IOWA STATE UNIVERSITY
Bioeconomy Institute






Phosphate sorption onto modified biochar surface

Biochar & Bioenergy 2019

Santanu Bakshi*, Ryan G. Smith and Robert C. Brown

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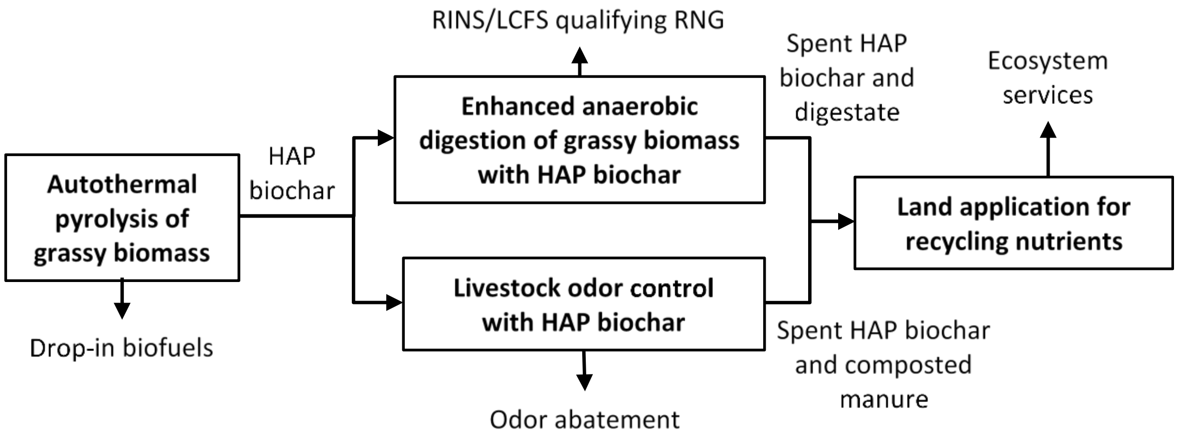
Innovations exploration

- Produce high alkalinity/porosity (HAP) biochar through autothermal pyrolysis of herbaceous feedstocks
- Assess the utility of HAP biochar to improve various performances
  - biogas quality from anaerobic digestion (AD)
  - livestock odor control
  - use of biochar + digestate and biochar + composted manure in land application for recycling nutrients



Hypotheses of this study

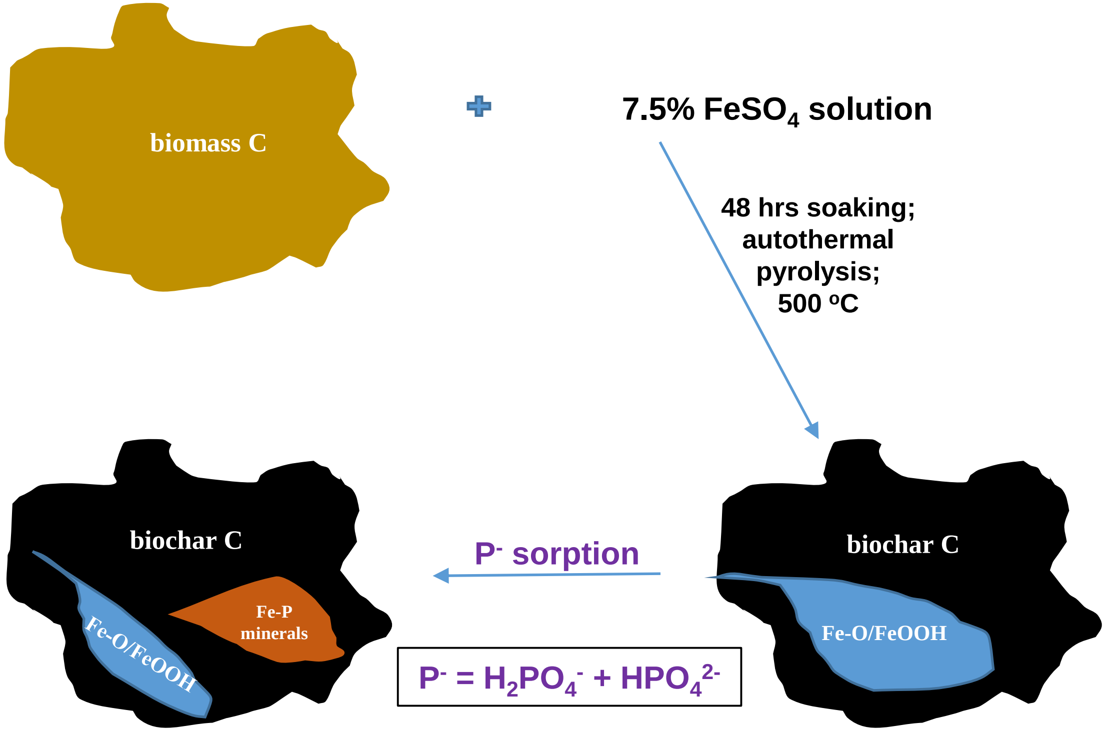
- **Modified biochars can be produced by alterations in biochar physical and chemical properties**

- **Co-composting of modified biochars with animal manures can retain phosphate**

- **Application of phosphate retained biochar can be used as a highly beneficial soil amendment to improve soil health**

Pyrolysis process of Fe-impregnation

Chemical precipitation



pK_a of phosphates

$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$
($pK_a \approx$ 2.12)

$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$
($pK_a \approx$ 7.21)

$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$
($pK_a \approx$ 12.67)

Desired pH > 7.2

Types of biochar and chemical properties

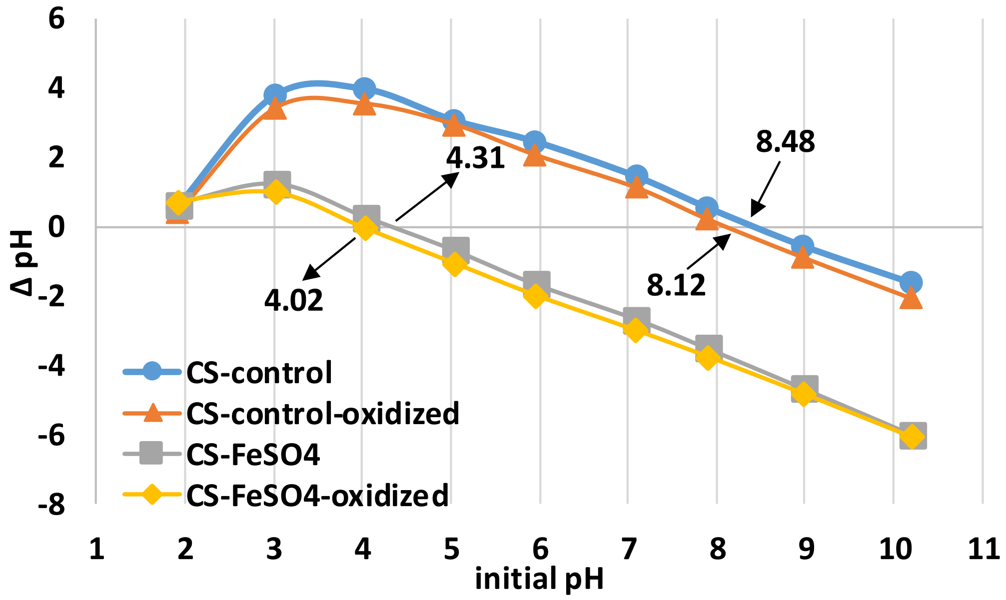
Biochar	Ultimate analysis (%)					Proximate analysis (%)				pH (1:15 solid : water)
	C	N	H	S	H/C (mol/mol)	moisture	VM	FC	ash	
CS-control	54.76	1.02	2.093	0.06	0.274	4.51	23.95	37.15	34.4	9.2 (0.05)
CS-control-oxidized*	48.56	1.26	1.983	0.09	0.245	2.34	26.18	32.58	38.9	8.8 (0.02)
CS-$FeSO_4$	36.42	1.21	1.63	5.03	0.268	2.24	33.98	23.98	39.8	5.4 (0.07)
CS-$FeSO_4$-oxidized	27.85	1.42	0.97	6.017	0.209	1.42	34.91	14.35	49.5	5.1 (0.04)

*Xiao and Pignatello, 2016. Effects of post-pyrolysis air oxidation of biomass chars on adsorption of neutral and ionizable compounds. Environ. Sci. Technol. 50. 6276-6283

