Evaluating the Adsorption Dynamics of Emerging Contaminants in Aqueous Solution onto Biochar Derived from Different Feedstocks

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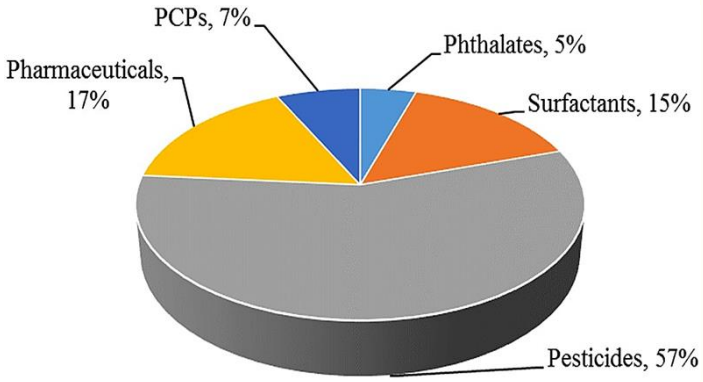
Emerging Contaminants Overview

- Over 700 ECs are listed EU aquatic environment
- Pharmaceuticals and pesticides are prominent classes



Contamination of Emerging Contaminants in Indian Aquatic Sources: First Overview of the Situation

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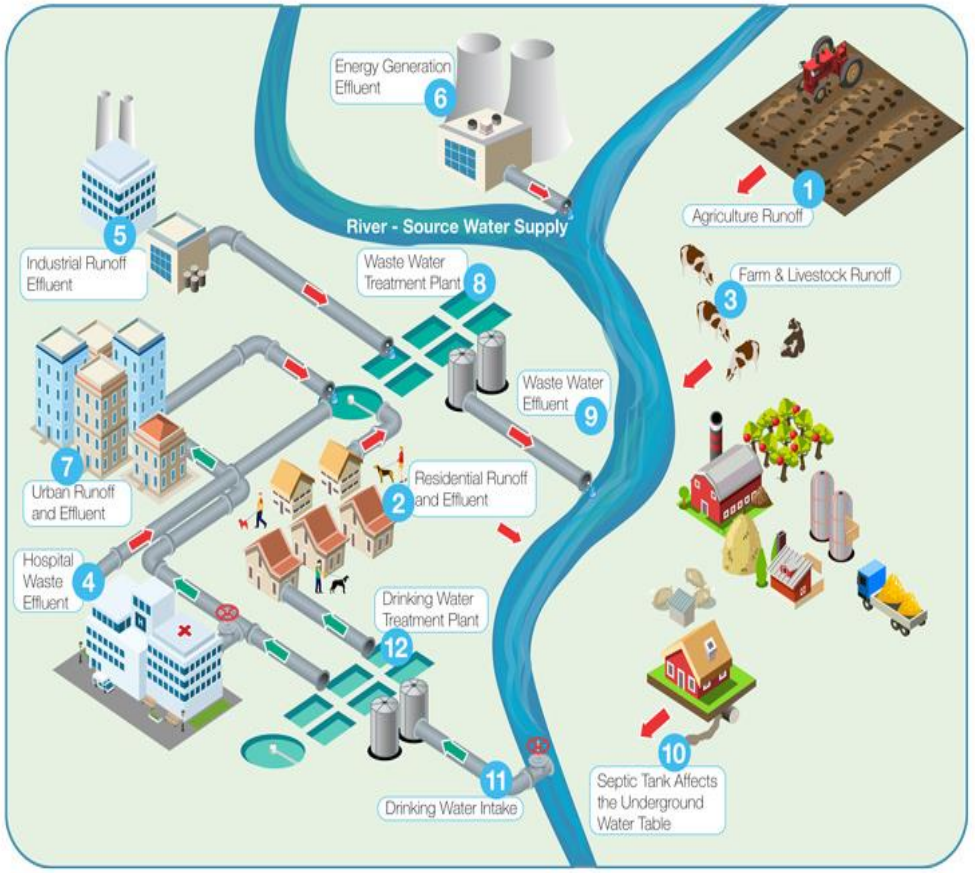
Abstract: This paper provides a first review of the contamination level of emerging contaminants (ECs) in aquatic sources of India. Contaminants reported so far belong to pesticides, pharmaceuticals, personal care products (PCPs), surfactants, and phthalates. A total of 41 publications are reported with a maximum share of pesticides (57%) followed by pharmaceuticals (17%), surfactants (15%), PCPs (7%), and phthalates (5%). The concentration of detected contaminants in all aquatic sources range as not detected (ND) to 10,000 ng/L



www.thermofisher.com/uk/en/home/industrial/environmental/environmental-learning-center/contaminant-analysis-information/emerging-contaminants-analysis.html

- Encompasses a wide range of point and non-point sources
- Harmful to both aquatic and terrestrial life

Biochar diversity

- Emerging as a promising low-cost economical substitute to the activated carbon
- Widely available feedstocks and pyrolysis methods
- Varying sorption results limit predictability among biochars materials
- Limited understanding of the mechanisms driving biochar-contaminants interactions

Goal of this study

- Evaluate sorption performance of locally produced biochar from selected feedstocks in the removal of emerging contaminants from wastewater.

