Supplementary Information (SI) for New Journal of Chemistry.

Supporting Information

Investigating Nalidixic Acid Adsorption onto Ferrihydrite and Maghemite Surfaces: Molecular-Level Insights via Continuous-Flow ATR-FTIR spectroscopy

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A. Substrates synthesis

Synthesized substrates were characterized by X-ray Diffraction (XRD) and results are coherent with protocols used. Indexation proposed is based in literature[59–61].

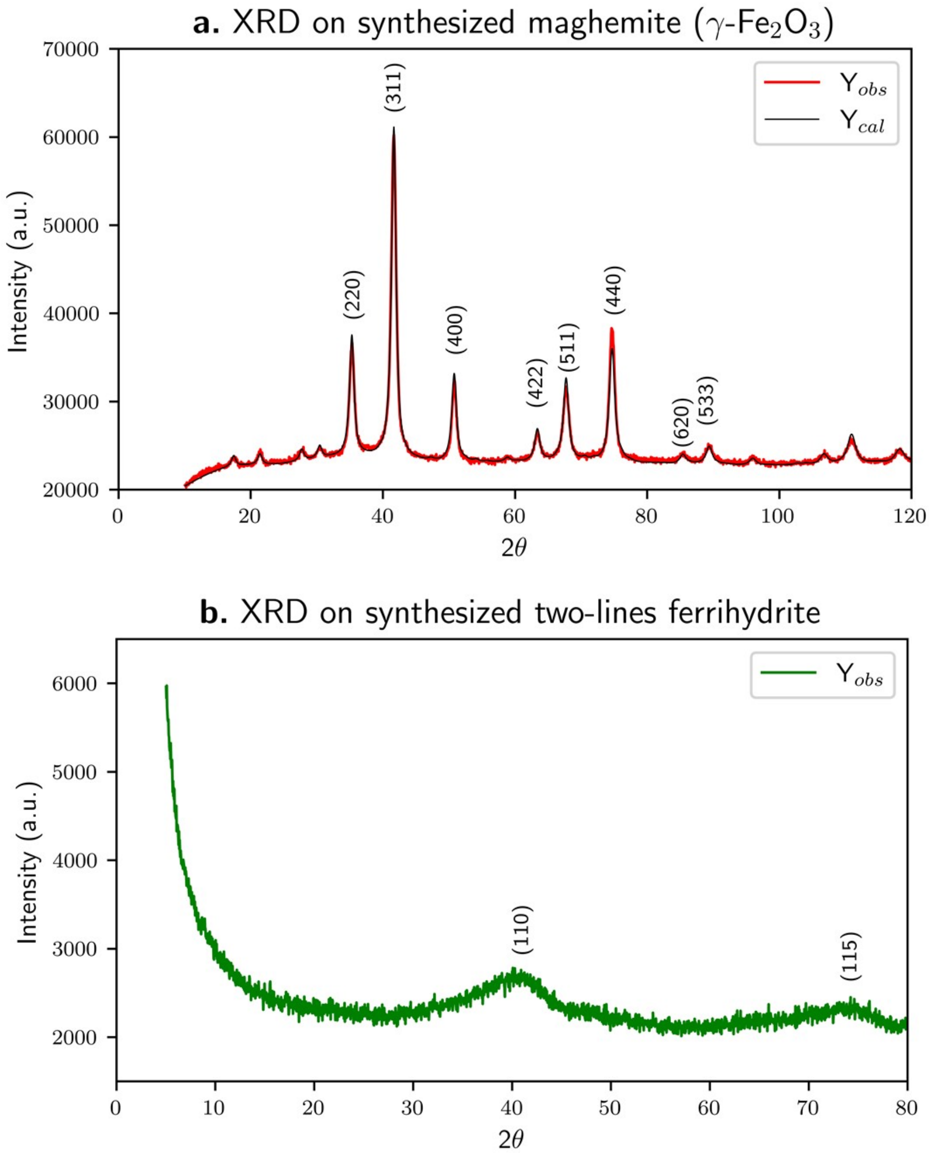

Figure S1. Powder XRD patterns of synthetic (**a**) nano-maghemite and (**b**) two-lines ferrihydrite samples. Result of the Rietveld refinement of the Mh pattern is shown with fitting curve in red color and experimental curve in black color (see text and Table 1).

