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Factors affecting sorption of halogenated phenols to polymer/biomass-derived biochar: Effect of pH, hydrophobicity, and deprotonation

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Biochar production in South Korea

- Since 2013, approximately 15% of biosolids (~1,000 ton/d) from WWTFs have been disposed via pyrolysis/carbonization.




- Biosolid biochar is being used for supplementary fuels for local power plants.
- One commercial biochar is available from Kyungdong Agro. Co.

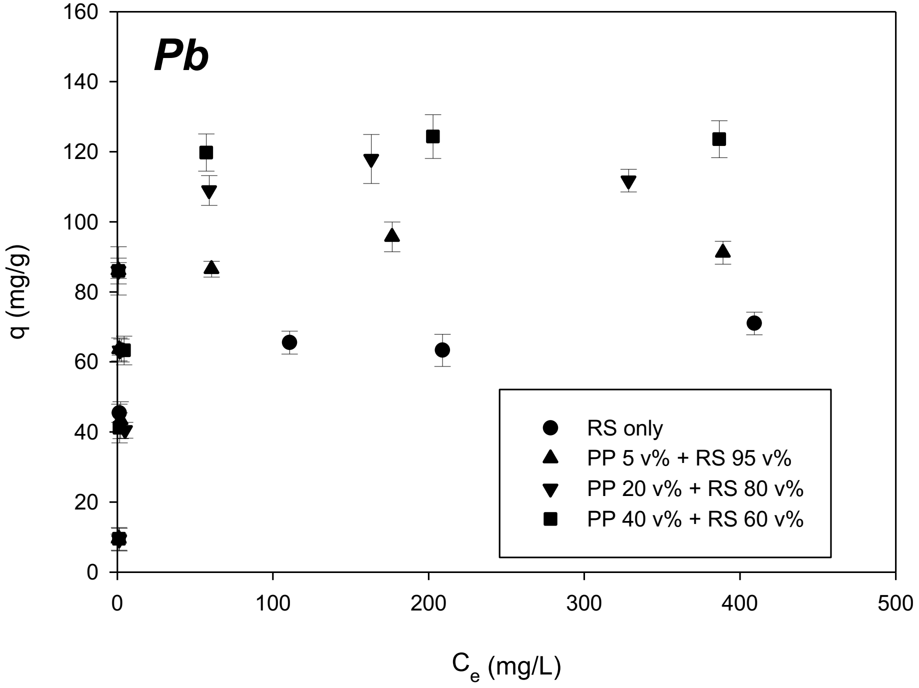
Polymer wastes: plastics

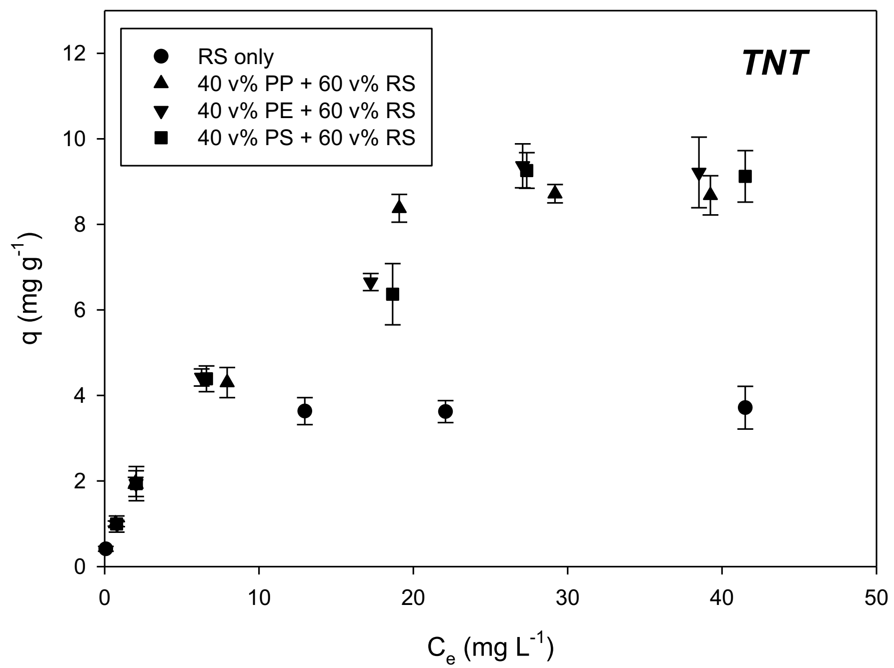
- Used in everyday life
- Global plastic production: 264 million tons (2010)
- In South Korea,
  - Plastic/polymer wastes generation: 6000 tons/day (2014)
  - About 60% recycling
- Resistant to biodegradation
- Final disposal: incineration and landfilling
- Pyrolysis of plastic wastes: pyrolysis oil and gas

Co-pyrolysis of polymer and biomass wastes

- Significantly improves the quality of bio-oil due to the synergistic effect of the high content of carbon and hydrogen in the polymers.
- Increases yield of bio-oil and higher heating values.
- Reduces acidity, density, and oxygen content.
- Studies on char produced from co-pyrolysis of biomass and polymers were limited.

Chars co-pyrolyzed with biomass and polymer wastes





(Oh and Seo, 2016, BT; Oh et al., 2018, JEQ)

Co-pyrolysis of polymer and biomass wastes

- Co-pyrolysis of polymer and biomass wastes improved the properties of biochar.

