Interactions of Emerging Contaminants-Antibiotics with Functionalized Biochar

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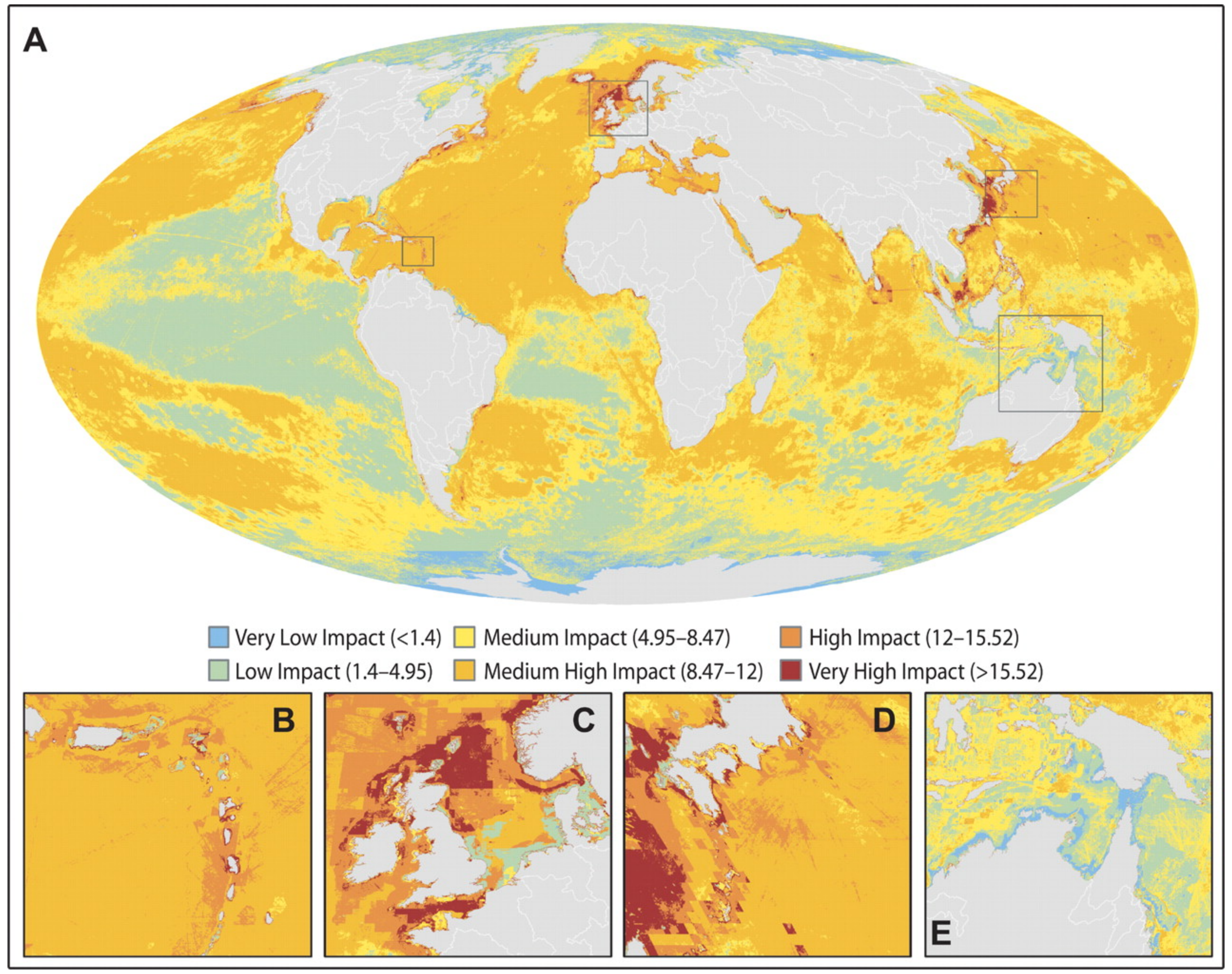
Outline of the Talk

1. Antibiotic residues in the environment
2. Preparation and characterization of functionalized biochar
3. Application of functionalized biochar in antibiotic removal from water and wastewater
4. Conclusions

Emerging Contaminants in the Environment

- Pharmaceuticals and personal care products (PPCPs)
- Nano-materials
- Disinfection by-products
- New pesticides
- Degradation products



Halpern et al. (2008) Science 319, 948

Pharmaceutical Residues in the Environment

- Of the greatest concern worldwide are pharmaceuticals, in particular antibiotic residues:

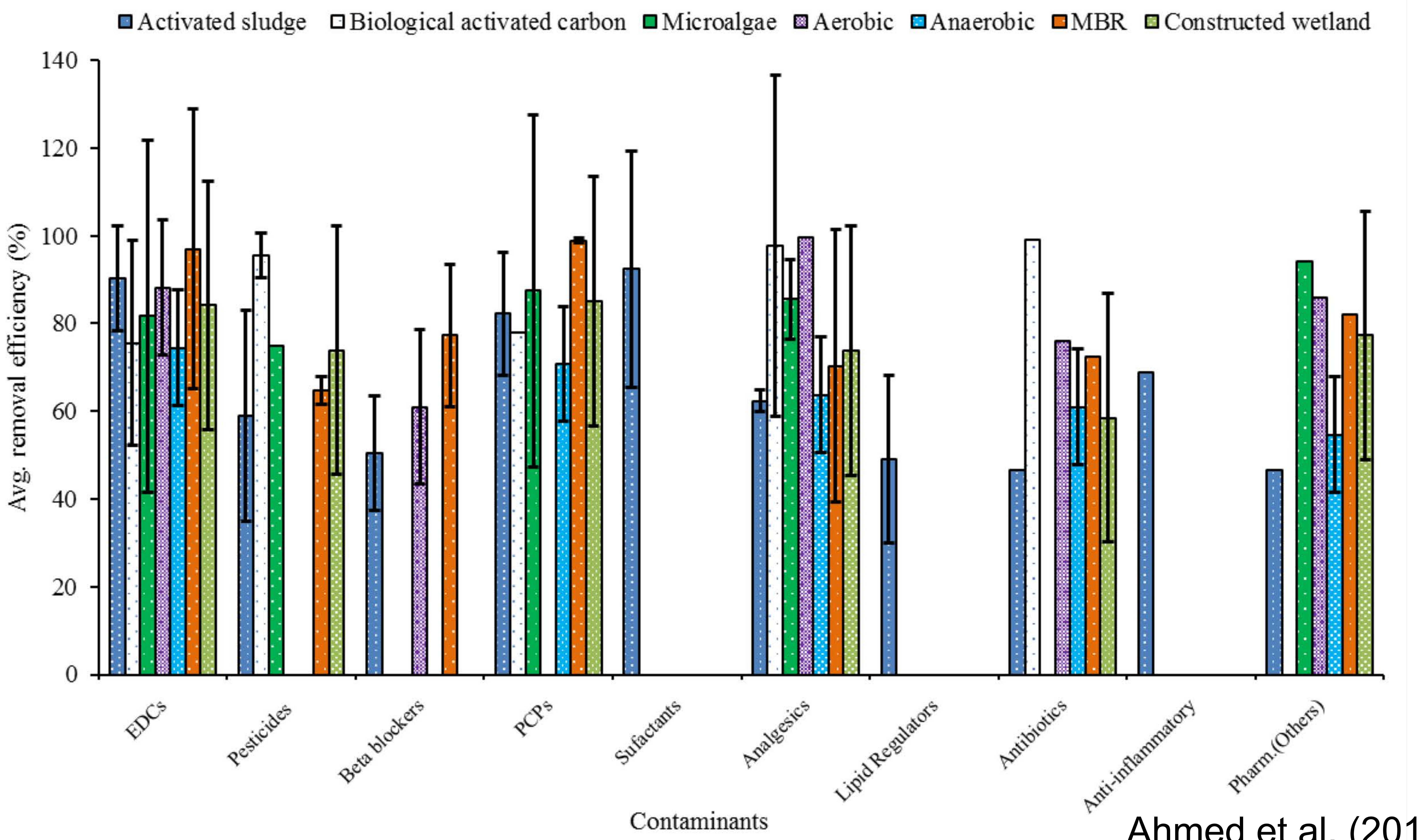
✓ Produced in large quantity, e.g. > 25000 tons per annum produced in China alone.

✓ Between 80-90% are excreted unmetabolized once consumed in human and animals.

✓ Poorly removed in sewage treatment plants.

✓ Potential to cause antibiotic resistance, leading to the so-called “superbugs” with antibiotic resistance genes.

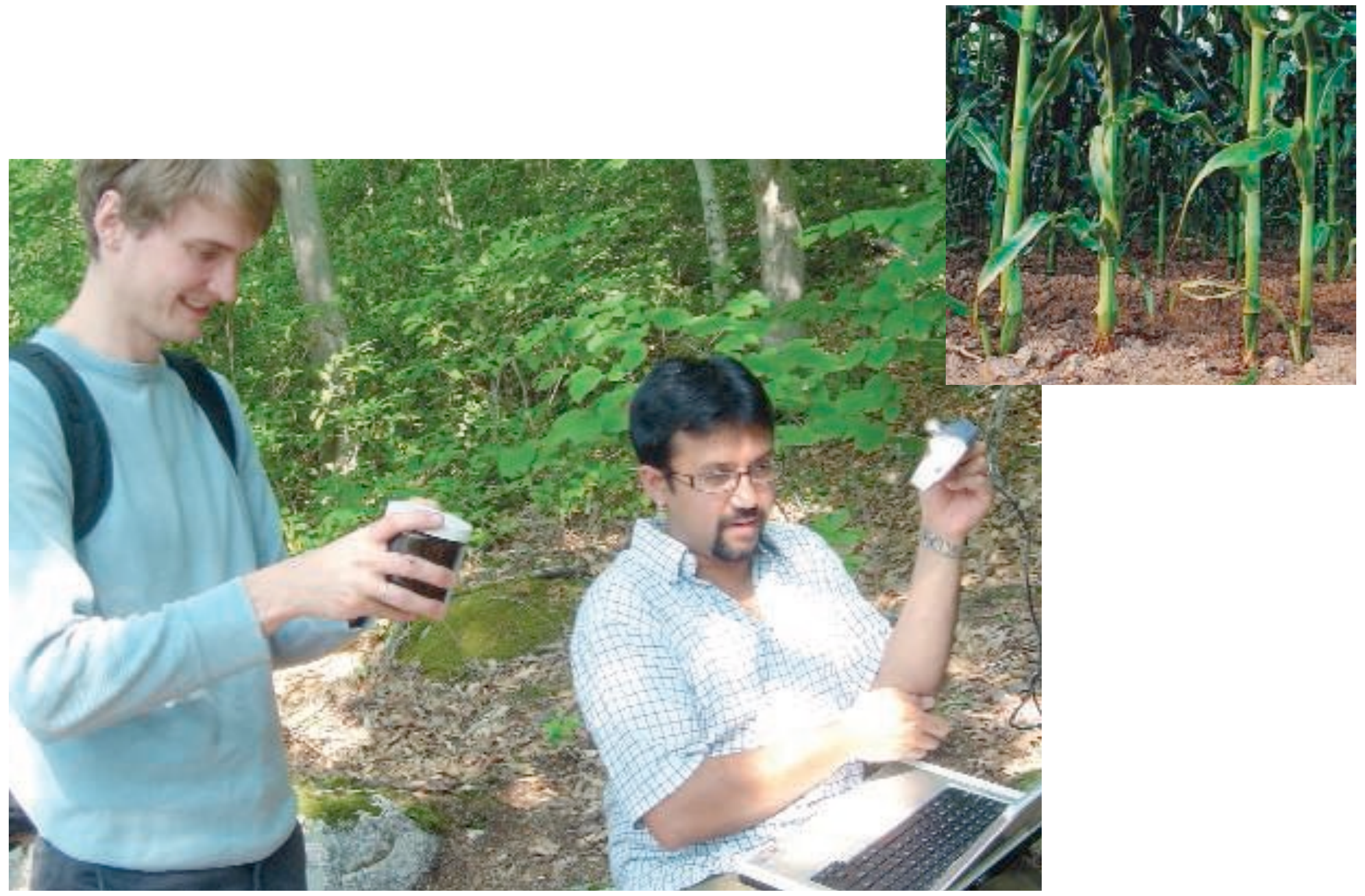
Comparative Removal Efficiency of Emerging Contaminants

