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Outstanding Student Poster & PICO Contest

NOVEL USE OF MAGNETIC BIOCHARS FOR THE REMEDIATION OF SOILS CONTAMINATED BY CONTAMINANTS OF EMERGING CONCERN (CECs)

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PETROLEUM TECHNOLOGY DEVELOPMENT FUND PTDF

School of Civil Engineering and Geosciences

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FIGURE 1: PRODUCTION OF MAGNETIC BIOCHAR ACCORDING TO (Han et al, 2015)

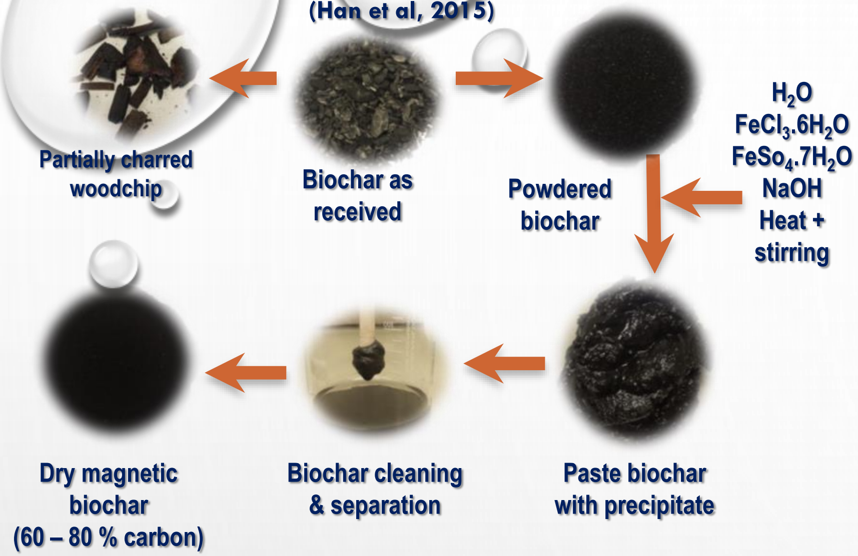


FIGURE 2: RECOVERY OF BIOCHAR (72 TO 98% RETRIEVED)

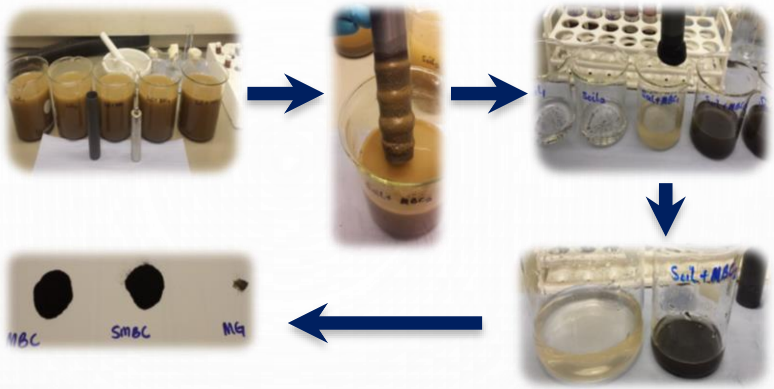


TABLE 1: SORBENT PROPERTIES (Han et al, 2015)

Sorbent	CoAC	MCoAC	Bio-1	MBio-1
Surface area (m^2g^{-1})	975	643	261	219
Pore volume (cm^3g^{-1})	0.47	0.41	0.17	0.23
MPV (cm^3g^{-1})	0.43	0.26	0.10	0.05
Pore size (Å)	37.1	91.1	52.1	66.9
pH_{PZC}	10.4	6.3	9.2	9.0