- Increasing carbon content and the development of surface functional groups significantly enhanced the sorption capacity of NACs and Pb on polymer/rice straw (RS)-derived biochar.

Can ionizable aromatic compounds be sorbed to polymer/RS-derived biohars more effectively?

Hypothesis

- Polymer/RS-derived biochar may promote the sorption capacity of halogenated phenols through various sorption mechanisms and that some factors may significantly affect the sorption of halogenated phenols onto polymer/RS-derived biochar.

Objectives

• To synthesize polymer/RS-derived biochar.

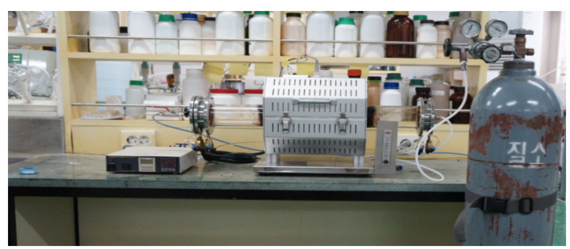
• To investigate the sorption of halogenated phenols onto polymer/RS-derived biochar.

• To examine affecting factors such as pyrolysis temperature, number of chlorinated functional groups, equilibrium pH, competition among halogenated phenols, and dissolved metals.

Biochar production

- Biomass: rice straw (RS)
- Polymers: polypropylene (PP), polyethylene (PE), polystyrene (PS)
- Mixing ratio of polymer:RS = 40:60 v/v

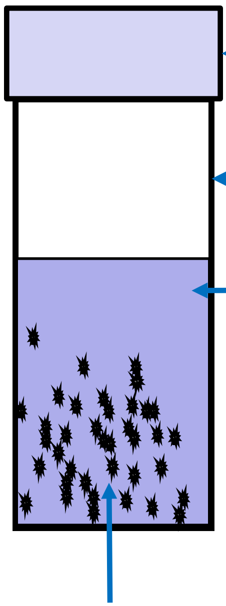
Rice straw



Co-pyrolysis
(550-900 ^{o}C, 4 h,
under N_2 at 1000 cc/min)

Biochar

Batch experiments



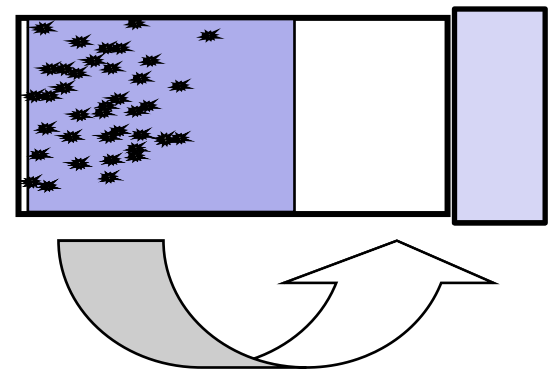
Screw cap

40-mL vial

20 mL of solution including,
1) Halogenated phenols: TCP/DCP/DFP/DBP/4CP/2CP/phenol
2) Initial conc.: 25-800 mg/L
3) pH 7.4/4.7 (HEPES/acetate)

Polymer/RS-derived biochar (0.1-5.0 g)

Duplicates
Control without sorbents



- At 25 ^{o}C
- 180 rpm shaking
- Duplicate sampling
- Equilibrium time: 24 h
- Filtration: 0.025-µm cellulose membrane filter
- Chemical analysis: HPLC (Ultimate®3000, Dionex)

Properties of polymer/RS-derived biochar

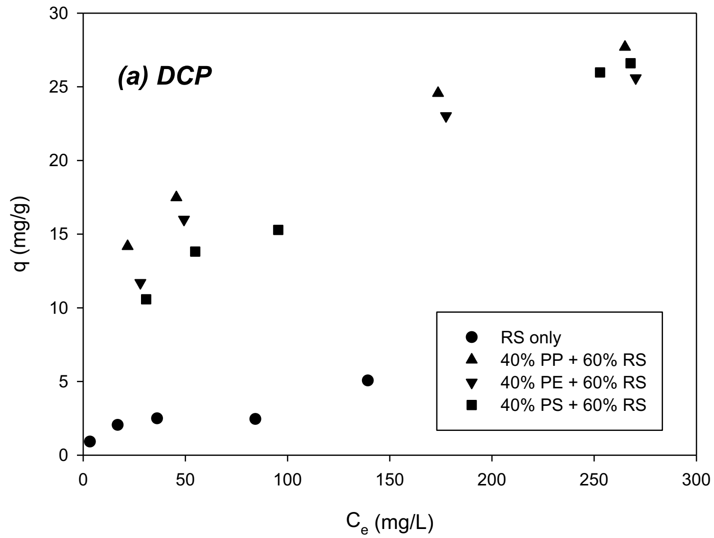
Polymer Type	Polymer Content Before Pyrolysis (v.%)	Pyrolysis Temp. (ºC)	pH	BET SA (m^2/g)	CEC (cmol/kg)	PZC	Elemental Contents (%)			
							C	H	O	N
-	0	550	9.12	16.4	77.5	8.4	55.8	2.88	13.1	2.02
PE	40	550	10.4	25.7	260	10.4	57.7	2.13	6.64	0.52
PS	40	550	10.5	20.0	191	9.8	58.1	1.56	4.71	0.54
PP	40	550	11.1	27.5	321	9.7	57.9	2.10	7.43	0.54
	40	700	11.1	33.6	99.9	9.8	56.8	1.55	6.46	0.40
	40	900	11.4	34.8	98.9	10.0	56.6	0.75	5.14	0.37