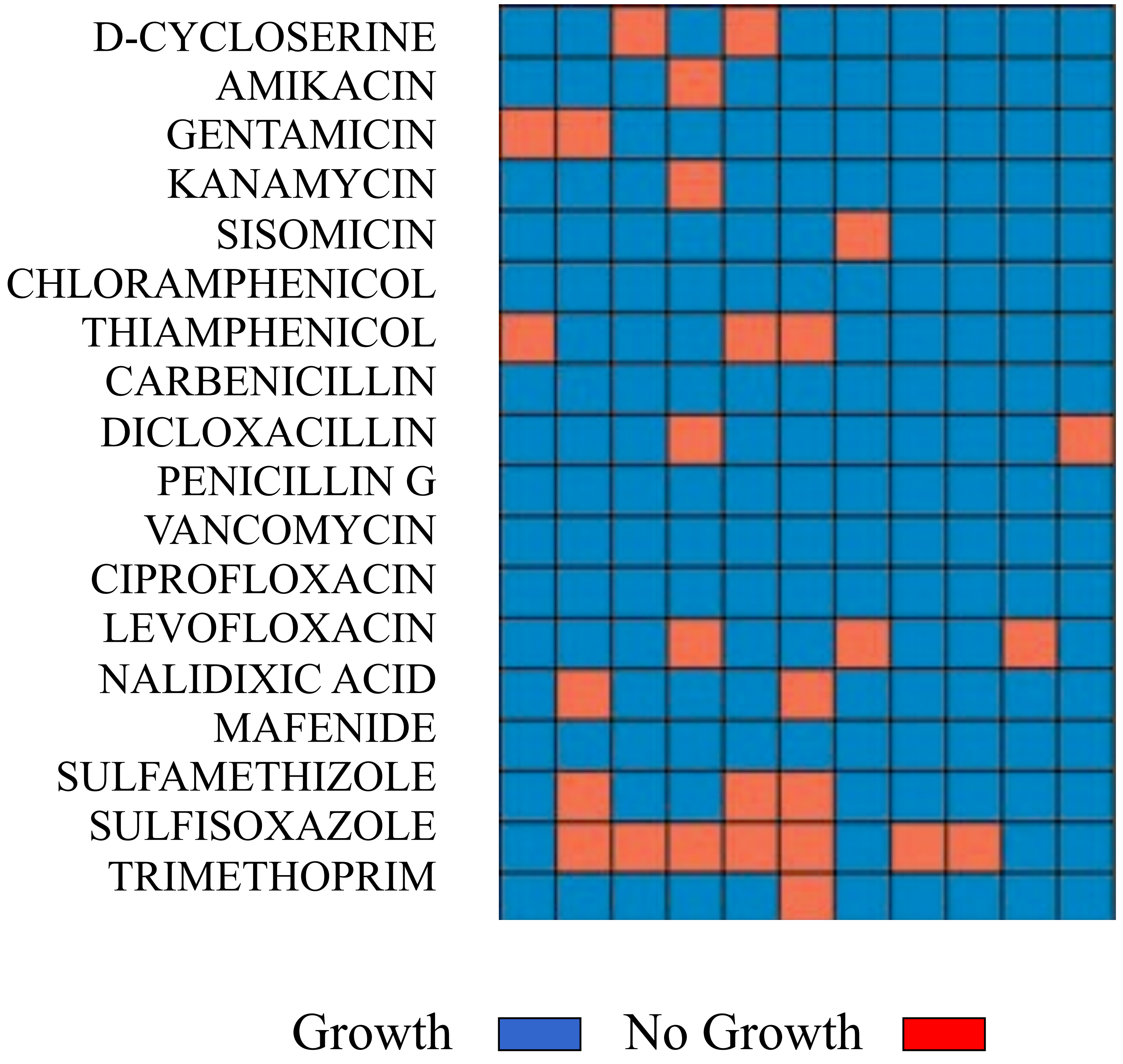


Ahmed et al. (2017) JHM 323, 274-298

Antibiotic Resistance

Germs Take a Bite Out of Antibiotics

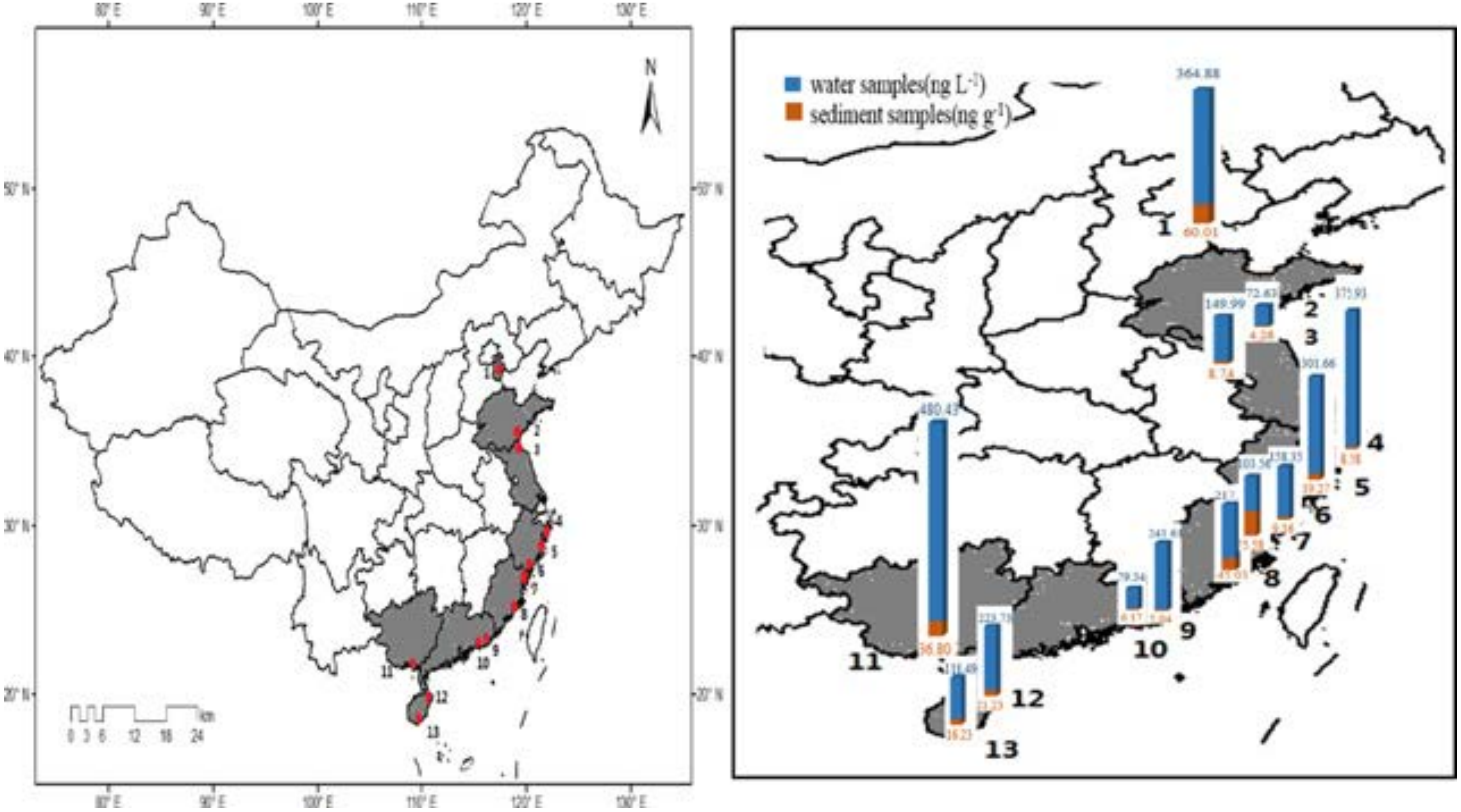




Taste test. Harvard University researchers Morten Sommer and Gautam Dantas and colleagues used soil samples from a Massachusetts forest and a cornfield (*inset*) to screen for antibiotic-eating microbes.

Science (2008) 320, 33

Antibiotics in Water and Sediments from Mariculture Sites in China



Chen et al. (2017) STOTEN 580, 1175

Outline of the Talk

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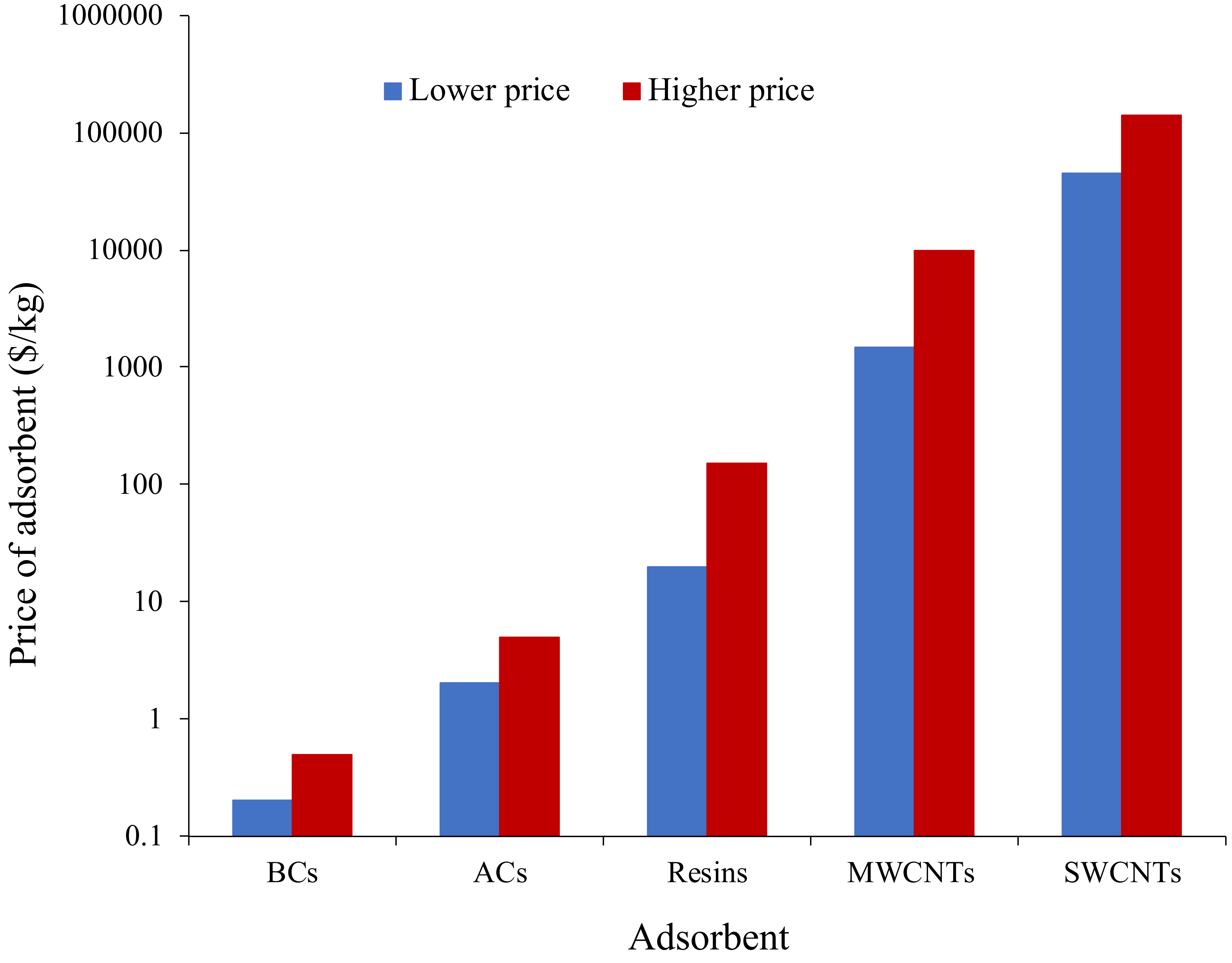
Why Biochar and Functionalized Biochar?

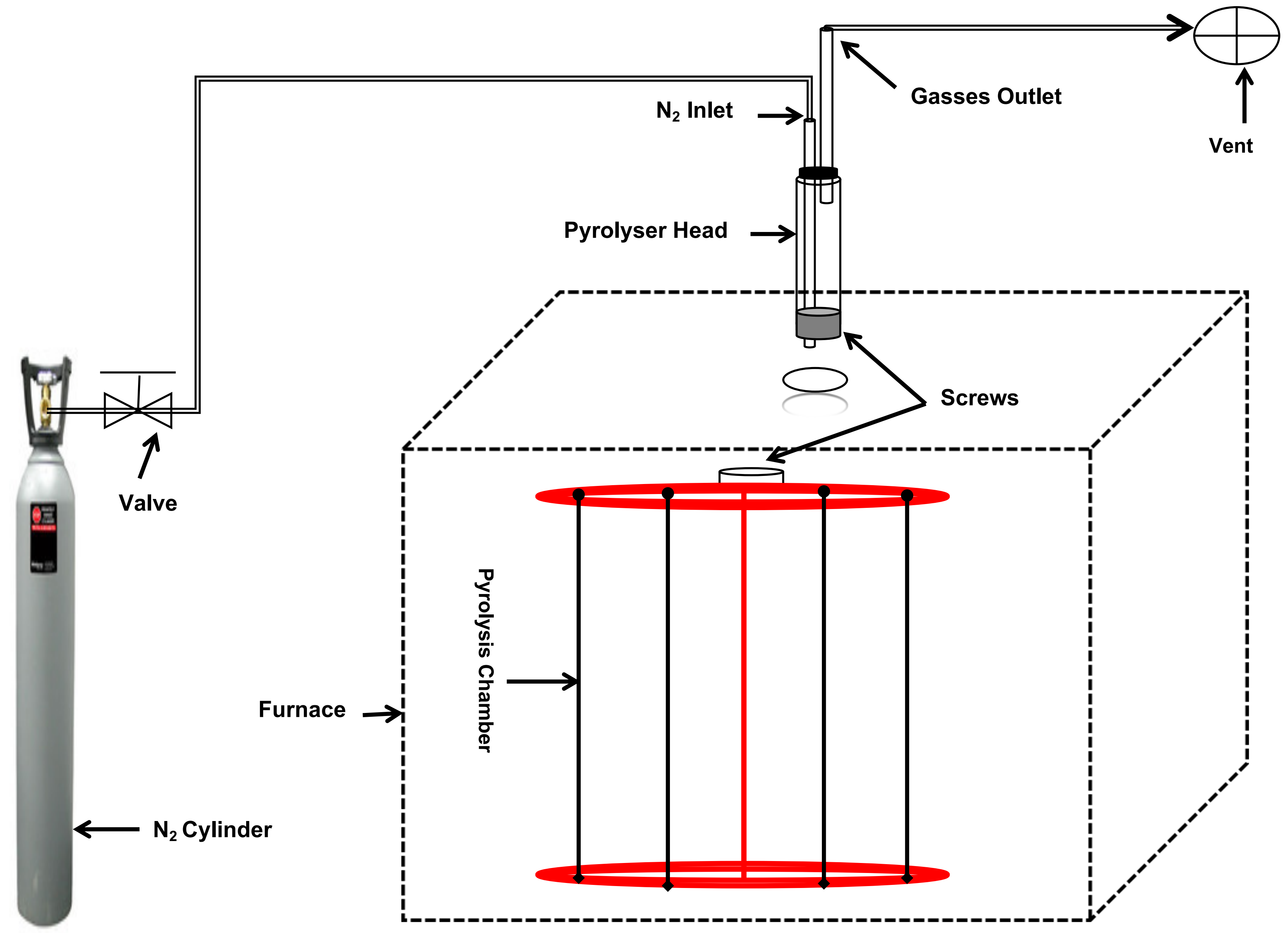


- Biochar is a C-rich product obtained when biomass is heated at elevated temperature in a closed reactor with little or no available air.
- Functionalized biochar (fBC) is obtained when biochar is further treated either chemically or physically in order to improve its functional groups and sorption performance.

Ahmed et al. (2015) STOTEN 532, 112-126

Preparation of Biochar and Functionalized Biochar

Biomass → Cut into small sizes → Wash & drying at 105 °C → Pyrolysis at 380 °C for 2 h at 2 psi → Increased N_2 pressure 10 psi at 380 °C for 15 min → Cooling at room temp. → Crushed into desired size, wash with DI & drying → **Biochar (BBC380)**



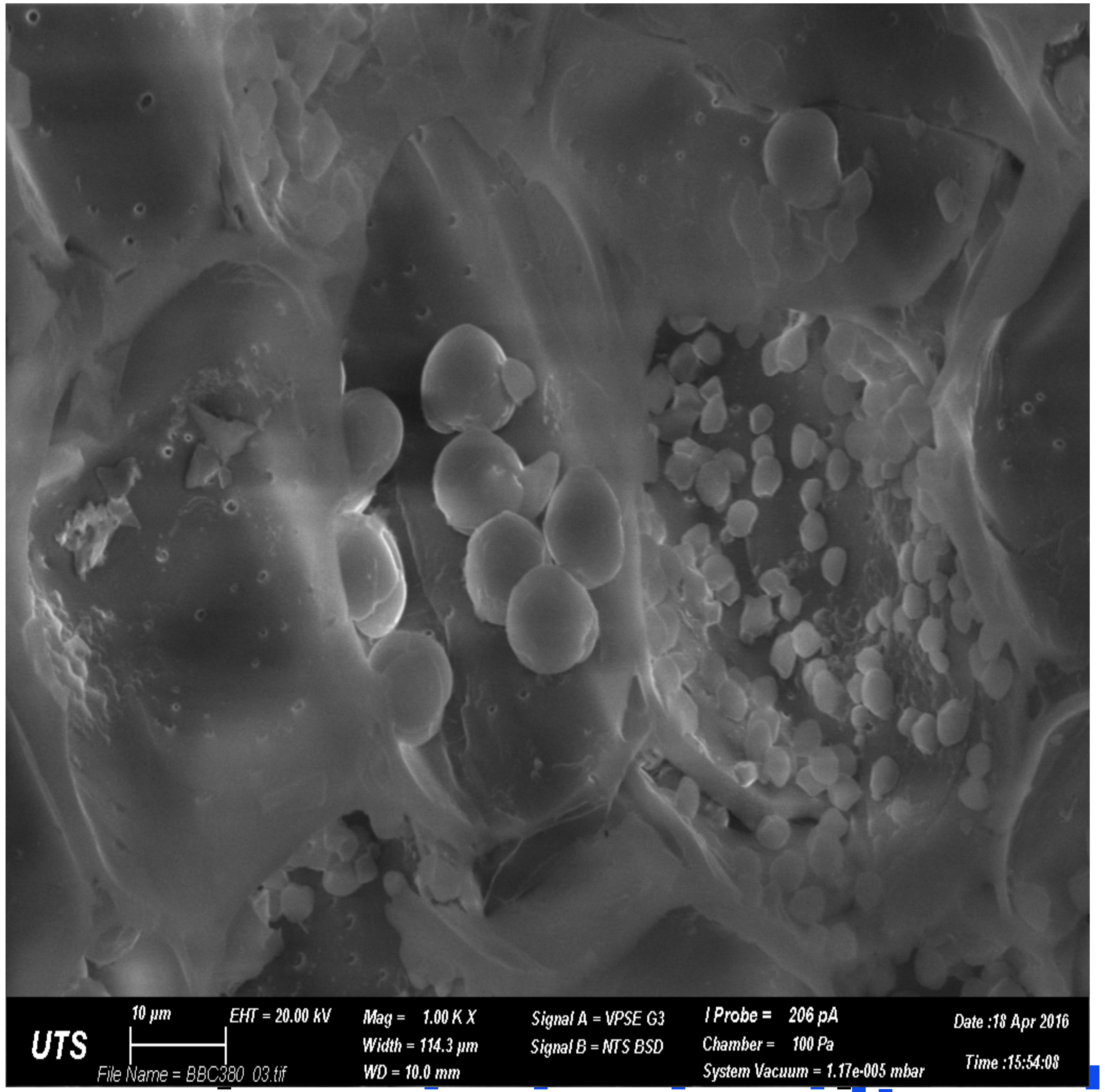
Biochar → Soaking in 50% phosphoric acid solution → Leave at 50 °C for 3 h → Heated at 600 °C for 2 h at 2.0 psi → Cooling in room temp. → Wash with DI & adjust pH to 7.0 and dry → **fBC**

