

Supporting information

Water flow variability affects adsorption and oxidation of ciprofloxacin onto hematite

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12 Pages, 6 Figures, 2 Tables, 2 Texts

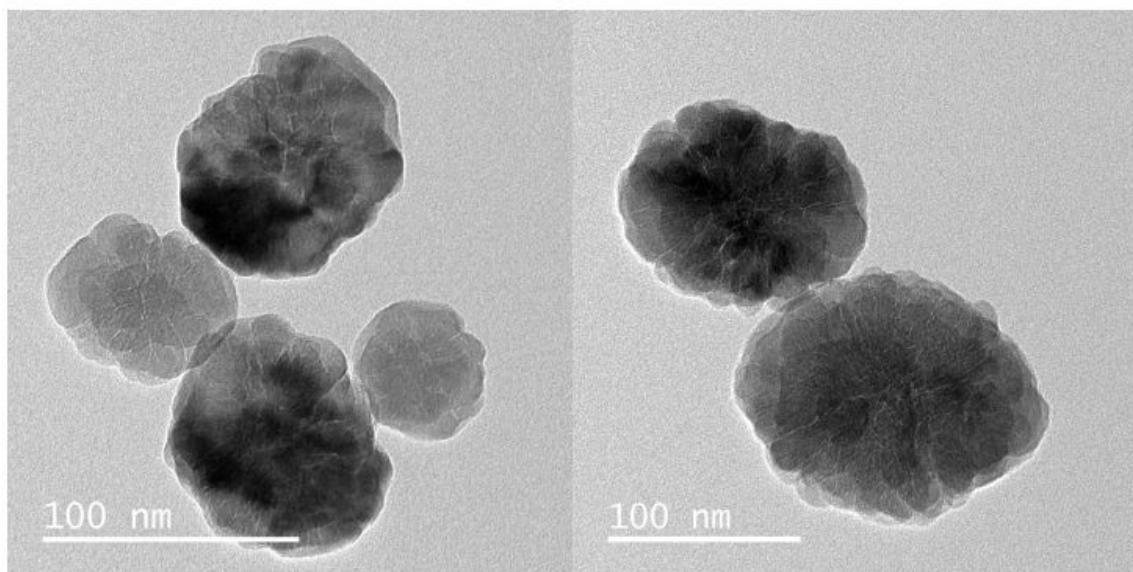


Fig.S1 Transmission electron microscopy images of synthetic hematite

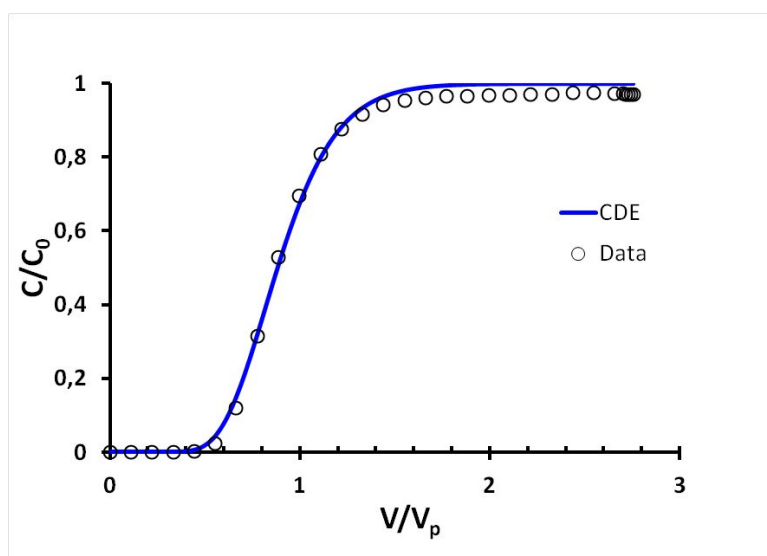


Fig.S2 Experimental breakthrough curve of the Br non-reactive tracer, and calculated curve (line) based on a CDE model. Inflow conditions: 10 mM KBr and 10 mM NaCl. PV=3.7 mL and 0.1 mL/min