Mass lost during PPAO:
CS-control: 11.2%, CS w/$FeSO_4$: 14.8%

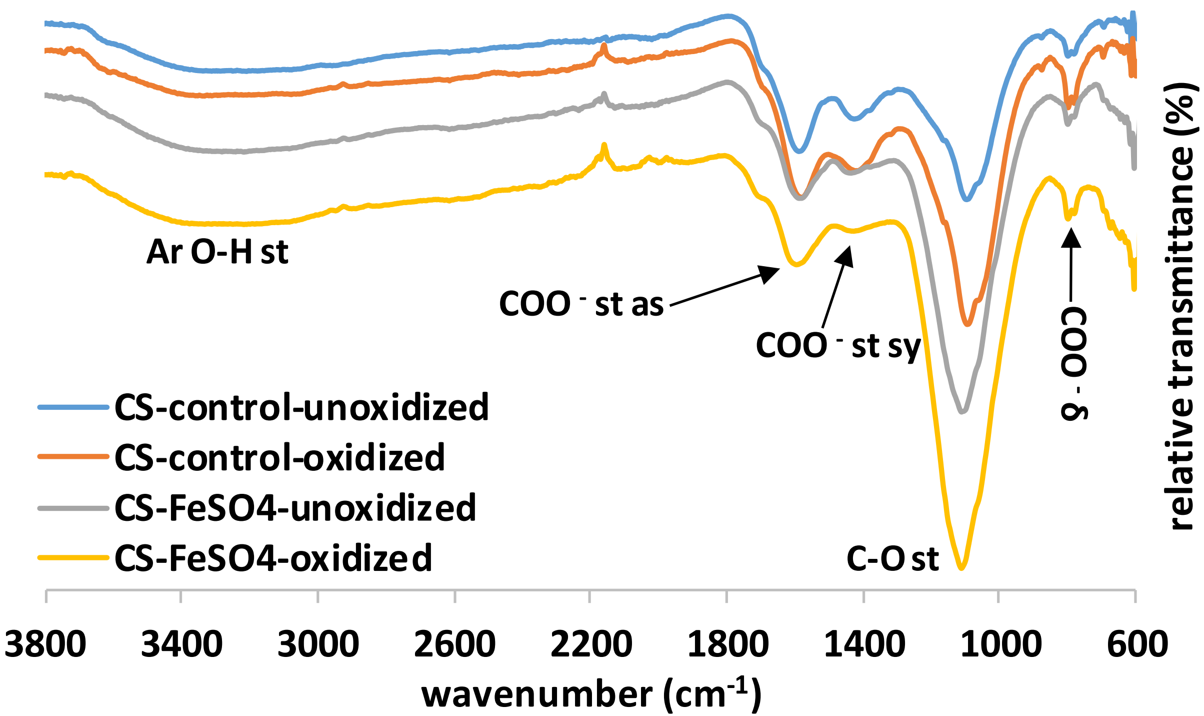
Zero point charge (ZPC)

(0.1 g biochar + 20 mL 0.1 M NaCl; adjusted to pH 2-10 range with HCl or NaOH; shaking for 24 hrs)

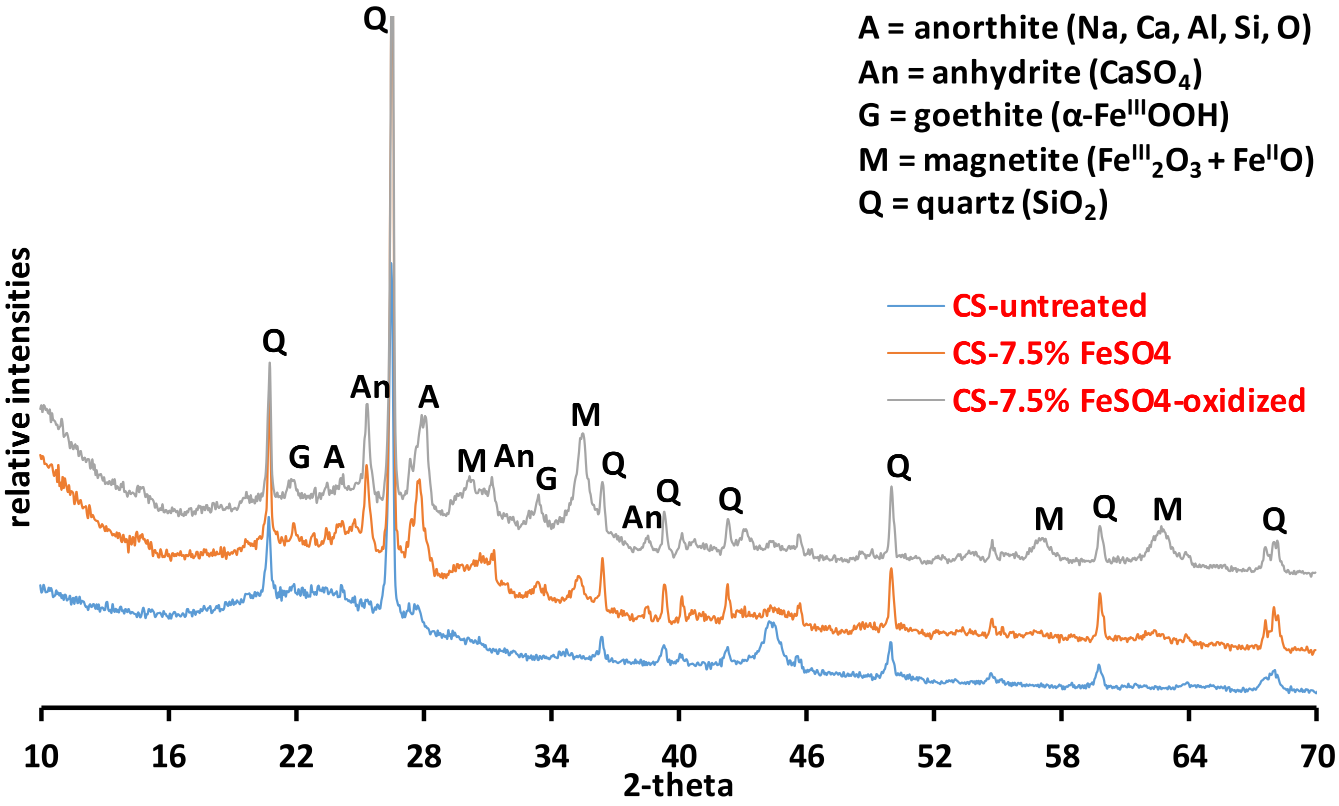


- **Positively charged surface for control biochar @ pH 2-8**
- **Positively charged surface for Fe impregnated biochar @ pH 2-4**

FTIR analysis

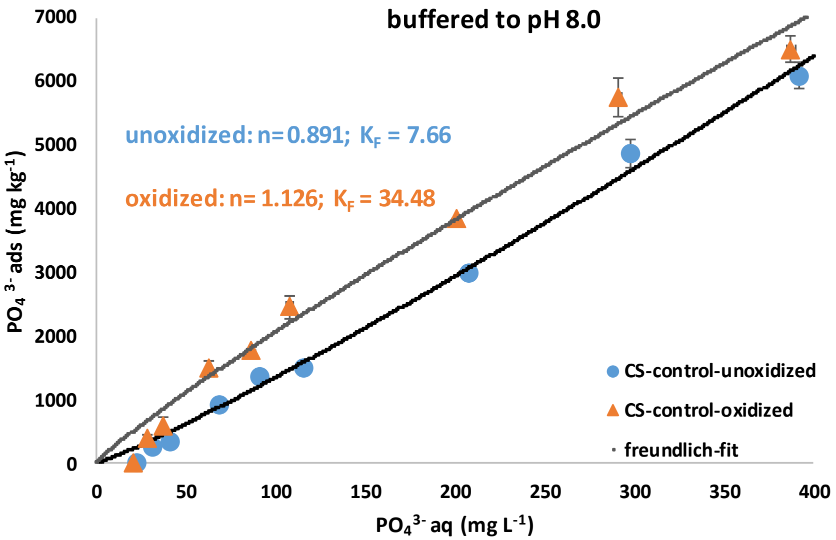


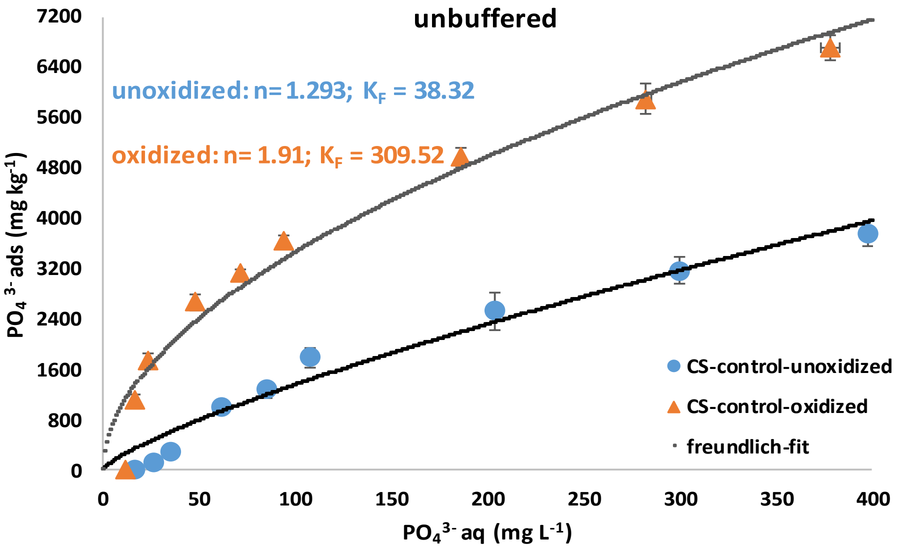
XRD analysis



Sorption isotherm: control biochar

(sorption equilibrium with 0-400 mg L^{-1} of pH 8.0 PO_4^{3-} solution for 48 hrs; solid loading rate 5 g/L)



