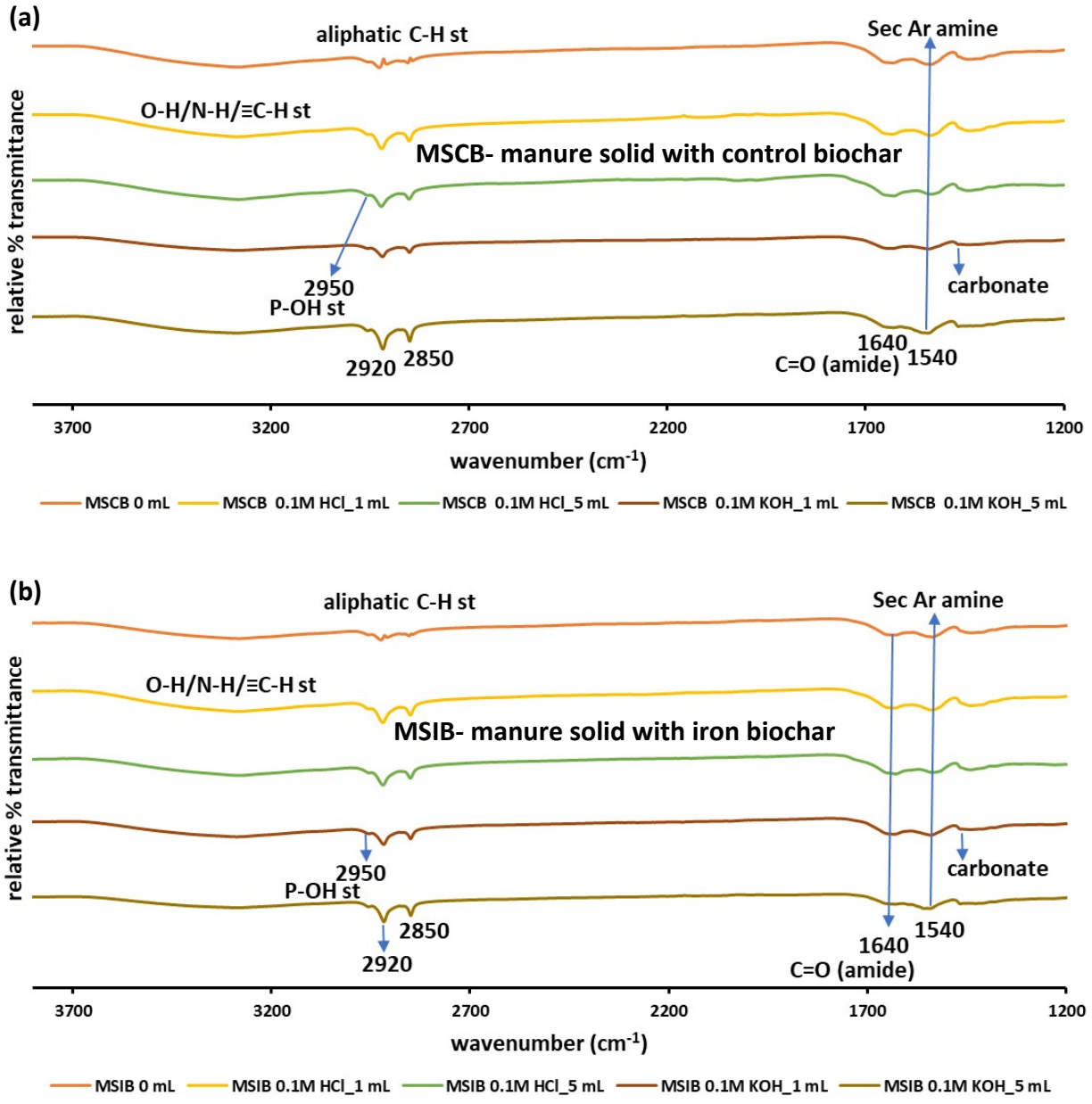
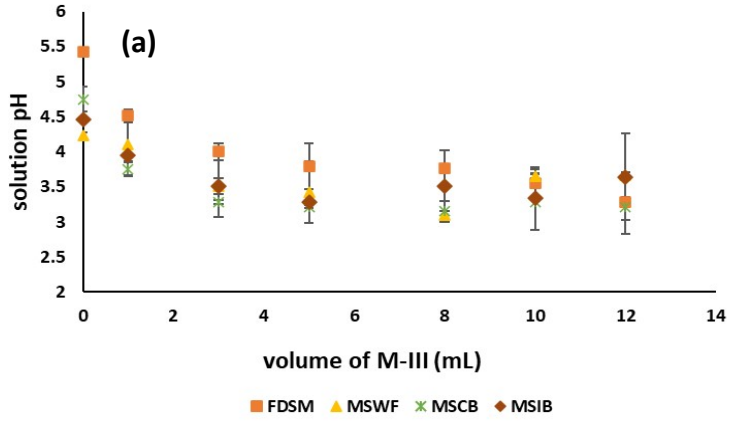
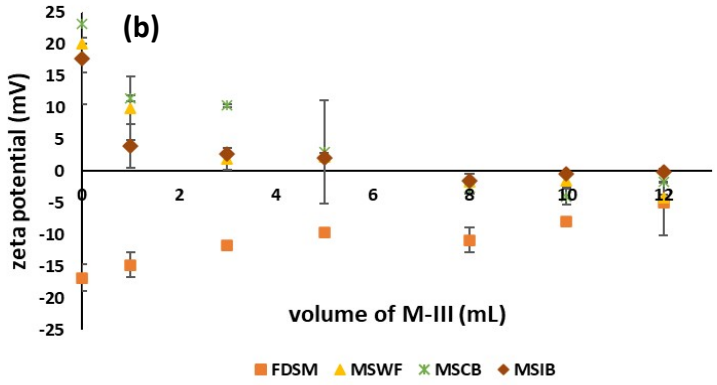