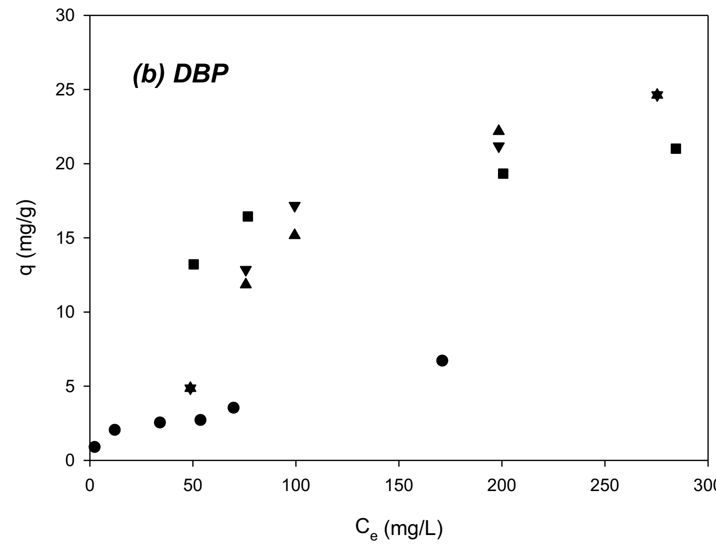
Properties of halogenated phenols

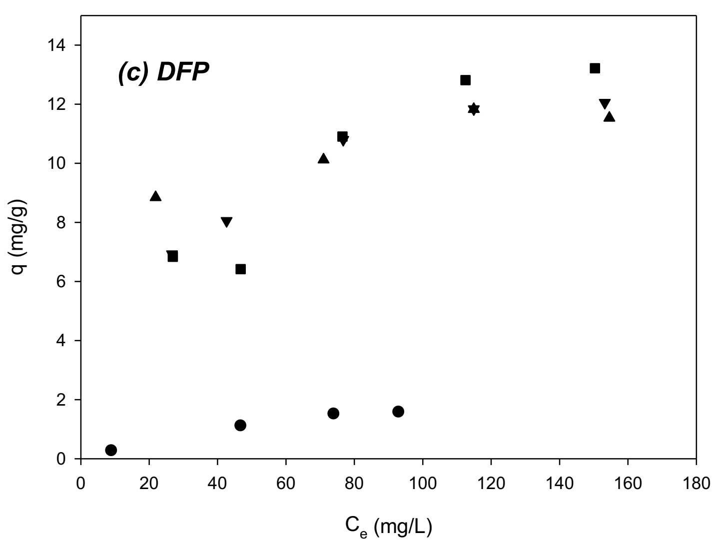
Name	Chemical Formula	Molecular Weight	$logK_{ow}$	pK_a	Water Solubility (mg/L)
2,4,6-trichlorophenol (TCP)	$C_6H_3Cl_3O$	197.45	3.69	6.23	800
2,4-dichlorophenol (DCP)	$C_6H_4Cl_2O$	163.0	3.20	7.90	4500
2-chlorophenol (2CP)	C_6H_5ClO	128.56	2.15	8.48	28500
4-chlorophenol (4CP)	C_6H_5ClO	128.56	2.39	9.41	24000
2,4-dibromophenol (DBP)	$C_6H_4Br_2O$	251.9	3.22	7.79	1900
2,4-difluorophenol (DFP)	$C_6H_4F_2O$	130.09	1.91	8.72	8109
Phenol	C_6H_6O	94.11	1.46	9.95	82800

Sorption to polymer/RS-derived biochar:

Types of halogenated functional groups



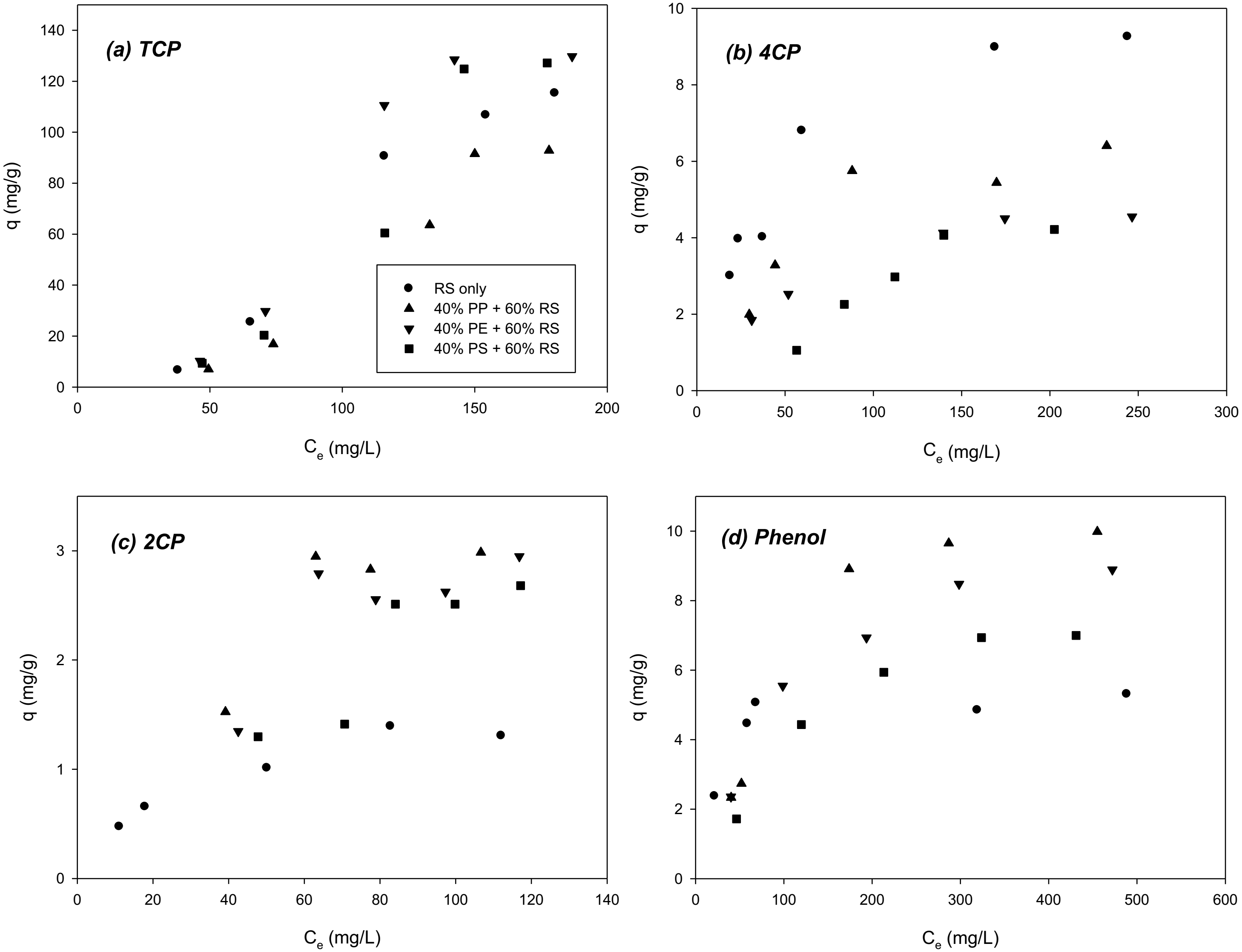




- Log K_{ow}(pH) of DCP, DBP, and DFP = 2.71, 2.83, and 0.26
- Equilibrium pH of RS- and polymer/RS-derived biochars = 9.1 and 10.1-10.3
- PZC of RS- and polymer/RS-derived biochars = 8.4 and 9.7-10.4

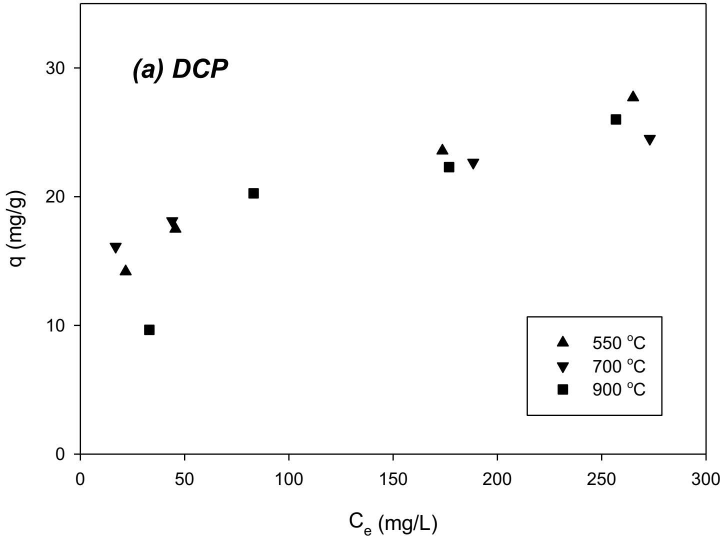
Sorption to polymer/RS-derived biochar:

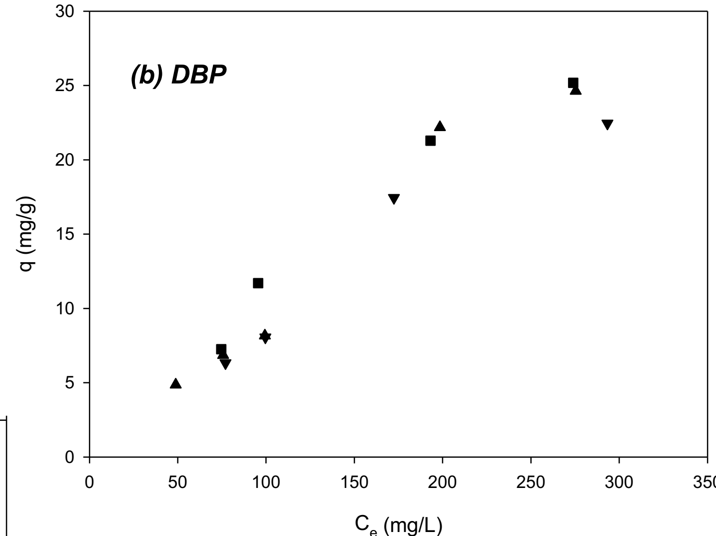
Numbers of chlorinated functional groups