FIGURE 3: IBUPROFEN SORPTION ISOTHERMS FOR (a) ACS AND (b) BCS

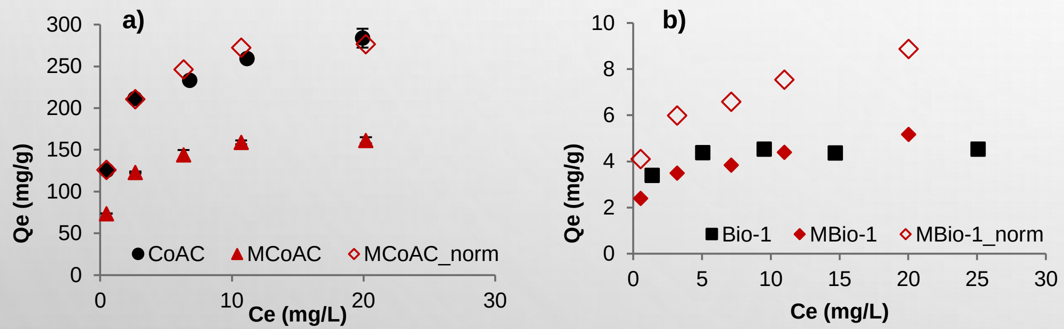


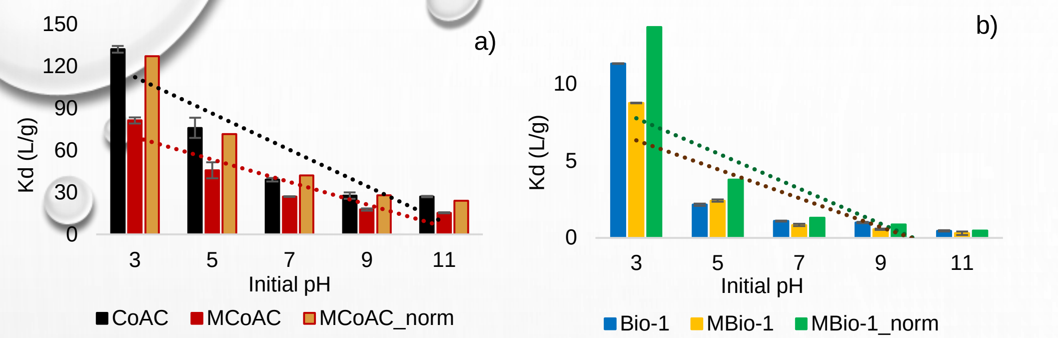
TABLE 2: SORPTION OF IBUPROFEN ON COAC: RESULTS OF OPTIMISED ERROR FUNCTIONS

Err. Fxn	LANG_L	FR_L	RP_L	LANG	FREU	RED-PET	DA	PDM
CoD	0.9301	0.9622	0.9907	0.9557	0.9639	0.9912	0.9854	0.9854
HYBRID	424.30	99.20	28.84	100.97	95.84	27.58	49.59	0.24
MPSD	17.70	7.02	3.50	6.37	6.99	3.47	4.62	4.62
ARE	9.02	4.11	1.66	3.99	3.62	1.64	2.02	2.34
EABS	74.71	41.85	19.63	62.02	38.48	19.47	25.37	0.16
ERSSQ	1819.20	630.13	136.71	734.45	533.64	125.07	218.05	0.01
ASE*	390.84	130.39	31.73	151.31	113.10	29.54	49.94	1.23

TABLE 3: SORPTION OF IBUPROFEN ON ACS AND BCS: MODEL PARAMETERS ACCORDING TO OPTIMISED MODEL FITTING

Model	Linear	Langmuir				Freundlich				Redlich-Peterson					Dubinin-Ashtakov				
Parameters	Kd	Qm	K_L	R^2	ASE	1/n	K_F	R^2	ASE	K_R	A_R	β	R^2	ASE	Qo	E	b	R^2	ASE
CoAC	250.56	294.85	0.86	0.9690	151.31	0.19	162.99	0.9663	113.10	784.13	3.86	0.89	0.9915	29.54	293.72	20.48	1.75	0.9853	49.94
CoAC*	8.71	198.84	0.04	0.9490	64.50	0.60	13.30	0.9715	27.19	354.27	25.95	0.41	0.9713	30.91	264.36	9.36	0.45	0.9875	15.92
MCoAC	154.81	287.96	1.22	0.9813	35.70	0.19	165.53	0.9357	80.48	607.70	2.64	0.92	0.9921	11.69	167.16	18.43	2.19	0.9961	6.06
MCoAC*	4.00	97.12	0.04	0.9774	10.19	0.56	8.48	0.9848	8.01	12.80	0.96	0.54	0.9852	8.22	73.62	9.79	1.05	0.9845	9.03
Bio-1	2.49	4.58	2.82	0.9482	0.97	0.08	3.49	0.7418	2.35	9.89	2.13	1.00	0.9441	1.11	4.48	12.68	5.99	0.9784	0.60
MBio-1	4.43	5.43	0.56	0.8859	81.66	0.22	2.64	0.9836	16.95	7284.62	2760.56	0.78	0.9837	18.64	7.97	32.44	0.63	0.9912	1.03

Figure 4: Effect of pH on sorption of ibuprofen on (a) ACs and (b) BCs



- pH has a negative influence on the sorption of ibuprofen.
- the sorption of neutral species is relatively favoured (Limousin *et al.*, 2007).
- likely due to van der Waals interaction and/or hydrogen bonding (Baccar *et al.*, 2012).
- At high pH electrostatic repulsion impairs sorption

Figure 5: Plot of sorption kinetics for ibuprofen on (a) ACs and (b) BCs

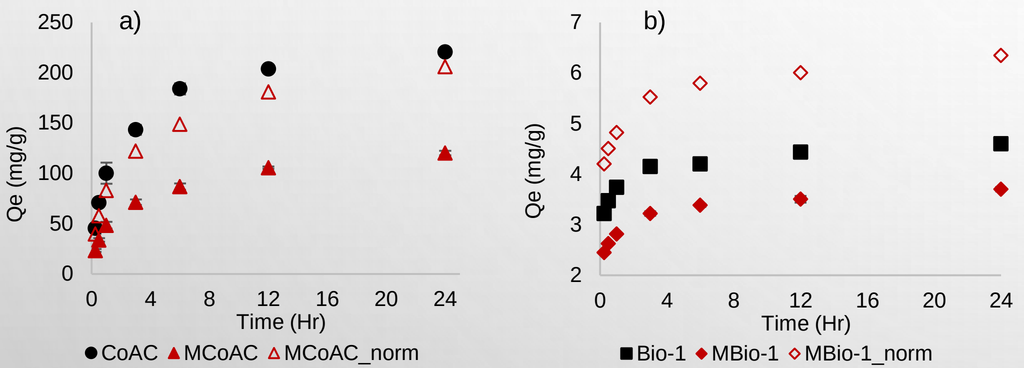


Figure 6: Ibuprofen sorption kinetics fractional uptake

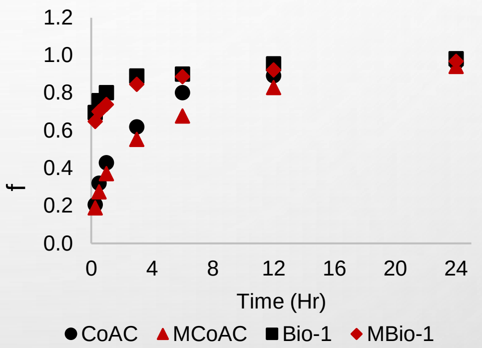


TABLE 4: OPTIMISED MODEL PARAMETERS FOR KINETICS OF SORPTION OF IBUPROFEN ON ACS AND BCS.