Fig. S6. Fourier transform infrared spectra of manure solids (MSCB and MSIB) after pH metric analysis of 0 mL (without acid or base), 1 mL, and 5 mL of 0.1M HCl and 0.1M KOH solution. (MSCB- manure solid with control biochar, MSIB- manure solid with iron biochar).


(a)
solution pH
volume of M-III (mL)
FDSM
MSWF
MSCB
MSIB


(b)
zeta potential (mV)
volume of M-III (mL)
FDSM
MSWF
MSCB
MSIB

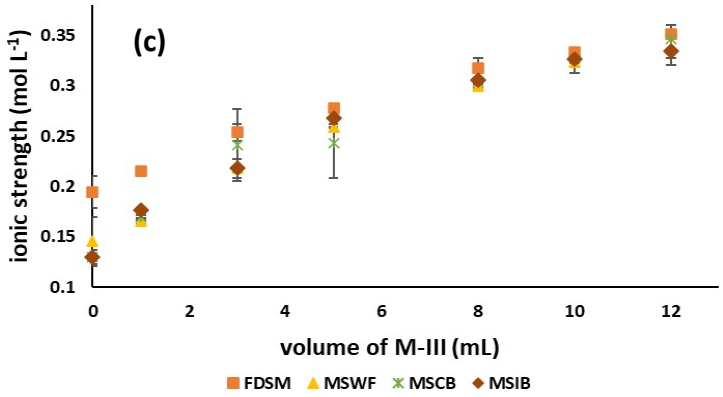

(c)
ionic strength (mol L-1)
volume of M-III (mL)
FDSM
MSWF
MSCB
MSIB

Fig. S7. Mehlich-III (M-III) extraction of different manure solids (a) solution pH, (b) zeta potential, and (c) ionic strength. (FDSM- freeze-dried swine manure, MSWF- manure solid with $FeCl_3$, MSCB- manure solid with control biochar, MSIB- manure solid with iron biochar).