- Hypothesis: The selected feedstock biochar can significantly removed contaminants in wastewater.

Material - Biochar production

Unique micropores distribution

Biomass

- Coconut Shell
- Corn Cob
- Coconut Husk
- Rice Straw

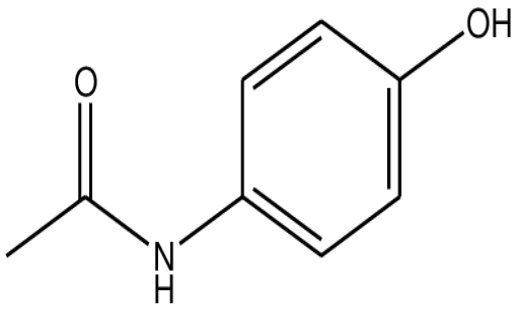
Pyrolysis method selection was based on the wide availability of instruments, low-cost production and low operational skills requirement.

Images source: Thunchanok Thongsamer, KMUTT

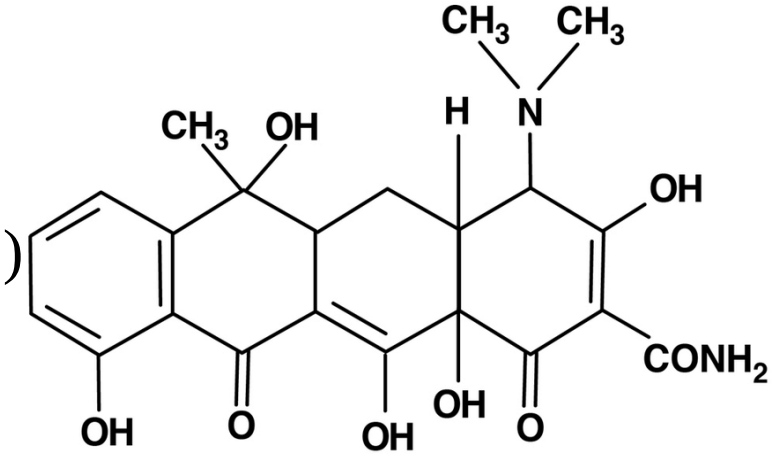
Material - Contaminants

Pharmaceuticals

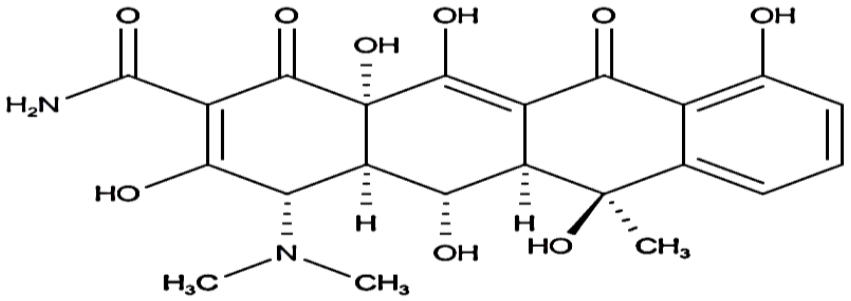
- Acetaminophen (ACM)



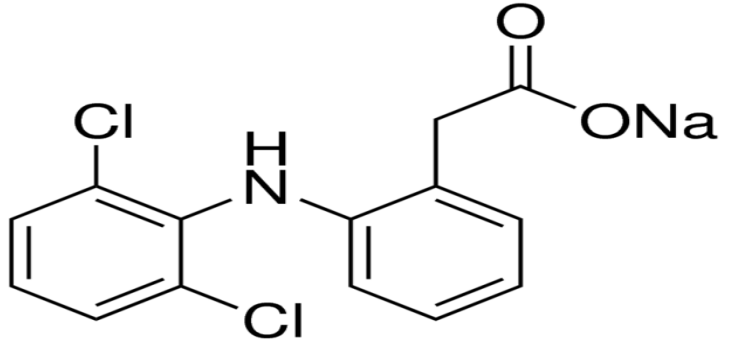
- Tetracycline (TC)



- Oxytetracycline (OTC)

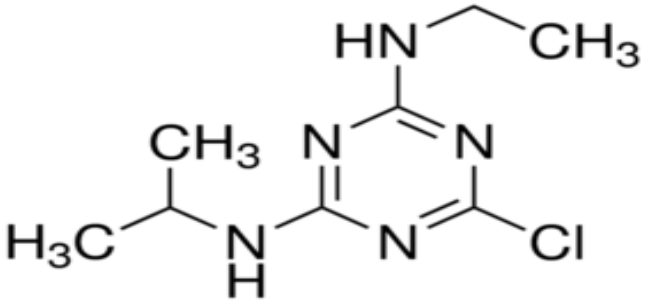


- Diclofenac (DIC)