Model	1st				2nd				
Parameters	Qe	k_1	R^2	ASE	Qe	k_2	R^2	ASE	Qe*
CoAC	205.90	0.01	0.9820	402.78	227.48	5.30E-05	0.9879	101.19	229.00
MCoAC	111.93	0.01	0.9521	199.65	122.34	7.2E-05	0.9785	74.49	127.5
Bio1	4.34	0.06	0.7149	8.23	4.59	0.01	0.9352	1.60	4.65
MBio1	3.49	0.05	0.7132	4.21	3.70	0.01	0.9232	2.21	3.8

Model	Elovich				Intra-particle				
Parameters	α	β	R^2	ASE	k_{id}	z	R^2	ASE	D
CoAC	8.53	0.03	0.9924	43.80	31.28	0.28	0.9515	289.15	8.59E-10
MCoAC	3.65	0.05	0.9943	14.41	13.33	0.31	0.9827	38.85	5.03E-10
Bio1	2535.16	3.54	0.9834	0.57	2.77	0.07	0.9729	0.74	1.64E-08
MBio1	151.16	3.66	0.9931	0.40	1.98	0.09	0.9851	0.60	1.26E-08

CECs SOURCES AND PATHWAYS

MANY STUDIES HAVE BEEN CARRIED OUT

Science of the Total Environment 473–474 (2014) 530–536

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Sorption behavior of nonylphenol (NP) on sewage-irrigated soil: Kinetic and thermodynamic studies

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Geoderma 189–190 (2012) 462–468

Contents lists available at SciVerse ScienceDirect

Geoderma

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Sorption and mobility of two micropollutants in three agricultural soils: A comparative analysis of their behavior in batch and column experiments

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Journal of Contaminant Hydrology

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Effect of biochar on the fate of volatile petroleum hydrocarbons in an aerobic sandy soil

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ABSTRACT

Biochar addition to soil is currently being investigated as a novel technology to remediate polluted sites. A critical consideration is the impact of biochar on the intrinsic microbial pollutant degradation, in particular at sites polluted with a mixture of readily biodegradable and more persistent organic pollutants. We therefore studied the impact of biochar (2% on dry weight basis) on the fate of volatile petroleum hydrocarbons in an aerobic sandy soil with batch and column studies. The soil–water partitioning coefficient, K_d, was enhanced in the biochar-amended soil up to a factor 36, and petroleum hydrocarbon vapor migration was retarded accordingly. Despite increased sorption, in particular of monoaromatic hydrocarbons, the overall microbial respiration was comparable in the biochar-amended and unamended soil. This was due to more rapid biodegradation of linear, cyclic and branched alkanes in the biochar amended soil. We concluded that the total petroleum hydrocarbon degradation rate was controlled by a factor other than substrate availability and the reduced availability of monoaro-

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A critical evaluation of magnetic activated carbon's potential for the remediation of sediment impacted by polycyclic aromatic hydrocarbons

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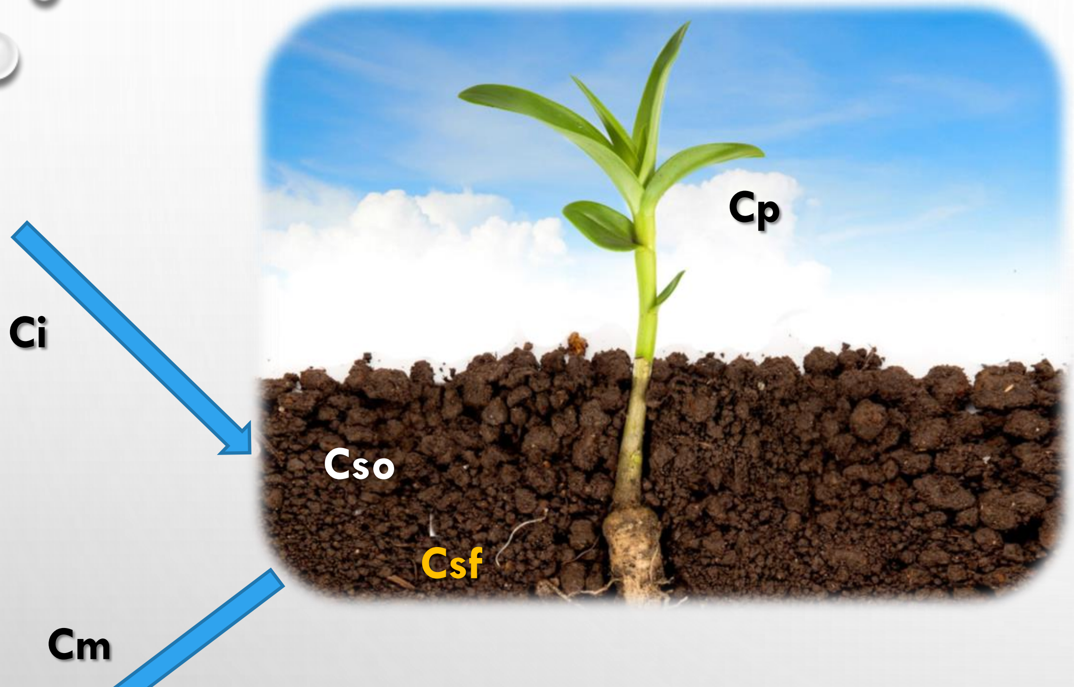
HIGHLIGHTS