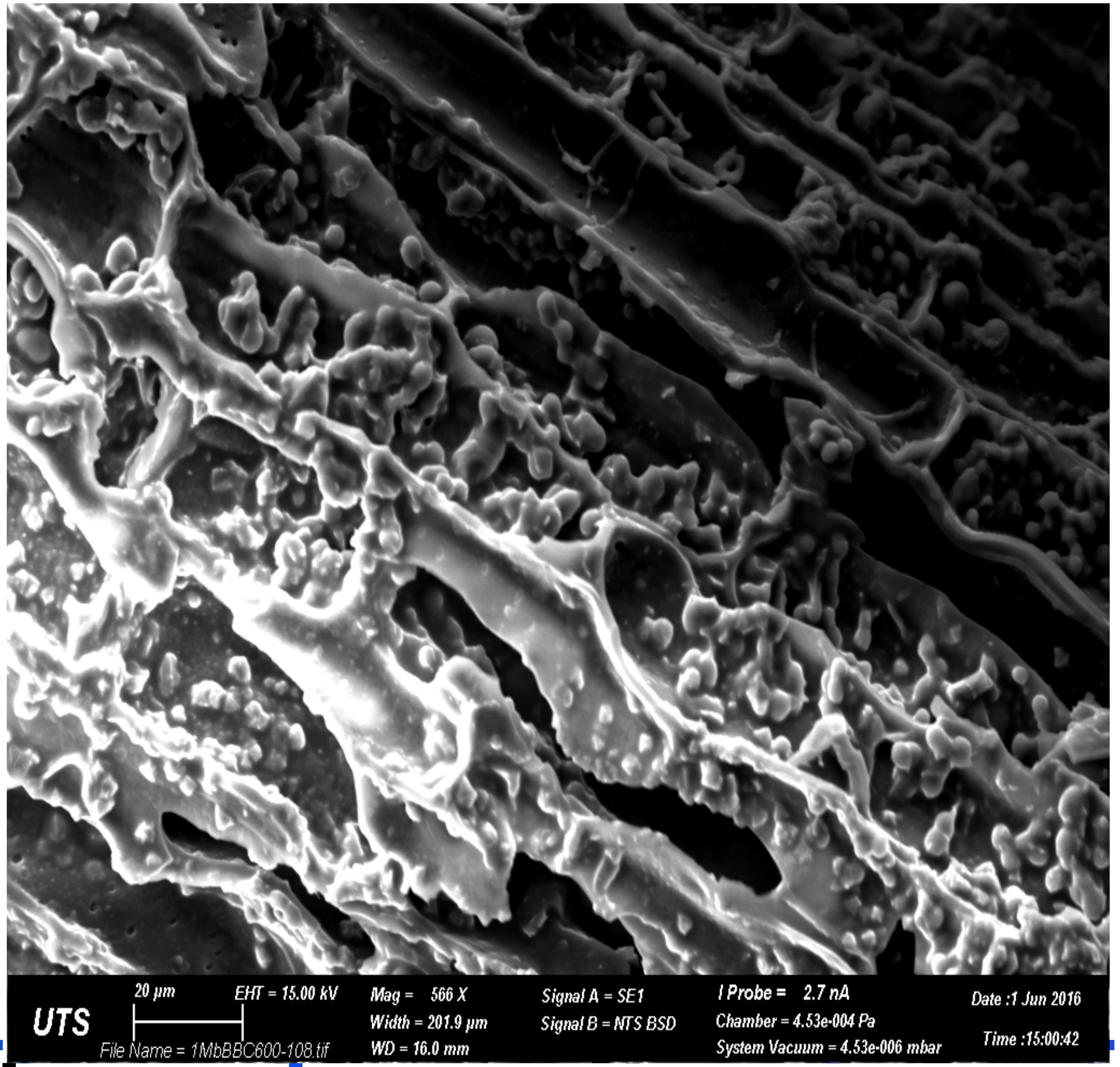
Physicochemical Properties of Biochar & fBC

Sample	Composition data				
	$Yield_{dry\ basis}$ (%)	Moisture content (%)	Ash (%)	Volatile mater (%)	Fixed carbon (%)
Biomass		5.61	12.93	63.83	26.67
BBC380	43.50				
			1MbBBC600		
Initial pH	1.62	3.00	4.35	6.13	10.00
Final pH	1.15	2.74	3.39	4.09	8.28
Zeta potential (mV)	5.34±0.32	-3.25±0.24	-12.76±1.23	-19.6±1.15	-45.9±4.67

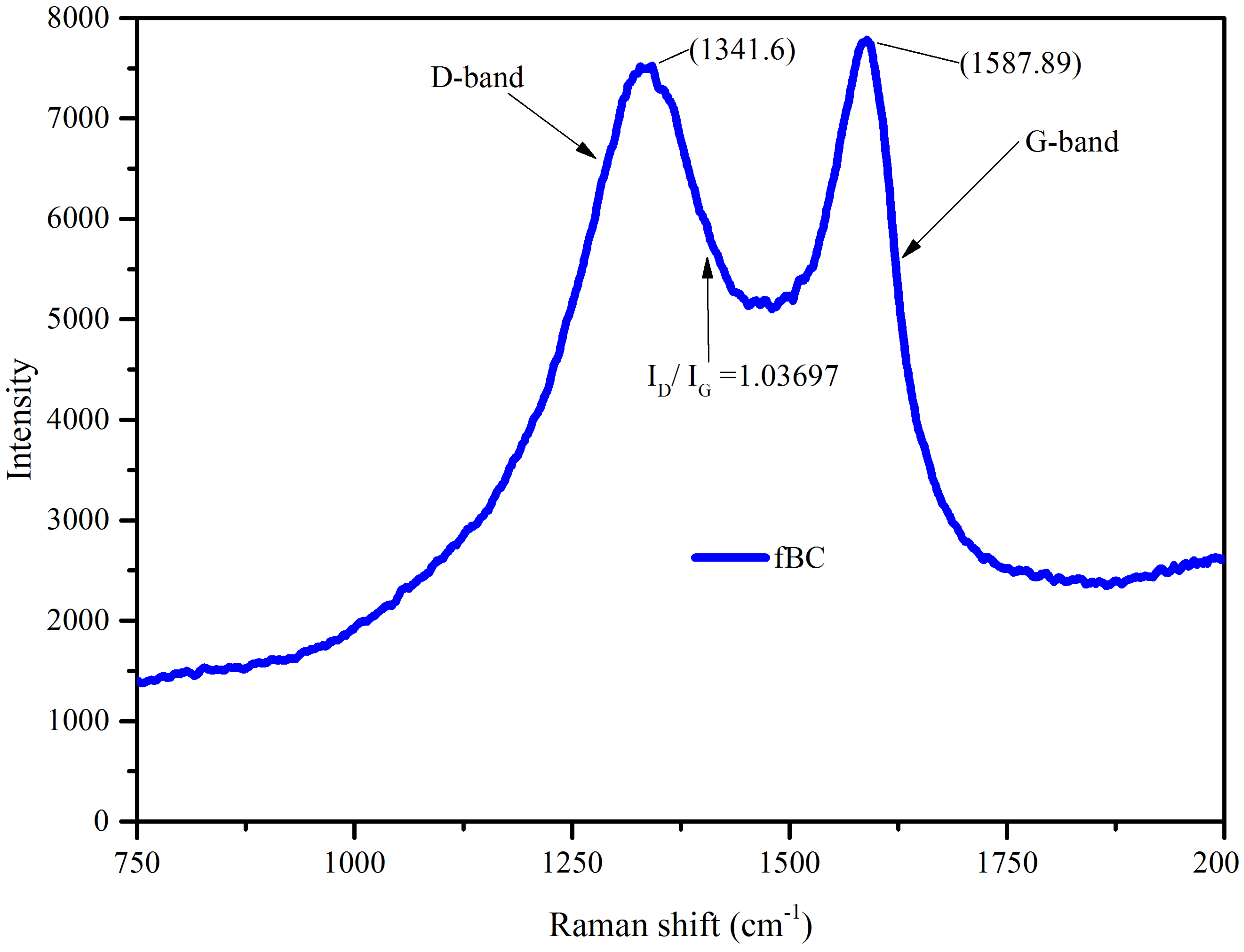
Sample	EDS analysis				BET surface area	BJH Adsorption pore diameter
	C %	O%	P%	Molar O/C		
BBC380	81.18	18.83	-	0.232	0.50 $m^2\ g^{-1}$	113.5 Å
1MbBBC600	51.96	39.52	8.16	0.761	1.12 $m^2\ g^{-1}$	83.8 Å

SEM of BBC380 and 1MbBBC600

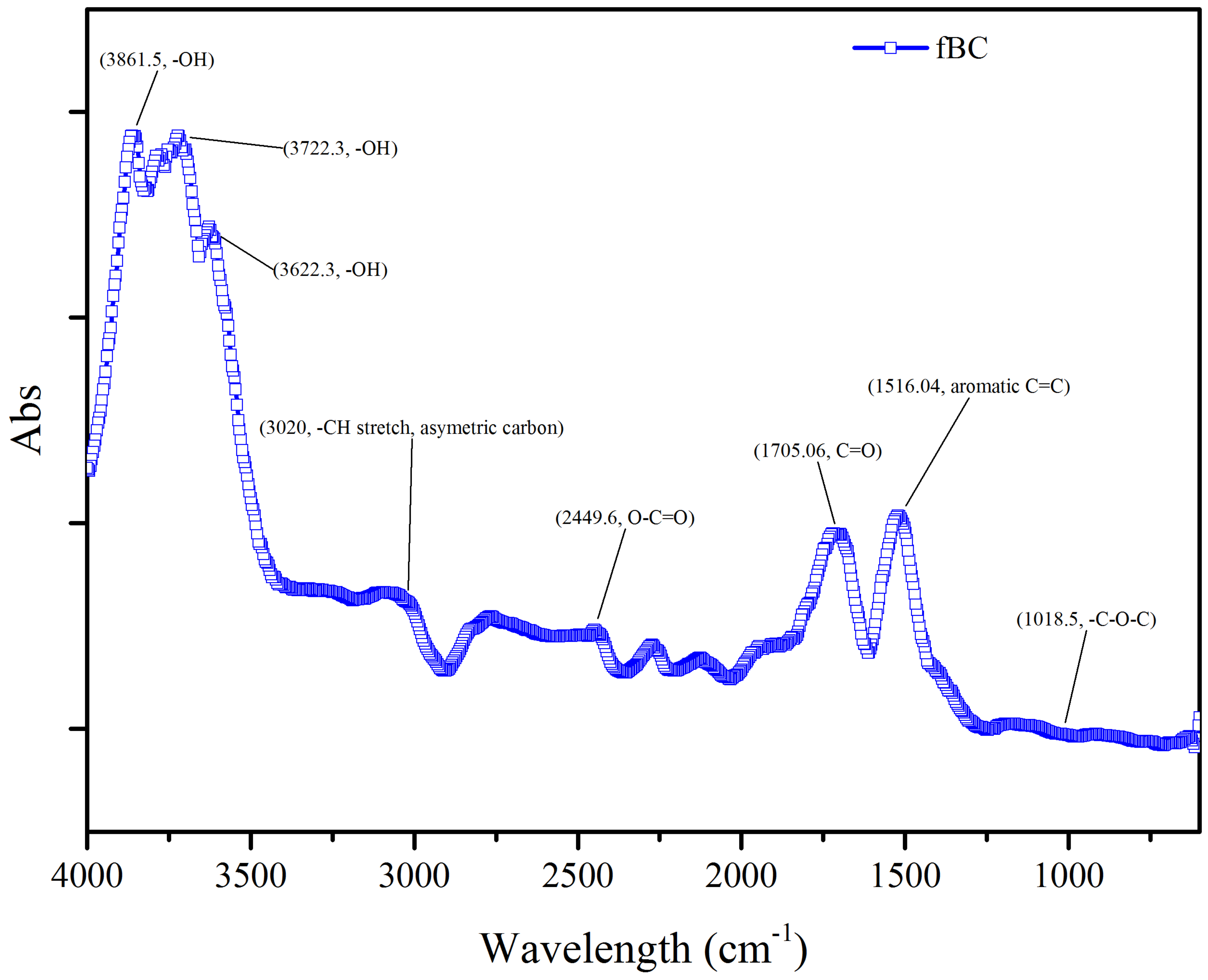




Raman Spectra of fBC



FTIR Spectra of fBC



Zeta Potential Value of fBC is 2.20

XPS Spectra of fBC

Name	Peak BE	Atomic %	Surface group	Assignment
C (1s) A	284.8	56.98	C=C	Graphitic carbon
C (1s) B	286.27	13.6	C-O-	Phenolic, alcoholic, etheric
C (1s) C	287.8	4.15	C=O	Carbonyl or quinone
C (1s) D	289	3.13	COO-	Carboxyl or ester
C (1s) E	290.54	2.77	C=O/ C=C	Carbonate, ocluded CO, p-electrons in aromatic ring
C (1s) F	292.35	1.13	π-π* transition	The transition due to conjugation
N (1s)	401.47	0.8	C–N$^+$H-C	Forms of quaternary nitrogen, protonated pyridinic ammonium ions, nitrogen atoms replacing carbon in graphene,
O (1s) B	533.3	8.52	C-O-	Oxygen singly bonded to carbon in aromatic rings, in phenols and ethers
O (1s) A	531.62	4.8	C=O	Oxygen doubly bonded to carbon
P (2p)	133.79	2.3	C-O-PO_3	Polyphosphates and/or phosphates