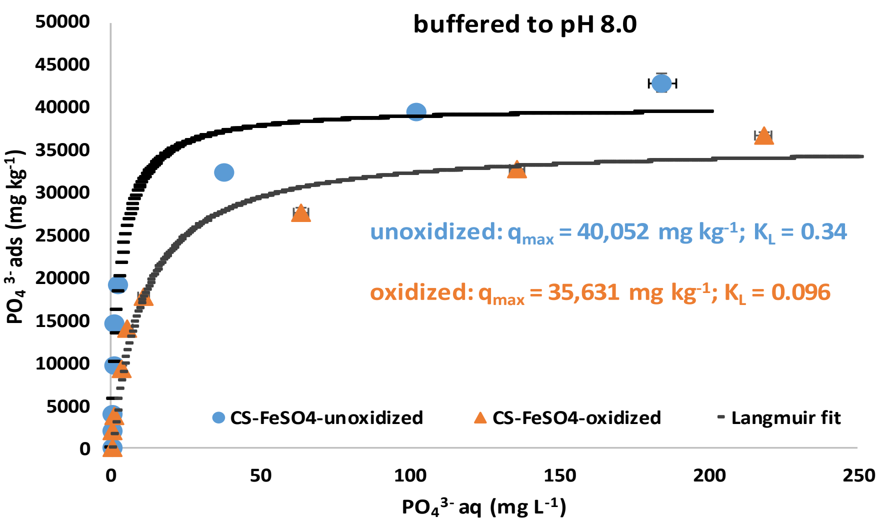


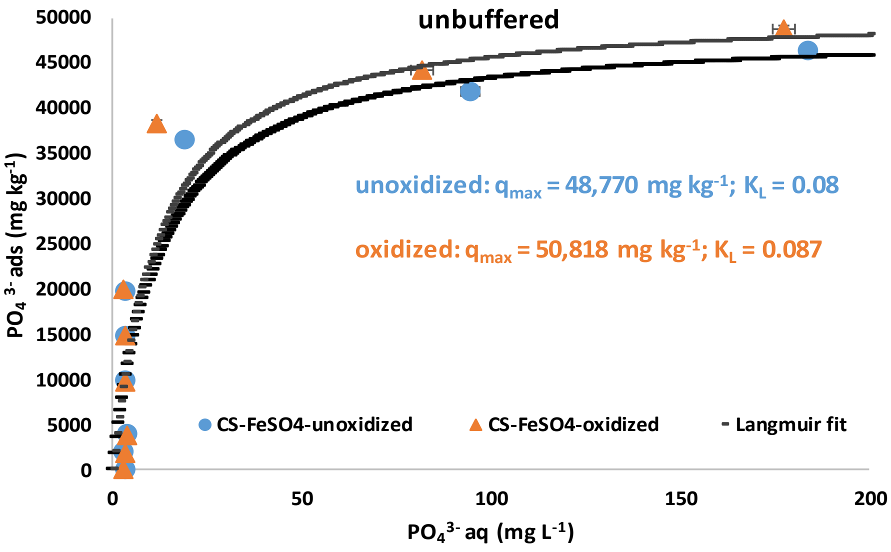
Equilibrium pH
Unoxidized: 7.64-8.33
Oxidized: 7.39-7.98

Equilibrium pH
Unoxidized: 8.2-8.73
Oxidized: 8.1-8.5

Sorption isotherm: $FeSO_4$ PT biochar

(sorption equilibrium with 0-400 mg L^{-1} of pH 8.0 PO_4^{3-} solution for 48 hrs; solid loading rate 5 g/L)



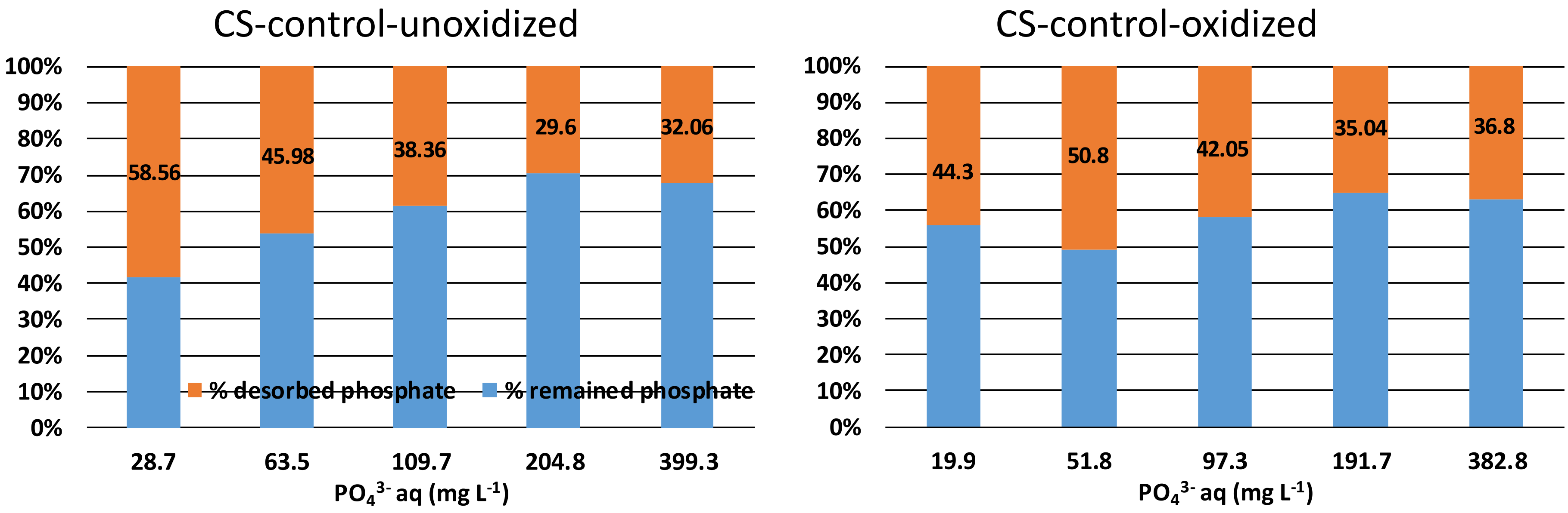


Equilibrium pH
Unoxidized: 7.04-7.62
Oxidized: 6.9-7.56

Equilibrium pH
Unoxidized: 5.28-5.64
Oxidized: 4.93-5.38

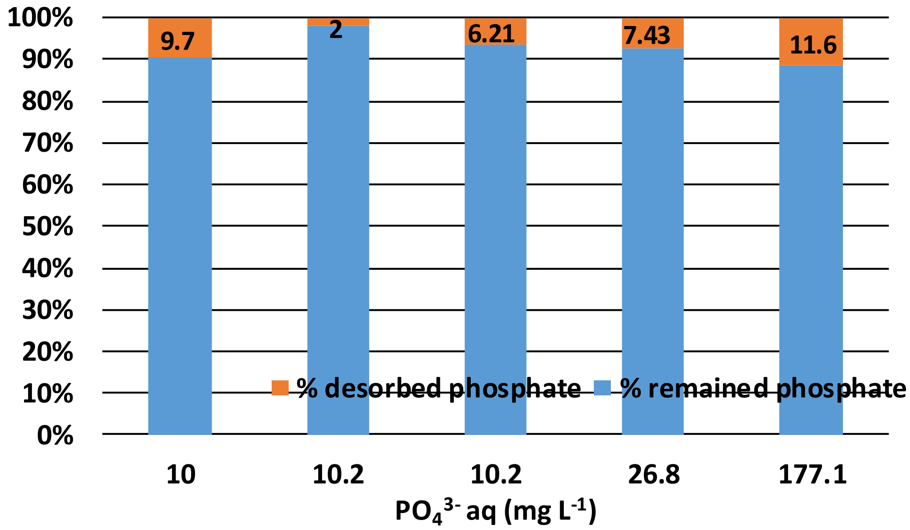
Desorption isotherm: control biochar

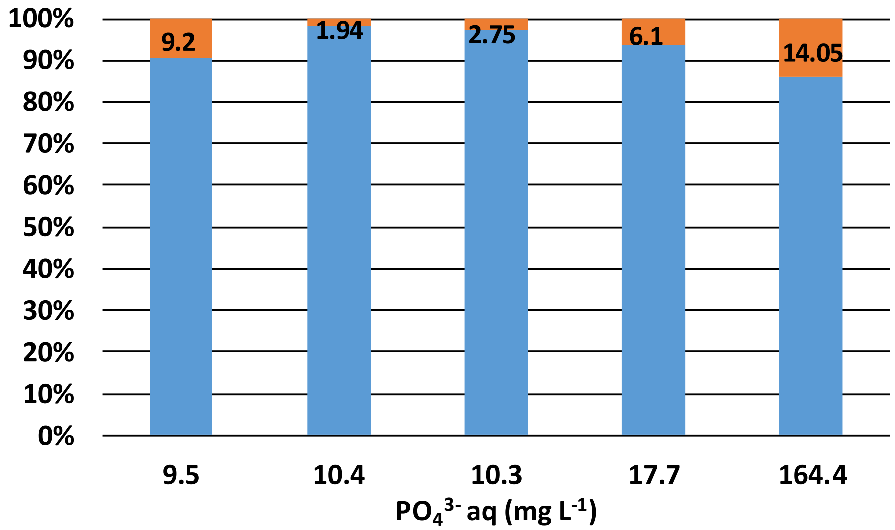
(After sorption, desorption step was done for 48 hrs each with de-ionized water for 3 times; solid loading rate 5 g/L)