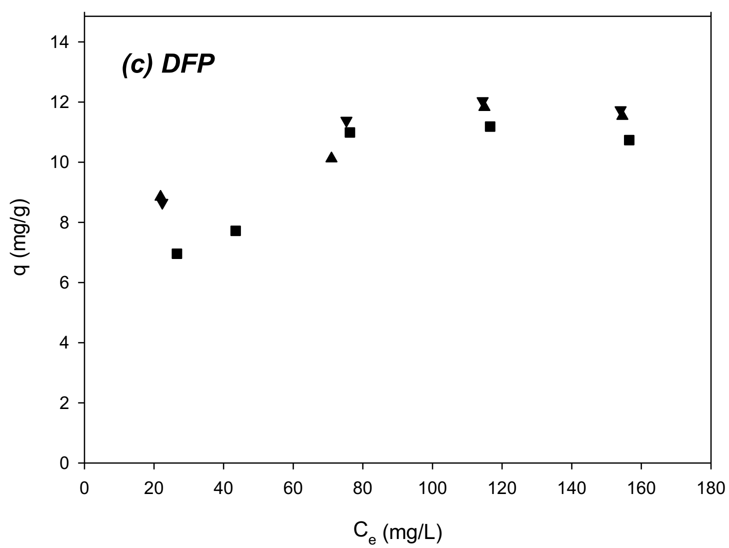


- Log K_{ow}(pH) and pK_a of TCP = 3.67 and 6.23
- Log K_{ow}(pH) and pK_a of 4CP = -0.12 and 9.41
- Log K_{ow}(pH) and pK_a of 2CP = 0.89 and 8.48
- Log K_{ow}(pH) and pK_a of phenol = -1.32 and 9.95

Effect of pyrolysis temperature:
PP/RS-derived biochar



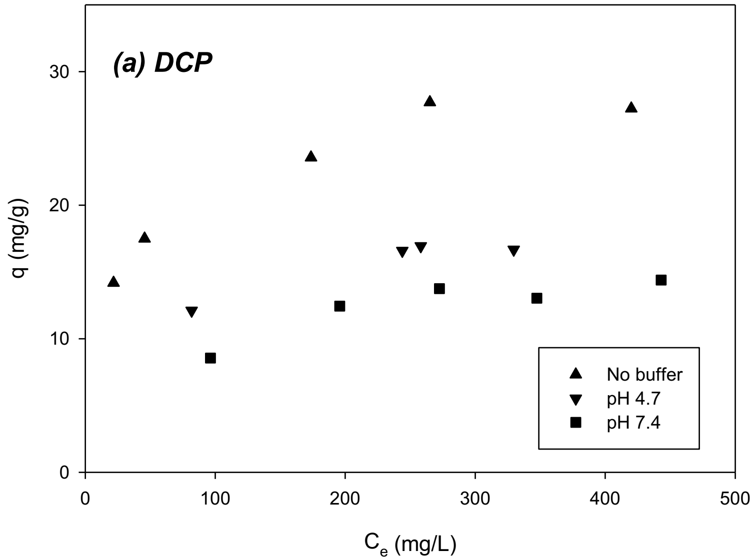


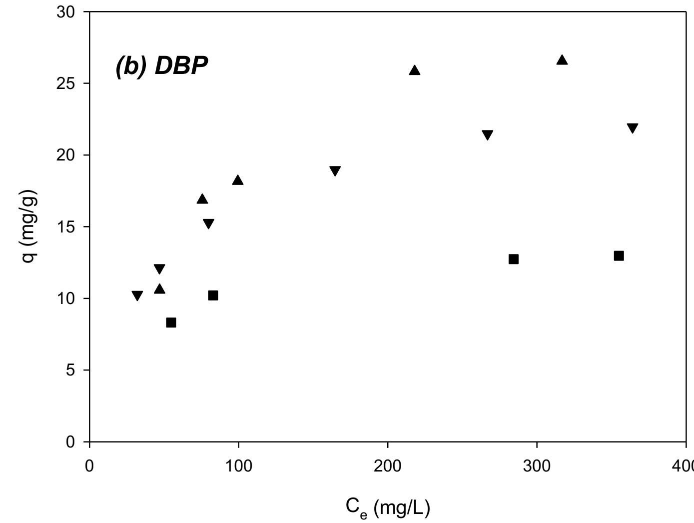


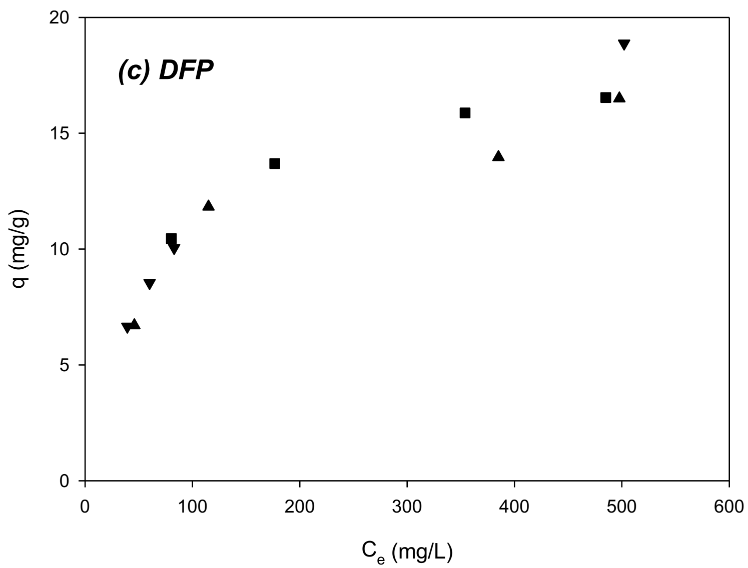
Hydrophobicity
vs. aromaticity (EDA interactions)