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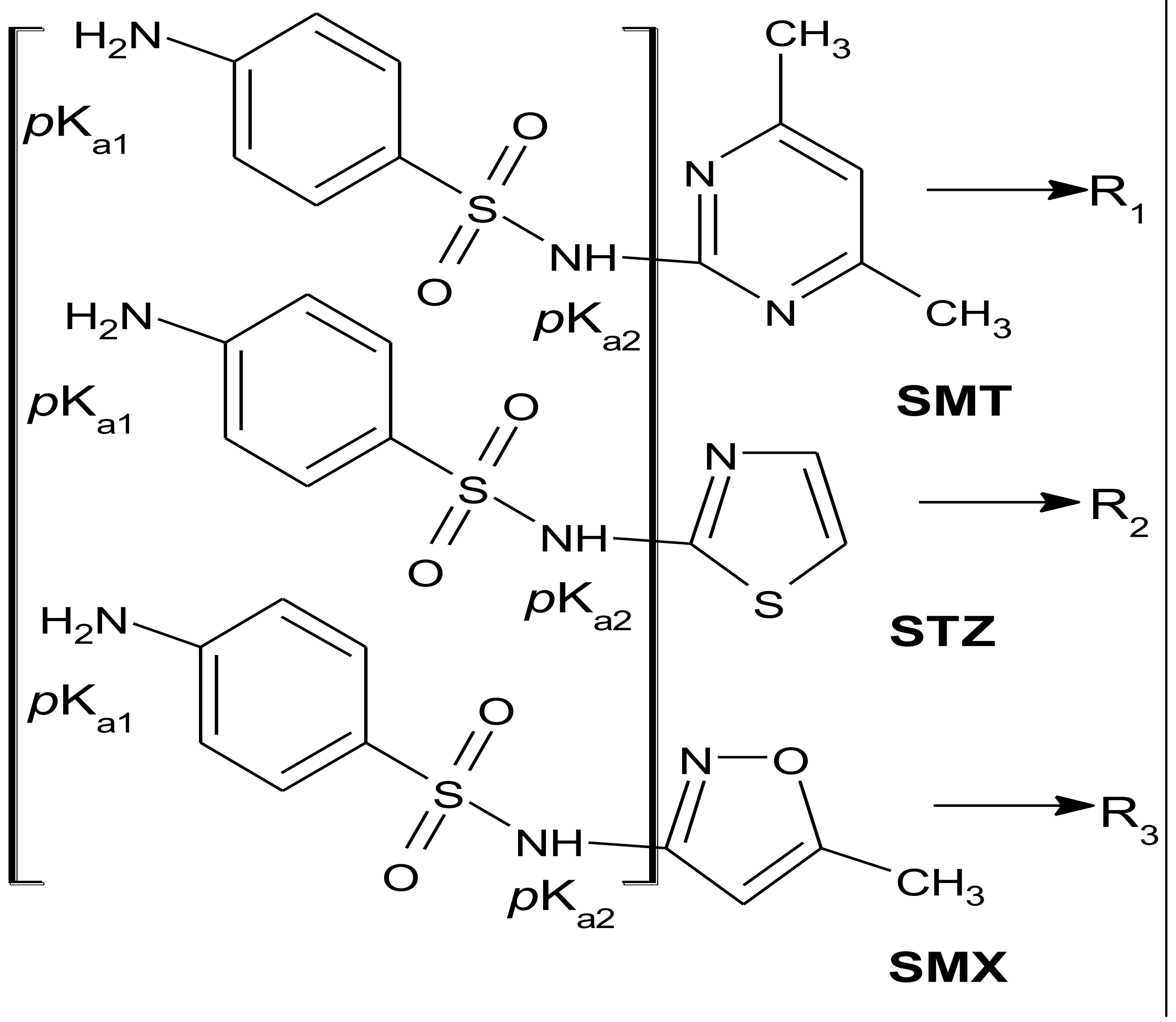
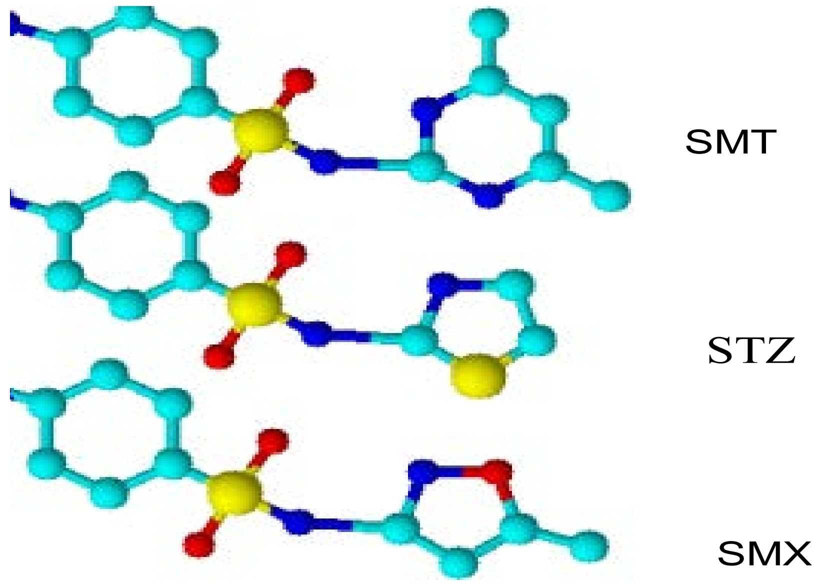
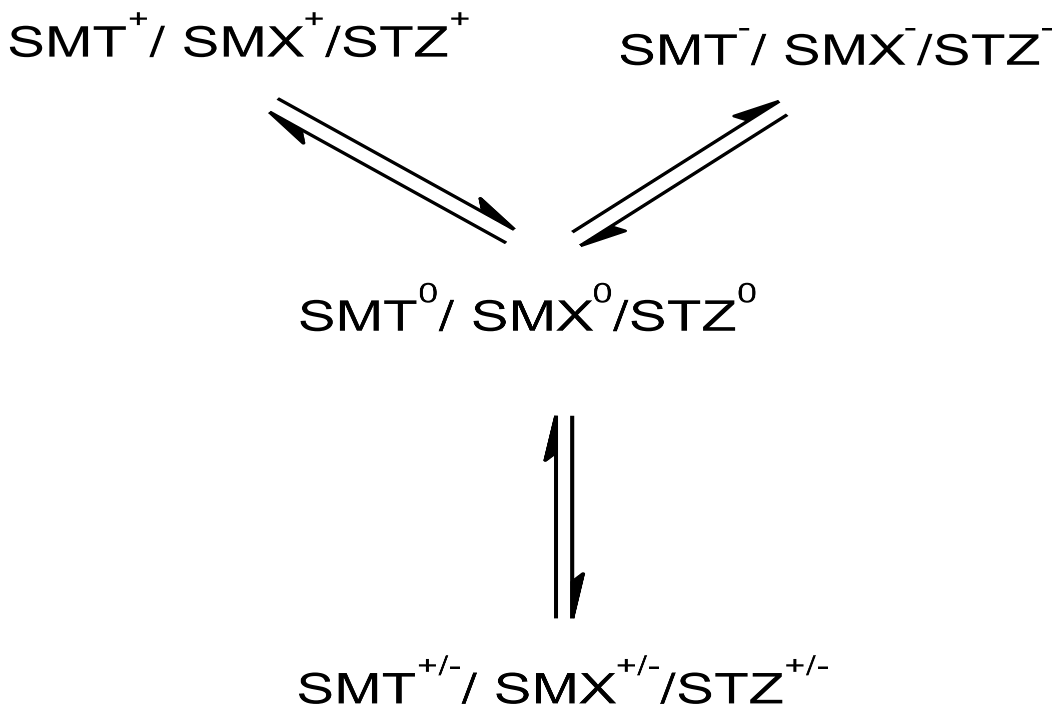
Single and Competitive Sorption of Sulfonamides by fBC



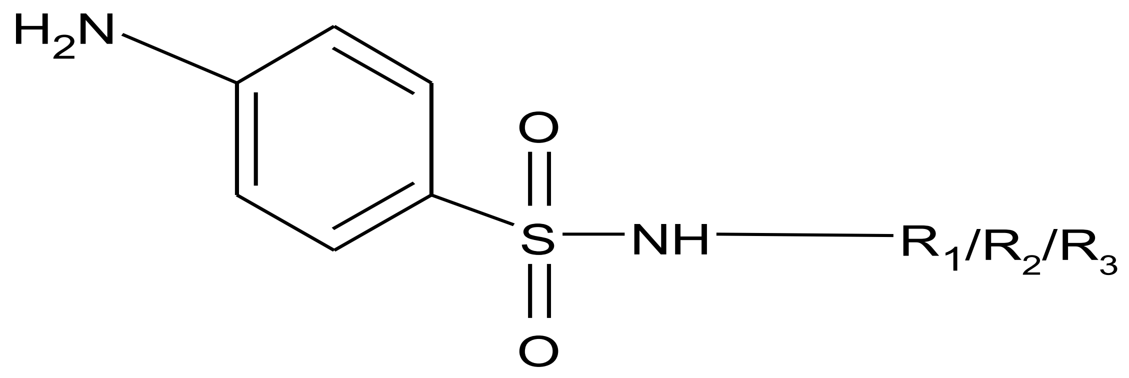
Sulfonamide structures



Sulfonamide 3D structures



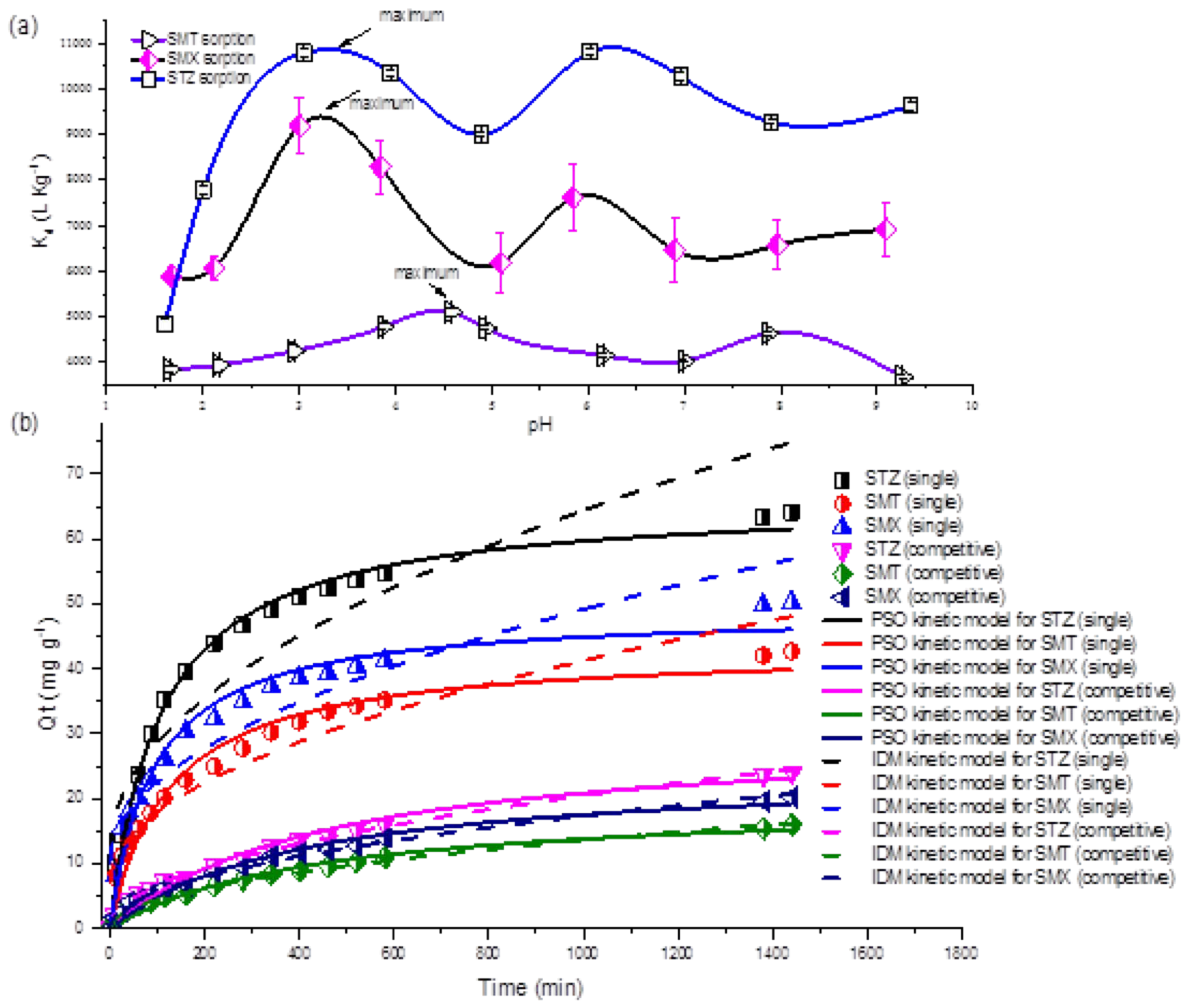
Sulfonamide species



General formula of sulfonamides

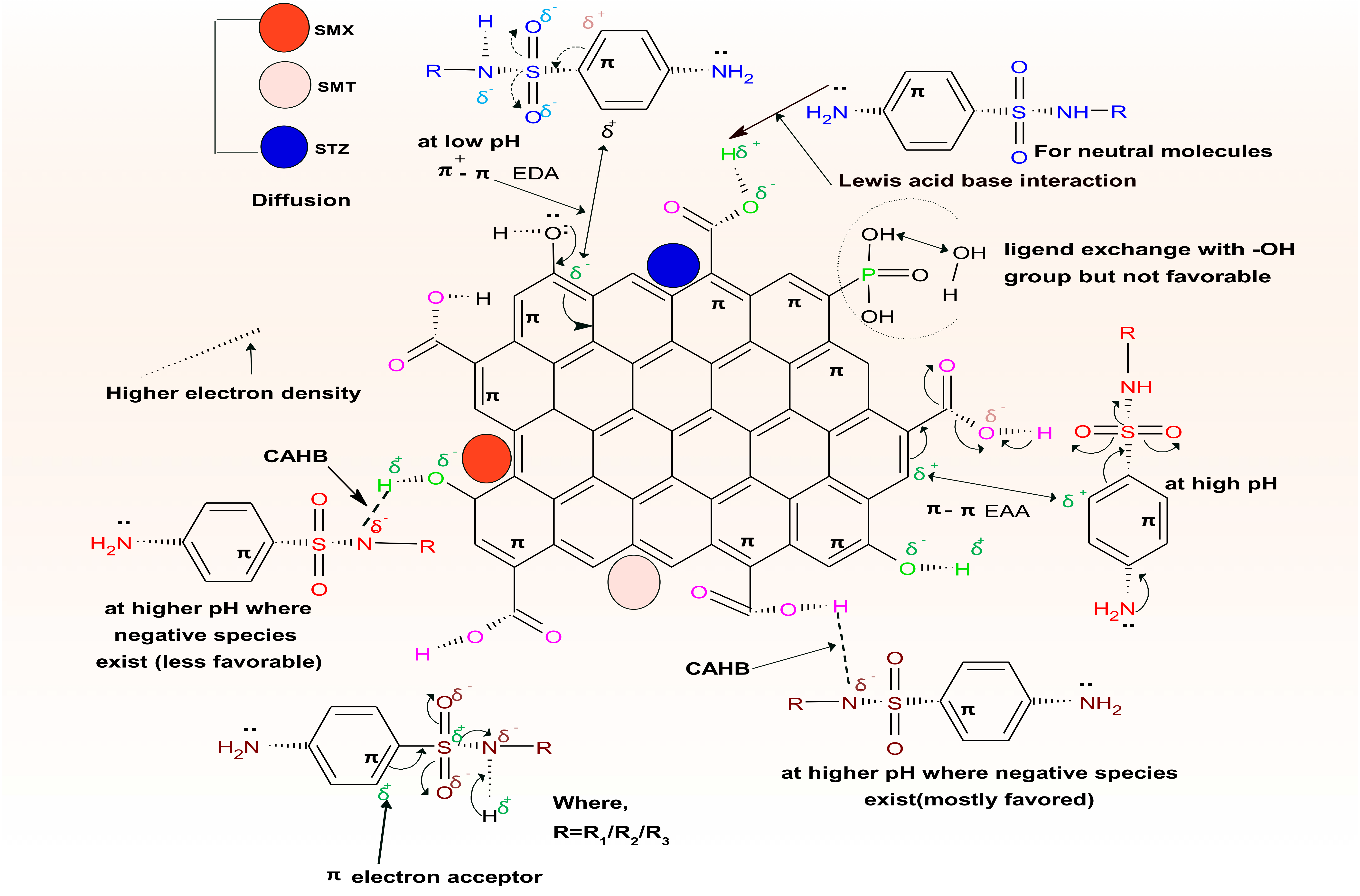
pH Effect on Sorption

- Functionalized biochar can sorb antibiotics in both single and competitive mode
- Sorption capacity for antibiotics was three times higher in single mode than in competitive mode
- Sorption capacity decreases as sulfathiazole > sulfamethoxazole > sulfamethazine
- Solution pH is a significant parameter for removing ionisable sulfonamides
- Sorption is mostly governed by the H-bond formation and π-π interactions