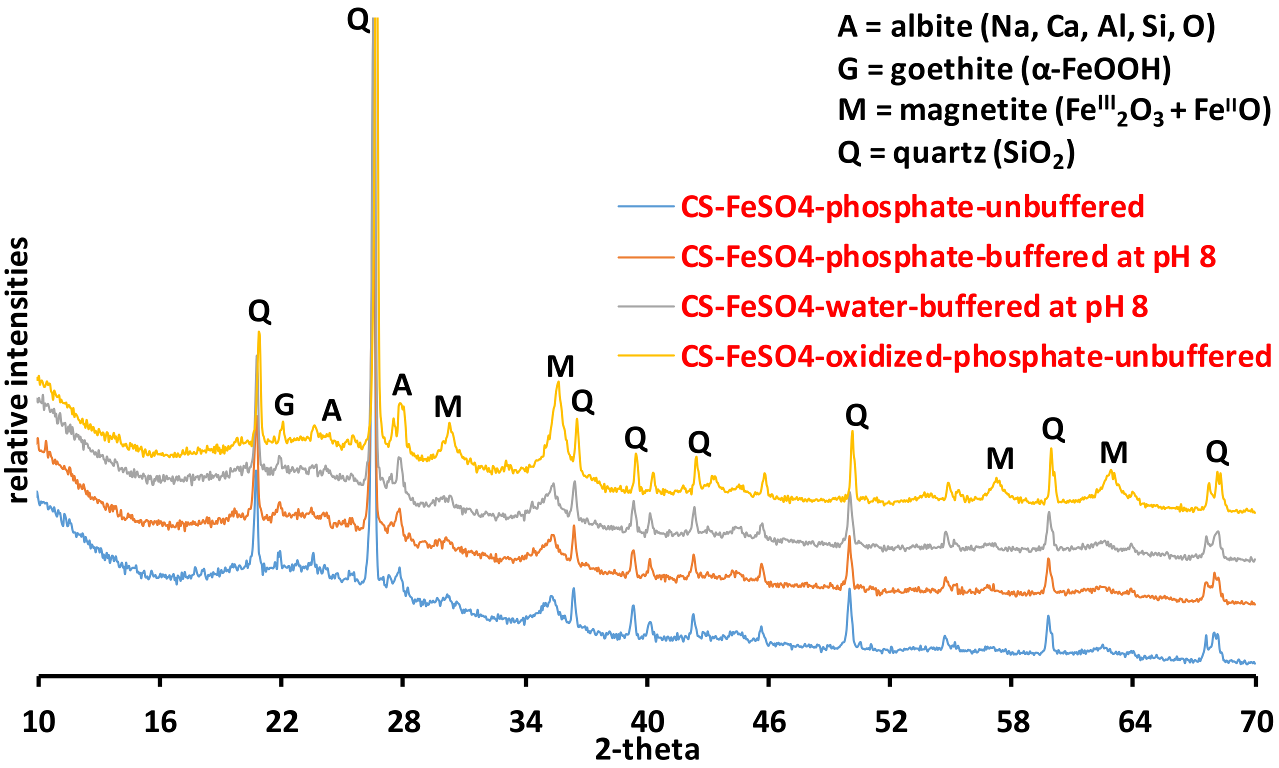
Desorption isotherm: $FeSO_4$ PT biochar

(After sorption, desorption step was done for 48 hrs each with de-ionized water for 3 times; solid loading rate 5 g/L)



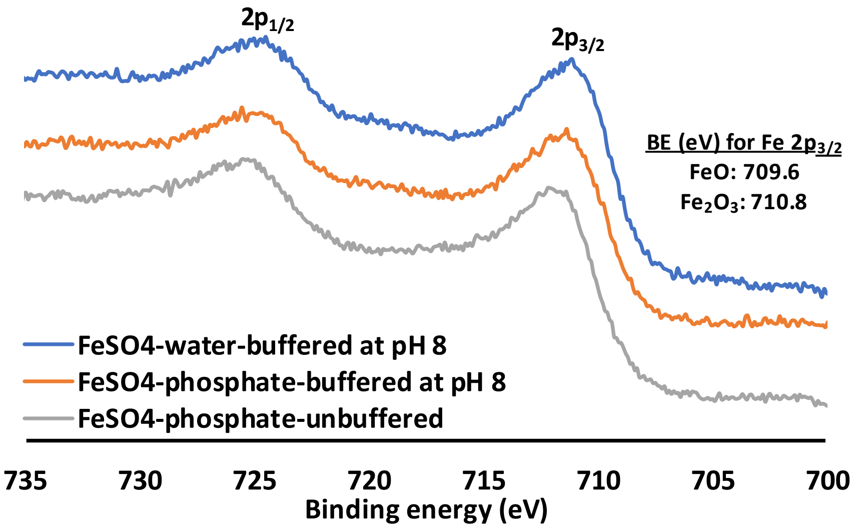


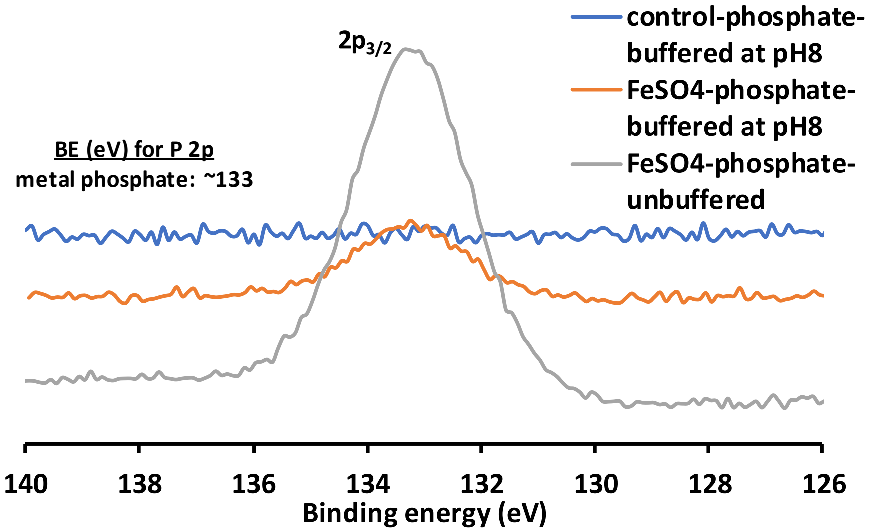
XRD analysis of phosphate sorbed biochar



Unfortunately, no new phosphate mineral of Fe was found by XRD

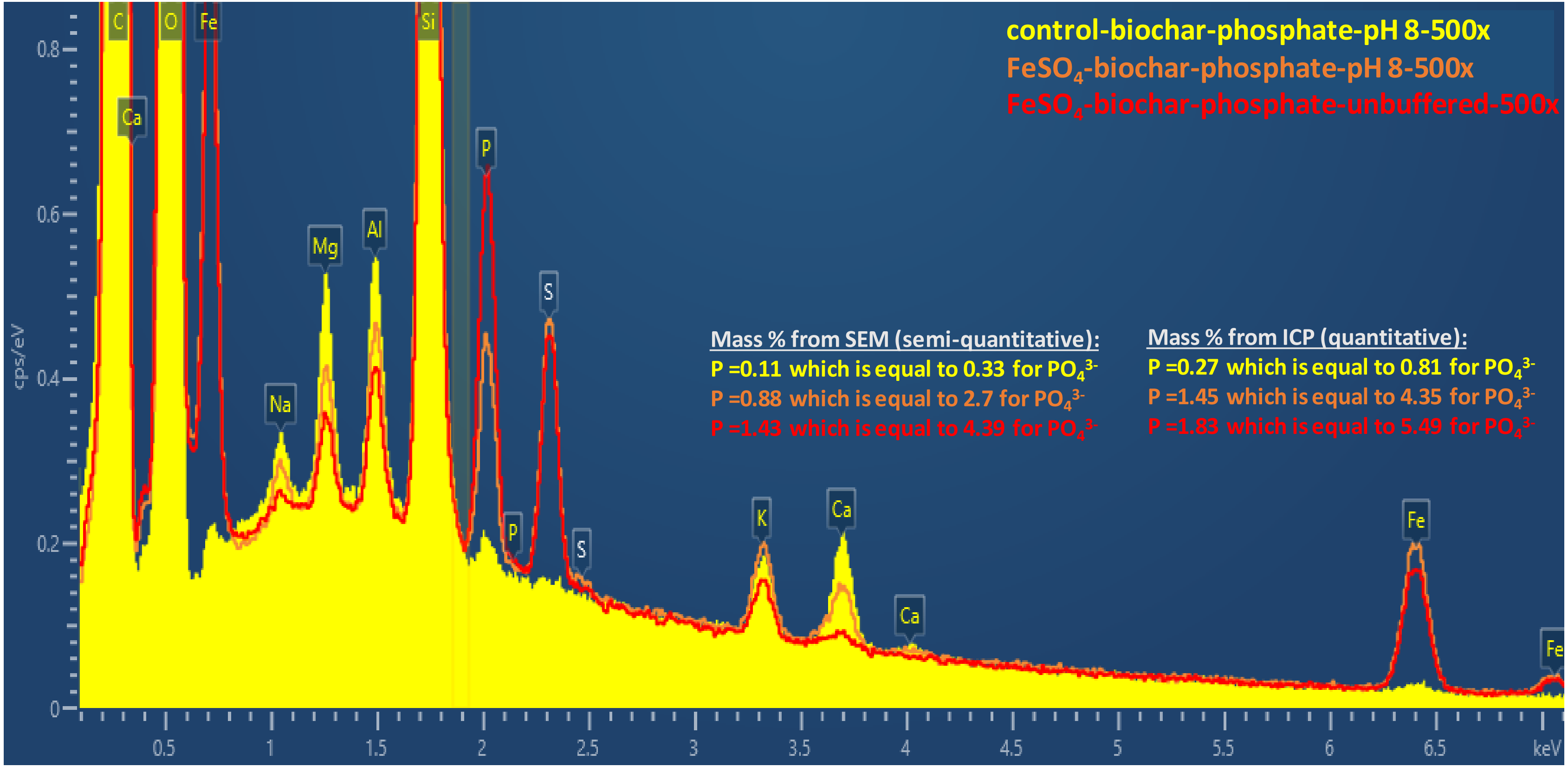
XPS analysis of phosphate sorbed biochar





