Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Biomass@MOF nanohybrid materials for competitive drug adsorption: analysis by conventional macroscopic models and statistical physical models

Bryan Fernando Rivadeneira-Mendoza[1, 2], Luis Santiago Quiroz-Fernández[1], Fausthon Fred da Silva[3], Rafael Luque[4,5]*, Alina M. Balu[2], Joan Manuel Rodríguez-Díaz [1,6]*

[1] Laboratorio de Análisis Químicos y Biotecnológicos, Instituto de Investigación, Universidad Técnica de Manabí, S/N, Avenida Urbina y Che Guevara, Portoviejo 130104, Ecuador.

[2] Departamento de Química Orgánica, Universidad de Córdoba, Edificio Marie Curie (C-3), Campus de Rabanales, Ctra. Nnal. IV-A, Km 396, E14014, Córdoba, Spain.

[3] Departamento de Química, Universidade Federal da Paraíba (UFPB), 58.051-900 João Pessoa, PB, Brazil.

[4] Universidad ECOTEC, Km. 13.5 Samborondón, Samborondón, EC092302, Ecuador, E-mail: rluque@ecotec.edu.ec

[5] National University of Science and Technology Polytehnica Bucharest, 1-7 Gh. Polizu str., Bucharest, Romania, E-mail: rafael.alvarez@upb.ro

[6] Departamento de Procesos Químicos, Facultad de Ciencias Matemáticas, Físicas y Químicas, Universidad Técnica de Manabí, Portoviejo, Ecuador. E-mail: joan.rodriguez@utm.edu.ec

Table S1. Combinations of initial concentrations of KTC and NPX for a competing system

$C_{0KTC} \rightarrow C_{0NPX}$ $C_{0NPX} \rightarrow C_{0KTC}$		$C_{0KTC} \rightarrow C_{0NPX}$ $C_{0NPX} \rightarrow C_{0KTC}$	
0.1	0	0.1	0.1
0.3	0	0.3	0.1
0.5	0	0.5	0.1
0.7	0	0.7	0.1
0.9	0	0.9	0.1
0.1	0.3	0.1	0.5
0.3	0.3	0.3	0.5
0.5	0.3	0.5	0.5
0.7	0.3	0.7	0.5
0.9	0.3	0.9	0.5
0.1	0.7	0.1	0.9
0.3	0.7	0.3	0.9
0.5	0.7	0.5	0.9
0.7	0.7	0.7	0.9
0.9	0.7	0.9	0.9

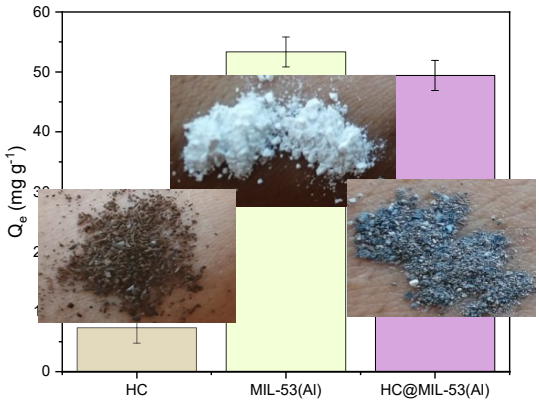

Fig. S1. Comparison of the adsorption capacity (Qe) of the pristine materials and the new composite separately