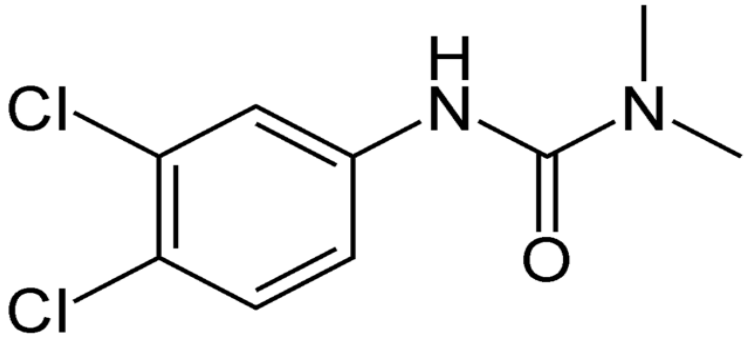


Pesticides

- Atrazine (ATR)



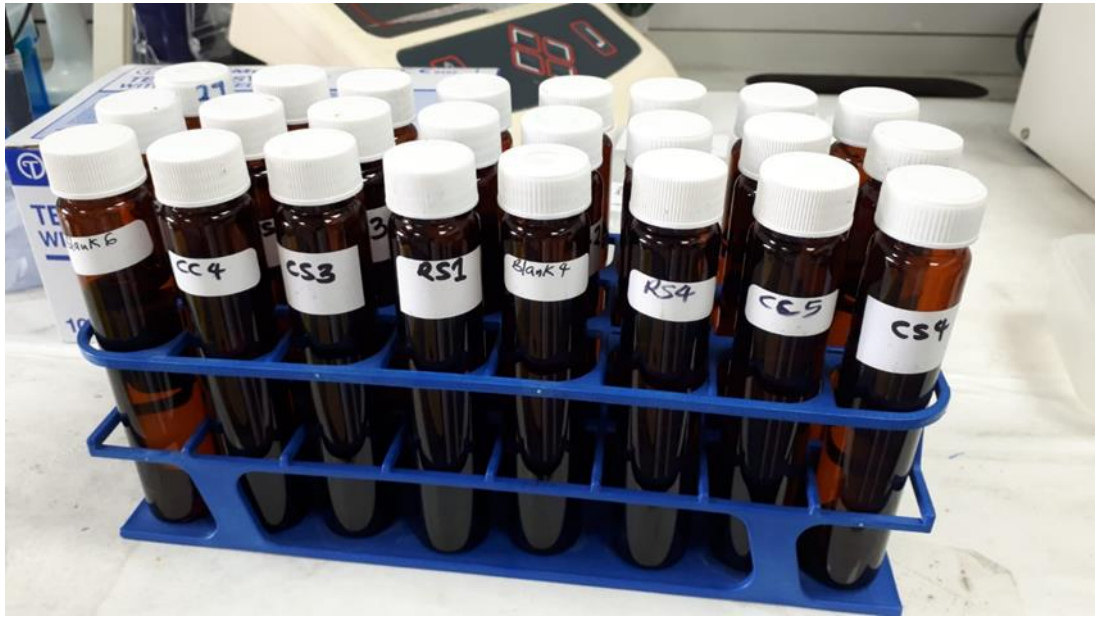
- Diuron (DRN)



Method - Batch adsorption study

Research Objective

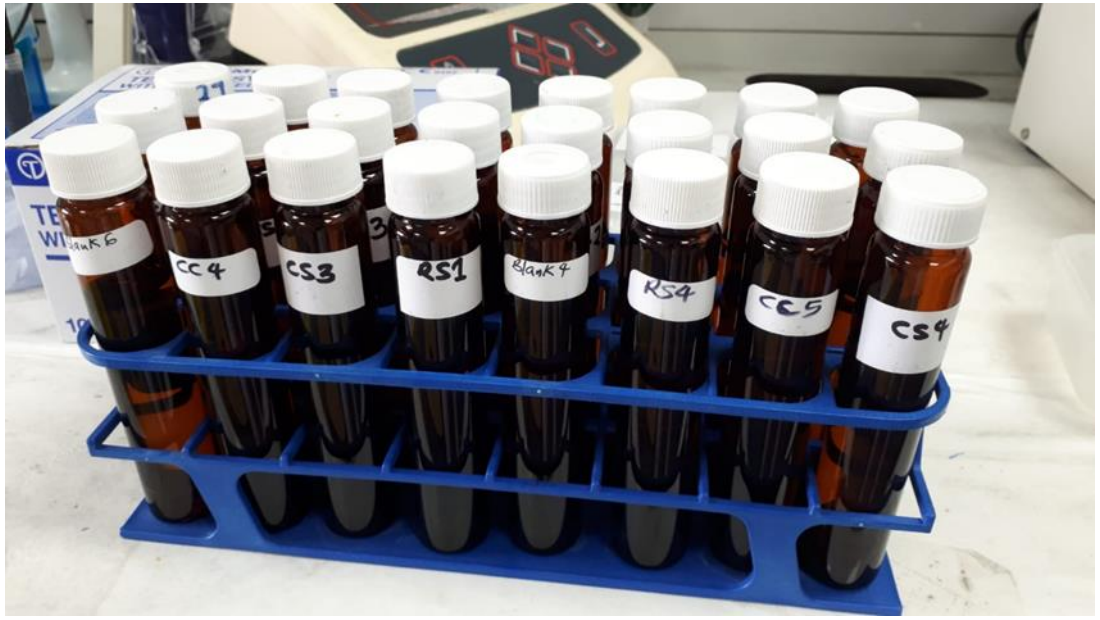
- To investigate the adsorption dynamics of selected micropollutants onto biochars derived from selected feedstocks.