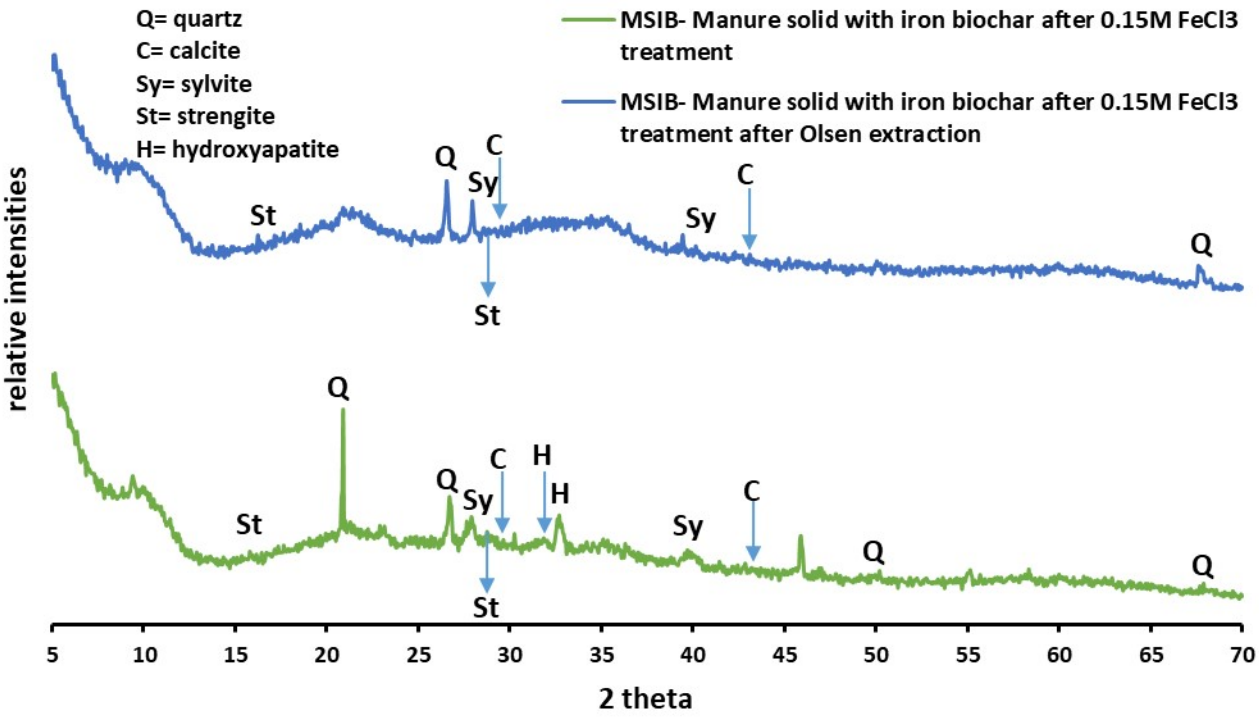
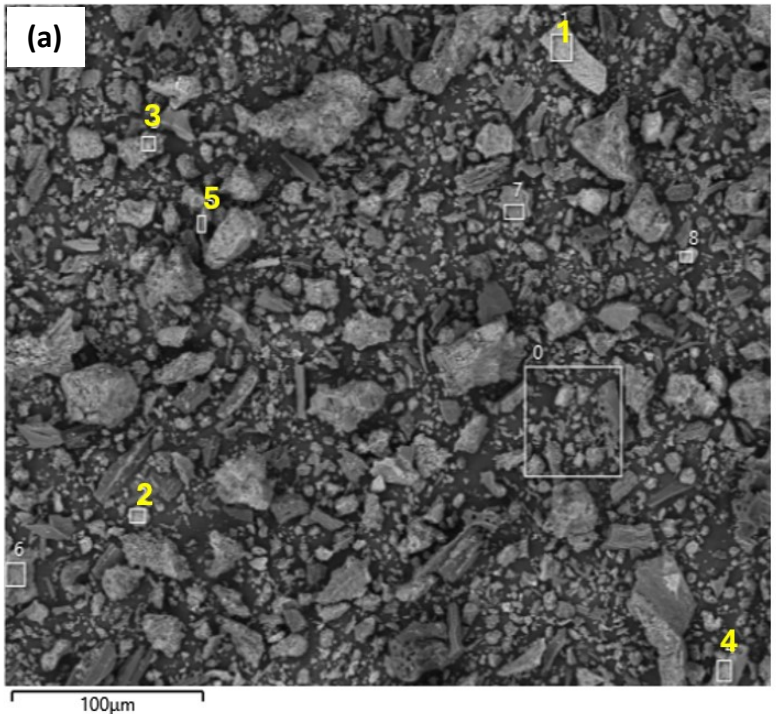
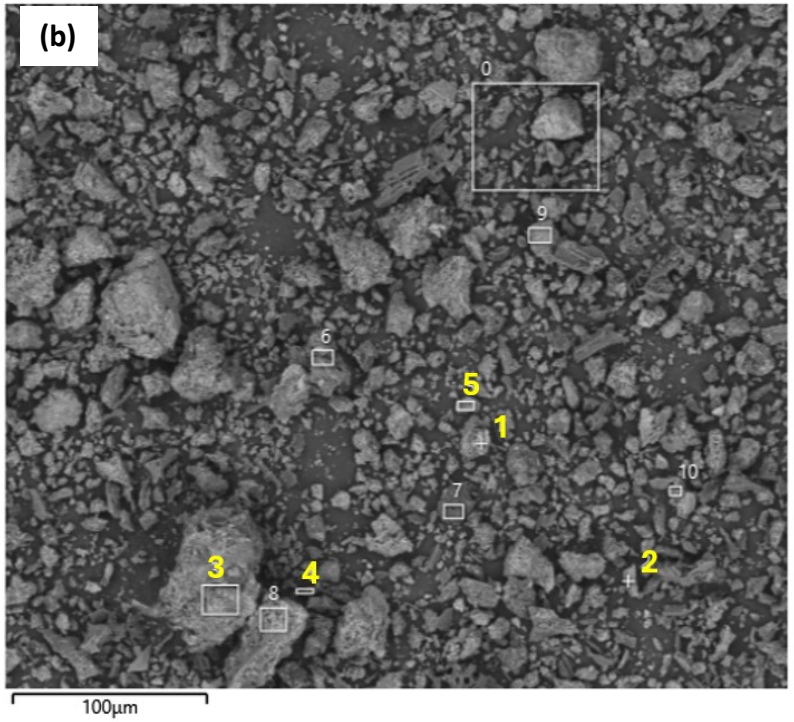


