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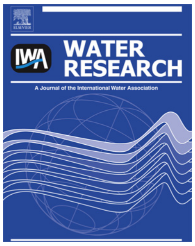

Kinetics of hydrophobic organic contaminant extraction from sediment by granular activated carbon

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A B S T R A C T

Ex situ solid phase extraction with granular activated carbon (GAC) is a promising technique to remediate contaminated sediments. The methods' efficiency depends on the rate by which contaminants are transferred from the sediment to the surface of GAC. Here, we derive kinetic parameters for extraction of polycyclic aromatic hydrocarbons (PAH) from sediment by GAC, using a first-order multi-compartment kinetic model. The parameters were obtained by modeling sediment-GAC exchange kinetic data following a tiered model calibration approach. First, parameters for PAH desorption from sediment were calibrated using data from systems with 50% (by weight) GAC acting as an infinite sink. Second, the estimated parameters were used as fixed input to obtain GAC uptake kinetic parameters in sediment slurries with 4% GAC, representing the *ex situ* remediation scenario. PAH uptake rate constants (k_{GAC}) by GAC ranged from 0.44 to 0.0005 d^{-1}, whereas GAC sorption coefficients (K_{GAC}) ranged from $10^{5.57}$ to $10^{8.57}$ L kg^{-1}. These values are the first provided for GAC in the presence of sediment and show that *ex situ* extraction with GAC is sufficiently fast and effective to reduce the risks of the most available PAHs among those studied, such as fluorene, phenanthrene and anthracene.

1. Introduction

In industrialized regions, aquatic sediments are often contaminated with toxic and persistent hydrophobic organic compounds (HOCs), such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorine hydrocarbons, thus posing a threat to the chemical and ecological status of water systems (Larsson, 1985). Emissions and transport of HOCs have resulted in HOC concentrations exceeding sediment and water quality criteria, particularly in densely inhabited or highly industrialized areas, depositional

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Table 1 – Sediment characteristics and first-order desorption rate parameters with standard errors (SE) obtained from Tenax and GAC tests at infinite sink condition (Eq. (5)).

First-order exponential model (Eq. (5))

Sorbate	Number of rings	C_{SED} (mg/kg)	Reduction of C_{SED}, %	F_{fast}	SE	k_{fast} (1/d)	SE	F_{slow}	SE	$k_{slow} \times 10^{-3}$ (1/d)	SE	R^2	RMSE*
Tenax:SED 1:1 ratio													
FL	3	99.8 (6.5)[a]	89	0.789	0.018	2.546	0.345	0.211	0.008	5.489	1.035	0.998	0.070
PHE	3	304.8 (16.9)	84	0.739	0.020	2.455	0.360	0.261	0.009	4.340	0.830	0.998	0.060
ANT	3	116.7 (5.3)	69	0.567	0.034	1.403	0.290	0.433	0.016	3.039	0.785	0.990	0.062
FLU	4	323.5 (14.6)	79	0.688	0.010	2.288	0.156	0.312	0.004	3.221	0.327	0.999	0.026
PYR	4	199.5 (5.9)	80	0.728	0.014	1.842	0.131	0.272	0.006	2.648	0.490	0.999	0.039
BaA	4	106.9 (9.2)	64	0.579	0.014	1.382	0.100	0.421	0.006	1.473	0.294	0.998	0.025
CHR	4	96.6 (11.4)	68	0.571	0.025	0.826	0.097	0.429	0.013	2.449	0.591	0.994	0.040
BbF	5	92.0 (11.9)	48	0.406	0.009	0.498	0.024	0.594	0.005	1.219	0.148	0.999	0.012
BkF	5	40.7 (4.1)	41	0.359	0.015	0.464	0.044	0.641	0.01	0.732	0.231	0.996	0.018
BaP	5	105.9 (15.3)	58	0.509	0.016	0.401	0.029	0.491	0.011	1.376	0.340	0.998	0.025
DBA	6	10.0 (3.2)	43	0.329	0.014	0.189	0.019	0.671	0.012	1.372	0.246	0.997	0.016
BghiP	6	45.9 (4.4)	51	0.384	0.015	0.141	0.013	0.616	0.015	1.914	0.308	0.998	0.017
InP	6	51.3 (4.2)	42	0.296	0.013	0.147	0.014	0.704	0.012	1.573	0.218	0.998	0.013
Σ13 EPA PAHs		1604.3 (90.2) **40**[b]											
TPH (mg/kg)		5370 (410)											
TOC; OC; BC (%)		4.46; 2.61; 1.85											