- To publish potential adsorption mechanisms.

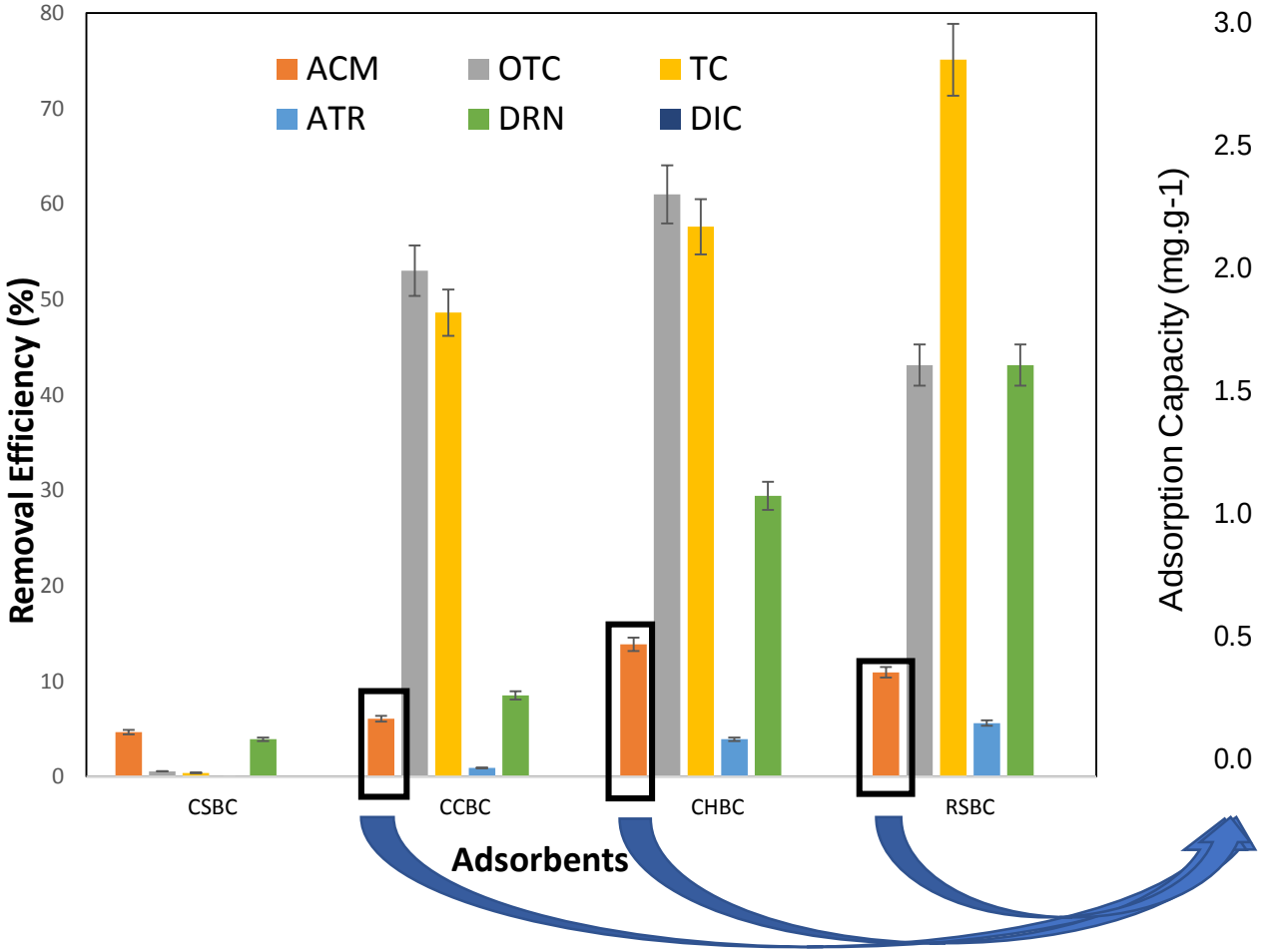
Method - Batch adsorption study

- ✓Dosage of adsorbents was each set at 5g·L^{-1}
- ✓Initial sorbate concentrations in matrix was each set at 10mg·L^{-1}
- ✓Solution was sterile with an initial pH of 6.0 (avg)
- ✓Solution was agitated on laboratory shaker at 170 rpm for 10 days at 25 ^{o}C
- ✓Aliquots were removed at preset time intervals through filtration with PVDF Filters.
- ✓Sorbate concentrations was measured by HPLC.
- ✓All experiments were carried out in triplicate and blanks were performed.