Effect of pH:

PP/RS-derived biochar



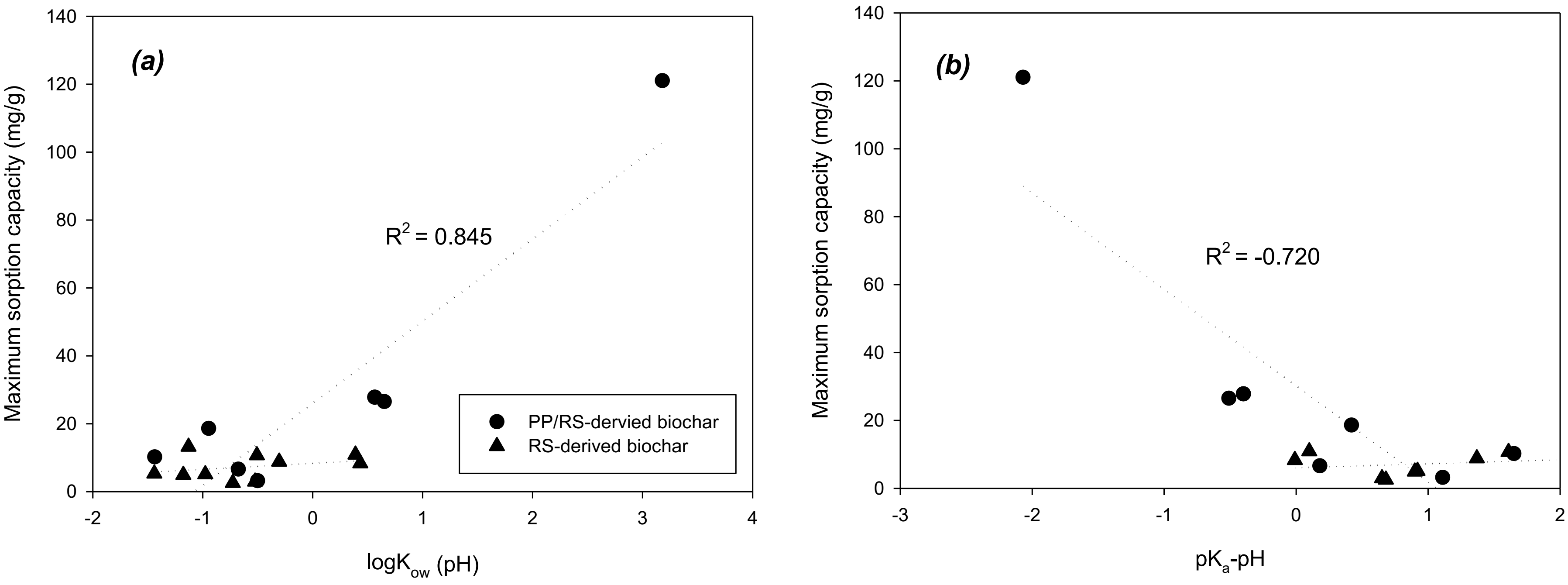




- $\log K_{ow}(pH)$ of DCP at pH 10.0, 7.4, and 4.7 = 2.71, 0.33, and 0.30
- $\log K_{ow}(pH)$ of DBP at pH 10.0, 7.4, and 4.7 = 2.83, 0.36, and 0.32
- $\log K_{ow}(pH)$ of DFP at pH 10.0, 7.4, and 4.7 = 0.26, -0.99, and -0.98