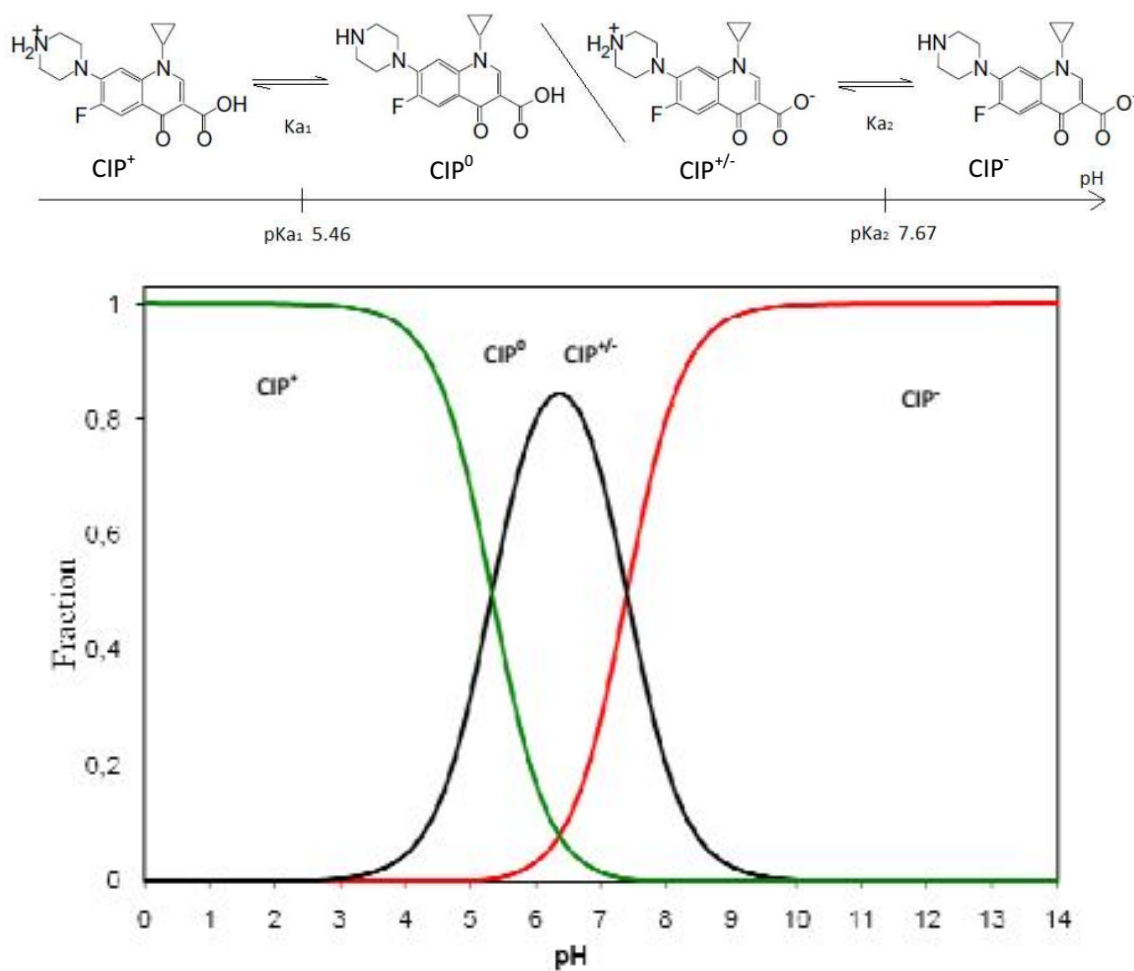


Fig.S3 Chemical speciation of ciprofloxacin versus pH.

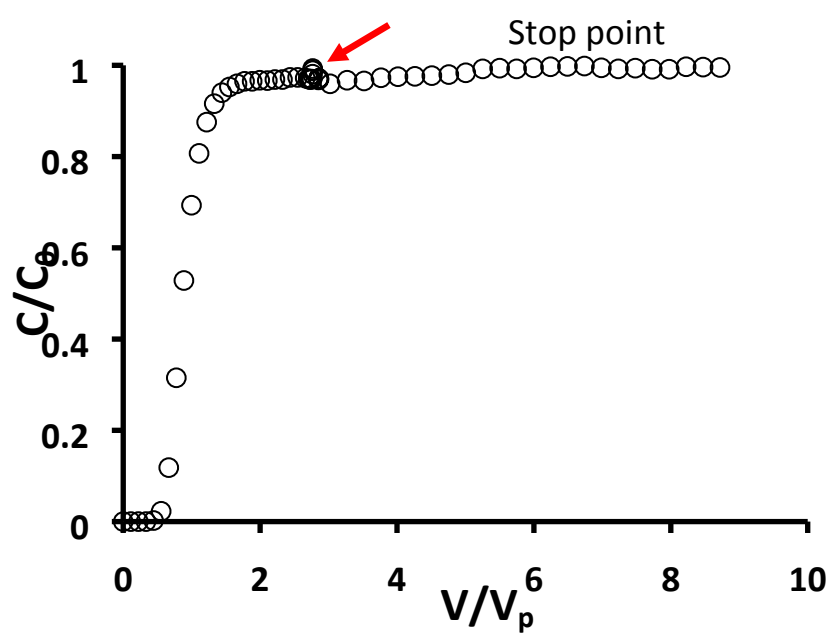


Fig.S4. Experimental BTC of bromide. Inflow conditions: 10 mM KBr and 10 mM NaCl. PV=3.7 mL and 0.1 mL/min. The arrow indicates the moment of flow-interruption (duration 16h).