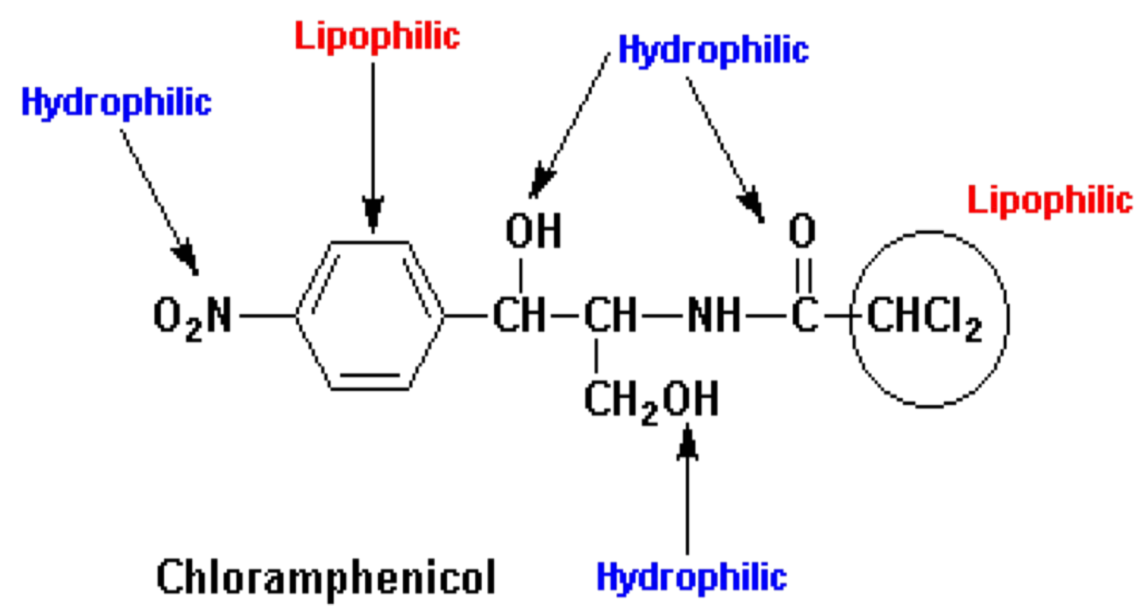


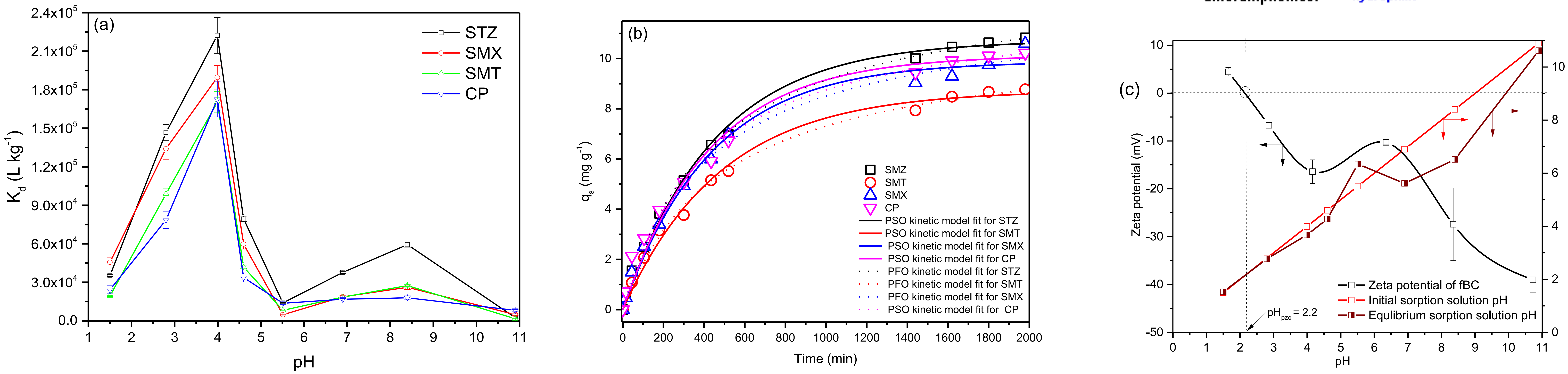
Ahmed et al. (2017) CEJ 311, 348-358

Proposed Sorption Mechanism



Sorption of Chloramphenicol



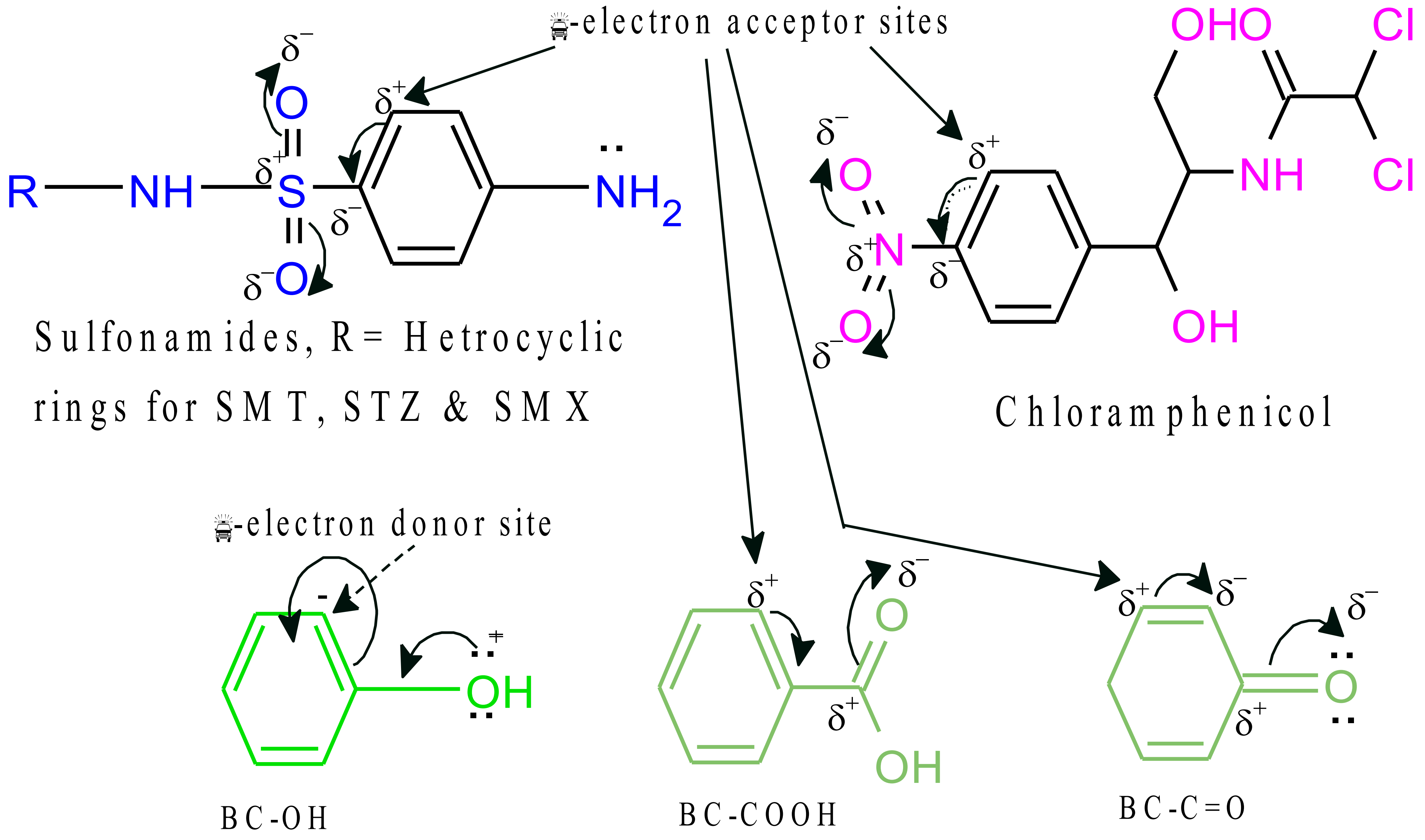


(a) Effect of pH on K_d, (b) Sorption kinetics, (c) zeta potential of functionalized biochar

Ahmed et al. (2017) BT 238, 306-3112

Sorption of Chloramphenicol: Mechanism

Resonance Structures



Sorption Affinity Mechanisms

Competitive Sorption Affinity: STZ> SMX> CP >SMT

At very low pH:

(i). Repulsion interactions

(ii). BC-OH + sulfonamides/CP = EDA interactions

At pH 4.0-4.25:

(i). BC-COO$^-$.....H$^+$....$^-$O$_2$N-chloramphenicol = CAHB formations with EDA interactions

(ii). BC-COO..H + sulfonamides (NHSO$_2$-/NH/ -NH$_2$/CH$_3$) = H-bond formations

At pH above 7.0:

(i). Repulsion interactions

(ii). Sulfonamides-N$^-$+ H$_2$O = sulfonamides-NH + -OH$^+$

(iii). BC-O....H + $^-$N....sulfonamides =BC-O$^-$.....H$^+$....$^-$N..sulfonamides = CAHB

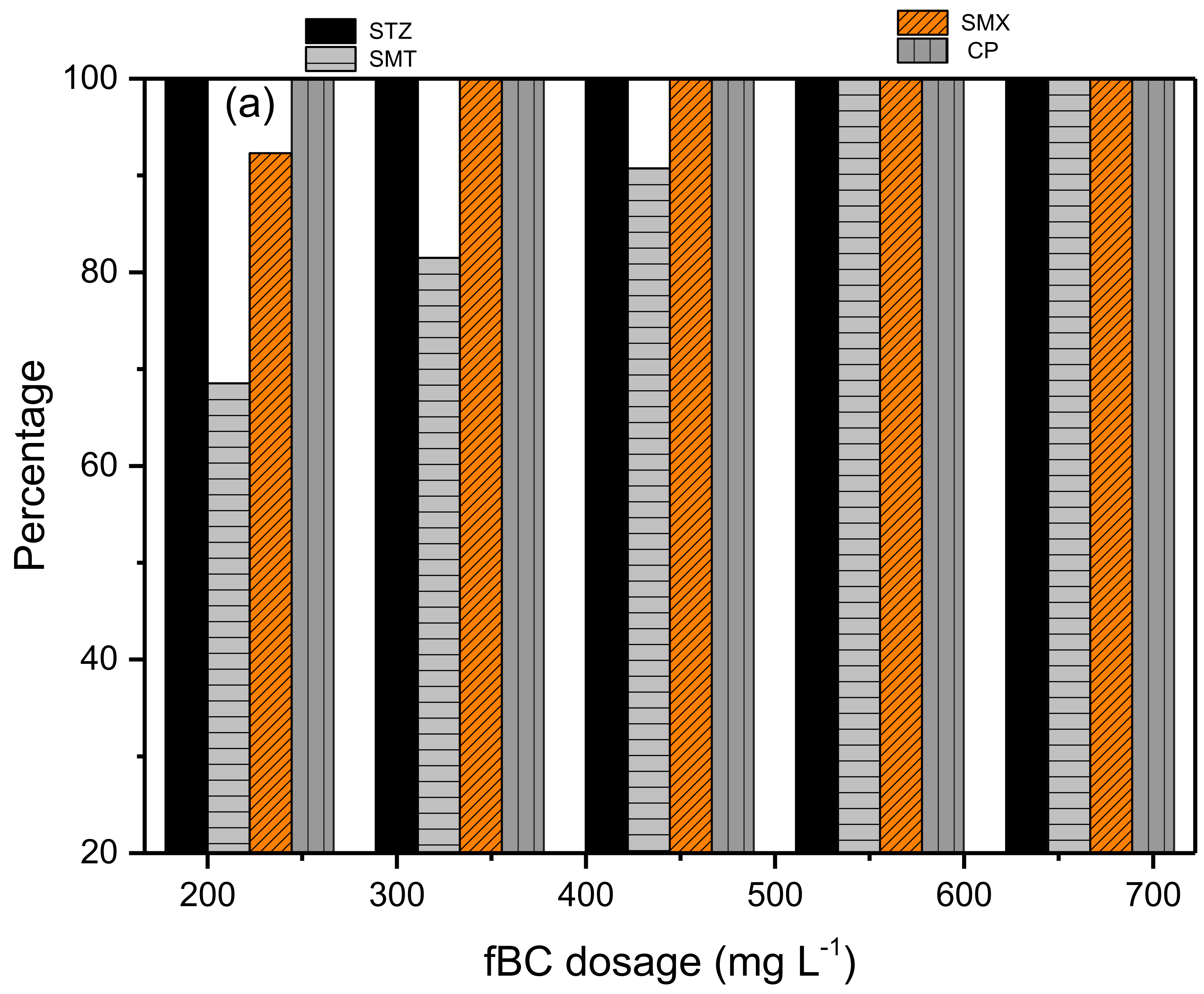
(iv). BC-OH + chloramphenicol (H$^+$/-OH/NO$_2$/-NH-/-Cl) = H-bond formations

Comparative Treatment Trend:

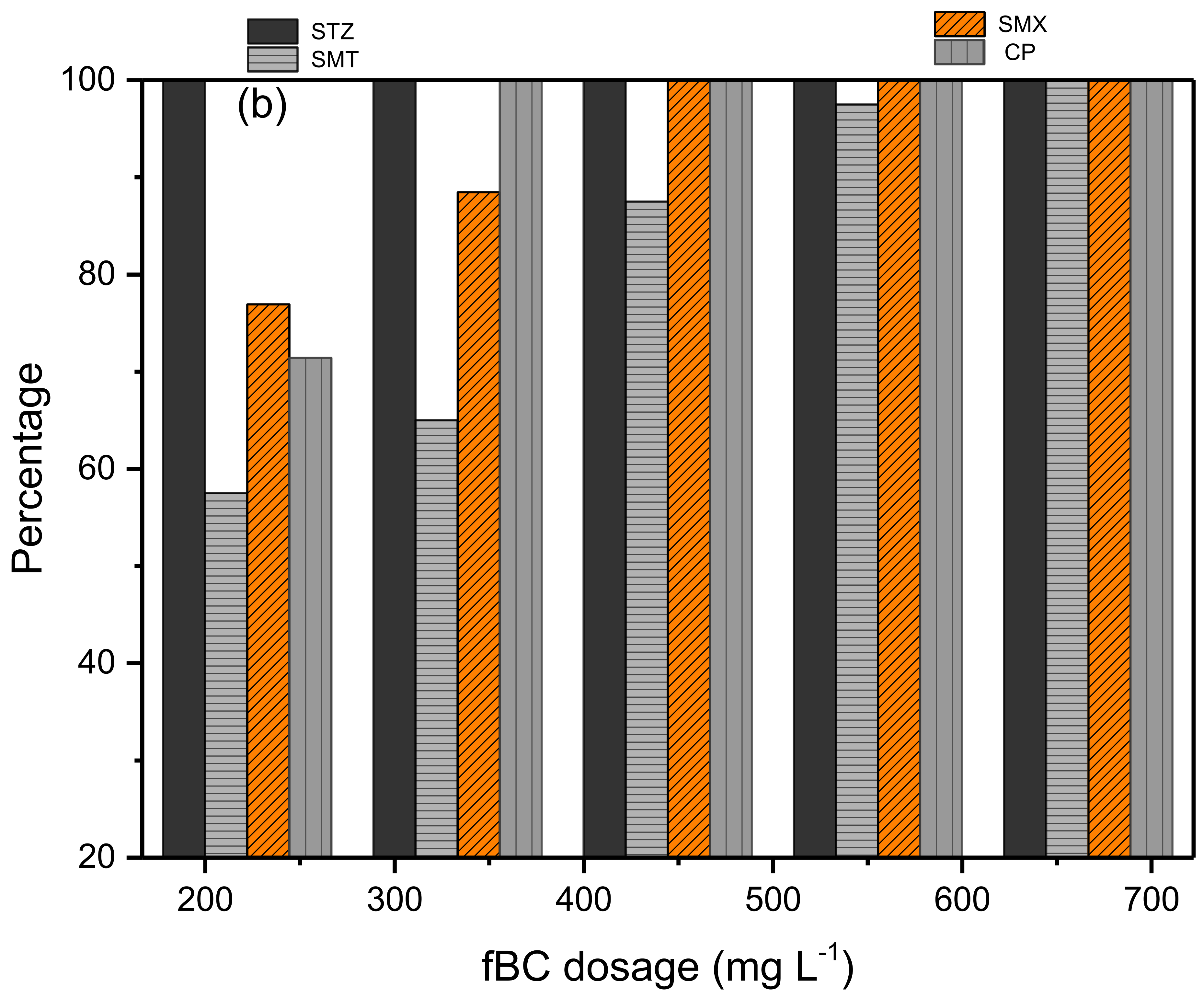
Deionized water> Lake water > Synthetic wastewater