Sorbate	Number of rings	Reduction of C_{SED}, %	F_{fast}	SE	k_{fast} (1/d)	SE	F_{slow}	SE	$k_{slow} \times 10^{-3}$ (1/d)	SE	R^2	RMSE*
GAC:SED 1:1 ratio												
FL	3	93	0.807	0.021	2.757	0.415	0.193	0.010	7.192	1.505	0.998	0.100
PHE	3	84	0.744	0.024	2.225	0.302	0.256	0.011	5.010	1.088	0.997	0.098
ANT	3	77	0.686	0.033	1.165	0.146	0.315	0.017	3.790	1.143	0.994	0.090
FLU	4	79	0.652	0.028	2.164	0.379	0.349	0.013	5.198	0.951	0.995	0.085
PYR	4	78	0.635	0.045	2.075	0.560	0.365	0.020	5.586	1.478	0.988	0.123
BaA	4	64	0.425	0.082	0.778	0.347	0.596	0.047	4.384	1.643	0.949	0.100
CHR	4	52	0.406	0.082	0.573	0.250	0.621	0.050	2.767	1.433	0.940	0.090
BbF	5	53	0.256	0.049	0.486	0.201	0.760	0.033	4.274	0.812	0.976	0.050
BkF	5	55	0.403	0.033	0.566	0.101	0.585	0.020	1.708	0.573	0.986	0.044
BaP	5	37	0.326	0.056	0.548	0.205	0.708	0.033	0.612	0.742	0.935	0.052
DBA	6	29	0.166	0.024	0.228	0.078	0.836	0.020	1.390	0.337	0.983	0.022
BghiP	6	39	0.355	0.035	0.404	0.086	0.674	0.023	0.857	0.522	0.980	0.034
InP	6	43	0.212	0.052	2.942	4.688	0.789	0.022	3.294	0.656	0.950	0.059

RMSE* = Root mean square error.

[a] SD between parenthesis.

[b] Threshold level for intervention (Circulaire bodemsanering, 2012).

zones and industrial harbors. Typically, HOCs bind to organic matter components in the sediment, like amorphous and condensed carbon phases, often referred to as black carbon (BC) (Koelmans et al., 2006).

In the past decade, *in situ* addition of activated carbon (AC) to polluted sediments has received considerable interest as a remediation approach aiming at reducing risks of sediment-bound contaminants, and improving the quality of marine and freshwater habitats (Ghosh et al., 2011; Rakowska et al., 2012). Several field studies have demonstrated the high potential of sediment and soil amendments with AC as a means to reduce aqueous concentrations and bioaccumulation of HOCs in aquatic organisms in various environmental settings (Ghosh et al., 2011; Beckingham and Ghosh, 2011; Cho et al., 2009; Cornelissen et al., 2011; Hale et al., 2012; Kupryianchyk et al., 2013a). Since addition of carbonaceous sorbents leads to significant reduction of contaminant mobility and availability for biouptake (Janssen et al., 2011; Kupryianchyk et al., 2011), the number of *in situ* applications is continuously increasing. However, *in situ* treatment may be incompatible with local regulations or ecological protection goals, or may be less desirable if reuse options for dredged sediments exist. Therefore, in a recent study, we proposed an alternative sediment treatment using mixing of granular AC (GAC) with the contaminated sediment, followed by subsequent removal of the contaminant loaded GAC as a beneficial reuse approach for dredged or disposed sediments (Rakowska et al., 2013). A central criterion for the applicability of this technique is sufficient transport of HOCs from the sediment to the GAC during the mixing stage. Consequently, an improved understanding of desorption and adsorption time scales in mixed sediment-GAC systems is required. This includes constraining kinetic parameters for short- and long-term sorption processes for a range of chemicals.

To date, desorption kinetics of HOCs from sediments are usually described using multi-compartment first order