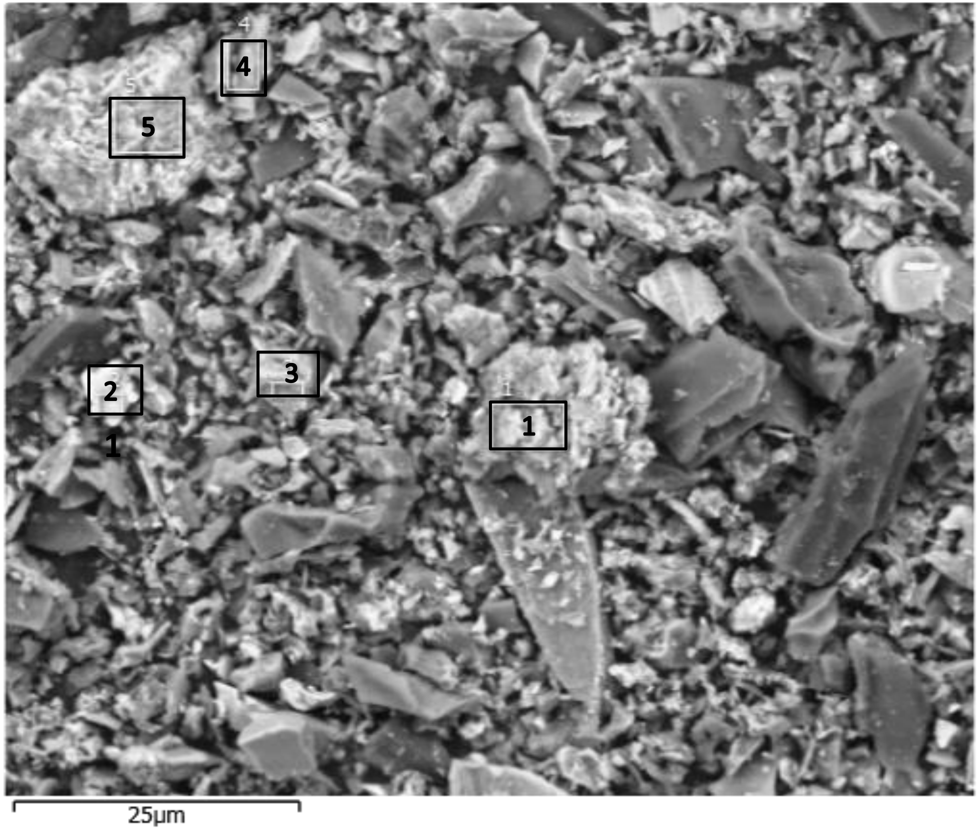
- BE Fe 2p suggests the “ferric” state
- BE P 2p suggests the “phosphate” state

SEM analysis of phosphate sorbed biochar

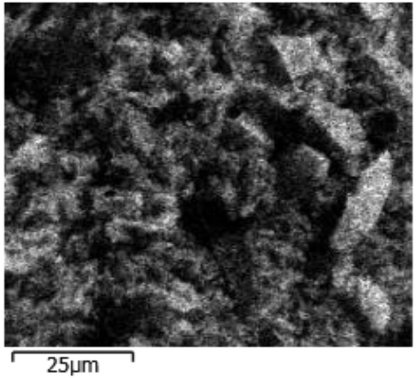


SEM analysis of phosphate sorbed biochar

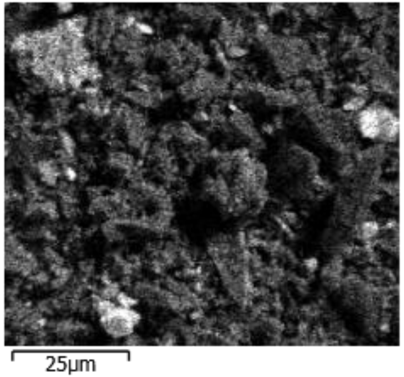
FeSO4-biochar-phosphate_ph8 area-1 1500x bse