B. The re-circulating set-up

The system is organized in four parts. As starting point there is a (i) mixing chamber (Flask A), followed by a (ii) laminar chamber (Flask B), a HATR-FTIR flow-through cell (accessory acquired from PIKE Technologies) and a (iv) peristaltic pump pulling the solvent and assuring constant circulation. Precision soft-walled tubing (Tygon, ϕ 1.59) was used to connect all parts and secured by Teflon barbed-to-male or barbed-to-female Luer joints. The entry/exit on each flask was supported by stainless steel needles (ϕ 0.6 and 0.9). It is noteworthy that, flask A possesses a magnetic stirrer to ensure flux homogeneity, while flask B contains a pH meter for flow monitoring and acts as a bubble trap (it does not contain stirrer), ensuring laminar flow state before entering the HATR cell. Nonetheless, a filter (Minisart 0.2 µm) was positioned before flux re-enter flask A to ensure nanoparticles removal in the case of coating detachment.

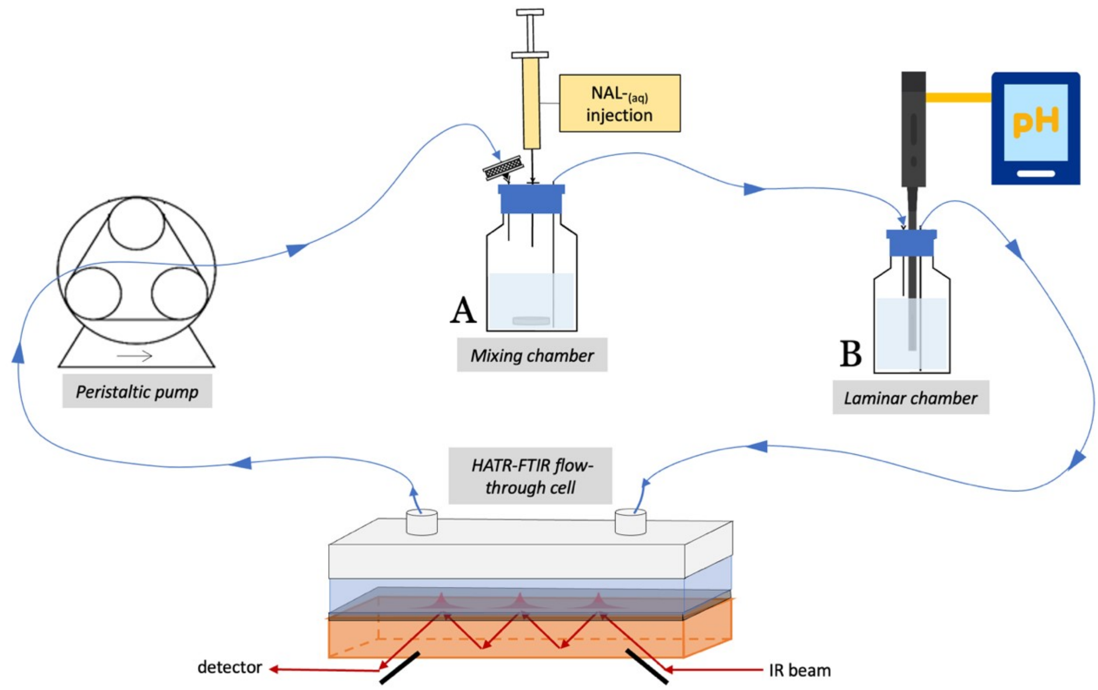

Figure S2. Schematics of the dynamic re-circulating flow system, easily attachable to the FTIR spectrometer.