- Within three months, 8.1% amended magnetic activated carbon (MAC) reduced sediment aqueous PAHs by 98%.
- The effectiveness of MAC in reducing sediment aqueous PAHs is almost as high as that of pristine activated car-

GRAPHICAL ABSTRACT

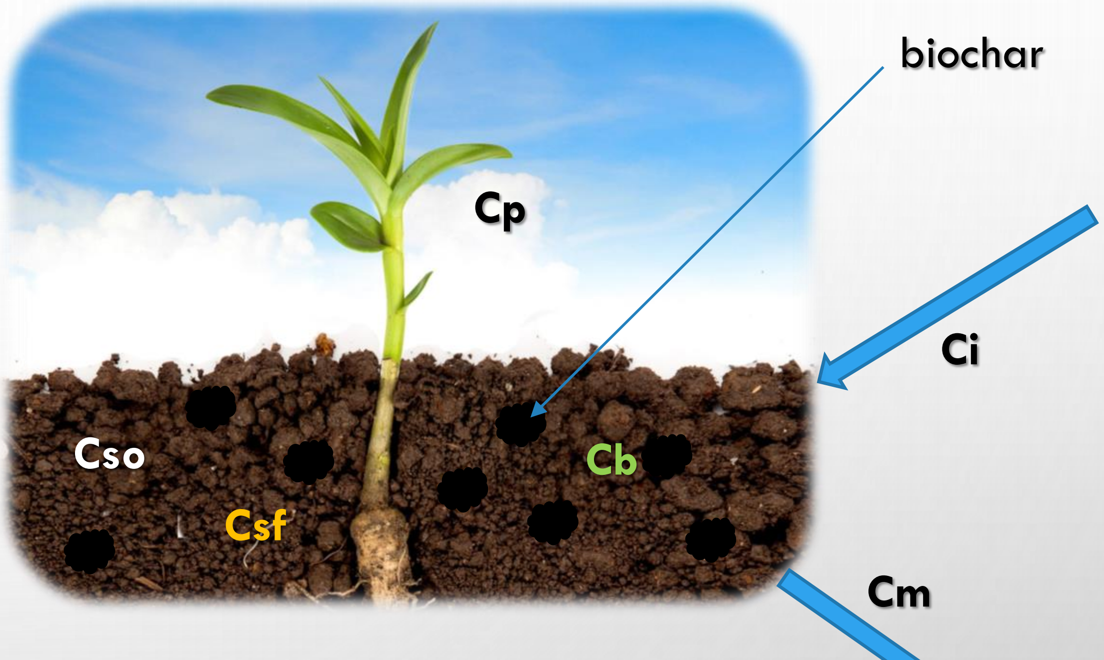
MASS BALANCE FOR CECs IN THE SOIL

A. Without biochar amendment



Ci + Cso = Cp + Csf +Cm

B. With biochar amendment



Ci + Cso = Cp + Csf +Cm + Cb

Ci + Cso ≈ Cb

Ci = amount of CECs introduced
Cso = CECs existing in the soil
Csf = final amount of CECs adsorbed to the soil
Cp = amount of CECs transferred to crops
Cb = amount of CECs adsorbed to the biochar
Cm = amount of CECs taken by other environmental phenomena.

FATE OF CECS IN BIOCHAR

3. With time the biochar attains full saturation.

1. Biochar keeps sorbing contaminants in soil.

2. Conditions in soil may change and the biochar is forced to release it contaminant loading back to the soil.

For reasons mentioned in 2 & 3 above, and similar, there may be the need to remove the biochar from the soil.

RESEARCH CONCEPT

Problem: Biochar needs to be removed for some probable reasons and cannot easily be removed from soil.

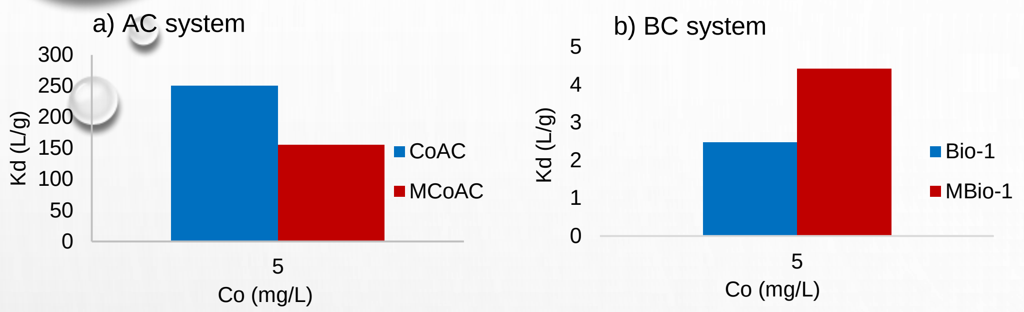
Solution: Magnetise the biochar and separate using principles of magnetism.

Problem: Magnetisation alters the surface properties and thus sorption characteristics of biochar.

Solution: Evaluate the trade-offs that exist between the need for magnetisation and change in sorption characteristics.