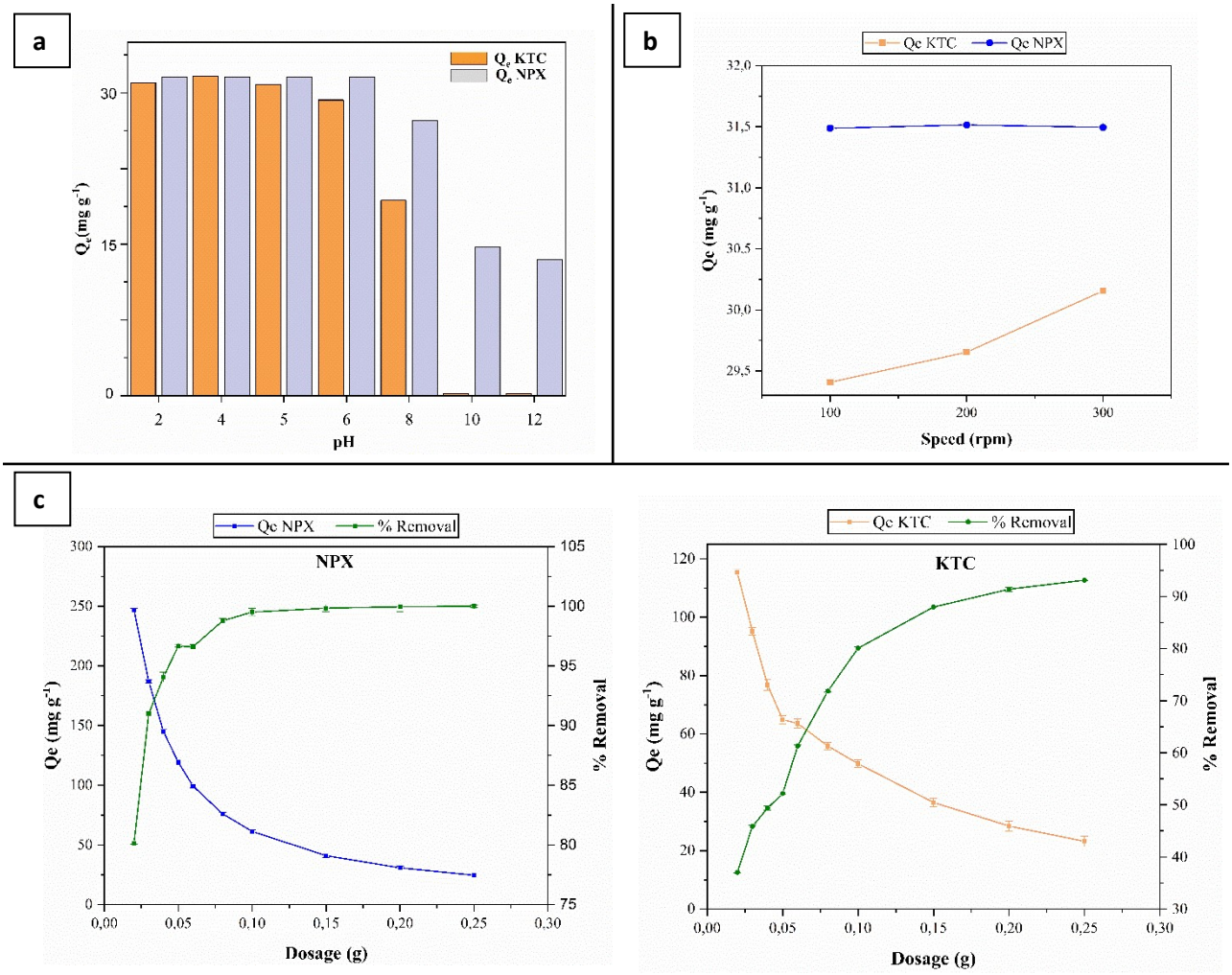

Fig. S2. Main parameters of the ADS: pH study **(a)**, agitation speed study **(b)** and dosage study **(c)**.