Sorption of Antibiotics in Mixture Mode

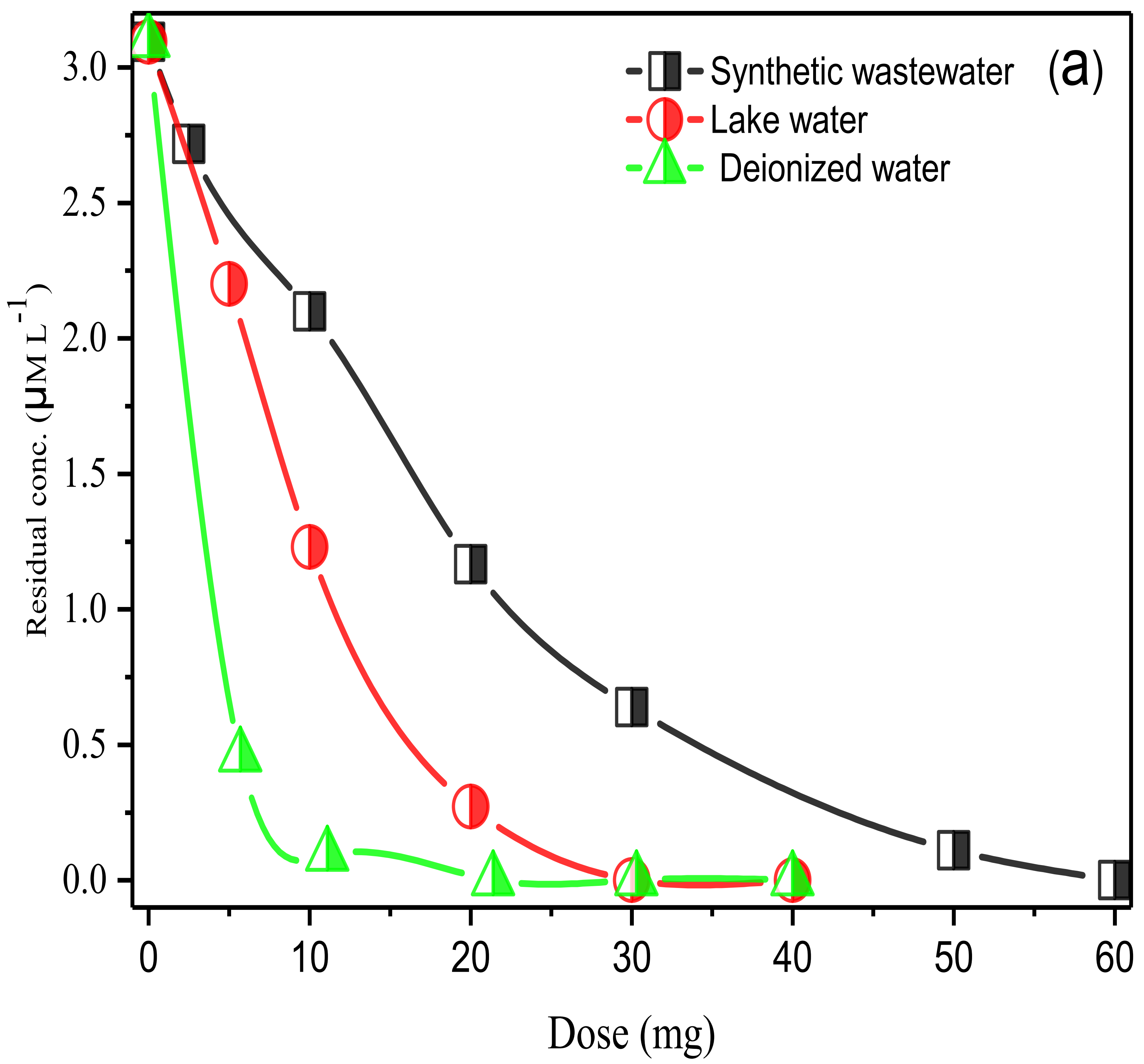
Lake water

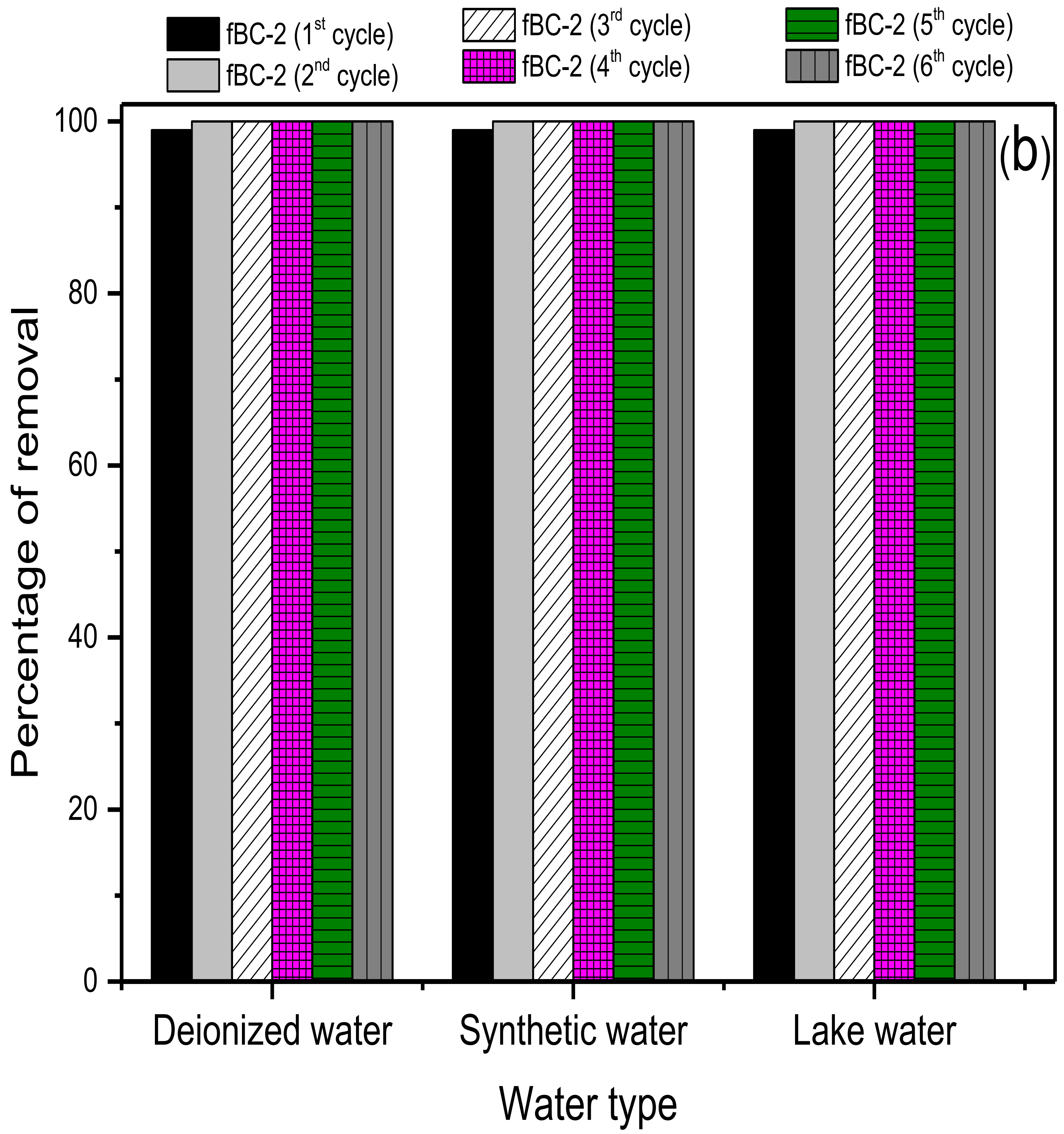


Synthetic wastewater



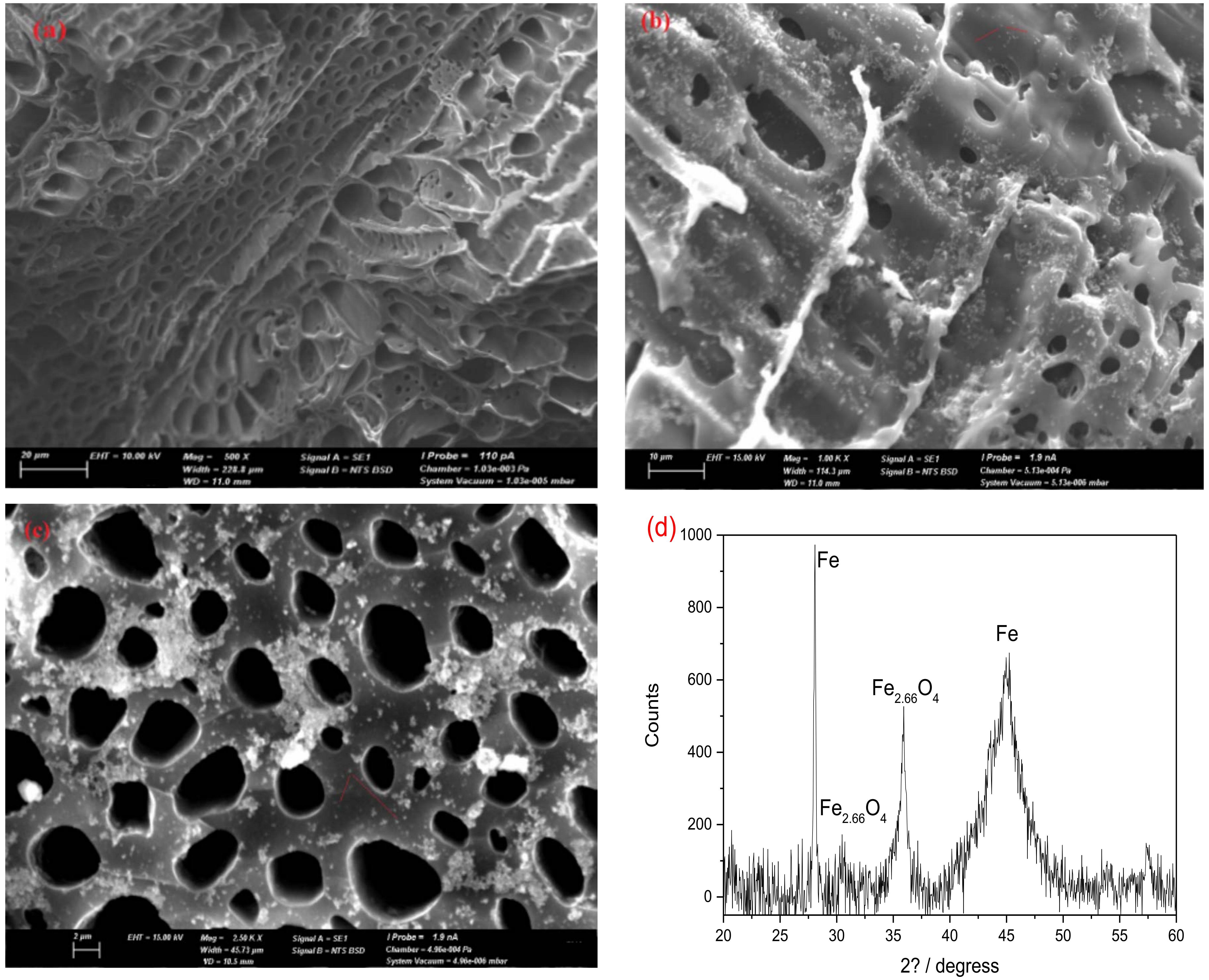
(a) Effects of Sample Composition on Chloramphenicol Sorption
(b) Regeneration of Functionalized Biochar at 300 °C





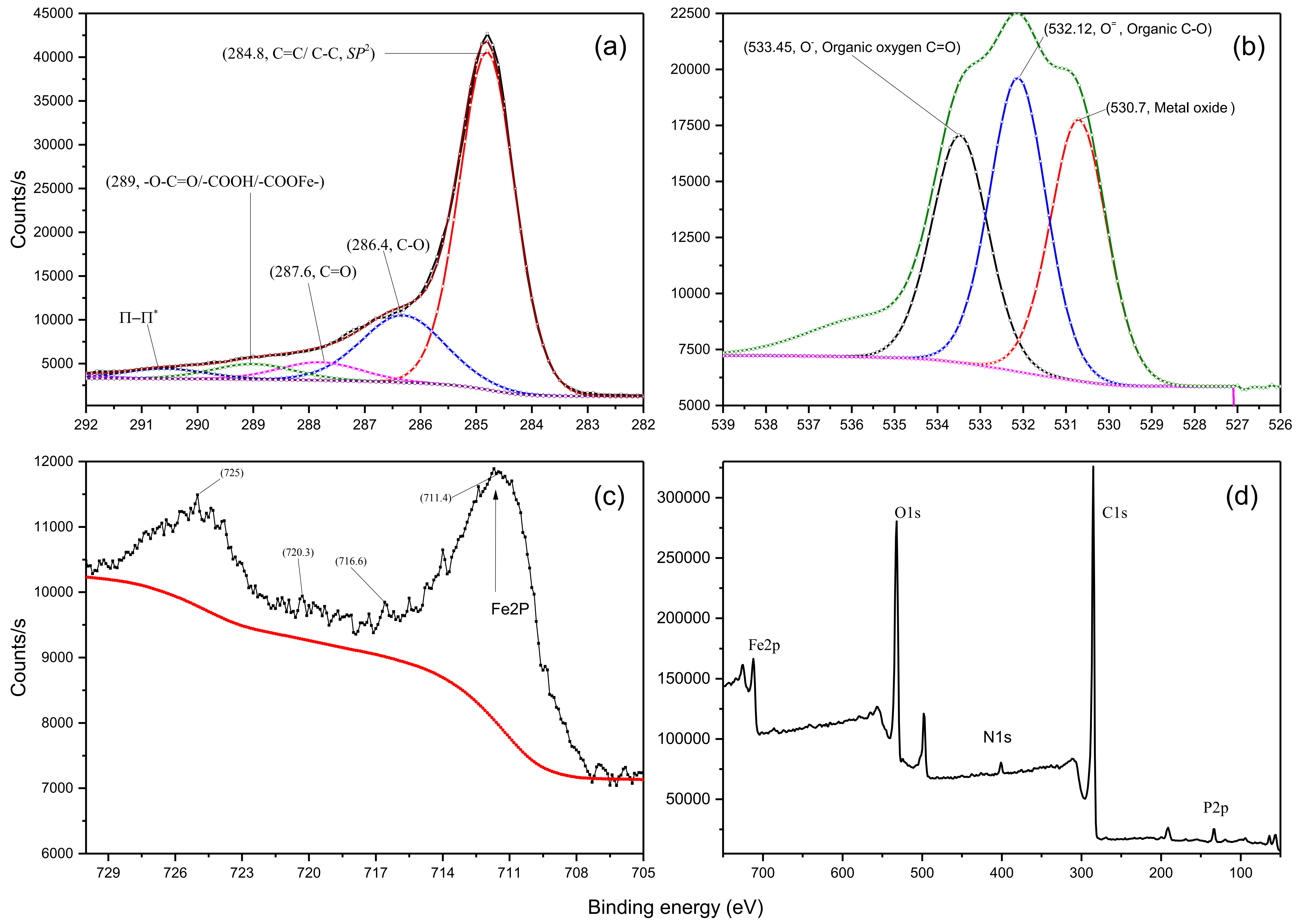
Ahmed et al. (2017) STOTEN 609, 885-895

SEM of fBC, nZVI-fBC and nFe3O4-fBC Composite (a-c) using SEM with energy dispersive spectrometer (EDS) and XRD pattern of nZVI (d).