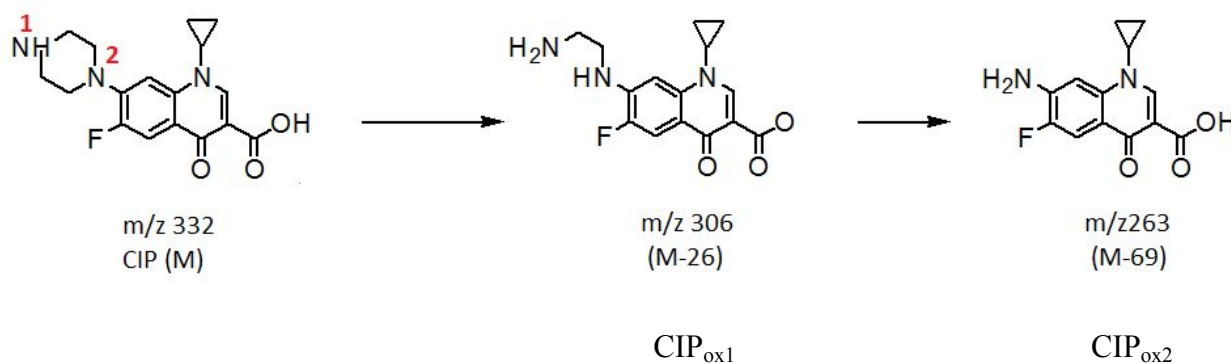


Fig.S5. Ciprofloxacin and identified oxidation byproducts by LC/MS (the M-X indicates the net mass loss of the product from the parent CIP).

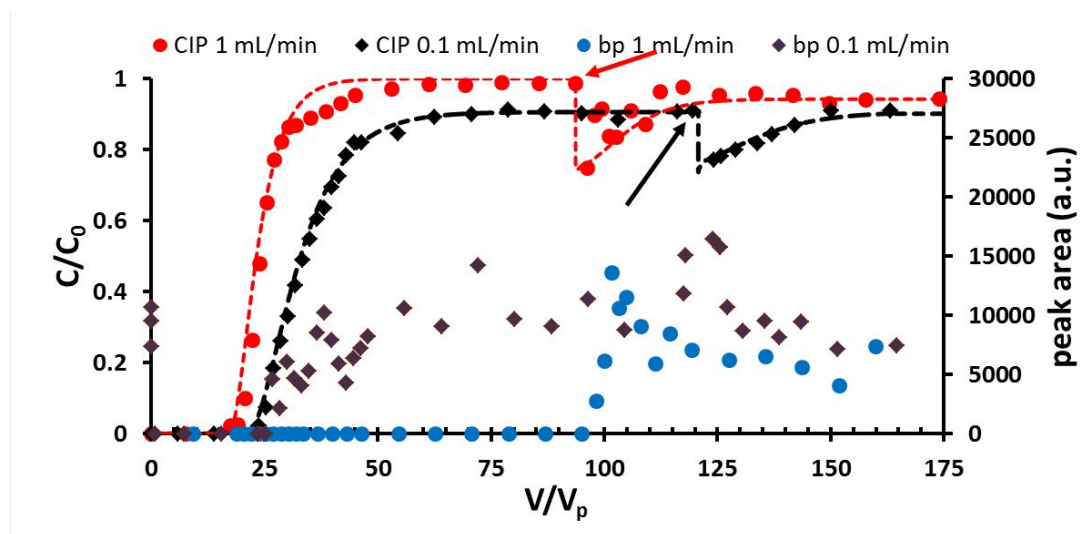


Fig.S6 Experimental and calculated BTCs of CIP. Inflow conditions: pH_{in} 5.5; 20 μ M, 10 mM NaCl $V_p=3.7$ mL. Solid lines represent the calculated BTC. The arrow indicates the moment of flow-interruption (duration 16h). The flow rate is constant before and after flow interruption in this case (Col-8).