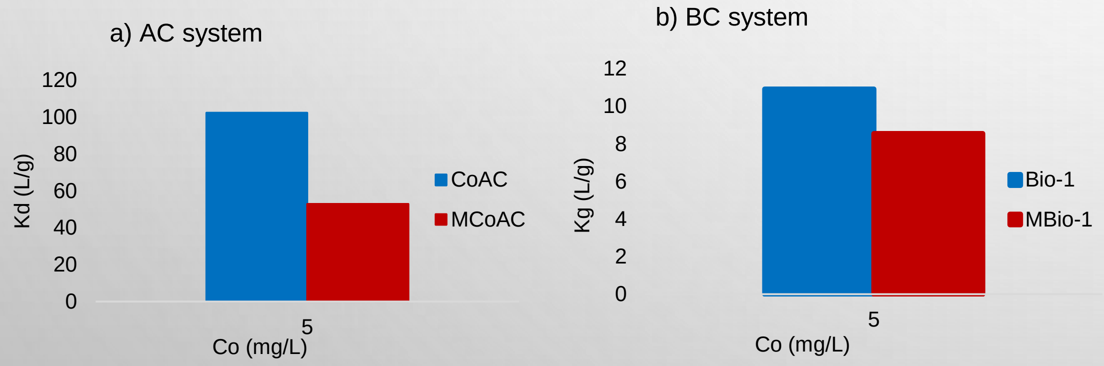
SORPTION CAPACITIES

Figure 7: Ibuprofen sorption partition coefficient



- two order of magnitude higher ibuprofen affinity for the ACs compared to the BCs, see figure 7. This could be due to amplified surface area (A_S) and pore structure in the case of the ACs.
- The higher *Kd* value of the CoAC against the MCoAC also suggest that in the ACs sorption is influenced mostly by the A_S.
- Accordingly, the higher *Kd* value of MBio-1 against Bio-1 indicates the significance of pore volume in the sorption of ibuprofen on the biochars.

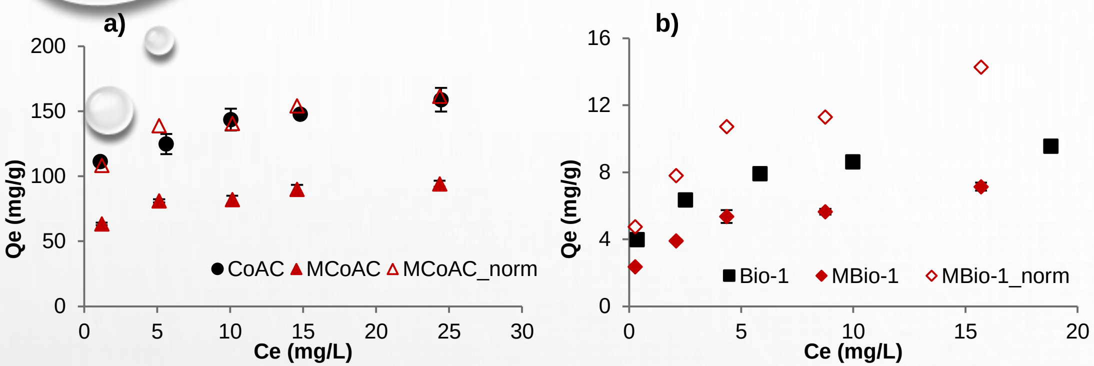
Figure 8: Diclofenac sorption partition coefficient



- The ACs outperformed the BCs in the uptake of diclofenac up to by about two order of magnitude, see figure 8.
- Pore volume does not influence the sorption of diclofenac as observed in sorption of ibuprofen

SORPTION CAPACITIES

Figure 9: Sorption of diclofenac isotherm plot for (a) ACs and (b) BCs



- The isotherms for the ACs overlap when MCoAC is normalised with respect to the actual carbon content.
- In the case of the BCs however, the normalised isotherm (MBio-1_norm) overshoots the Bio-1 isotherm due to the influence of pore volume.

TABLE 5: SORPTION OF DICLOFENAC ON COAC: RESULTS OF OPTIMISED ERROR FUNCTIONS

Err. Fxn	LANG_L	FR_L	RP_L	LANG	FREU	RED-PET	DA	PDM
CoD	0.7654	0.9506	0.9496	0.8106	0.9565	0.9564	0.9649	0.9650
HYBRID	390.00	17.76	27.14	89.03	17.65	26.56	23.85	0.08
MPSD	18.61	3.74	4.63	8.12	3.74	4.58	4.04	4.07
ARE	8.97	2.23	2.25	4.25	1.84	1.89	1.72	1.81
EABS	53.28	14.53	14.67	28.89	11.86	11.98	10.85	0.03
ERSSQ	1320.51	68.02	69.28	359.49	66.57	66.79	52.91	0.00
ASE	298.60	17.72	19.67	81.66	16.95	18.64	15.57	1.00

TABLE 6: SORPTION OF DICLOFENAC ON ACS AND BCS: MODEL PARAMETERS ACCORDING TO OPTIMISED MODEL FITTING

Model	Linear	Langmuir				Freundlich				Redlich-Peterson					Dubinin-Ashtakov				
Parameters	Kd	Qm	KL	R^2	ASE	1/n	KF	R^2	ASE	KR	AR	β	R^2	ASE	Qo	E	b	R^2	ASE
CoAC	102.34	164.19	0.81	0.8071	81.66	0.13	105.74	0.9546	16.95	172778.98	1633.20	0.87	0.9545	18.64	17016.14	0.74	0.22	0.9631	15.57
CoAC*	7.26	173.87	0.04	0.9564	37.14	0.63	10.76	0.9743	17.63	3407.58	315.68	0.37	0.97428	20.53	42042.63	5.29	0.78	0.9755	19.51
MCoAC	53.03	97.09	0.92	0.9270	14.97	0.13	63.10	0.9624	7.24	505.63	7.25	0.91	0.9699	6.35	123.28	42.40	2.63	0.9676	7.03
MCoAC*	3.38	84.84	0.05	0.9801	6.69	0.60	6.52	0.98302	7.26	7.20	0.45	0.59	0.9844	6.83	311.06	20.42	2.16	0.9842	6.93
Bio-1	10.92	9.76	0.74	0.9600	5.39	0.22	5.20	0.9903	1.18	58.19	10.05	0.82	0.9964	0.80	16.51	35.73	2.40	0.9977	0.62
MBio-1	8.56	8.07	0.44	0.9427	8.83	0.27	3.36	0.9754	2.24	1584.99	480.17	0.72	0.9754	2.65	79.83	18.80	0.91	0.9754	2.92