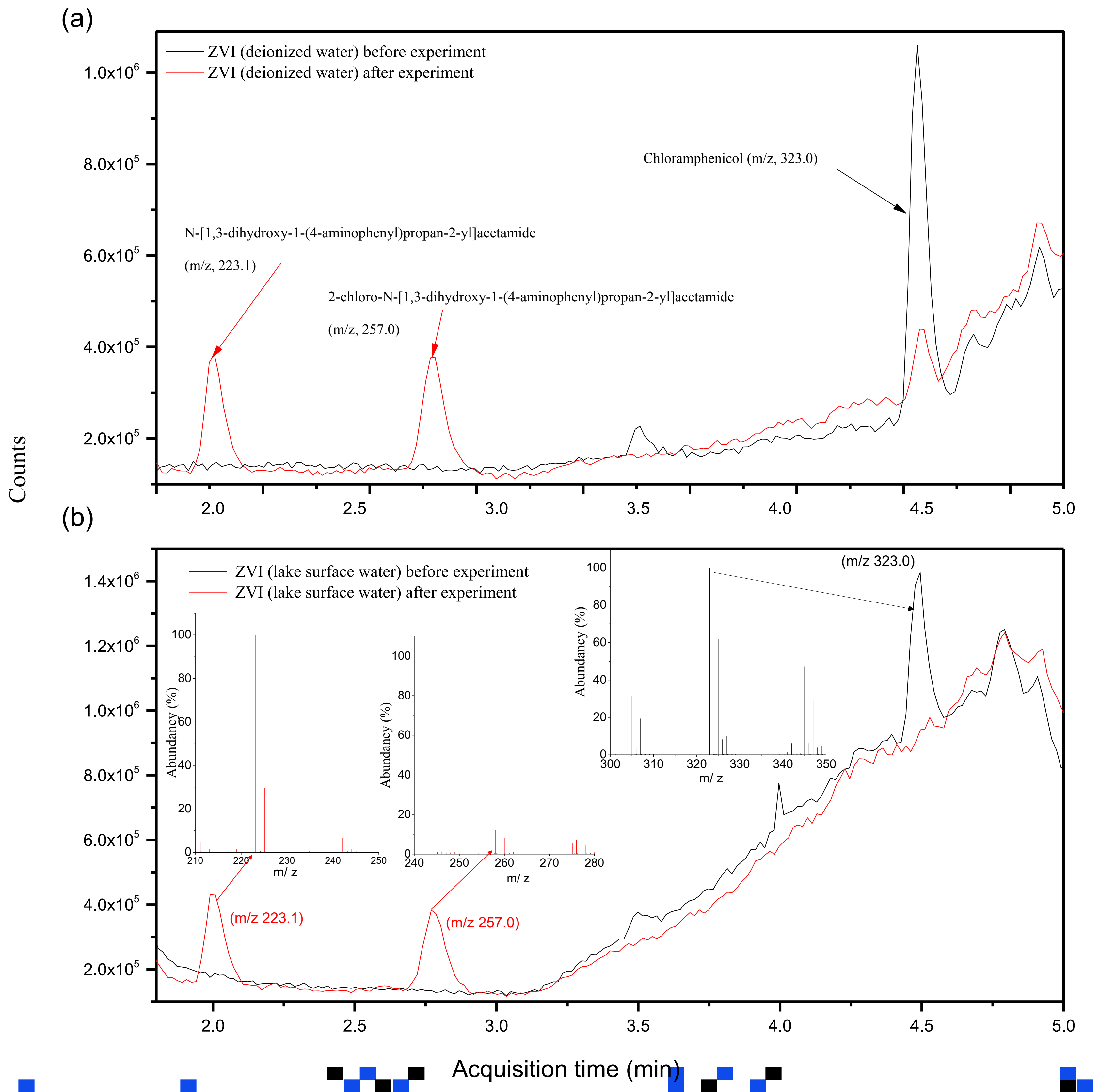


Ahmed et al. (2017) CEJ 322, 571-581

XPS of nZVI-fBC Composite before Sorption Experiments



Chloramphenicol Transformation By-products Identified by Their Retention Times (2.1 min, 2.7 min) by LC-MS/QTOF from Deionized Water (a) and Lake Water (b).

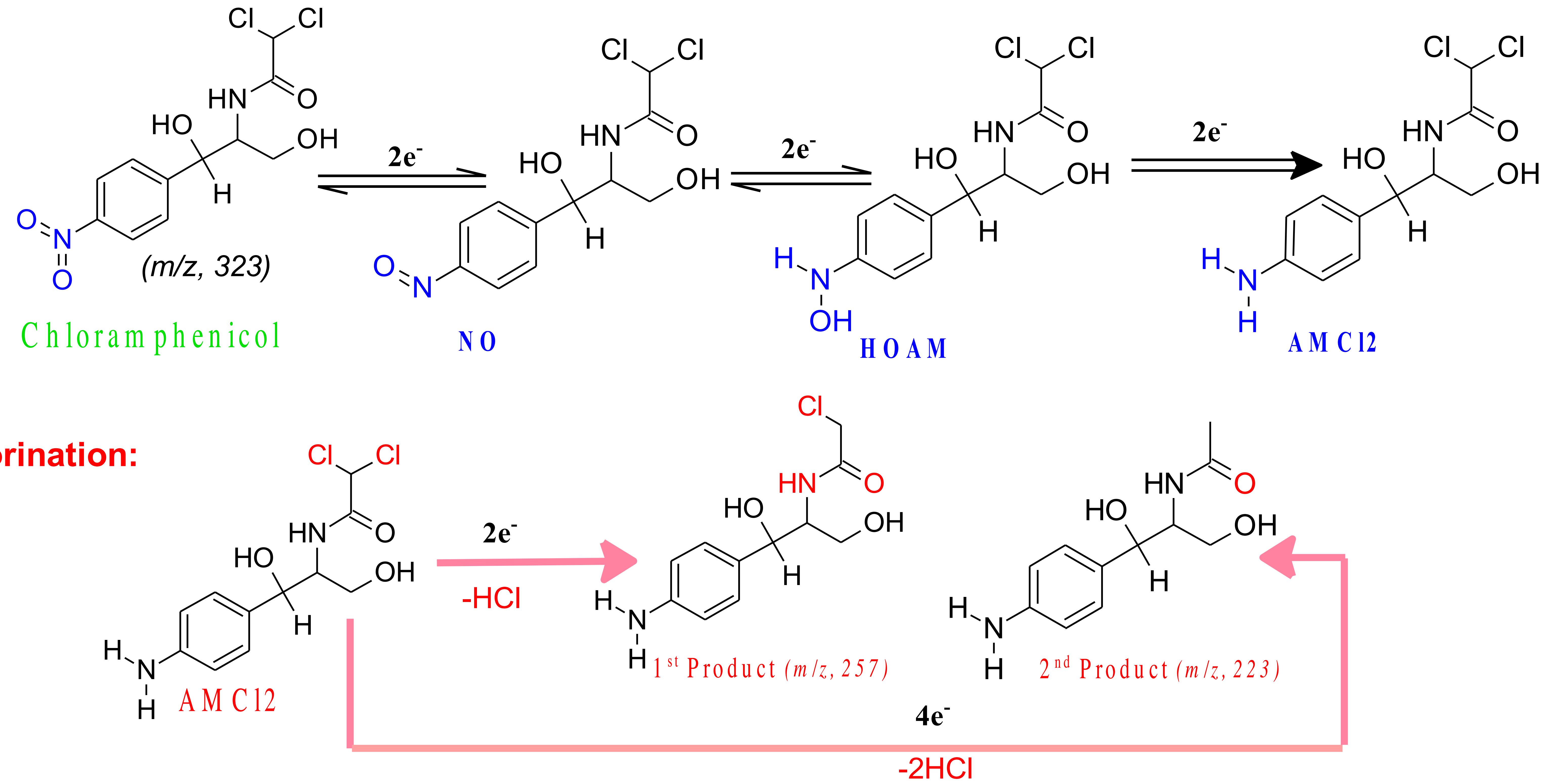


Proposed Reduction and Dechlorination Mechanism for Chloramphenicol from Water and Wastewater

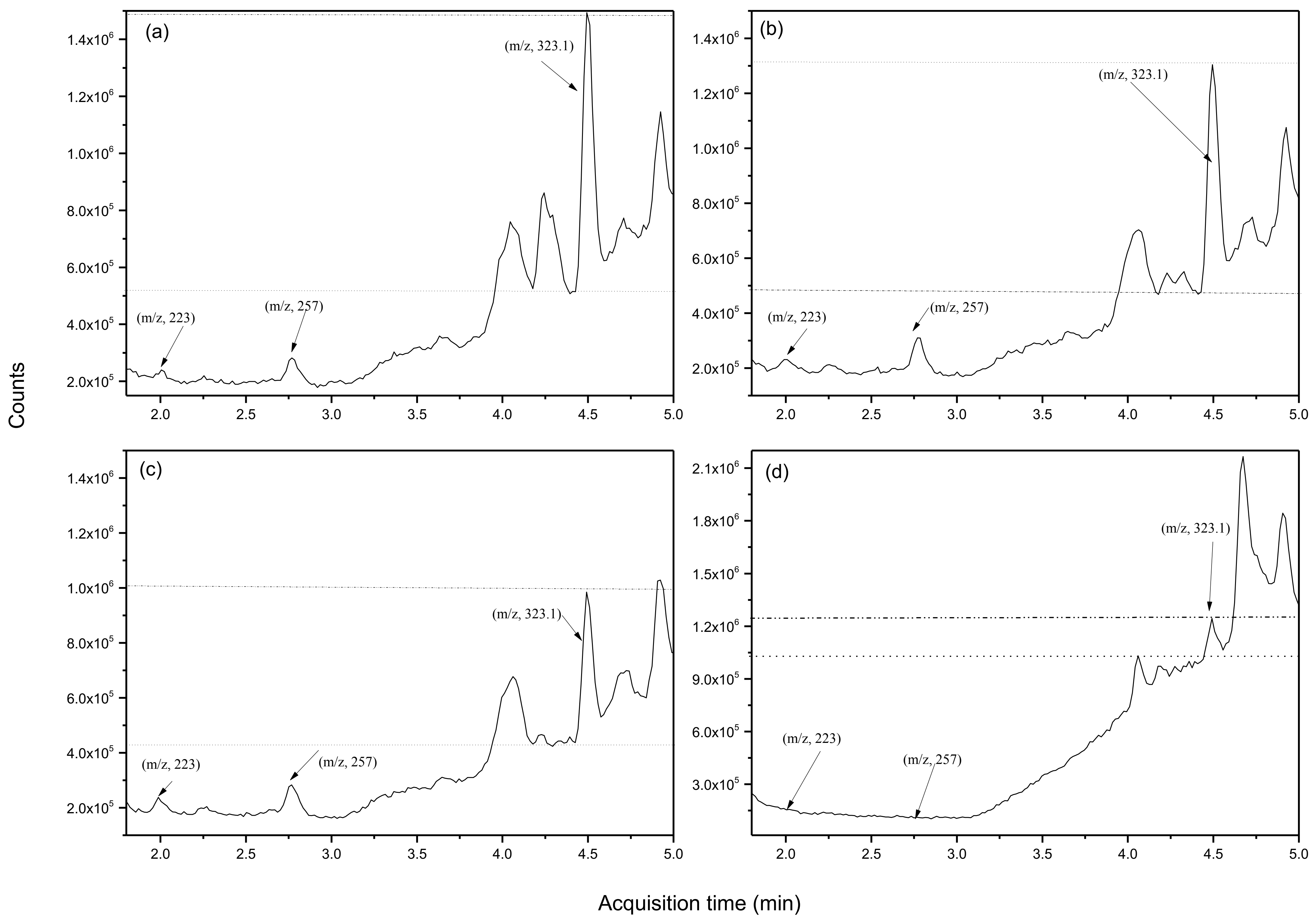
Fe^0 (nZVI)+$2H_2O-2e^-$ ⟶ $Fe^{2+} + 2OH^- + H_2$ & nZVI-fBC composite (unstable) —Transformation⟶ nFe_3O_4-fBC composite (Stable)

Reduction of nitro group:

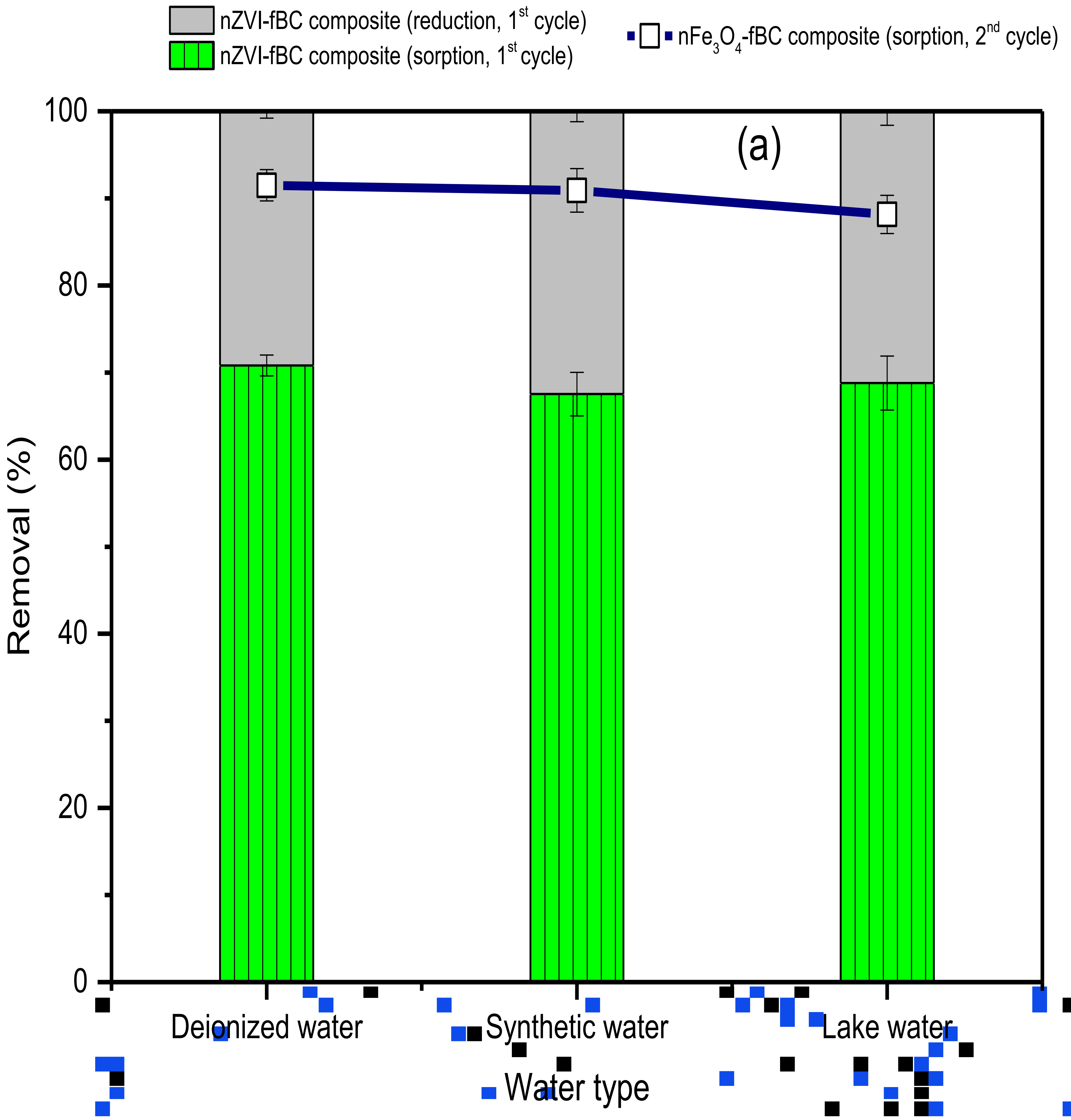
De-chlorination:



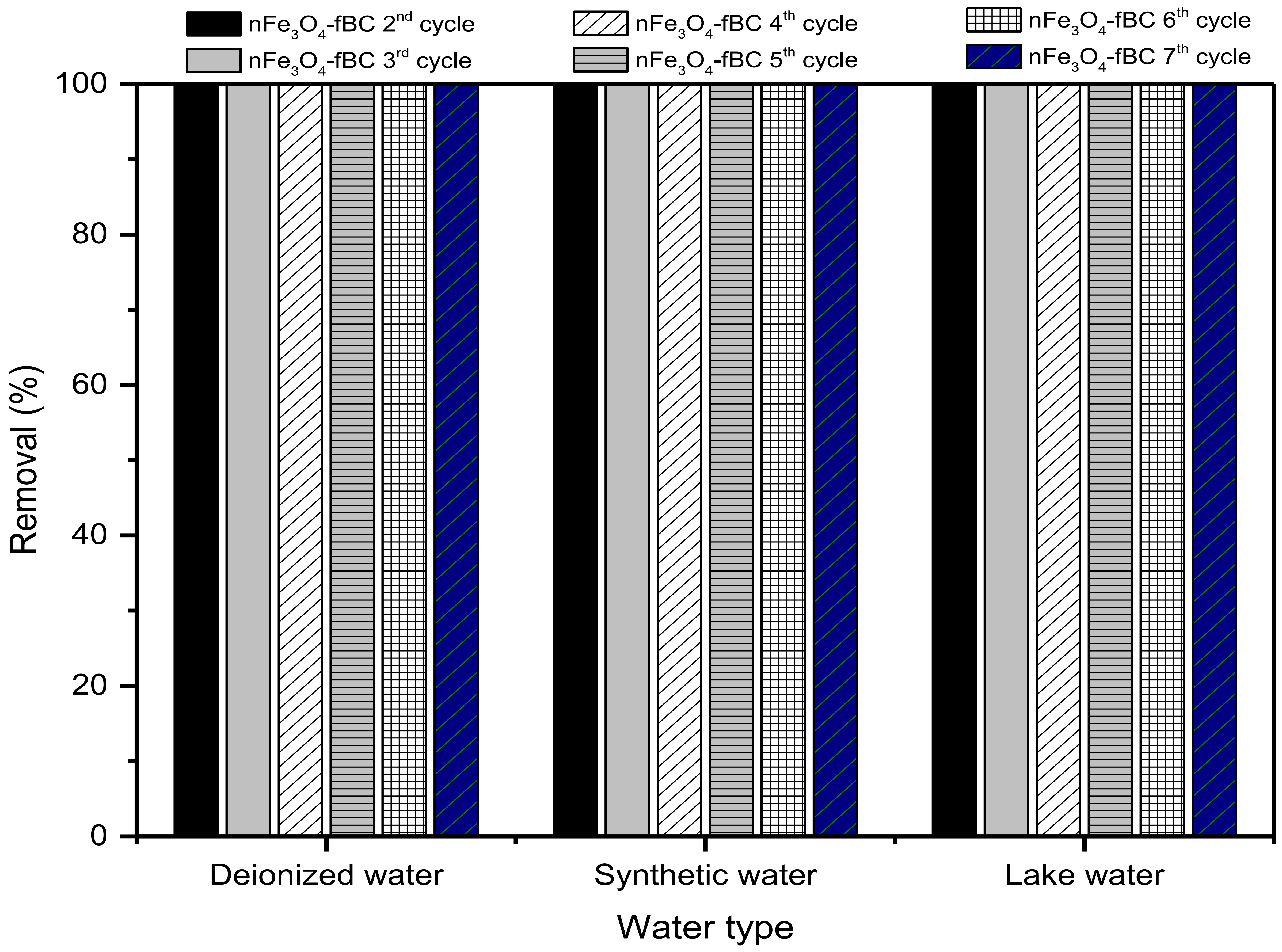
Chloramphenicol Transformation Products Highlighted by Their Retention Times after 10 min (a), 30 min (b), 150 min (c), and 12 h (d) Treatment using nZVI-fBC in synthetic wastewater



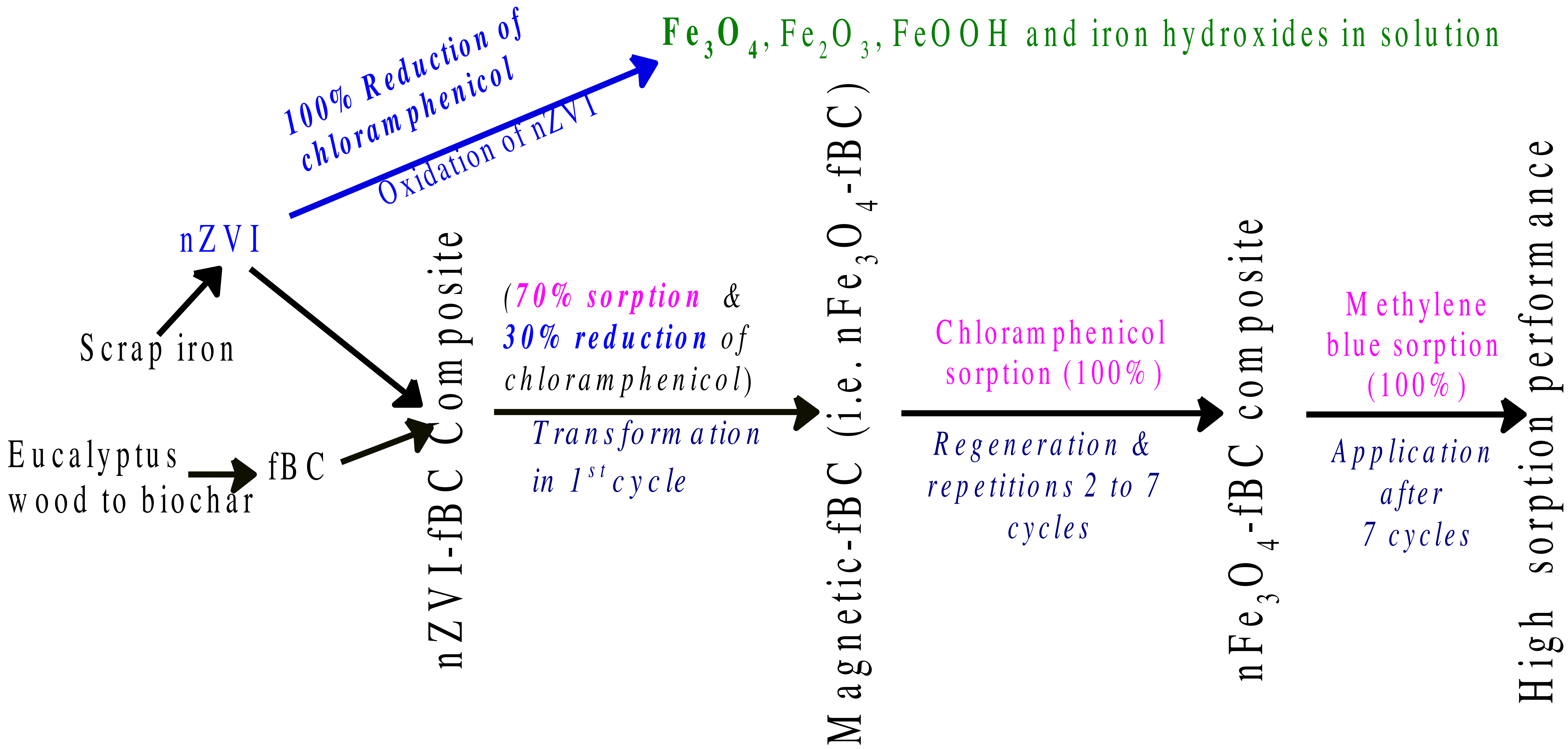
Sorption and Reduction of Chloramphenicol using nZVI-fBC Composite (in the 1st cycle) followed by Sorption onto nFe_3O_4-fBC Composite



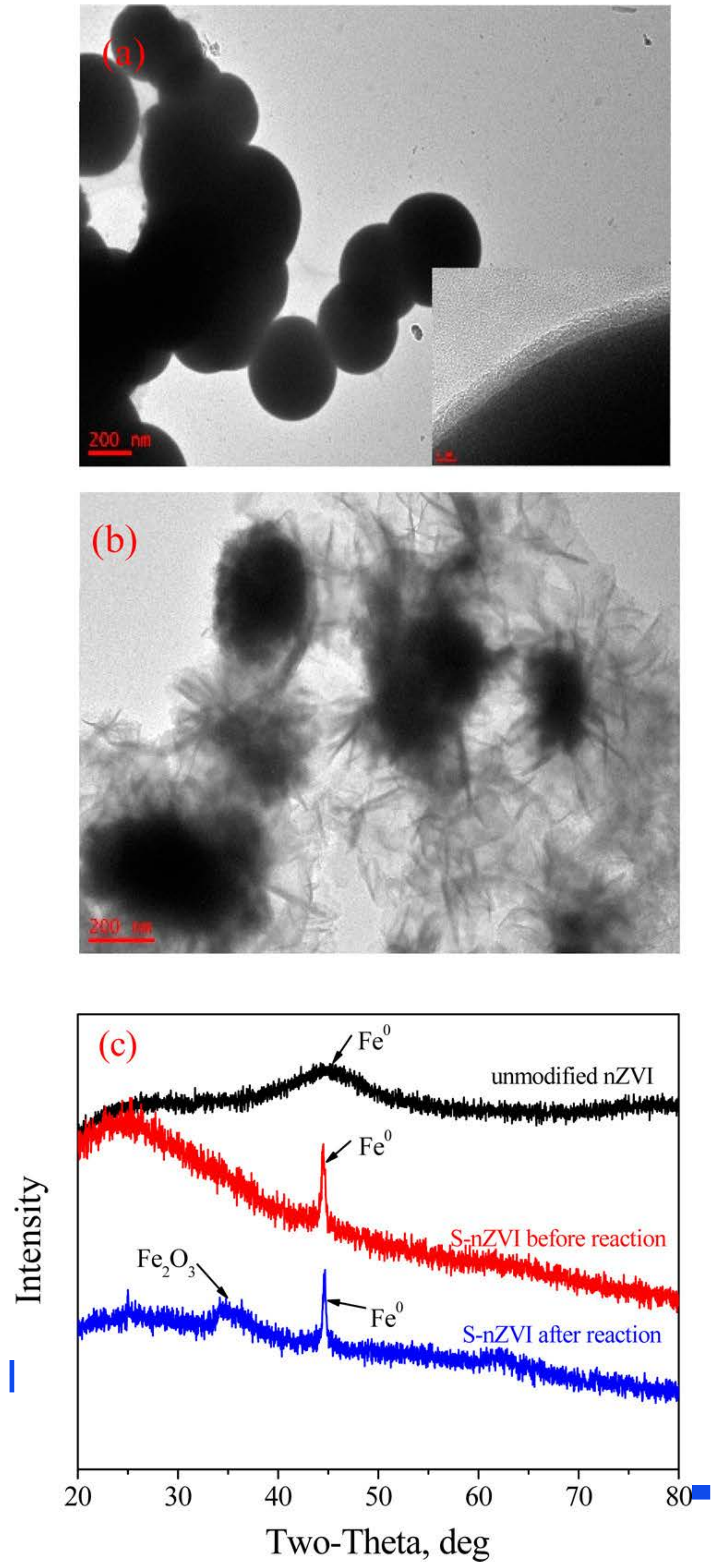
Regeneration of nFe_3O_4-fBC Composite by Methanol for Repetitive Applications (up to 7 cycles) for Chloramphenicol



fBC-nZVI Composite

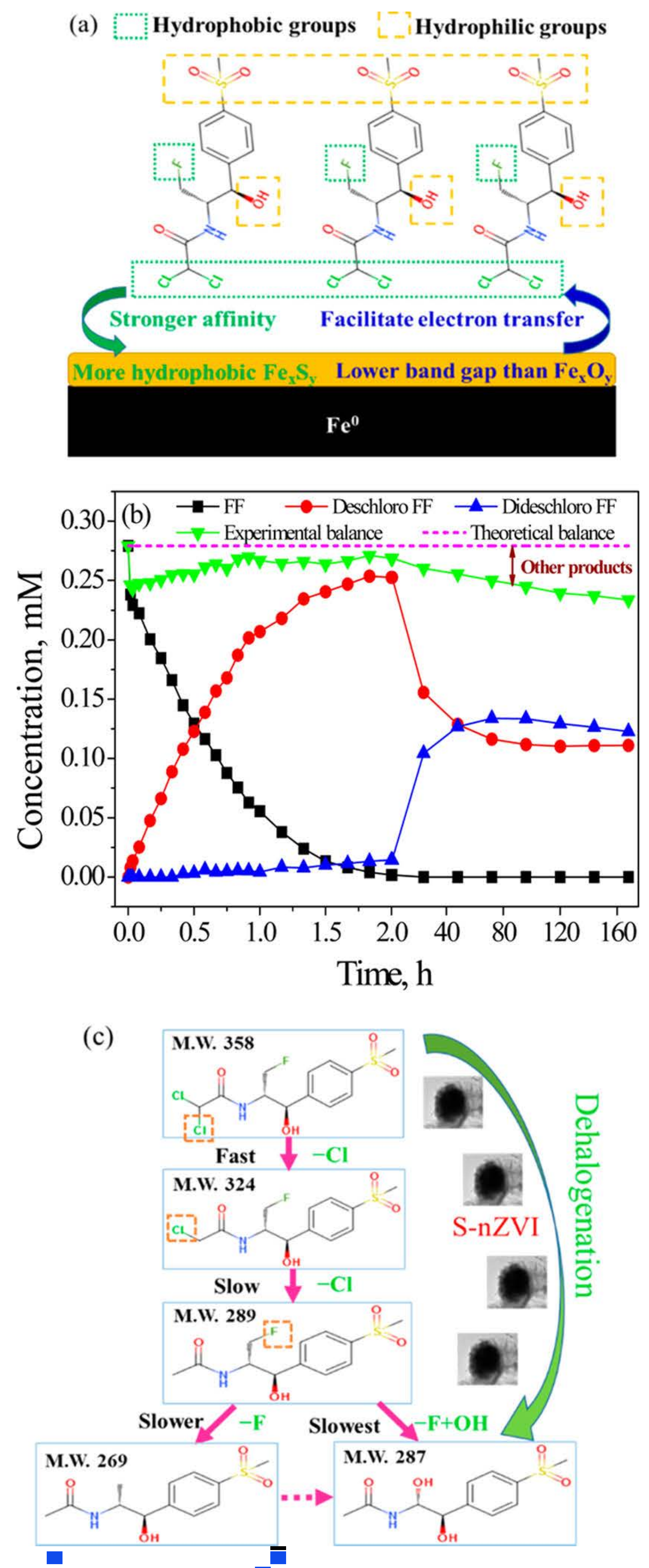


TEM Images of (a) Unmodified nZVI and (b) S-nZVI; and (c) XRD Spectra of Unmodified nZVI and S-nZVI (1.0 g/L nZVI with 0.14 molar ratio of S/Fe)



Cao et al. (2017) EST 51, 11269-11277

Schematic Mechanism of Enhanced Florfenicol (FF) Removal by S-nZVI, (b) Mass Balance of FF and Dechlorinated FF during reaction, and (c) Pathway of FF Removal



Conclusions

1. Antibiotic residues in the environment are of global concern due to potential adverse effects e.g. inducing antibiotic resistance genes.
2. Functionalized biochar has been prepared with significant capacity for the removal of antibiotic residues from water and wastewater.
3. H-bond formation, π-π electron donor acceptor and electrostatic interactions were the main sorption mechanisms at different pH.
4. Functionalized biochar is effective in immobilizing nZVI to form composite which can sorb and reduce antibiotic compounds.
5. Future research is needed to develop novel biochar-based composite materials for enhanced sorption and reduction capabilities, and with regeneration potential.

Thank you for listening !

Questions?