Table S1. Experimental conditions for dynamic column breakthrough experiments

column ID	Inflow pH	Flow rate (mL/min)	Input boundary condition	Number of FI events	Duration of each FI event
Col-1	pH 5.5	1	Step	-	-
Col-2	pH 5.5	0.1	Step	-	-
Col-3	pH 7	1	Step	-	-
Col-4	pH 7	0.1	Step	-	-
Col-5	pH 5.5	1-0.1	Flow-interruption	1	16h
Col-6	pH 5.5	0.1-0.1	Flow-interruption	1	16h
Col-7	pH 5.5	1	Flow-interruption	4	16h
Col-8	pH 5.5	1-1	Flow-interruption	1	16h

Table S2. Degradation rate coefficient (k , min⁻¹) calculated from multiple flow-interruption events using eq. 6.

Column ID	FI-1	FI-2	FI-3	FI-4
Col-5	1.0×10^{-4}	-	-	-
Col-6	5.8×10^{-5}	-	-	-
Col-7	1.3×10^{-4}	4.0×10^{-5}	5.7×10^{-5}	2.5×10^{-5}
Col-8	1.3×10^{-4}	-	-	-

Text S1. Sensitivity Analysis

During curve-fitting, 4 parameters were estimated including the parameters of adsorption isotherms K_d (the empirical distribution coefficient) and β (the index constant determining the linearity or nonlinearity of sorption isotherm), first-order kinetic sorption rate ω and the first-order degradation rate μ_s . In Hydrus 1-D, least-squares optimization method is used for parameter estimation. The goodness of fit and the problem of parameter non-uniqueness can be analyzed by comparing parameters including R^2 , confidence interval (95% CI) and standard error of the coefficient.

The BTCs (flow rate 0.1 mL/min, pH5.5) obtained by both step injection and flow interruption method were selected to test the fitting procedure. As isotherms for many organic compounds have β values less than 1 (Brusseau, 1989a), a relatively rough estimation was firstly conducted by setting a range of β (0.2 - 1.2) and adjusting the other parameters to fit the experimental data. Figure S1-1 and Table S1-1 showed the fitted curves and the corresponding results of parameter estimation respectively.

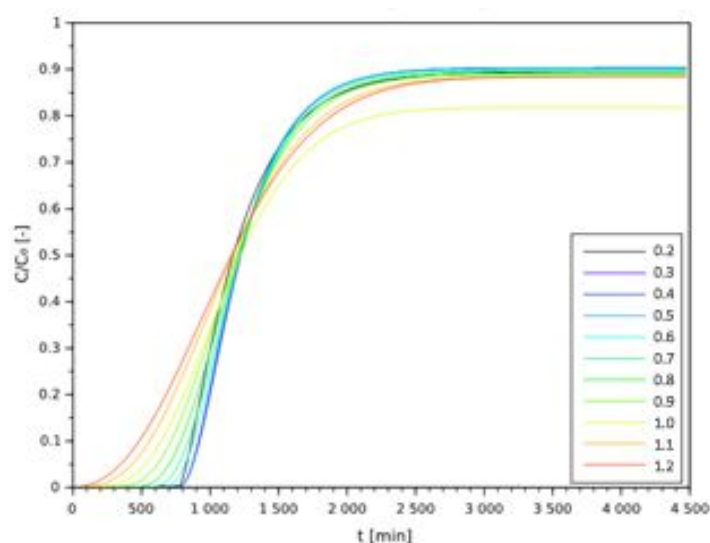


Figure S1-1. Fitted curves by setting a range of β and adjusting other 3 parameters