SORPTION CAPACITIES

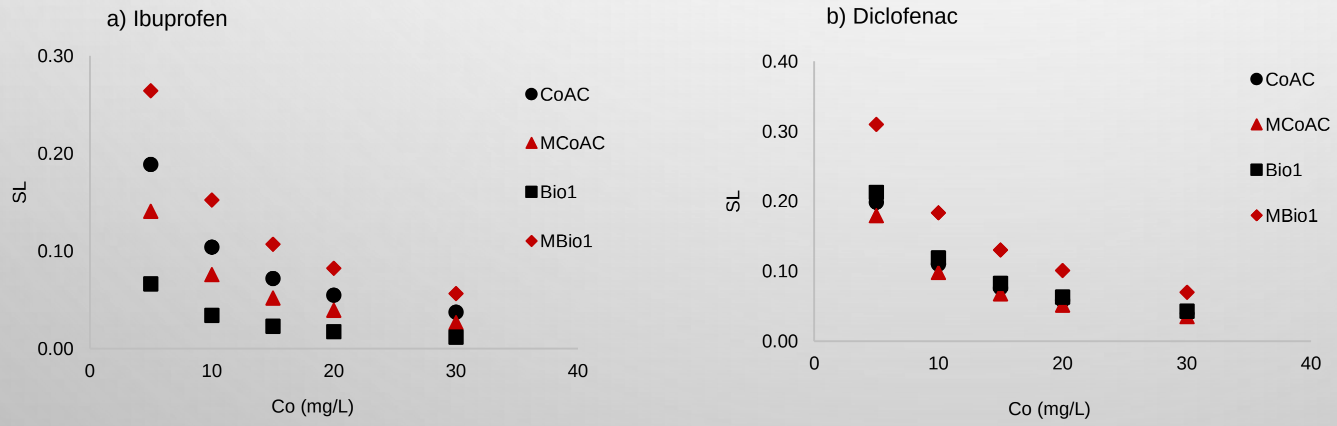
Table 7: Ibuprofen sorption: correlation of normalised model capacity factors and sorbent properties

Model	Parameters	As	V_P	V_{MP}	PS
Linear	Kd	0.8208	0.9304	0.7882	0.0252
Langmuir	Qm	0.5440	0.7307	0.5096	0.1914
Freundlich	KF	0.5214	0.7096	0.4878	0.2078
Dubinin-Ashtakov	Qo	0.8625	0.9541	0.8303	0.0109

Table 8: Diclofenac sorption: correlation of normalised model capacity factors and sorbent properties

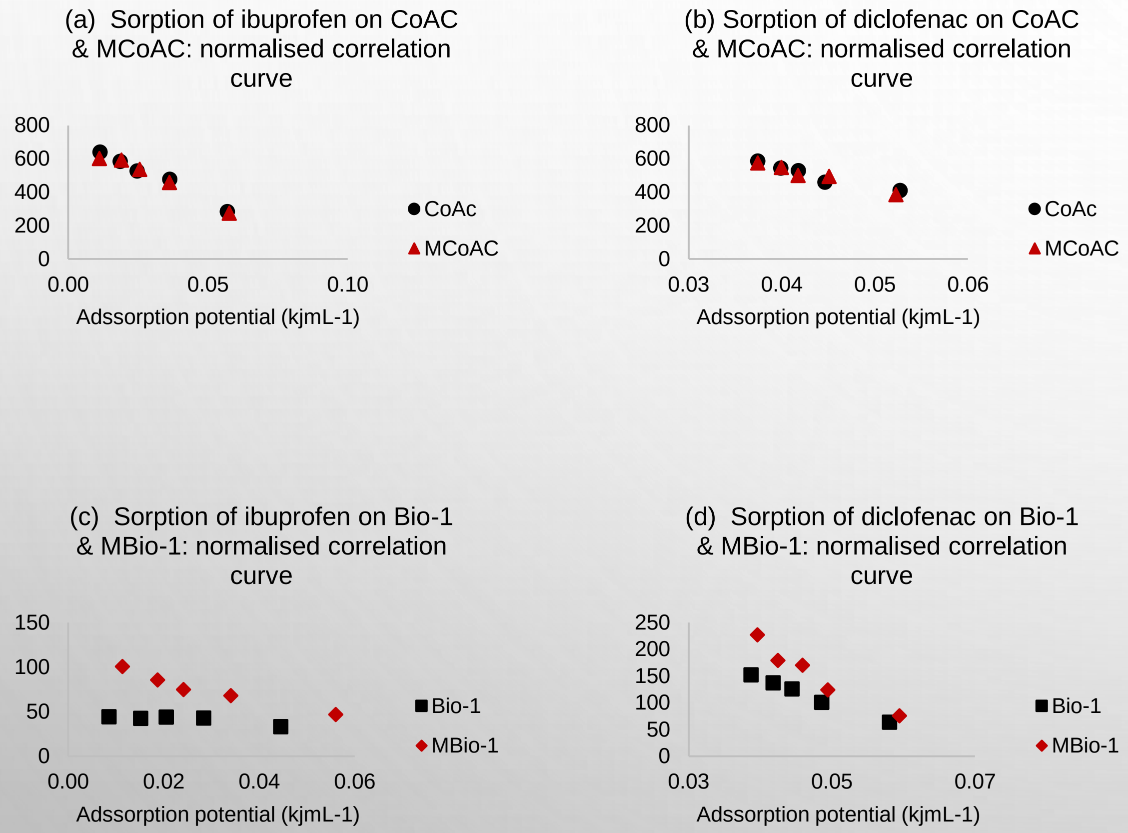
Model	Parameters	As	Vp	V_{MP}	PS
Linear	Kd	0.9095	0.9742	0.8789	0.0010
Langmuir	Qm	0.8432	0.9435	0.8108	0.0170
Freundlich	KF	0.8401	0.9366	0.8093	0.0176
Dubinin-Ashtakov	Qo	0.7166	0.4958	0.7318	0.5061