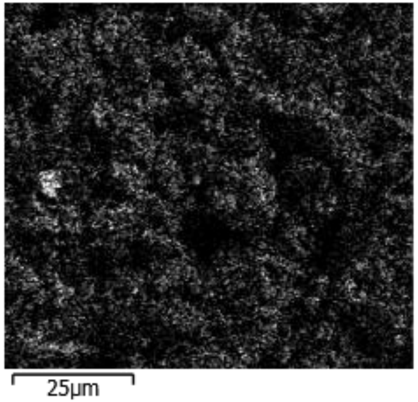
C K series



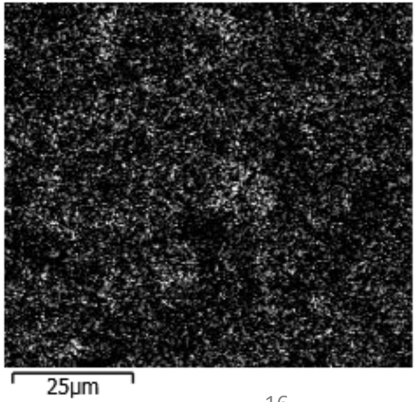
O K series



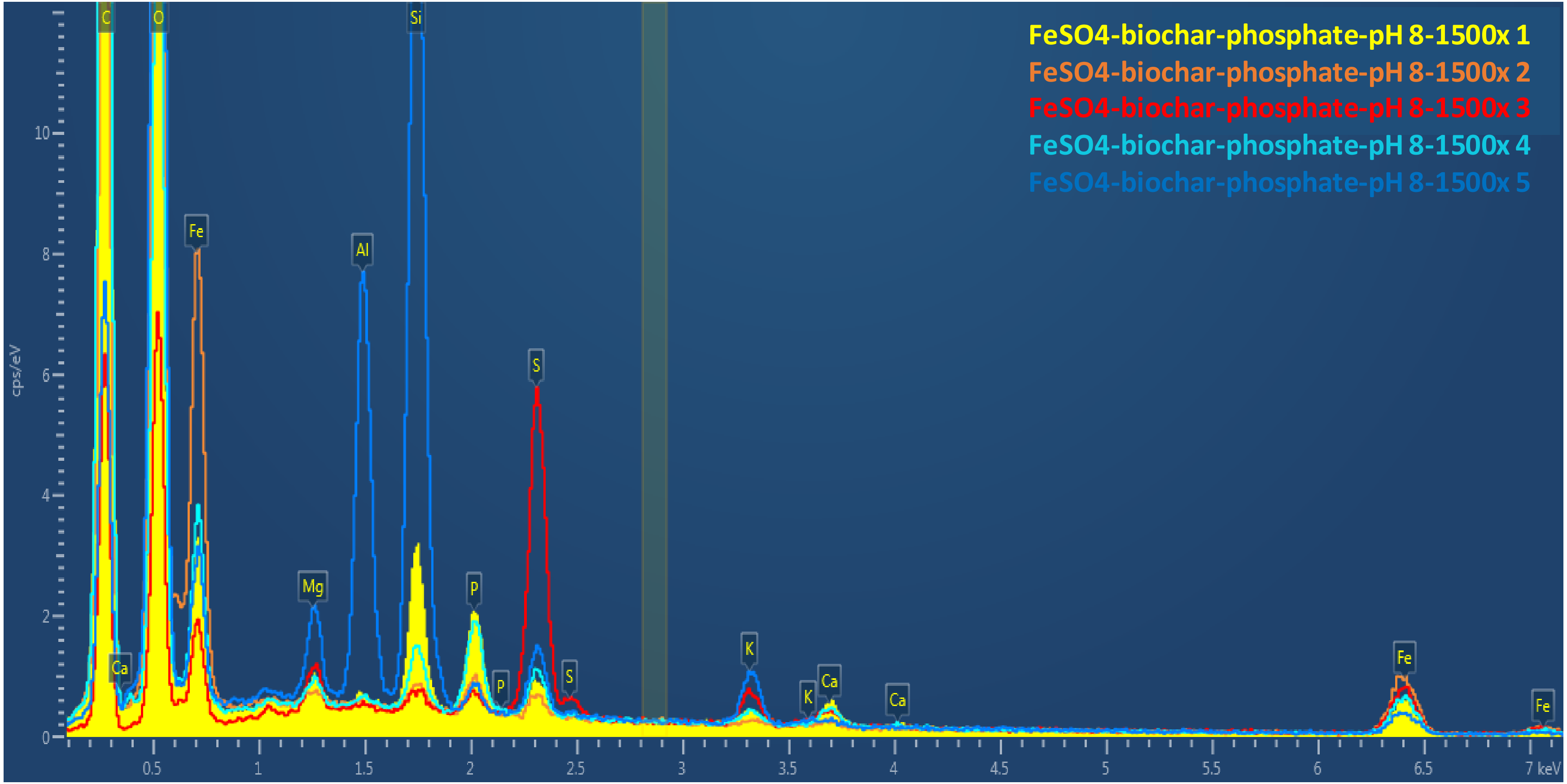
Fe L series



P K series



SEM analysis of phosphate sorbed biochar



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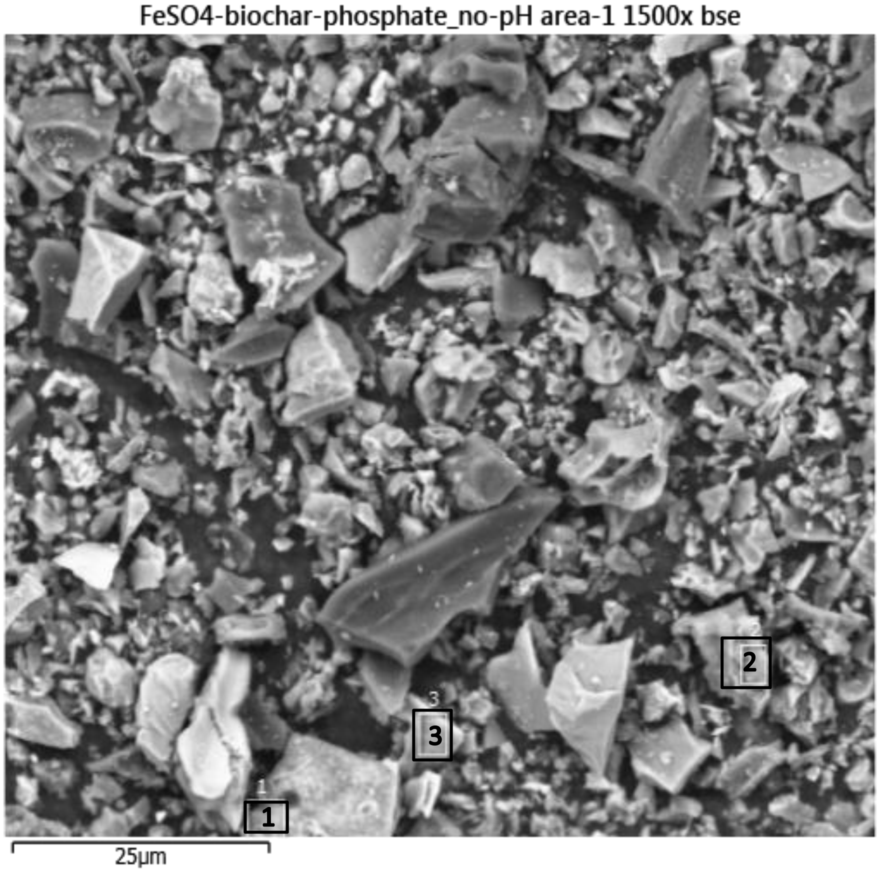
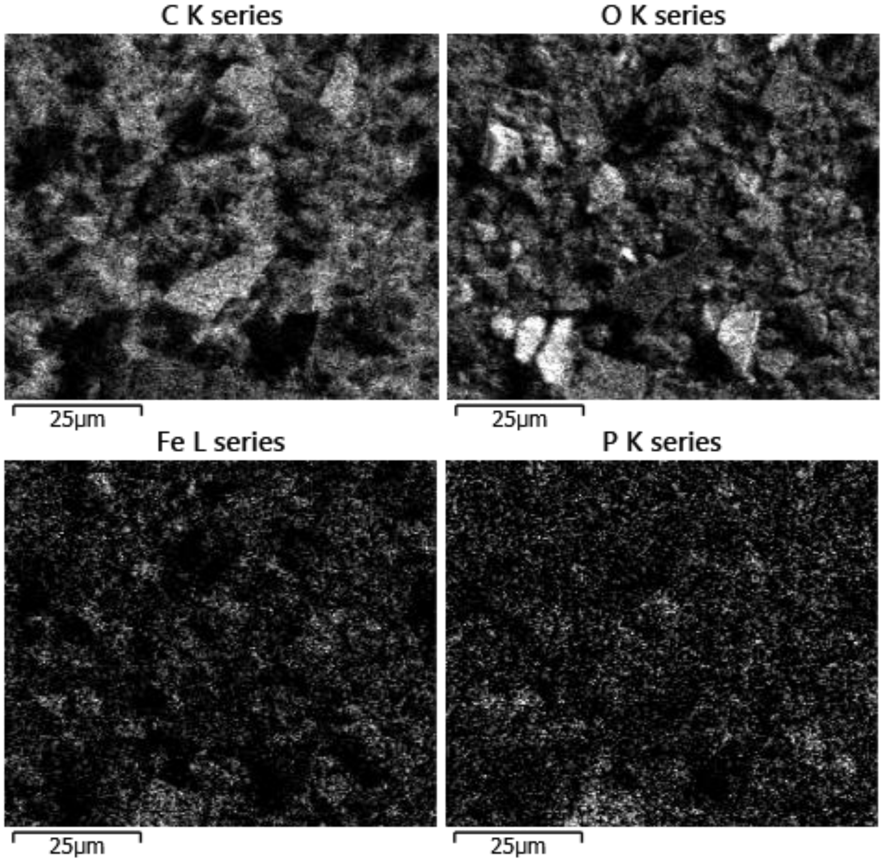
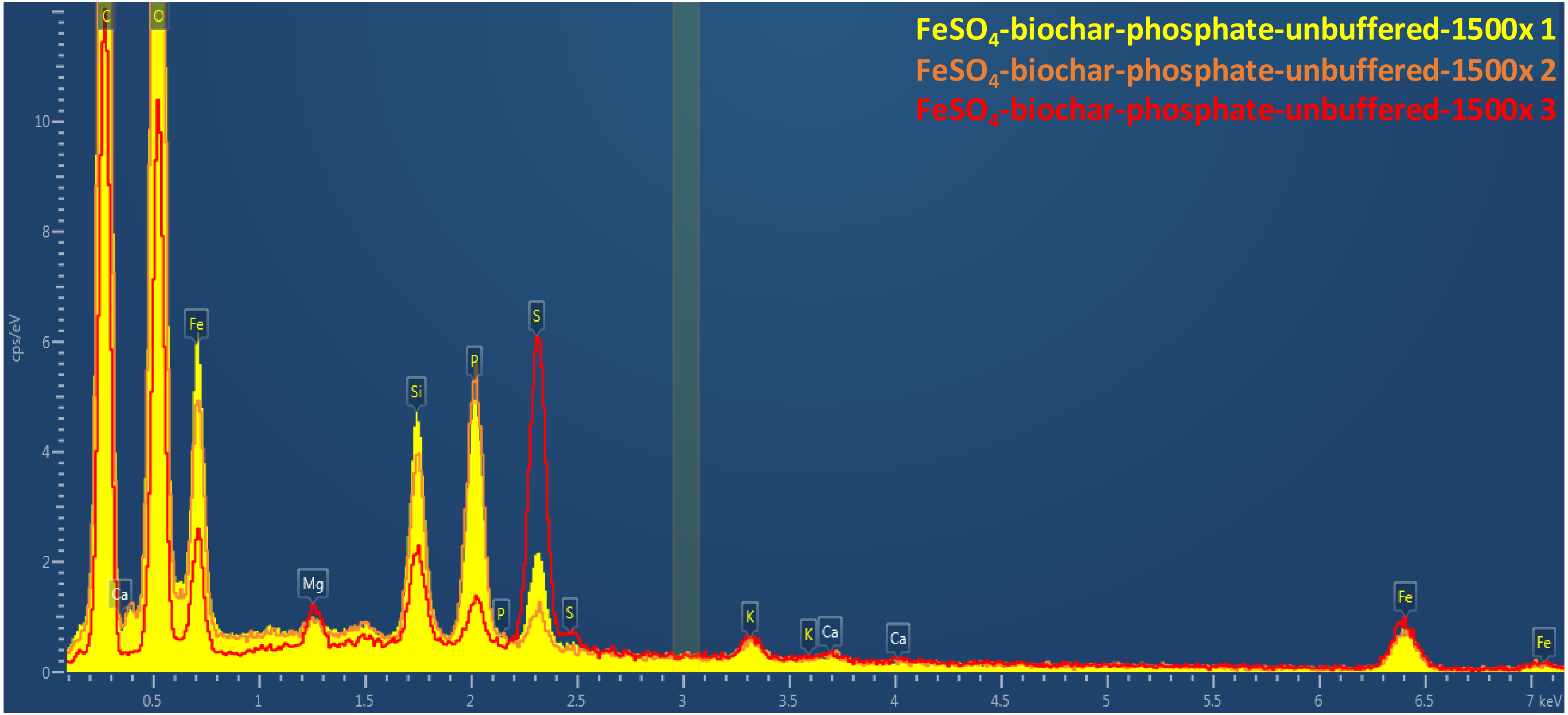
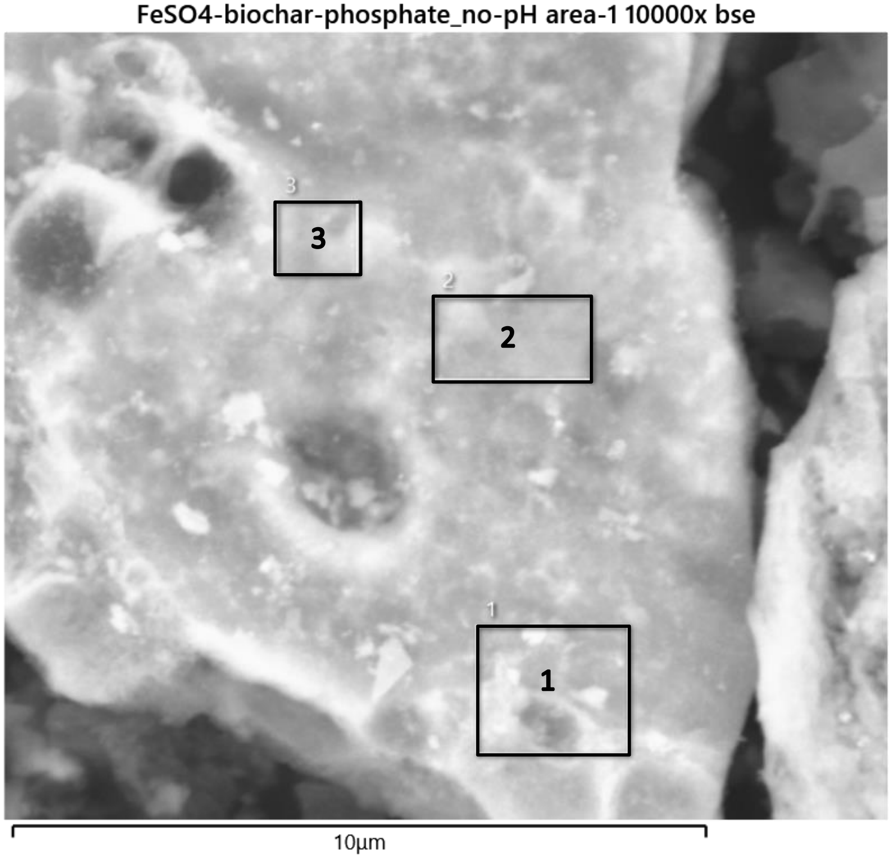