Table S1-1. Parameter estimation from least-squares analysis

$\beta(-)$	R^2	Variable	Value	S.E.Coeff	95% confidence limits	
					Lower	Upper
0.2	0.9930	$K_d (\text{mol}^{1-\beta}\text{cm}^{3\beta}\text{g}^{-1})$	7.65	1.21×10^{-1}	7.39	7.91
		$\mu_s (\text{min}^{-1})$	9.08×10^{-5}	1.14×10^{-5}	6.64×10^{-5}	1.15×10^{-4}
		$\omega (\text{min}^{-1})$	3.46×10^{-3}	8.36×10^{-4}	1.67×10^{-3}	5.25×10^{-3}
0.3	0.9985	$K_d (\text{mol}^{1-\beta}\text{cm}^{3\beta}\text{g}^{-1})$	7.78	5.53×10^{-2}	7.66	7.90
		$\mu_s (\text{min}^{-1})$	8.35×10^{-5}	5.85×10^{-6}	7.10×10^{-5}	9.61×10^{-5}
		$\omega (\text{min}^{-1})$	6.69×10^{-3}	2.99×10^{-4}	6.05×10^{-3}	7.33×10^{-3}
0.4 Best fit	0.9986	$K_d (\text{mol}^{1-\beta}\text{cm}^{3\beta}\text{g}^{-1})$	7.78	3.87×10^{-2}	7.70	7.86
		$\mu_s (\text{min}^{-1})$	8.25×10^{-5}	5.20×10^{-6}	7.13×10^{-5}	9.36×10^{-5}
		$\omega (\text{min}^{-1})$	5.86×10^{-3}	3.35×10^{-4}	5.14×10^{-3}	6.58×10^{-3}
0.5	0.9984	$K_d (\text{mol}^{1-\beta}\text{cm}^{3\beta}\text{g}^{-1})$	7.71	7.19×10^{-2}	7.56	7.86
		$\mu_s (\text{min}^{-1})$	8.47×10^{-5}	6.35×10^{-6}	7.11×10^{-5}	9.84×10^{-5}
		$\omega (\text{min}^{-1})$	7.40×10^{-3}	2.92×10^{-4}	6.77×10^{-3}	8.02×10^{-3}
0.6	0.9975	$K_d (\text{mol}^{1-\beta}\text{cm}^{3\beta}\text{g}^{-1})$	7.69	1.05×10^{-1}	7.47	7.92
		$\mu_s (\text{min}^{-1})$	8.67×10^{-5}	9.03×10^{-6}	6.74×10^{-5}	1.06×10^{-4}
		$\omega (\text{min}^{-1})$	9.20×10^{-3}	4.43×10^{-4}	8.25×10^{-3}	1.02×10^{-2}
0.7	0.9954	$K_d (\text{mol}^{1-\beta}\text{cm}^{3\beta}\text{g}^{-1})$	7.65	1.67×10^{-1}	7.29	8.01
		$\mu_s (\text{min}^{-1})$	9.09×10^{-5}	1.38×10^{-5}	6.14×10^{-5}	1.21×10^{-4}
		$\omega (\text{min}^{-1})$	1.17×10^{-2}	7.88×10^{-4}	1.00×10^{-2}	1.34×10^{-2}
0.8	0.9903	$K_d (\text{mol}^{1-\beta}\text{cm}^{3\beta}\text{g}^{-1})$	7.57	2.73×10^{-1}	6.98	8.15
		$\mu_s (\text{min}^{-1})$	9.69×10^{-5}	2.16×10^{-5}	5.05×10^{-5}	1.43×10^{-4}
		$\omega (\text{min}^{-1})$	1.45×10^{-2}	1.41×10^{-3}	1.15×10^{-2}	1.76×10^{-2}
0.9	0.9812	$K_d (\text{mol}^{1-\beta}\text{cm}^{3\beta}\text{g}^{-1})$	7.46	4.10×10^{-1}	6.59	8.34
		$\mu_s (\text{min}^{-1})$	1.03×10^{-4}	3.11×10^{-5}	3.59×10^{-5}	1.69×10^{-4}
		$\omega (\text{min}^{-1})$	1.73×10^{-2}	2.24×10^{-3}	1.25×10^{-2}	2.21×10^{-2}
1	0.9668	$K_d (\text{mol}^{1-\beta}\text{cm}^{3\beta}\text{g}^{-1})$	7.39	6.71×10^{-1}	5.95	8.83
		$\mu_s (\text{min}^{-1})$	1.77×10^{-4}	6.63×10^{-5}	3.48×10^{-5}	3.19×10^{-4}
		$\omega (\text{min}^{-1})$	1.93×10^{-2}	3.72×10^{-3}	1.13×10^{-2}	2.73×10^{-2}
1.1	0.9549	$K_d (\text{mol}^{1-\beta}\text{cm}^{3\beta}\text{g}^{-1})$	7.31	7.12×10^{-1}	5.78	8.83
		$\mu_s (\text{min}^{-1})$	1.10×10^{-4}	5.02×10^{-5}	1.85×10^{-6}	2.17×10^{-4}
		$\omega (\text{min}^{-1})$	2.08×10^{-2}	3.89×10^{-3}	1.24×10^{-2}	2.91×10^{-2}
1.2	0.9417	$K_d (\text{mol}^{1-\beta}\text{cm}^{3\beta}\text{g}^{-1})$	7.28	8.56×10^{-1}	5.44	9.12
		$\mu_s (\text{min}^{-1})$	1.10×10^{-4}	5.85×10^{-5}	-1.55×10^{-5}	2.36×10^{-4}
		$\omega (\text{min}^{-1})$	2.16×10^{-2}	4.52×10^{-3}	1.19×10^{-2}	3.13×10^{-2}

According to the results, the best fit ($R^2=0.9986$) was found when β was 0.4. Meanwhile, the 95% confidence intervals of the other 3 parameters were reasonable.