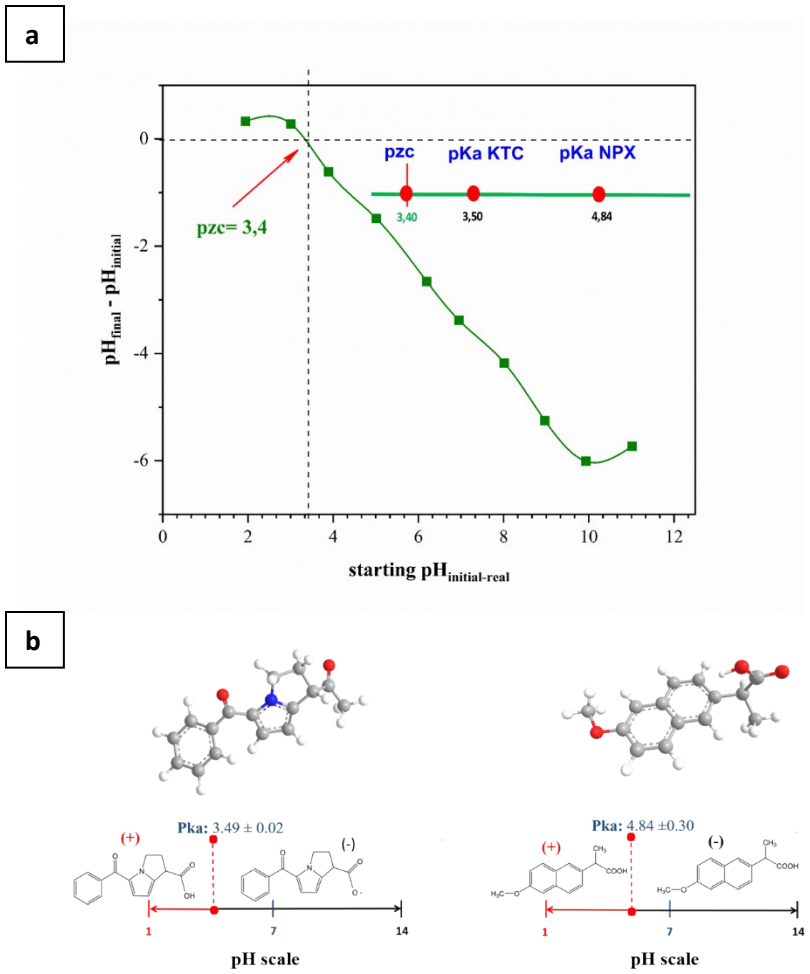

Fig. S.3. Point zero charge (PZC) of HC@MIL-53(Al) obtained by a graphical method **(a)** and related information to the PKa of KTC and NPX as a function of medium pH **(b)**.

Table S2. Kinetic fitting parameters and well-fitting models for the adsorption of KTC on HC@MIL-53(Al)

	C_0 KTC (mg L^{-1})						
Parámetros	**25.53**	**75.58**	**127.63**	**178.69**	**229.40**	**280.79**	**331.85**
Qe, exp (mg g^{-1})	6.623	19.074	29.875	42.429	52.046	64.406	74.928
Pseudo primer orden (PFO)							
Qe, cal (mg g^{-1})	6.573	18.631	29.056	41.178	49.917	50.871	72.445
k_1 (min^{-1})	3.284	3.284	0.382	1.358	25.29	39.38	0.217
R^2	0.649	0.649	0.910	0.981	0.953	0.745	0.979
MPSD	1.564	2.717	14.25	4.260	40.261	60.372	16.685
Pseudo segundo orden (PSO)							
Qe, cal (mg g^{-1})	3.081	6.620	30.292	41.17	52.306	66.903	77.131
k_2 (mg g^{-1} min^{-1})	2.726	0.224	0.023	0.028	0.026	0.005	0.004
R^2	0.969	0.961	0.966	0.990	0.993	0.991	0.986
MPSD	1.051	1.097	8.634	2.863	5.694	8.071	10.113
Avrami Fractionary							
Qe, cal (mg g^{-1})	2.692	18.631	26.045	41.779	47.201	63.73	58.745
k (min^{-1})	0.001	1.310	14.117	0.371	28.817	0.126	25.889
n	0.018	1.311	0.617	0.528	2.961	0.571	1.390
R^2	0.760	0.896	0.789	0.996	0.799	0.993	0.646
MPSD	4.320	13.67	11.400	1.409	23.55	5.780	57.189
Bangham							
k_y (min^{-1})	0.013	0.022	0.028	0.008	0.008	0.004	0.004
α (mg g^{-1} min^{-1})	0.011	0.013	0.018	0.005	0.104	0.228	0.109
R^2	0.897	0.983	0.895	0.761	0.845	0.637	0.701
MPSD	0.377	3.617	13.488	13.483	10.446	16.833	14.056
Difusión intrapartícula							
Región 1							
K_{id} (mg g^{-1} min^{-1})	0.036	0.664	4.022	4.022	4.402	5.123	4.485
$C_{intersept}$	5.25	8.67	13.87	7.24	9.74	10.05	15.24
MPSD	1.693	12.58	34.448	34.448	30.305	40.379	32.593
Región 2							
K_{id} (mg g^{-1} min^{-1})	0.009	0.020	0.097	0.097	0.165	0.644	0.956
$C_{intersept}$	10.01	14.95	31.92	25.79	37.95	16.76	10.22
MPSD	2.375	8.288	4.378	4.374	5.901	20.389	25.264
Región 3							
K_{id} (mg g^{-1} min^{-1})	0.001	0.03	0.015	0.015	0.023	0.042	0.066
$C_{intersept}$	12.92	16.66	20.75	29.73	40.59	21.23	14.47
MPSD	0.671	2.441	3.688	3.688	2.321	6.886	9.181