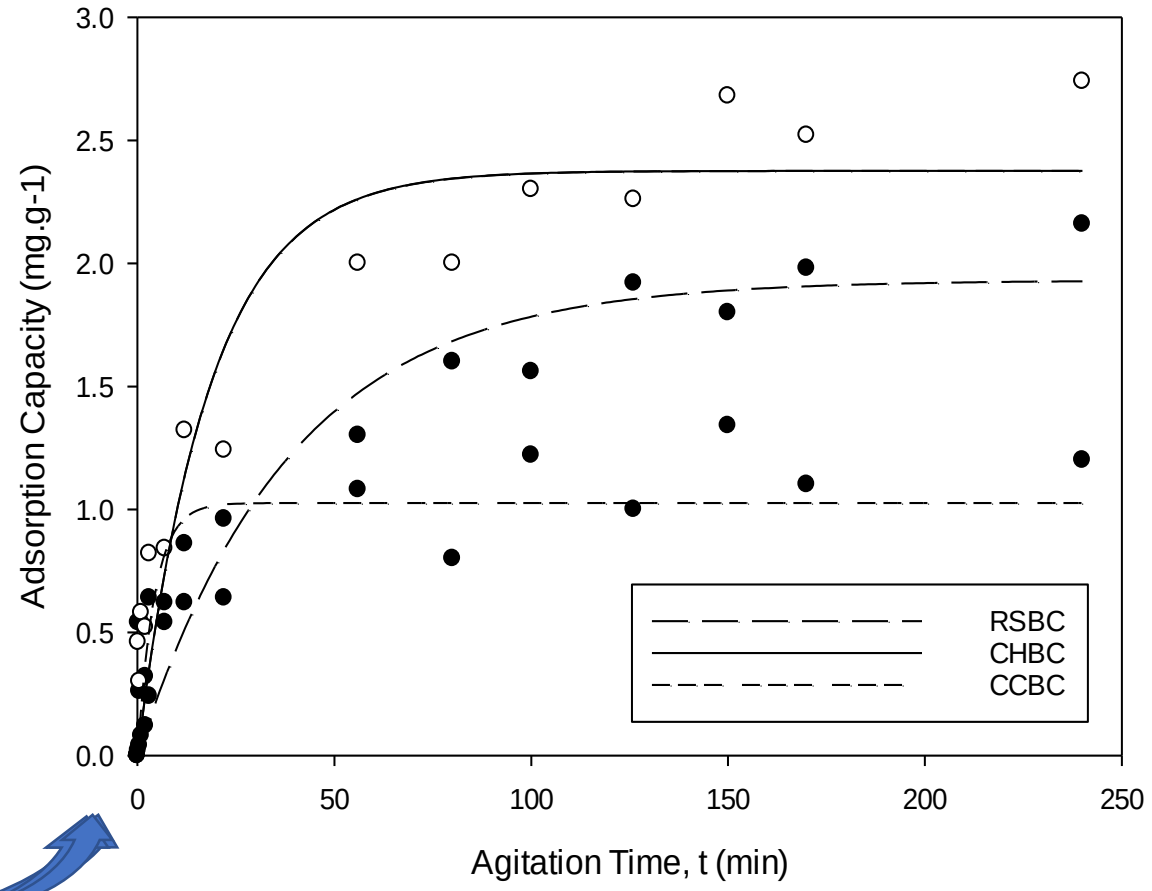


Results - Contaminants sorption

Removal efficiency of the pollutant mixture on selected biochar



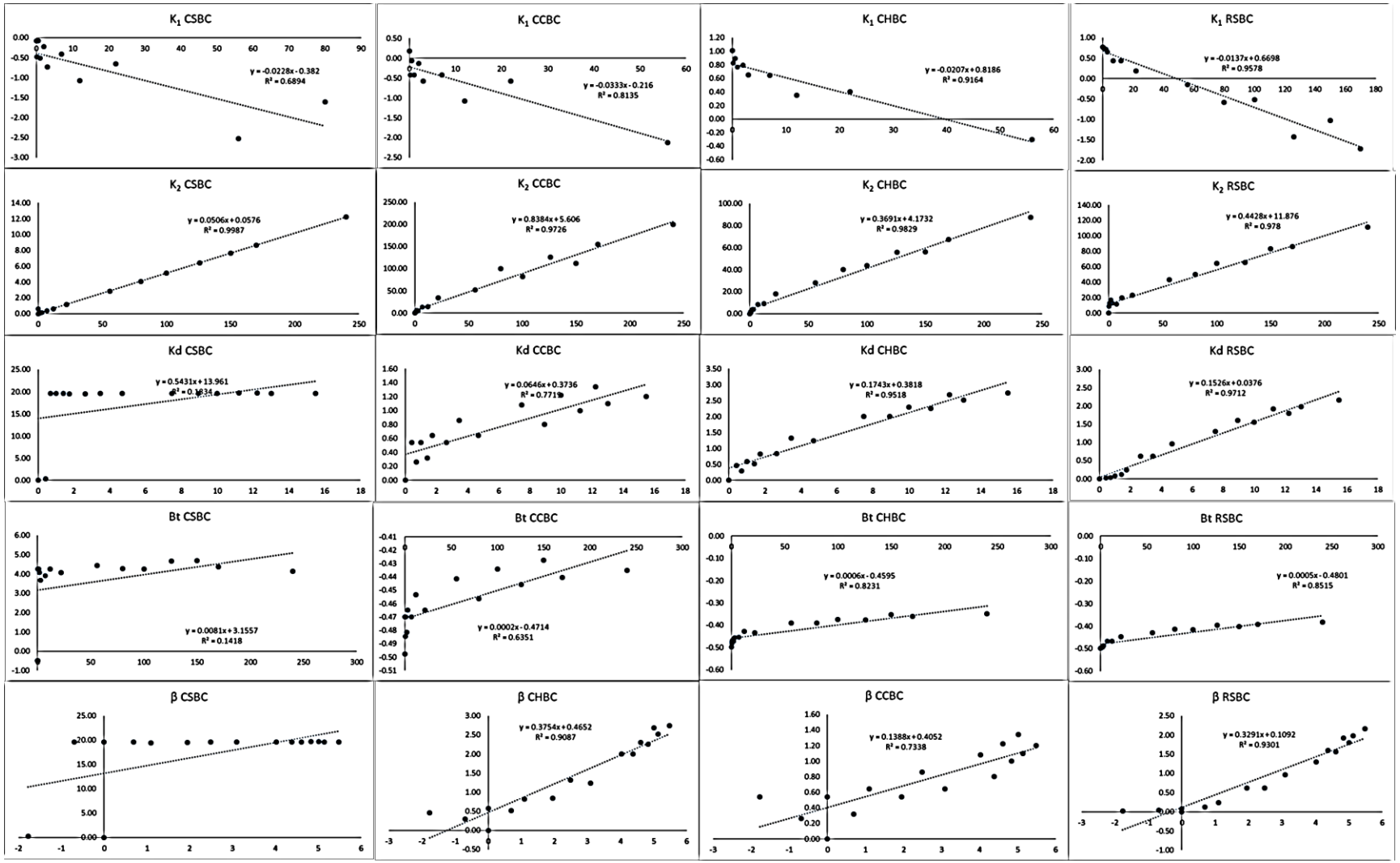
Kinetic fitting curve of ACM adsorption on thre adsorbents



Results - Adsorption Kinetics and Mechanism

Model plots for **ACM** adsorption on the tested adsorbents CSBC, CCBC, CHBC and RSBC

- Pseudo-first-order
  $\ln(q_e - qt) = \ln q_e - k_1 t$
- Pseudo-second order
  $\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} t$
- Inter-particle diffusion
  $q_e = kdt^{0.5} + I$
- Boyd model
  $Bt = -0.4977 - \ln(1 - F)$
- Elovich
  $q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t$



Results - Adsorption Kinetics and Mechanism

Table 2. Comparison of model parameters

Model	Parameter	Adsorbent			
		CSBC	CCBC	CHBC	RSBC
Pseudo First-Order Model	K_1 (min^{-1})	0.0102	0.0098	0.0098	0.0134
	q_e (exp) ($mg.g^{-1}$)	0.9200	1.2000	2.7400	2.1600
	q_e (cal) ($mg.g^{-1}$)	10.9600	10.6000	12.2000	8.6200
	R^2_{adj}	0.9973	0.9946	0.9351	0.9646
Pseudo Second-Order Model	K_2 (g/mg. min)	0.1328	0.1254	0.0326	0.0165
	q_e (exp) ($mg.g^{-1}$)	0.9200	1.2000	2.7400	2.1600