Then a sensitivity analysis was conducted around the best fit for all the four parameters to see how each parameter may affect the shape of BTC. For example, we set a range of K_d from

3 to 12 and kept the other 3 parameters identical to the values of the best fit. Similar procedures were also applied to β (0.2~1.2), ω (0.001~0.01 min⁻¹) and μ_s (0~ 8×10^{-6} min⁻¹).

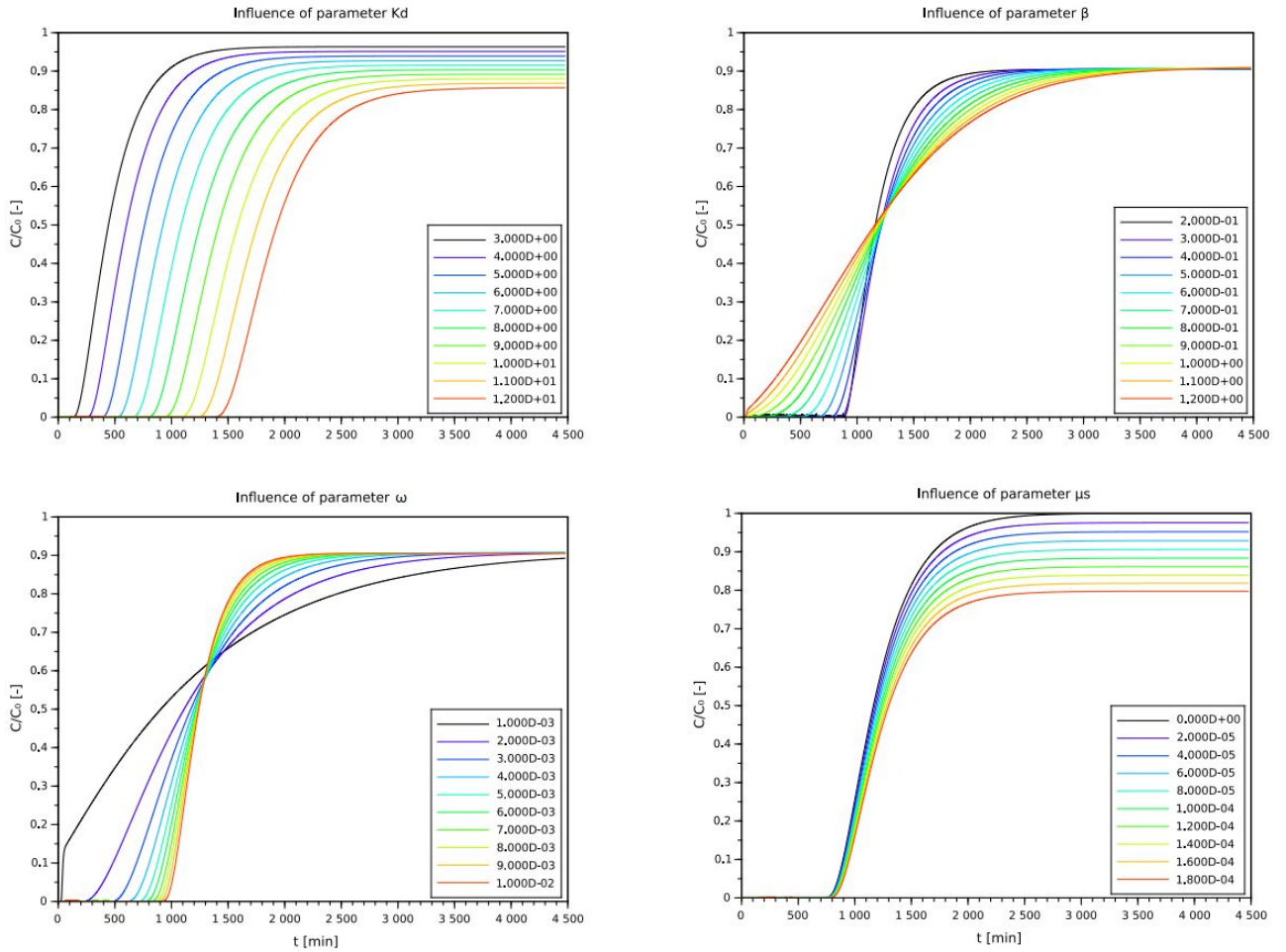


Figure S1-2. Sensitivity analysis around best fit.