Table S3. Kinetic fitting parameters and well-fitting models for the adsorption of NPX on HC@MIL-53(Al)

	C_0 NPX (mg L^{-1})						
Parámetros	**25.22**	**75.67**	**126.12**	**176.58**	**227.03**	**277.48**	**327.93**
Qe, exp (mg g^{-1})	6.135	18.000	31.199	43.235	55.089	67.784	80.923
Pseudo primer orden (PFO)							
Qe, cal (mg g^{-1})	6.135	17.991	30.790	43.132	54.925	65.376	78.418
k_1 (min^{-1})	3.284	1.716	0.381	0.686	0.805	39.382	0.217
R^2	0.999	0.981	0.856	0.974	0.968	0.669	0.696
MPSD	0.001	0.086	3.240	0.417	0.386	6.541	4.991
Pseudo segundo orden (PSO)							
Qe, cal (mg g^{-1})	6.141	18.010	31.362	43.371	55.179	67.364	80.312
k_2 (mg g^{-1} min^{-1})	4.711	2.727	2.023	1.156	1.024	0.005	0.004
R^2	0.941	0.983	0.965	0.989	0.992	0.894	0.910
MPSD	0.115	0.174	1.619	0.270	0.190	1.056	2.947
Avrami Fractionary							
Qe, cal (mg g^{-1})	6.135	17.996	31.227	35.025	55.021	68.016	77.302
k (min^{-1})	6.286	0.743	0.271	0.001	0.560	0.102	28.116
n	5.196	0.019	0.132	0.027	0.055	0.102	42.031
R^2	0.999	0.974	0.9807	0.752	0.993	0.962	0.659
MPSD	0.001	0.0518	1.281	6.797	0.185	2.552	7.583
Bangham							
k_y (min^{-1})	0.012	0.012	0.011	0.012	0.012	0.011	0.011
α (mg g^{-1} min^{-1})	0.013	0.001	0.028	0.008	0.021	0.046	0.037
R^2	0.597	0.887	0.948	0.812	0.804	0.878	0.896
MPSD	0.376	0.284	3.875	1.284	1.011	3.925	181.826
Difusión intrapartícula							
Región 1							
K_{id} (mg g^{-1} min^{-1})	0.015	0.050	1.139	0.549	0.576	1.281	1.485
$C_{intersept}$	10.57	16.04	17.61	22.99	39.14	44.36	40.21
MPSD	0.817	0.949	11.512	4.135	3.449	6.586	6.170
Región 2							
K_{id} (mg g^{-1} min^{-1})	0.001	0.001	0.017	0.008	0.012	0.159	0.166
$C_{intersept}$	12.97	13.99	18.22	30.88	42.94	46.31	61.33
MPSD	0.001	0.660	1.035	15.622	0.391	4.446	4.032
Región 3							
K_{id} (mg g^{-1} min^{-1})	0.002	0.001	0.003	0.001	0.002	0.001	0.005
$C_{intersept}$	11.36	15.49	24.67	31.50	43.11	47.29	63.66
MPSD	0.001	0.001	1.836	0.312	0.183	0.059	0.700

Table S4. Fitting parameters of bicomponent equilibrium isotherms for KTC adsorption and effect of temperature.

Isoterma	Parámetros	Temperatura (K)		
		298	**313**	**328**
Langmuir Extendida	q_{max}	50.1863	55.1507	54.2470
	b_{KTC}	0.4198	0.4049	0.5084
	b_{NPX}	0.0010	0.0000	0.0000
	MPSD	27.9083	61.8969	31.1766
	R^2	0.9093	0.9412	0.9573
Freundlich Extendida	K_{FKTC}	14.4914	16.9450	19.1311
	n_{KTC}	1.3768	2.8417	3.3008
	X_{KTC}	0.3796	7.6751	0.000
	Y_{KTC}	3.2227	2.0664	0.0022
	Z_{KTC}	0.5888	0.5306	1.9131
	MPSD	6.5711	3.4963	0.1992
	R^2	0.9875	0.9950	0.9987
Sips Extendida	q_{mKTC}	139.3417	5674.5346	1213.4858
	b_{KTC}	0.1194	0.0031	0.0162
	n_{KTC}	1.2571	693640.8368	3.2079
	b_{NPX}	1.0335	0.0843	0.0361
	n_{NPX}	561968.7726	693640.8368	562123.0339
	MPSD	5.8698	3.3928	0.2294
	R^2	0.9924	0.9950	0.9883

Table S5. Fitting parameters of bicomponent equilibrium isotherms for NPX adsorption and effect of temperature.