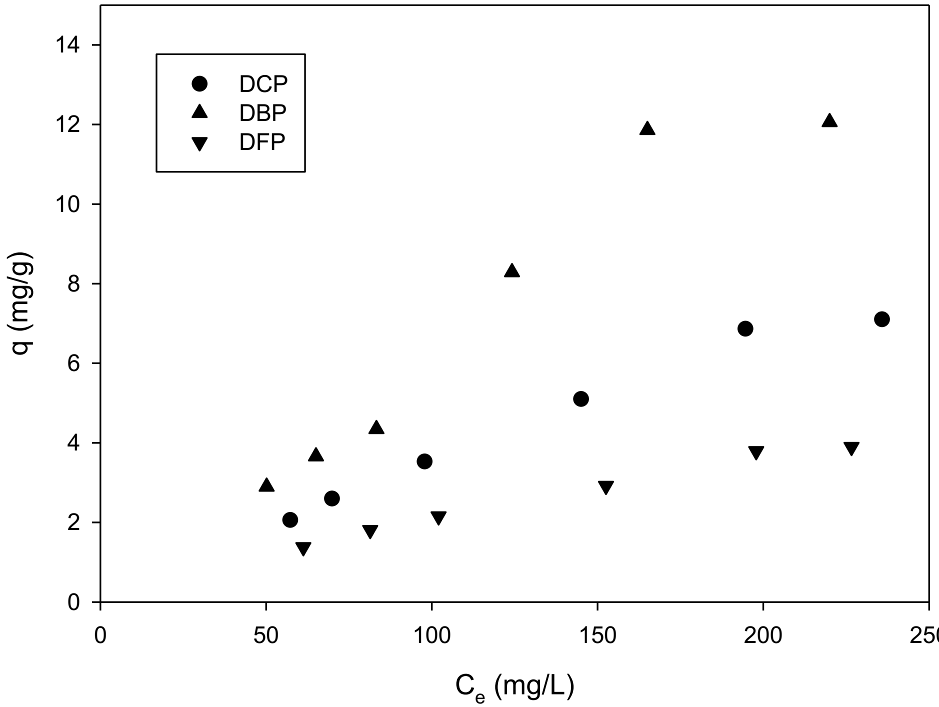
& degree of deprotonation

Correlation between the maximum sorption capacity (mg/g) and pH-modified octanol-water partition coefficient ($logK_{ow}(pH)$) or the degree of deprotonation (pK_a-pH).

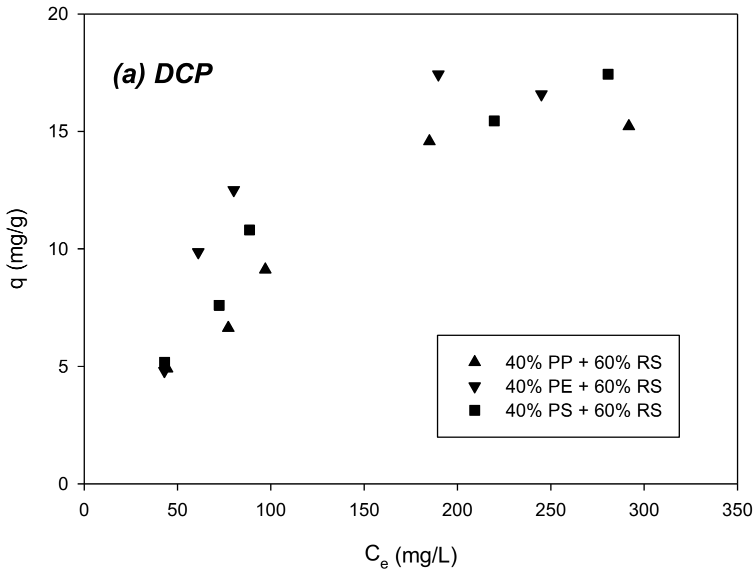


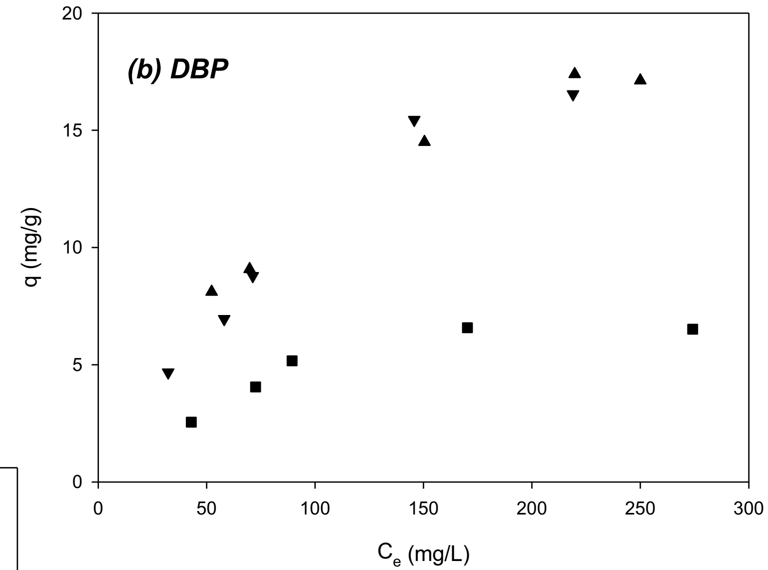
Effect of competition:

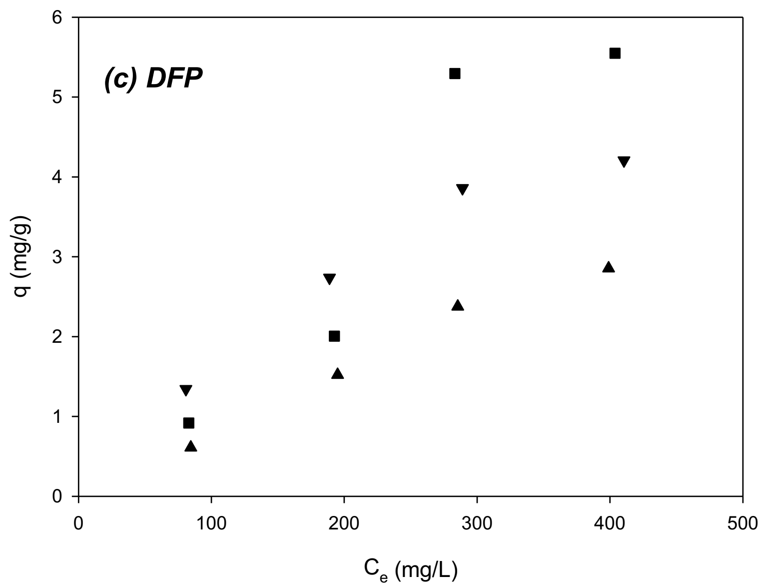
PP/RS-derived biochar



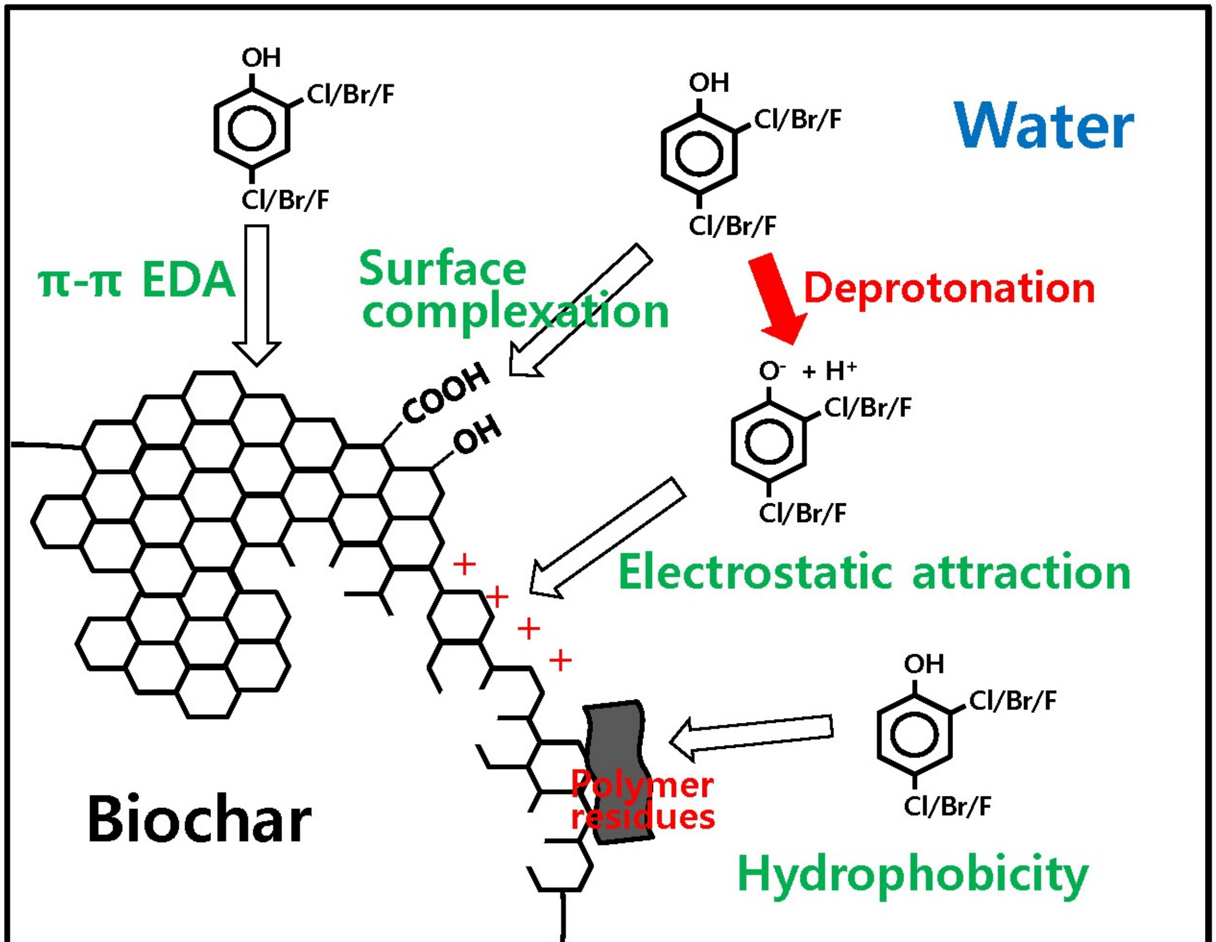
Effect of dissolved Zn^{2+} (~50 mg/L)







Schemes on sorption of halogenated phenols to polymer/RS-derived biochar



Conclusions

• Polymer/RS-derived biochar could significantly enhance the sorption of halogenated phenols according to polymer residues, net surface charge, and deprotonation of compounds.

• Increasing the pyrolysis temperature from 550 to 700 and 900^{o}C was not advantageous due to compensation between the removal of polymer residues and surface functional groups and increasing π-π EDA interactions.

• Solution pH was an important factor in controlling the hydrophobicity and deprotonation of compounds.

Conclusions

- Competition with other halogenated phenols and dissolved cations implied that similar sorption mechanisms existed and that surface complexation and EDA interactions were involved in sorption onto polymer/RS-derived biochar.

- Co-disposal of thermoplastic and biomass wastes through pyrolysis may be an effective option to produce high-performance upgraded biochar as a sorbent for various types of contaminants.

Acknowledgments

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Any questions?

Application of biochar in urban farming [Gwangju (Gyunggi-do), South Korea]

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