	q_e (cal) ($mg.g^{-1}$)	0.9405	1.1927	2.7092	2.2584
	R^2_{adj}	0.9744	0.9726	0.9829	0.9780
Intra-particle Diffusion Model	K_d ($mg/g.min^{0.5}$)	0.5413	0.0646	0.1743	0.1526
	I (mg/g)	13.9610	0.3736	0.3818	0.0376
	R^2	0.1834	0.7719	0.9518	0.9712
Boyd Kinetic Model	B	0.0081	0.0002	0.0006	0.0005
	D_i ($x10^{-11}$ m^2/s)	126.3208	3.1190	9.3571	7.7976
	R^2	0.1418	0.6351	0.8231	0.8515
Elovich Model	β (g. mg^{-1})	/	7.2046	2.6638	3.0386
	α (mg. g^{-1} min^{-1})	/	2.5718	1.2962	0.4586
	R^2	/	0.7338	0.9087	0.9301

- **Although R^2 >0.9, predicted a significantly higher values of q_e than the experimental values, which indicates the inapplicability**
- **Adsorption process agrees with Pseudo second-order.**
- **Good correlation coefficients for CHBC and RSBC but fail to pass through the origin.**
- **Suggested that the rate-determining step is the external mass transfer**
- **The good fitting indicates that pore diffusion plays a vital role in controlling the rate of reaction.**

Method – Small scale column study

Objective

- The objective of the small scale column test was to determine the suitability of CHBC to be used as an alternative medium for the removal of microcontaminants in pond water.