Fig. S8. XRD spectrum of MSIB (a) before and (b) after Olsen extraction. (MSIB- manure solid with iron biochar).





Weight (%)									
Point	**C**	**N**	**O**	**Na**	**Mg**	**P**	**K**	**Ca**	**Fe**
1	21.53	1.78	24.96	0.72	0.15	5.54	1.81	0.24	35.65
2	29.63	1.45	22.38	0.67	0.28	7.33	2.89	0.51	26.21
3	40.82	1.18	11.52	0.14	-	1.22	0.69	0.51	12.14
4	20.06	20.06	3.90	-	-	0.06	1.59	0.18	3.50
5	31.81	6.8	5.49	-	-	0.47	2.61	0.13	3.68

Weight (%)									
Point	**C**	**N**	**O**	**Na**	**Mg**	**P**	**K**	**Ca**	**Fe**
1	20.71	-	30.56	5.47	-	5.32	-	0.46	33.14
2	23.90	-	33.18	8.53	0.38	9.54	0.31	2.45	18.39
3	36.08	1.77	26.27	5.06	-	1.65	-	0.79	26.67
4	28.65	-	35.27	16.52	-	0.27	-	0.28	7.28
5	15.27	-	40.78	1.10	0.21	0.06	0.39	0.21	6.14

Fig. S9. SEM-EDS analysis of MSIB (a) before and (b) after Olsen extraction. (MSIB- manure solid with iron biochar).