From the results (Figure S1-2), BTC shifted to left and the position of plateau in the end of BTC would rise with the decrease of K_d . In addition, there was no change in the slope of early breakthrough part and tailing part with varying K_d . For μ_s , with the increase of degradation rate, the position of plateau in the end of BTC dropped down and the slope of early breakthrough part decreased slightly. Briefly, K_d determines the position of BTC front in x-axis and μ_s determines the plateau after reaching equilibrium. These two parameters could be determined from the previous best fit because both 95% CI are small. The parameter β and ω control the slope of early breakthrough part and tailing part, which correspond to the results of Brusseau et al. (1989a). Indeed, occurrence of nonequilibrium may be overlooked due to nonlinearity isotherms in traditional column experiments.

A further analysis was conducted to investigate the relation between β and ω with flow-interruption method. Three cases were selected to fit the BTC with flow interruption:

1) fit the experimental points with ω obtained from previous BTC with step injection in the condition of degraded $\beta=0.8$,

2) fit the experimental points with β obtained from previous BTC with step injection in the condition of degraded $\omega=0.0035$,

3) find the best fit by adjusting ω and β simultaneously.

In the 3 cases, K_d and μ_s values from the previous best fit are kept constant.

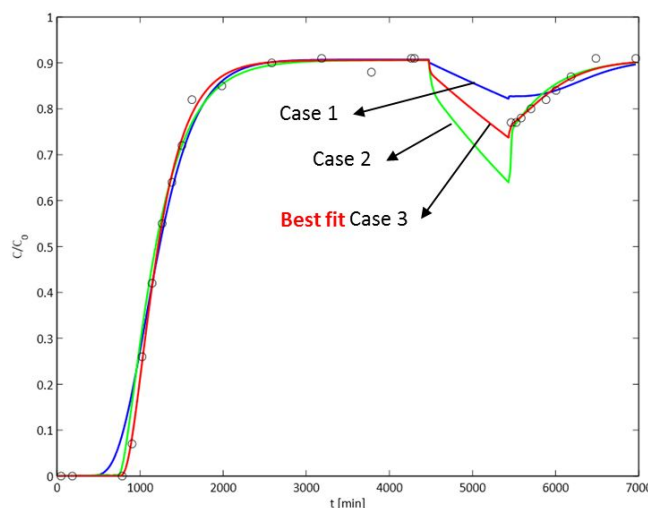


Figure S1-3. Three cases of curve-fitting by using flow interruption method

Table S1-2 Parameter estimation of three cases

Parameters	Case 1	Case 2	Case 3
K_d ($\text{mol}^{1-\beta}\text{cm}^3\text{g}^{-1}$)	7.80	7.80	7.80
β (-)	0.8	0.25	0.4 (95% CI 0.369~0.431)
ω (min^{-1})	1.37×10^{-2}	3.50×10^{-3}	5.87×10^{-3} (95% CI $5.61 \times 10^{-3} \sim 6.12 \times 10^{-3}$)
μ_s (min^{-1})	8.0×10^{-5}	8.0×10^{-5}	8.0×10^{-5}
R^2	0.9873	0.9928	0.9984

These results show that case1 and case2 could fit the BTC before stop-flow in a relatively good way, but both failed to fit the concentration drop during the flow-interruption period. Following the flow interruption method proposed by Brusseau et al. (1989b), the first order kinetic rate ω was determined in a more reliable way in Case3 (Fig. S1-3). The value β was in the valid confident interval. We compared the best fits from case 3 and the one from previous rough estimation. The results of parameter estimation were quite close, indicating that parameter non-uniqueness is of less importance. Therefore, our fitting procedure by setting a range of β is reliable when the goodness of fit is quite close to the best fit. Following this

method parameter estimation was conducted by fitting the breakthrough points from col-1, col-2, col-3, col-4 (Table S1-2).

As for BTC from col-5 and BTC from multiple stop-flow events, the parameters of sorption isotherms and first-order kinetic sorption rate ω were those of col-1. The degradation rate μ_s was determined by fitting the concentration drop during the flow-interruption period. The concentration drop was caused by not only non-equilibrium sorption but also the degradation reaction. However, the extent of concentration drop controlled by non-equilibrium sorption and degradation was different. If we assume that there is no change in the parameters of adsorption isotherms during the column experiment, we can improve the fit by adjusting degradation rate μ_s .

References:

- Brusseau M. L., Rao, P. S. C. & Gillham R. W. Sorption nonideality during organic contaminant transport in porous media, *Critical Reviews in Environmental Control*, *19*, **1989a**, 33-99.
- Brusseau, M. L., Rao, P. S. C., Jessup, R. E., & Davidson, J. M. Flow interruption: A method for investigating sorption nonequilibrium. *Journal of Contaminant Hydrology*, *4*, **1989b**, 223-240.