Figure 10: Separation factor for ibuprofen and diclofenac sorption



SORPTION CAPACITIES

Figure 11: Polanyi characteristic curves for ibuprofen and diclofenac sorption

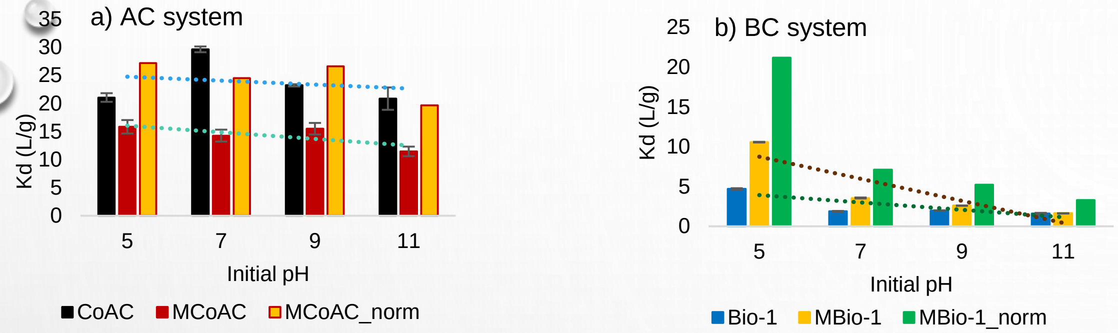


- The ACs correlation curves have collapsed to a single line when normalised with respect to their V_{MP}, i.e. figures (a) and (b).
- sorption takes place by pore filling mechanism, this is relatively satisfied with respect to both the isotherm fitting and characteristic curve.
- Therefore, van der Waals force and pore-filling play significant roles in the sorption of ibuprofen and diclofenac on these sorbents (Xu *et al.*, 2008).

- Correlation curves did not collapse in the case of the BCs, i.e. figures (c) and (d).
- the Polanyi theory was satisfied with respect to the isotherm fitting and not the characteristic curve
- Polanyi theory may still be applied to sorption due to open surface as has been reported in the sorption of organic sorbent on carbon nanotubes and nanosized particles with poor microporosity (Yang and Xing, 2010).

EFFECT OF PH ON SORPTION

Figure 12: Effect of pH on sorption of diclofenac



- the pH has little influence over the ACs' sorption system, hence a nearly horizontal trend was presented.
- Similar observation for diclofenac sorption on other materials (Bajpai and Bhowmik, 2010; Nam *et al.*, 2014) due too its hydrophobic nature.
- this non pH dependence sorption is related to the nature and concentration of functional groups present on the AC's surface that causes variations in both electrostatic interaction and other sorption deriving forces
- In theory, dissociated species are more soluble and therefore can be removed from solution after the hydrophilic forces are overcome by the sorption forces.