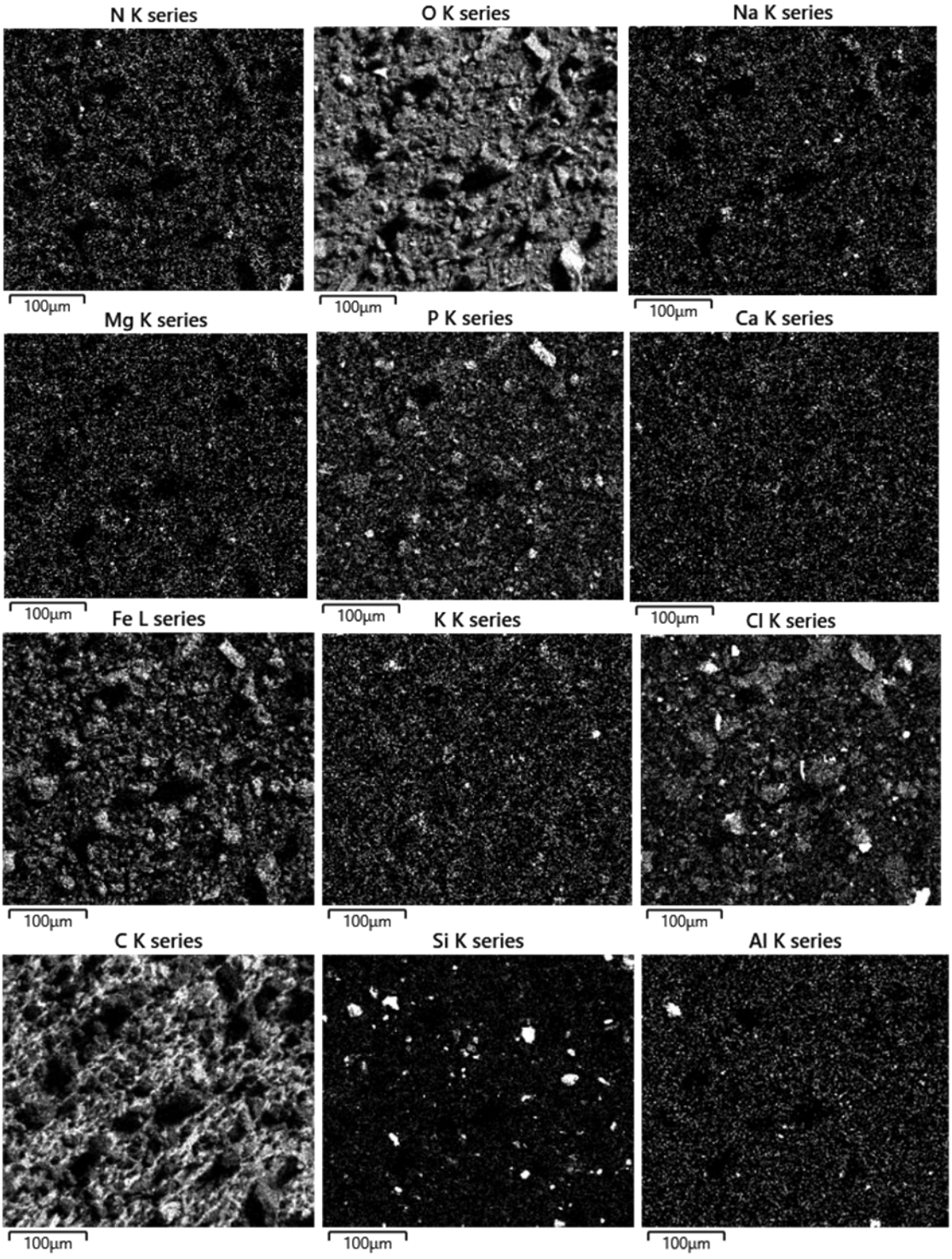


Fig. S10. EDS mapping of MSIB before Olsen extraction. (MSIB- manure solid with iron biochar).