Isoterma	**Parámetros**	**Temperatura (K)**		
		298	**313**	**328**
Langmuir Extendida	q_{max}	92.4868	126.2323	72.1714
	b_{NPX}	0.9691	16302.3670	4623653.7000
	b_{KTC}	0.0000	787.7512	4137.6072
	MPSD	2.4241	7.4815	2.0126
	R^2	0.9846	0.9521	0.9444
Freundlich Extendida	K_{FNPX}	55.1439	64.3508	70.6575
	n_{NPX}	4.6414	6.6552	8.7649
	X_{NPX}	5.7040	2.7596	0.0000
	Y_{NPX}	0.0048	0.1867	0.0358
	Z_{NPX}	0.0100	0.0013	0.0000
	MPSD	0.1867	0.0146	0.0586
	R^2	0.9876	0.9618	0.9602
Sips Extendida	q_{mNPX}	80.4258	316921.3400	8440.6945
	b_{NPX}	2.3759	0.0001	0.0082
	n_{NPX}	0.5507	3.8521	8.7036
	b_{KTC}	0.0000	0.0020	0.0084
	n_{KTC}	3.7128	571304.2300	567073.1200
	MPSD	1.3876	1.9490	0.0588
	R^2	0.9832	0.9805	0.9601

Table S6. Fit parameters of physical-statistical bicomponent equilibrium models for KTC adsorption.

Model	Parameter	Temperature (K)		
		298	**313**	**328**
SPM1	n	0.5724	0.3973	0.3055
	N_m	734.1320	16755.8340	1837.6107
	$C_{1/2}$	523.1203	12603243	58334.7820
	MPSD	10.7746	11.5883	1.2975
	R^2	0.9920	0.9934	0.9886
SPM2	n_1	0.5730	0.6888	0.3165
	Nm_1	362.0886	185.7735	508.8459
	n_2	0.5729	0.0055	0.3148
	Nm_2	362.0886	1085.7349	508.8459
	C_1	506.9288	106.7038	6126.5980
	C_2	506.9288	6174.7615	6126.5980
	MPSD	13.1970	1.1892	1.6613
	R^2	0.9920	0.9946	0.9874
SPM3	n_1	0.9995	0.9996	0.9997
	Nm_1	382.3922	594.9329	576.5847
	C_1	383.4175	596.8567	577.8935
	C_2	522.6401	805.8019	786.8564
	MPSD	6.08E-05	0.0002	0.0001
	R^2	0.9499	0.9524	0.9242

Table S7. Fit parameters of physical-statistical bicomponent equilibrium models for NPX adsorption.

Model	Parameter	Temperature (K)		
		298	**313**	**328**
SPM1	n	1.8157	1.0558	0.1773
	N_m	734.1320	101.8928	1706.6234
	$C_{1/2}$	523.1203	1.0792	490.2575
	MPSD	10.7746	0.3337	1.3677
	R^2	0.9920	0.9610	0.9500
SPM2	n_1	3.2438	0.4838	5.7373
	Nm_1	9.2546	0.0100	5.7636
	n_2	4.4042	1.0559	5.7373
	Nm_2	12.2645	101.8653	5.7636
	C_1	2.4081	0.3632	0.0101
	C_2	0.4322	1.0791	0.0101
	MPSD	0.2336	0.4087	7.1031
	R^2	0.9872	0.9610	0.9151
SPM3	n_1	1.8157	1	0.1875
	Nm_1	44.2924	118790	639.3025
	C_1	0.6208	466029.0700	1.5853
	C_2	2040.1167	14168420	63.0114
	MPSD	1.2979	209.4127	1.4836
	R^2	0.9832	0.9274	0.9496

Table S8. Thermodynamic parameters from microscopic models for KTC and NPX adsorption.