C. Experimental and Theoretical intensities

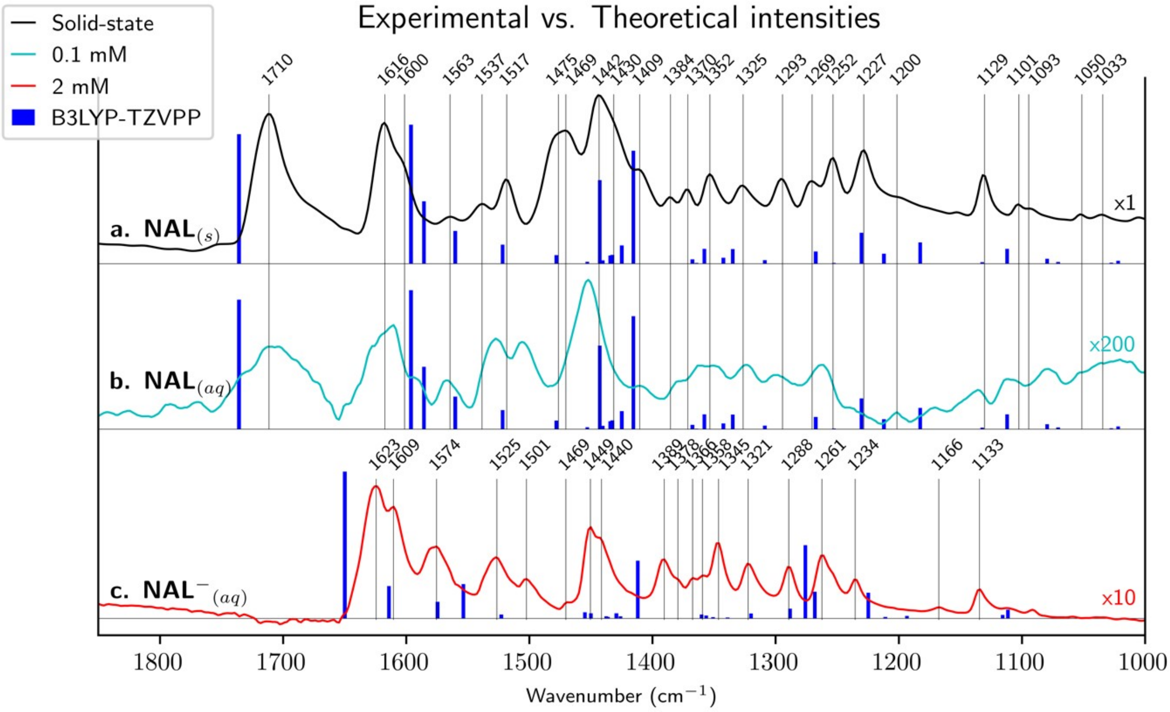

Figure S3. Comparison of experimental and calculated (DFT) spectra for NAL. ATR-FTIR spectra of (**a**) solid-state nalidixic acid ($NAL_{(s)}$) and (**b**) aqueous nalidixic acid ($NAL_{(aq)}$, pH 5) are compared to the calculated spectrum for the protonated molecule, while (**c**) aqueous nalidixate ($NAL^{-}_{(aq)}$, pH 9) is compared to the calculated spectrum for the deprotonated molecule (anion).

D. Following kinetics over time

To extract absorbance information at a precise wavenumber, a python script was generated due to the amount of data related – a spectrum by minute. For kinetics, we aim to follow the relative intensity for a precise peak position. This is doable by following the difference between a baseline and a peak maximum, whereas is relative since the baseline is constantly changing. For us, baseline was each time traced between a set range. For instance, to follow kinetics of peak 1451 cm^{-1}, for Mh-NAL^{-} we set the baseline between the range 1474 and 1419 cm^{-1}. See all specifications bellow.

Table S1. Range specifications for relative intensity data extraction and kinetics analysis.

Experiment	Target peak [cm^{-1}]	Limits applied for baseline [cm^{-1}]	
a. Mh-NAL^{-} adsorption 2 molecules/nm^2	1528	1690	1474
	1504		
	1451	1474	1419
b. Fh-NAL^{-} adsorption 2 molecules/nm^2	1521	1690	1470
	1498		
	1449	1470	1414