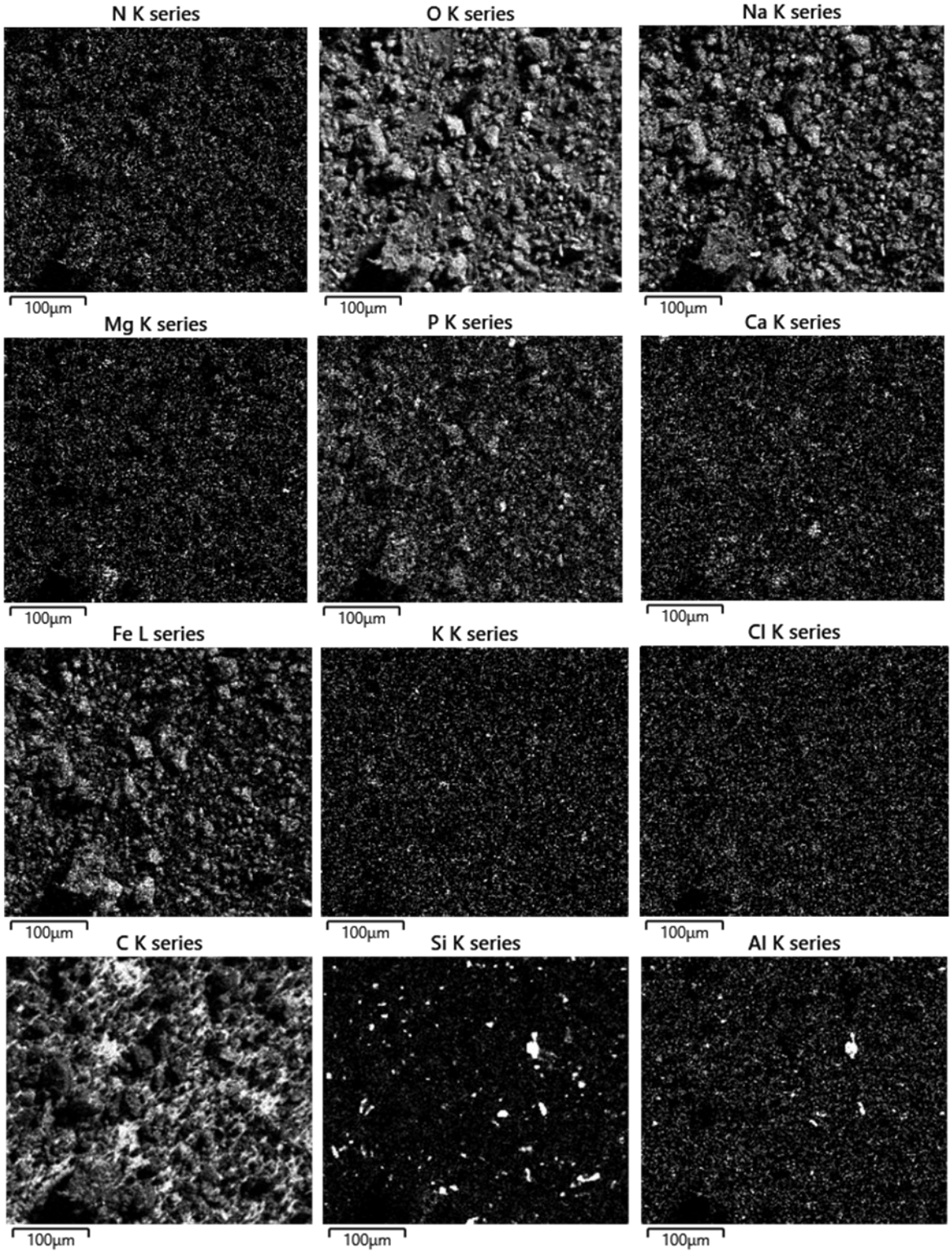


Fig. S11. EDS Mapping of MSIB after Olsen extraction. (MSIB- manure solid with iron biochar).