T (K)	$\Delta E_1\ (KJ\ mol^{-1})$	$\Delta E_2\ (KJ\ mol^{-1})$
KTC		
298	34.35	16.07
313	25.52	13.64
328	16.30	10.03
NPX		
298	8.57	8.03
313	14.35	10.42
328	20.02	7.54

Table S9. Combinations results of initial concentrations of KTC and NPX for a competing system

C_{0KTC}	C_{0NPX}	Ce KTC (ppm)	Qe KTC (mg g^{-1})	Rq KTC	C_{0NPX}	C_{0KTC}	Ce NPX (ppm)	Qe NPX (mg g^{-1})	Rq NPX
0.1	0	0	6.745	-	0.1	0	0	8.0425	-
0.3	0	0.794	19.744	-	0.3	0	0	18.96	-
0.5	0	3.837	31.60325	-	0.5	0	0.101	30.02725	-
0.7	0	9.623	45.09425	-	0.7	0	0.482	39.4345	-
0.9	0	22.53	55.95	-	0.9	0	5.312	54.7395	-
0.1	0.1	0	6.675	0.989	0.1	0.1	0	6.135	0.762
0.3	0.1	0	11.10975	0.562	0.3	0.1	0	8.12	0.428
0.5	0.1	6.378	29.2965	0.927	0.5	0.1	0	8.12225	0.270
0.7	0.1	17.785	40.22375	0.891	0.7	0.1	0	8.1425	0.206
0.9	0.1	29.235	52.71875	0.942	0.9	0.1	0	8.65	0.158
0.1	0.3	0.339	6.49275	0.962	0.1	0.3	0	18.96	2.357
0.3	0.3	1.487	19.158	0.970	0.3	0.3	0	18.01	0.949
0.5	0.3	12.714	27.6165	0.873	0.5	0.3	0	18.9525	0.631
0.7	0.3	31.091	36.93975	0.819	0.7	0.3	0	18.775	0.476
0.9	0.3	53.274	43.6665	0.780	0.9	0.3	0	18.98	0.346
0.1	0.5	0.781	6.63225	0.983	0.1	0.5	0	29.745	3.698
0.3	0.5	8.681	17.77225	0.900	0.3	0.5	0	29.3875	1.549
0.5	0.5	7.01	29.976	0.948	0.5	0.5	0.474	31.214	1.039
0.7	0.5	53.8	33.855	0.750	0.7	0.5	0.818	30.148	0.764
0.9	0.5	81.7	40.6575	0.726	0.9	0.5	1.238	30.243	0.552
0.1	0.7	9.51	4.3	0.637	0.1	0.7	19.4	34.7675	4.322
0.3	0.7	35.75	11.765	0.595	0.3	0.7	48.05	27.8375	1.468
0.5	0.7	53.96	18.38	0.581	0.5	0.7	31.86	31.5925	1.052
0.7	0.7	67.04	28.11	0.623	0.7	0.7	20.054	34.544	0.875
0.9	0.7	117.47	26.915	0.481	0.9	0.7	19.67	34.695	0.633
0.1	0.9	16.39	2.6275	0.389	0.1	0.9	21.54	50.6825	6.301
0.3	0.9	34.18	11.95	0.605	0.3	0.9	43.02	45.3125	2.389
0.5	0.9	67.8	17.8	0.563	0.5	0.9	43.93	45.085	1.501
0.7	0.9	115.54	18.1825	0.403	0.7	0.9	75.73	37.135	0.941
0.9	0.9	158.93	21.35	0.3815	0.9	0.9	81.07	35.8	0.654