SORPTION KINETICS

Figure 13: Plot of sorption kinetics for diclofenac on (a) ACs and (b) BCs

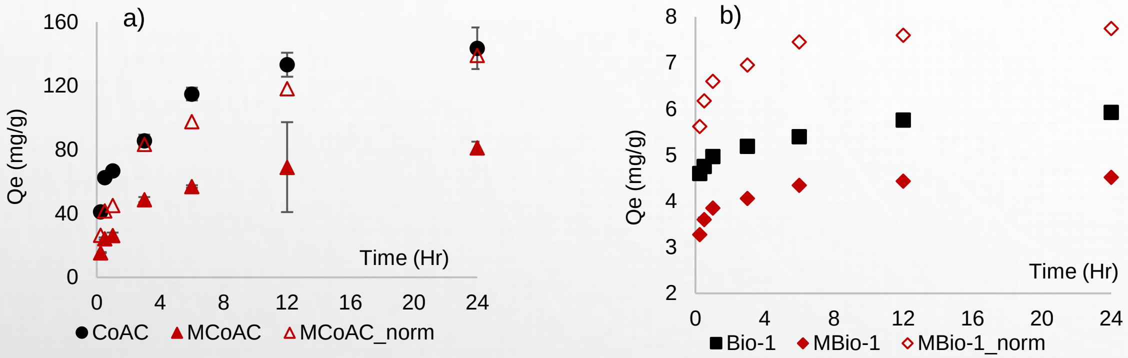


Figure 14: Diclofenac sorption kinetics fractional attainment of equilibrium

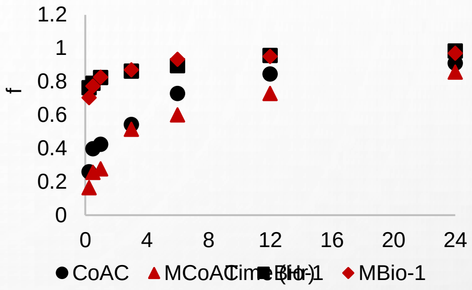
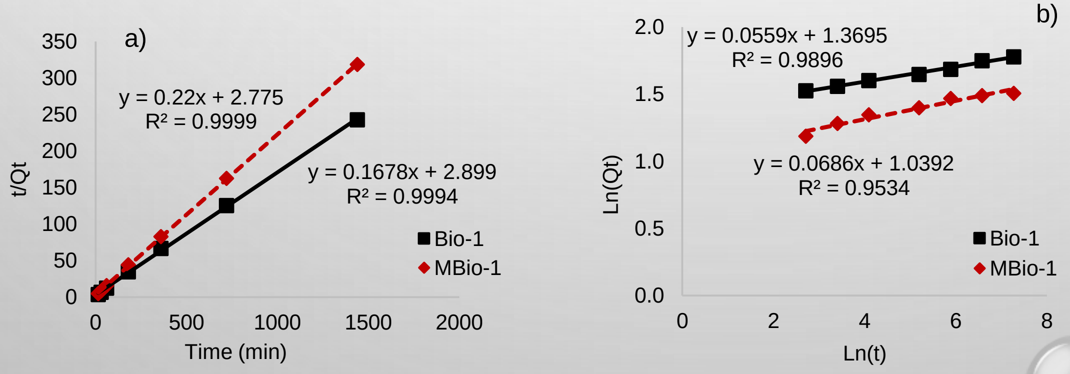


Figure 15: Sorption kinetics of diclofenac on BCs: (a) linear pseudo 2nd order kinetics model plot, (b) linear intra-particle kinetics model plot



SORPTION KINETICS

TABLE 9: OPTIMISED MODEL PARAMETERS FOR KINETICS OF SORPTION OF DICLOFENAC ON ACS AND BCS.

Err. Fxn	1st_L	2nd_L	Elovich_L	Intra-P_L	1st	2nd	Elovich	Intra-P
CoD	0.5018	0.6765	0.9837	0.9888	0.6758	0.7993	0.9840	0.9892
HYBRID	610.29	19.58	0.09	0.06	3.31	1.48	0.09	0.06
MPSD	108.74	20.50	1.30	1.06	7.87	5.25	1.30	1.06
ARE	91.64	11.28	0.92	0.74	5.48	3.86	0.86	0.69
EABS	33.32	3.78	0.34	0.28	2.06	1.47	0.31	0.26
ERSSQ	158.69	4.56	0.02	0.02	0.88	0.40	0.02	0.02
ASE	167.20	10.00	0.45	0.36	3.32	2.11	0.43	0.35

TABLE 10: MODEL PARAMETERS ACCORDING TO BEST FIT MODELS FOR KINETICS OF SORPTION OF DICLOFENAC ON ACS AND BCS

Model	1st				2nd				
Parameters	Qe	k1	R^2	ASE	Qe	k2	R^2	ASE	Qe*
CoAC	143.75	0.01	0.9451	448.46	160.50	5.87E-05	0.9510	206.06	157.70
MCoAC	86.27	0.00	0.9451	108.42	91.59	6.0E-05	0.9718	54.97	94.72
Bio1	5.79	0.05	0.5495	3.32	6.05	0.01	0.8282	2.11	6.03
MBio1	4.37	0.06	0.7257	2.90	4.67	0.01	0.9460	1.31	4.66

Model	Elovich				Intra-particle				
Parameters	α	β	R^2	ASE	kid	z	R^2	ASE	D
CoAC	9.34	0.04	0.9822	53.45	28.23	0.22	0.9647	62.10	1.47E-09
MCoAC	2.08	0.07	0.9860	23.22	9.39	0.30	0.9788	27.48	4.52E-10
Bio1	175258.22	3.52	0.9867	0.43	3.96	0.05	0.9874	0.35	2.00E-08
MBio1	7063.47	3.807	0.9671	0.77	2.958	0.06	0.9523	0.93	1.86E-08

- Kinetic plots exhibit nonlinear curves characterised by steep slope at the lower end of the plot with data points within the vicinity of the ordinate axis
- Also, the slopes of the pristine sorbents at the early stages are steeper than those of their corresponding magnetic pairs
- In this study, according to both linear fitting and correlation plots, the Elovich kinetic model describes the experimental kinetic data better
- Among sorbent pairs, α values for the nonmagnetic sorbents are larger than those of their corresponding magnetic pairs
- The Elovich constant β – the desorption constant - due to the BCs is higher compared to the ACs system. It is hence an evidence that the ACs have higher number of sites.

CONCLUSION

- Substantial retrieval (72.38%) of magnetic biochar added as 1.2% to agricultural soil was recorded.
- In general, analysis of data by nonlinear methods resulted in better data fit and as such returned more accurate model parameters.
- The difference in sorption capacities between the magnetic and nonmagnetic ACs and BCs was found to be due to the lesser content (ca. 35%) of carbon material in the composites.
- Hydrophobic interactions alone could not explain why the relatively more hydrophobic diclofenac sorbs less than ibuprofen.
- Elovich model had the best fitting to experimental data. The diffusion based fractional power intra-particle model also exhibited very good fitting.
- In the overall, the magnetised sorbents behaved in very similar manner with their corresponding pristine pair under all tested conditions.

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