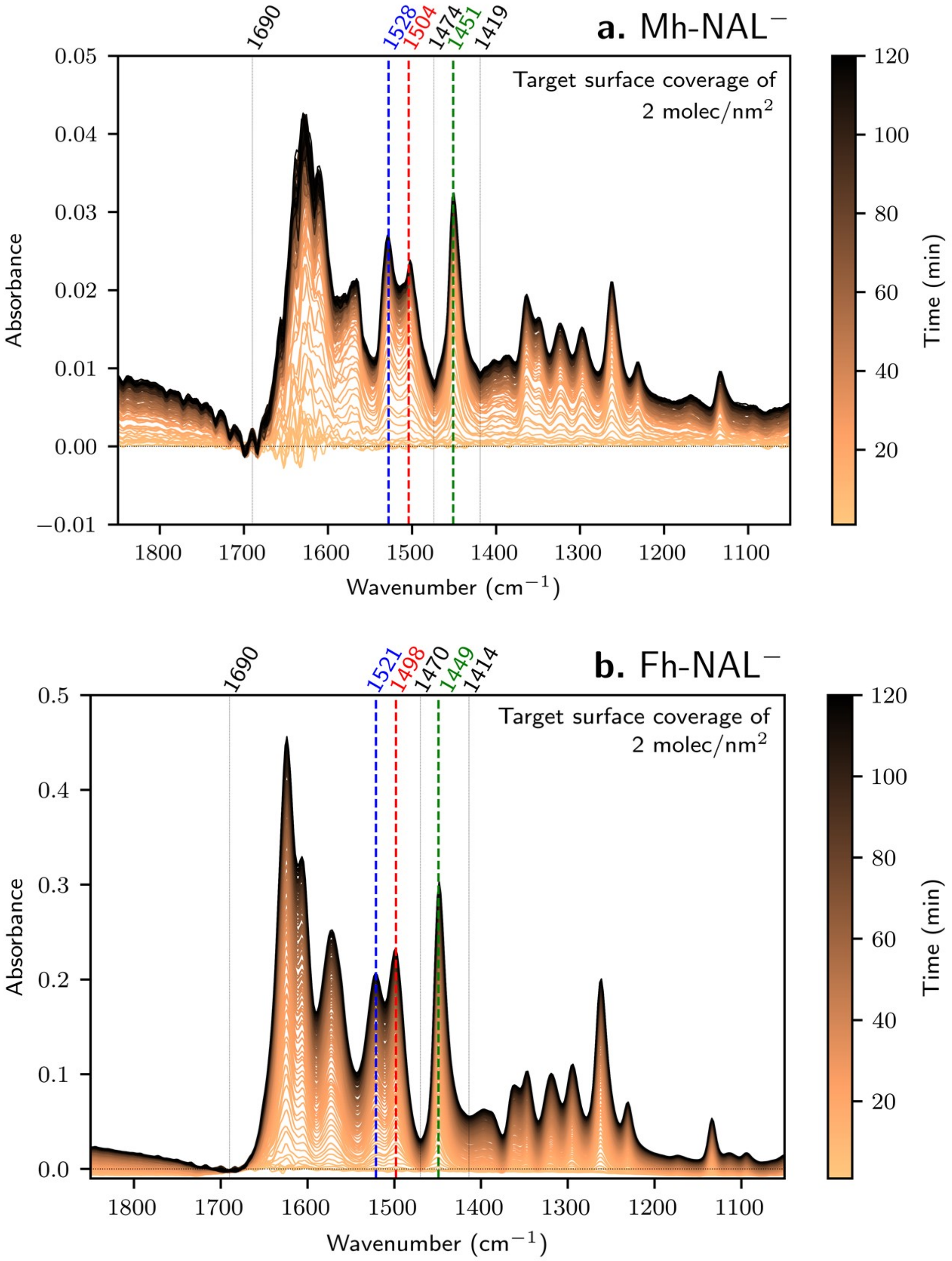

Figure S4. Full experiments performed via the dynamic approach. Sorption with a target surface coverage of 2 molecules/nm^2 on (a) Mh (in a 6-6.3 pH range) and (b) Fh (in a 6-6.9 pH range).

E. Kinetics fitting

Relative intensity data plotted in Figure 5 was fitted with exponential functions for further discussion using Origin software. The fittings were performed using exponential equations given by,

$$y = A_1 * e^{-x/t_1} + y_0$$

Tables bellow summarizes all detail values concerning the fitting performed for each substrate individually. Brief reminder that the sorption experiments here considered are only the ones performed under the dynamic approach.

The adsorption of NAL onto maghemite demonstrated a biexponential fitting.

Table S2. Mh-NAL$^-$ biexponential fitting values.

Fitting for Mh-NAL$^-$	Band [cm^{-1}]	y_0	A_1	t_1	A_2	t_2	Adjusted r^2
Biexponential	1528	0.033	-0.060	6.760	-0.018	275.287	0.994
	1504	0.022	-0.008	186.224	-0.010	6.821	0.991
	1451	0.042	-0.023	460.429	-0.012	7.236	0.997

The adsorption of NAL onto ferrihydrite demonstrated to adequately fit both mono or biexponential fitting. The fitting plotted in Figure 5b is the monoexponential.

Table S3. Fh-NAL$^-$ monoexponential and biexponential fitting values.

Fitting for Fh-NAL$^-$	Band [cm^{-1}]	y_0	A_1	t_1	A_2	t_2	Adjusted r^2
Monoexponential	1521	0.205	-0.190	46.081	-	-	0.998
	1498	0.228	-0.252	41.665	-	-	0.998
	1449	0.270	-0.305	39.436	-	-	0.997
Biexponential	1521	0.232	-0.044	17.058	-0.159	79.302	0.999
	1498	0.253	-0.051	15.038	-0.165	69.652	0.999
	1449	0.307	-0.074	15.786	-0.188	73.532	0.999