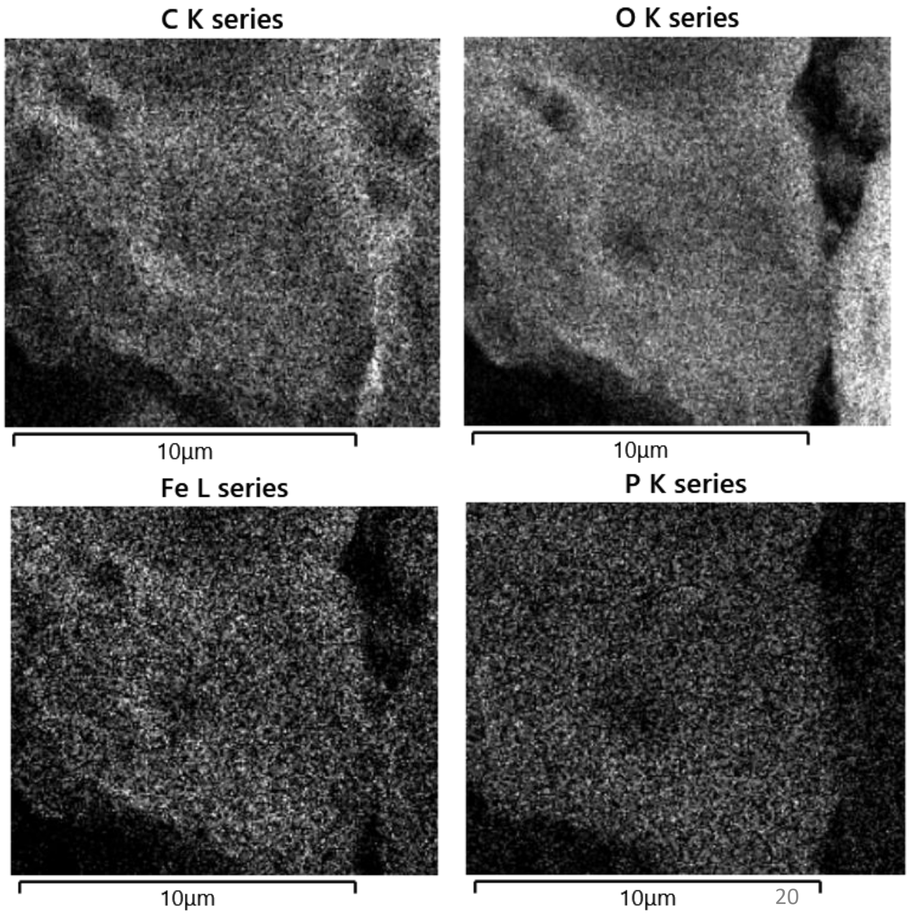


SEM analysis of phosphate sorbed biochar

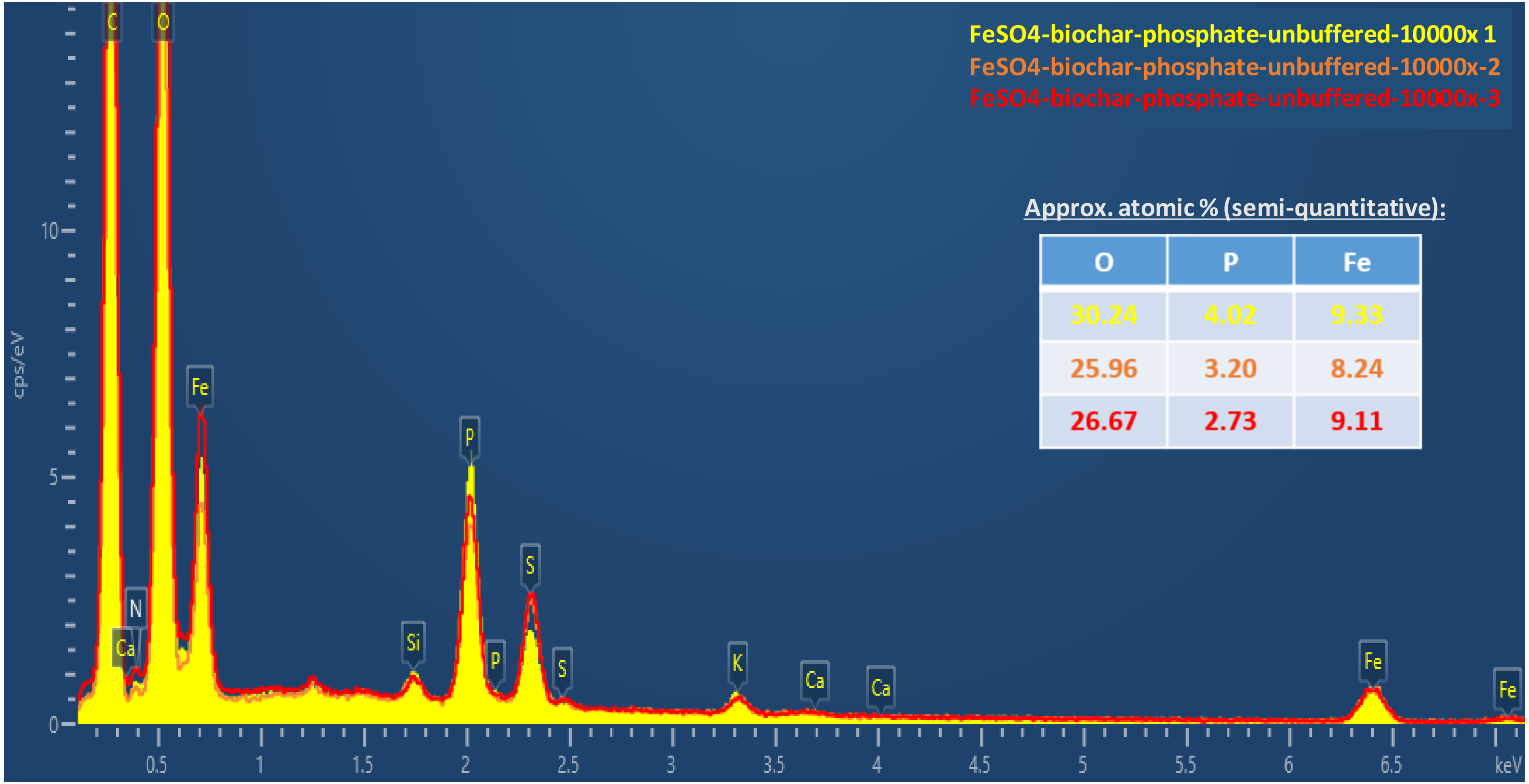


SEM analysis of phosphate sorbed biochar





SEM analysis of phosphate sorbed biochar

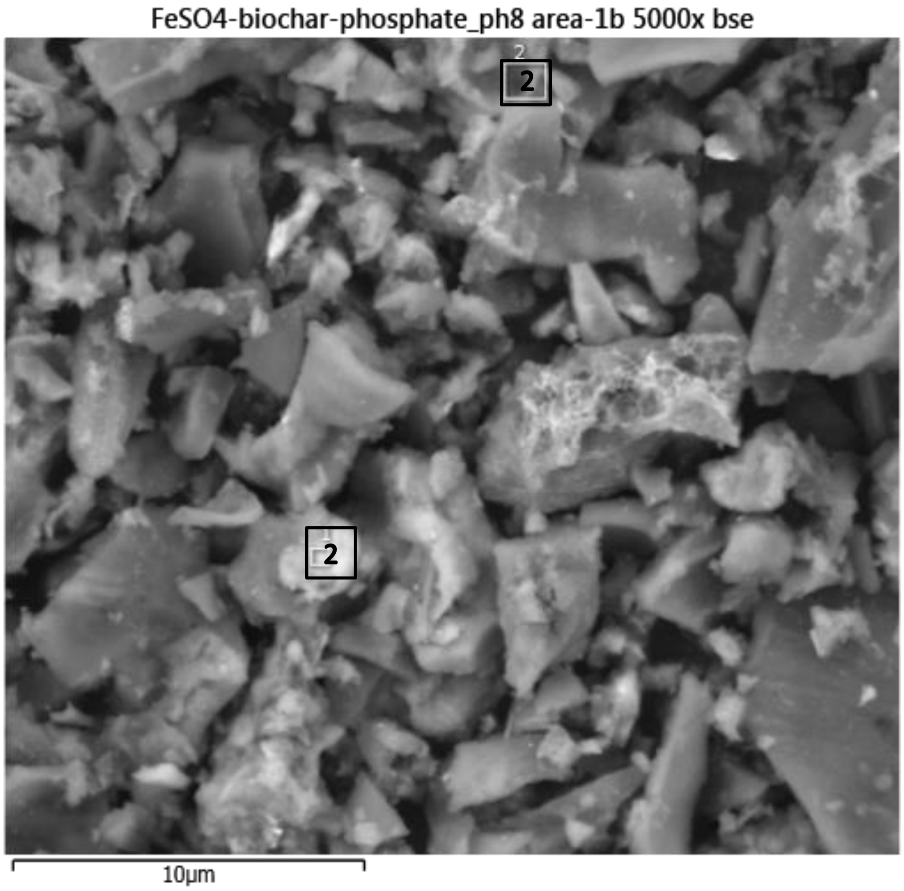


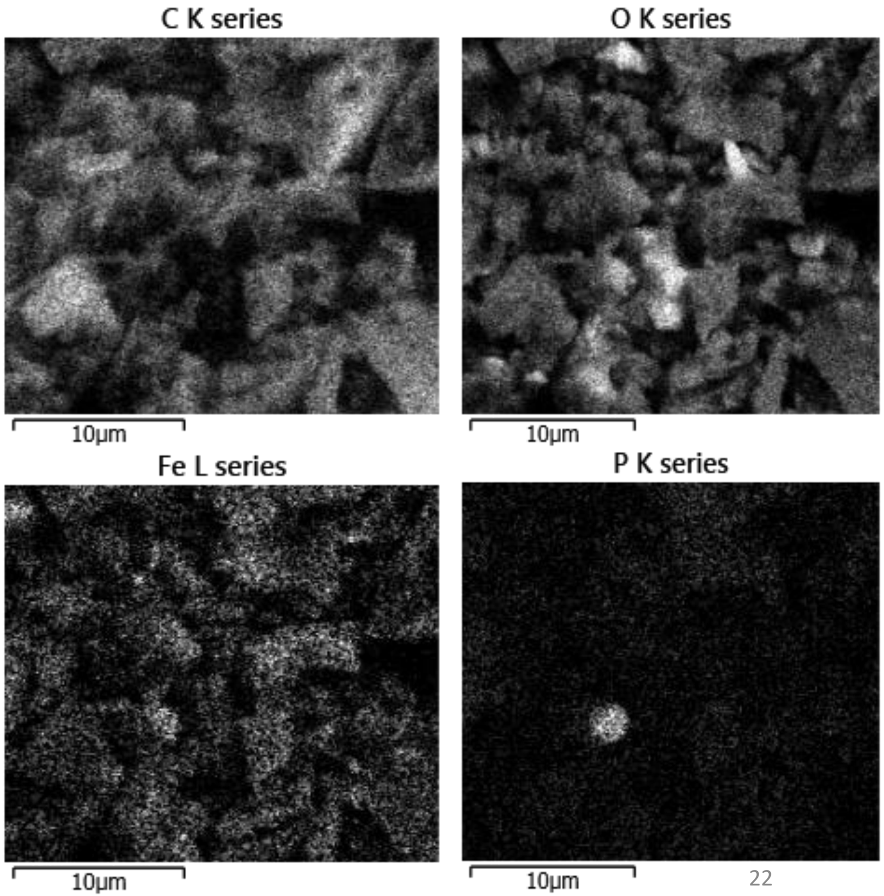
Approx. atomic % (semi-quantitative):

O	P	Fe
30.24	4.02	9.33
25.96	3.20	8.24
26.67	2.73	9.11

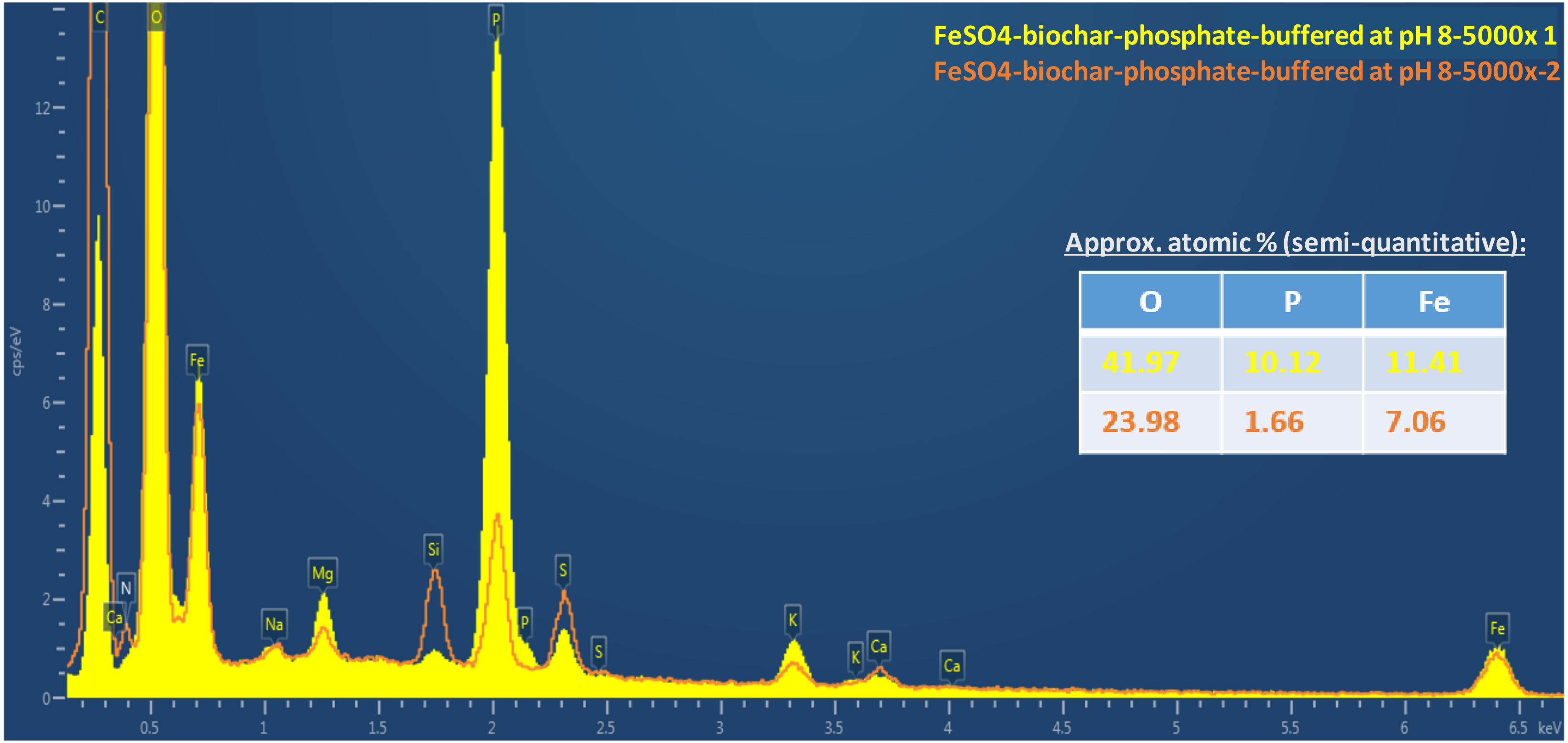
SEM-EDS analyses partially suggest the dominant form of phosphate is $H_2PO_4^-$ when the pH was unbuffered to form $Fe(H_2PO_4)_3$

SEM analysis of phosphate sorbed biochar





SEM analysis of phosphate sorbed biochar



Approx. atomic % (semi-quantitative):

O	P	Fe
41.97	10.12	11.41
23.98	1.66	7.06

SEM-EDS analyses partially suggest the dominant form of phosphate is HPO_4^{2-} when the pH was buffered to 8 to form $Fe_2(HPO_4)_3$

Conclusions

- ❑ **Fe-impregnation caused modifications on biochar surface**
- ❑ **Sorption of phosphate onto biochar surface depends on solution pH**
- ❑ **Phosphate can be slowly desorbed from biochar surface**
- ❑ **Surface complexation through ligand exchange is the dominant mechanism**

Future research

- ❖ **Reversibility of phosphate sorption in presence of competing ions**
- ❖ **Evaluation of plant available P**
- ❖ **Greenhouse study**