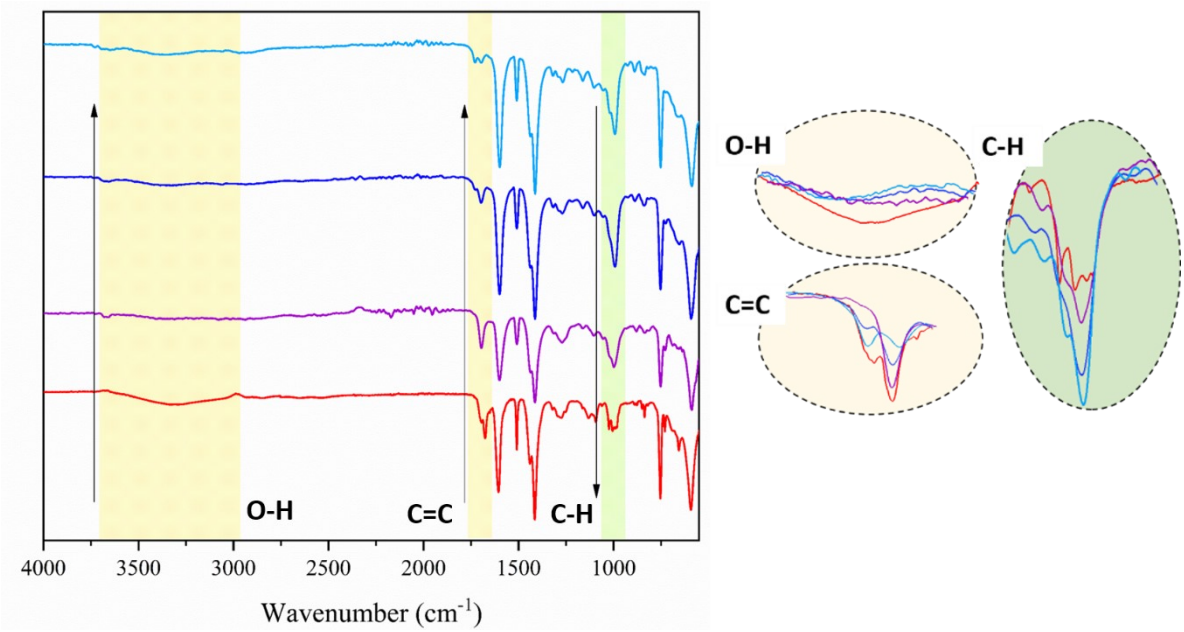

Fig. S4. Alteration of the main functional groups involved in the ADS process of KTC and NPX in saturated HC@MIL-53(Al) at different concentrations of both adsorbates.

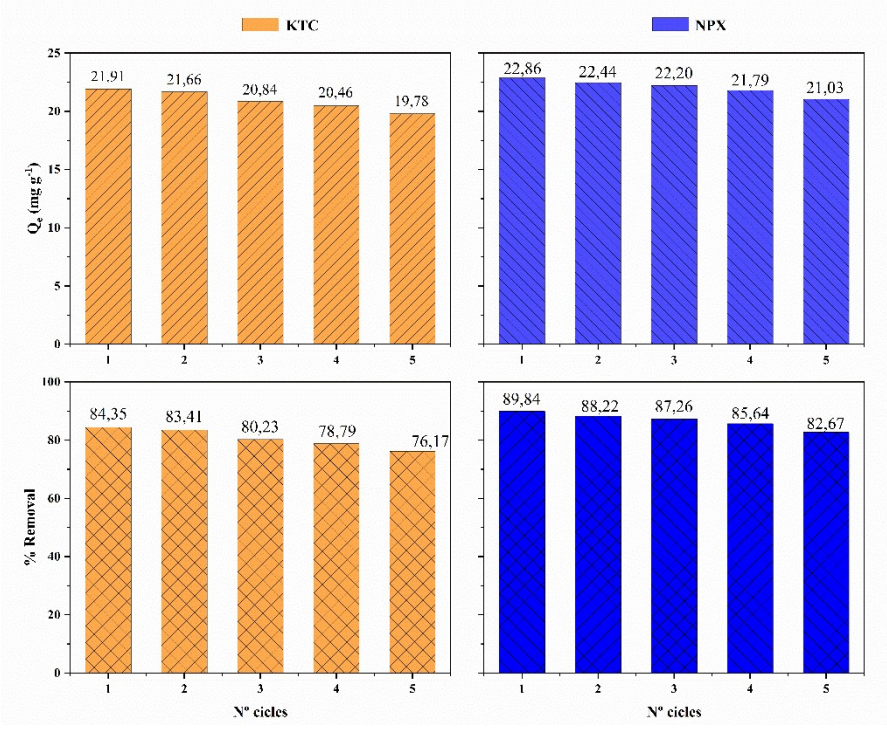

Fig. S5. ADS capacity (Qe) and removal (%R) of KTC (orange) and NPX (blue) as a function of the number of cycles.