Text S2. Kinetic study at two pH values

The disappearance kinetics of compounds undergoing adsorption/transformation process on metal oxides cannot be described by simple equations that include classical exponential functions (*e.g.*, pseudo-first order model). This behavior has been attributed to the complexity of involved reactions including formation of precursor complex, dissolution of reduced metal, accumulation of reaction products and/or a gradual change of the surface reactivity. Instead, we calculated an initial rate constant (k_{in} in min^{-1}) over the first stage of reaction (*e.g.* 5h) by plotting a linear regression of $-\ln([\text{CIP}]_{\text{tot}}/[\text{CIP}]_0)$ versus time, and only for total concentrations corresponding to the degradation reaction (Fig. S2-1). We found very comparable rates at two pH values: $5 \times 10^{-4} \text{ min}^{-1}$ at pH 5.5 and $6 \times 10^{-4} \text{ min}^{-1}$ at pH 7.

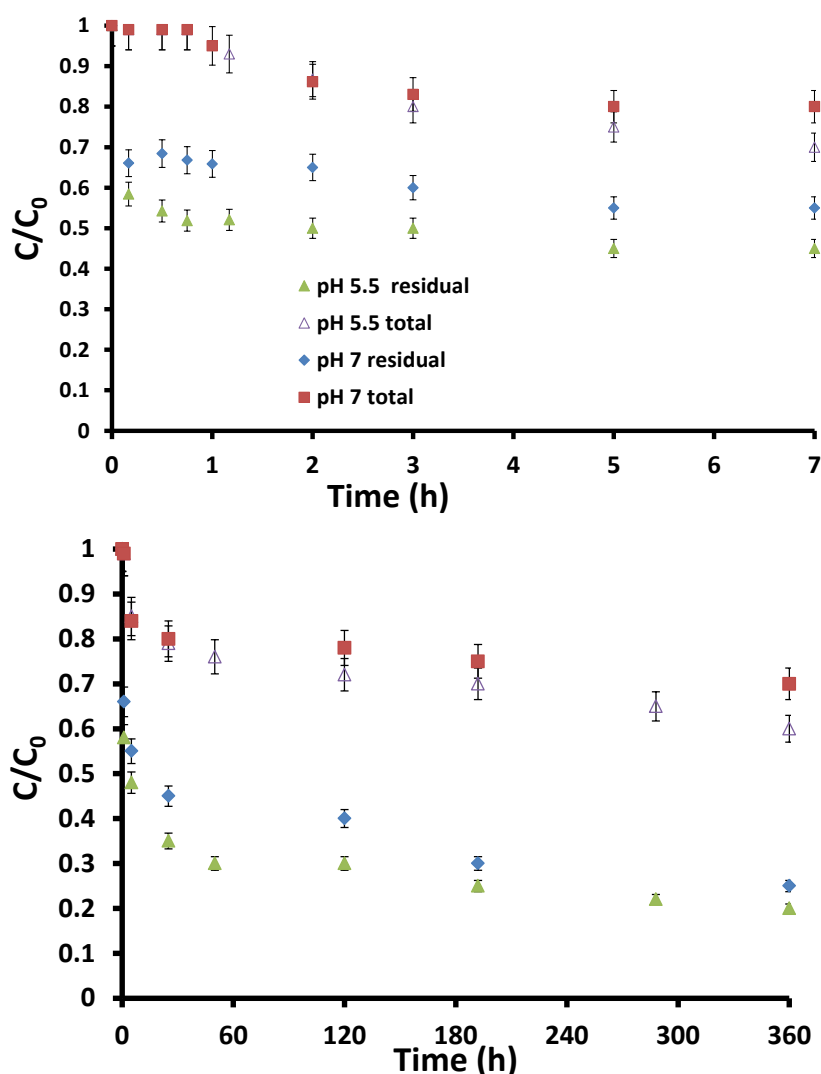


Figure S2-1. Removal kinetics of CIP at two pH values with an ionic strength of 0.01M (NaCl) and for two total durations: 7 hours-experiment and 15 days-experiment. 1 g/L of hematite ($39.3 \text{ m}^2/\text{g}$), CIP $20 \text{ }\mu\text{M}$, $20 \text{ }^\circ\text{C}$. Residual = aqueous residual concentration; total = total concentration representing both aqueous (residual) and adsorbed concentrations. The total concentration was measured after desorption by increasing pH of suspension to 10.