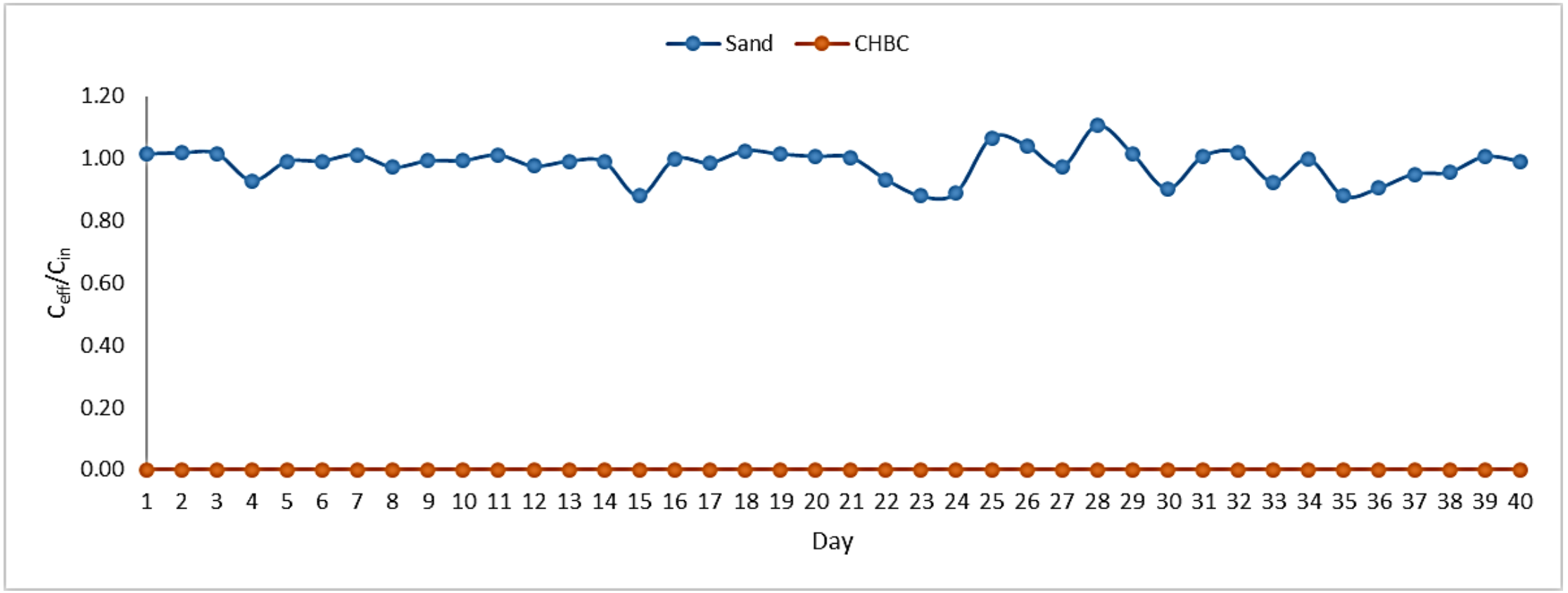
- To determine breakthrough and compare the results with field experiments carried out in Thailand.

Method – Small scale column study

- Columns size: 1.8cm diameter and 20cm bed length.
- 42.3g CHBC-sand mix (10% w/w) media and 77.7 g of fine sand (control media).
- Solution was pond water spiked with contaminants mix each at 100µg·L^{-1} at 25 ^{o}C.
- Experiment run: 12 hours continuous and 40 days intermittent samplings
- Effluent samples were taken at preset time intervals through filtration with PVDF membrane Filters and measured by HPLC.
- All experiments were carried out in triplicate and blanks were performed.
- Column deconstruction: microbial analysis.

Results – Small scale column study

Plot of effluent to influent **ACM** concentration ratio vs. time



Breakthrough curve for adsorption for column experiment could not be established due to influence rapid biodegradation.

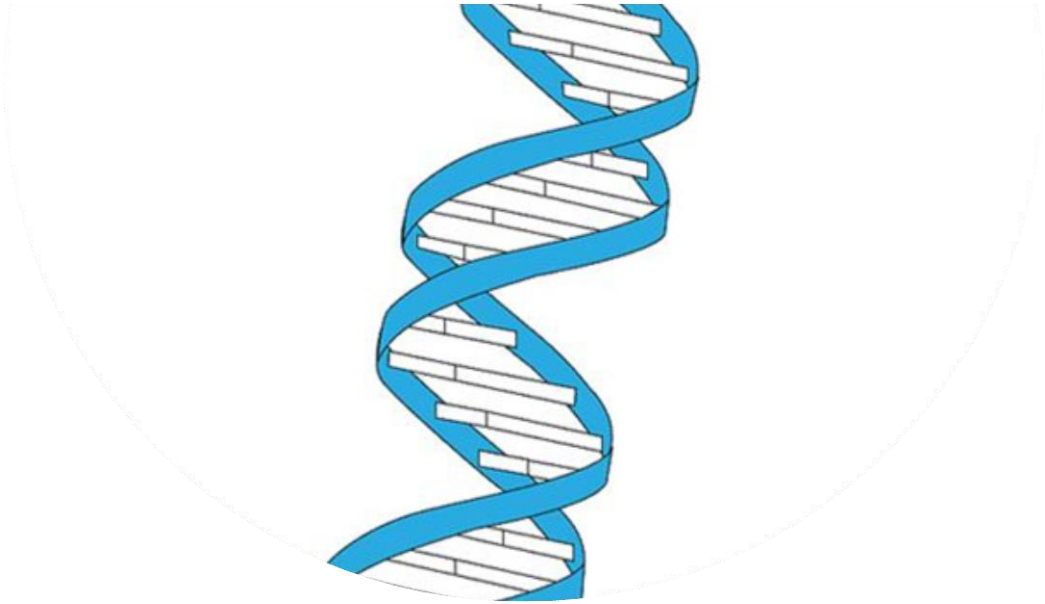
Conclusion

- The study demonstrated CHBC and RSBC are effective adsorbent for ACM removal.
- Over 75% of ACM removal was attained by RSBC.
- Adsorption of sorbate was also found to be dependent on contact time and sorbate type.
- Removal efficiency could increase with increased sorbate dosage and modification of biochar.
- No change in concentration of the control column suggests biochar is bio-active.
- This information can be used to properly select biochars for intended purposes and environments

Work in Progress

Lysimeter Leachate Analysis

- The objective of this research is to determine if biochar application on soil affects ground water quality.



Microbiology Study

- The objective is to determine the presence of biodegradation vis-à-vis adsorption in the small scale column experiment.

Acknowledgement

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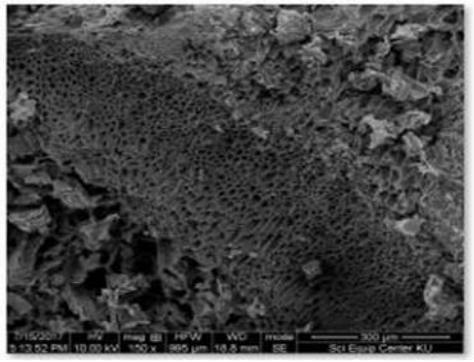
THANK YOU
FOR LISTENING

Material - Biochar characterisation

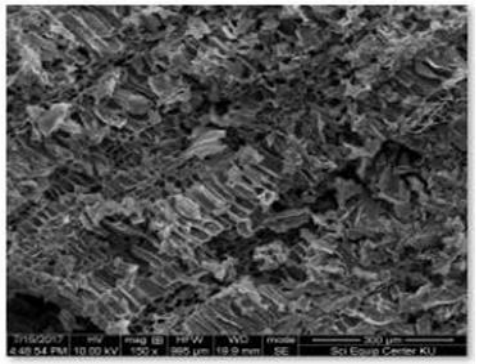
Table 1. Proximate & Ultimate Analysis [a]

Biomass	Max. Temp in Chamber (°C)	% Yield	Bulk density (g/cm3)	Iodine Number (mg/g)	pH (DI water)	BET surf. Area (m^2/g)	Elemental analysis (wt %)				
							C	H	N	S	O
CCBC	480	32.07	0.698	32.31	8.97	/	60.36	3.03	1.81	0.12	34.68
CHBC	378	33.65	0.661	68.36	9.75	11.00	68.48	3.53	0.06	0.15	27.78
CSBC	704	23.82	1.143	13.17	9.02	/	68.63	3.69	0.25	0.02	27.41
RSBC	303	10.00	1.692	3.06	8.94	14.60	/	/	/	/	/

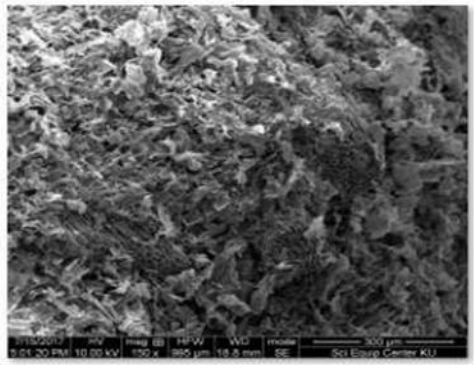
[a] determined by KMUTT



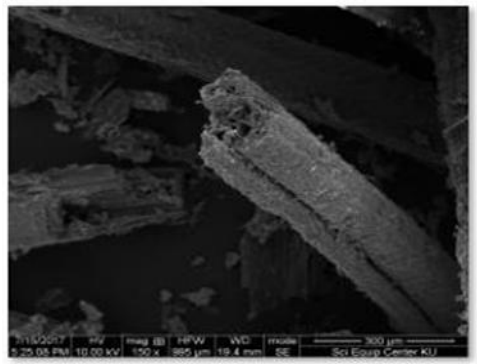
Corncob x150



Coconut husk x150



Coconut shell x150



Rice straw x150