Optimization of binary adsorption of metronidazole and sulfamethoxazole in aqueous solution enhanced with DFT calculations.

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Supplementary Material

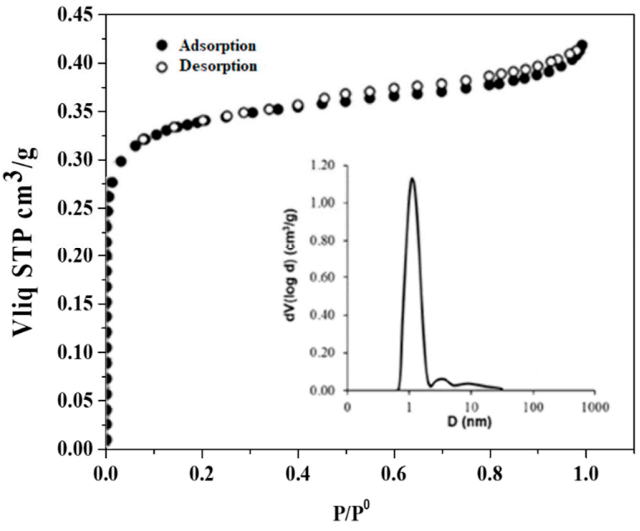

Figure S1.- Adsorption-desorption isotherm of N_2 at 77 K using CAG

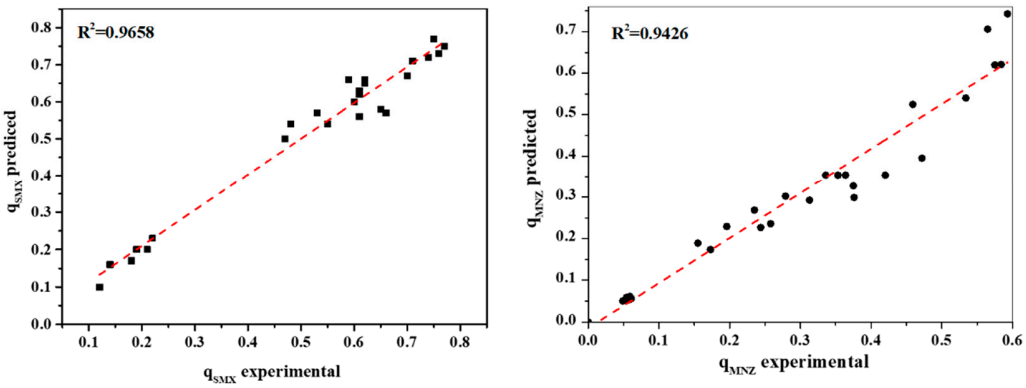

Figure S2.- Correlation between experimental values and predicted values in adsorption process for a) SMX, b) MNZ.

Table S1.- CAG textural properties (Serna-Carrizales et al., 2021)

Sample	S_{BET}	W_0 (N_2)	W_0 (CO_2)	L_0(N_2)	L_0 (CO_2)	$V_{0.95}$	V_{meso}
	$m^2\ g^{-1}$	$cm^3\ g^{-1}$	$cm^3\ g^{-1}$	nm	nm	$cm^3\ g^{-1)}$	$cm^3\ g^{-1}$
F400	756	0.317	0.244	1.27	0.64	0.360	0.066

S_{BET}: Specific area obtained by the adsorption isotherm of N_2 at 77 K.
W_0 (N_2): Micropore volumes obtained by N_2 adsorption.
W_0 (CO_2): Micropore volumes determined by CO_2 adsorption.
L_0(N_2) and L_0 (CO_2): Size of micropores determined by the Dubinin-Radushkevich equation.
$V_{0.95}$: Pore volume determined by Gurvich's law at a relative pressure of 0.95.
V_{meso}: Volume of mesopores calculated as Gurvich Volume

Table S2. Design of experiments for the binary adsorption process

Exp. No.	pH	Temperature °C	[MNZ] mmol L^{-1}	[SMX] mmol L^{-1}	q_{MNZ} mmol g^{-1}	q_{SMX} mmol g^{-1}	q_T mmol g^{-1}
1	10	10	0.16	0.16	0.376	0.371	0.747
2	2	25	0.02	0.16	0.058	0.418	0.476
3	2	25	0.30	0.16	0.313	0.373	0.686
4	10	25	0.02	0.16	0.051	0.378	0.429
5	5	40	0.30	0.16	0.534	0.497	1.032
6	5	25	0.16	0.16	0.420	0.430	0.850
7	2	25	0.16	0.02	0.353	0.040	0.393
8	5	10	0.30	0.16	0.565	0.370	0.935
9	10	25	0.16	0.30	0.065	0.043	0.107
10	5	10	0.16	0.02	0.472	0.046	0.518
11	5	25	0.02	0.30	0.049	0.502	0.551
12	2	25	0.16	0.30	0.163	0.487	0.650
13	5	25	0.30	0.30	0.584	0.550	1.134
14	5	40	0.16	0.30	0.244	0.596	0.840
15	5	10	0.02	0.16	0.059	0.343	0.403
16	5	25	0.30	0.02	0.575	0.033	0.608
17	2	10	0.16	0.16	0.279	0.356	0.635
18	10	25	0.30	0.16	0.593	0.218	0.811
19	10	40	0.16	0.16	0.364	0.308	0.672
20	5	40	0.21	0.02	0.460	0.049	0.509
21	2	40	0.16	0.16	0.156	0.390	0.546
22	5	25	0.16	0.16	0.353	0.278	0.631
23	5	40	0.02	0.16	0.061	0.380	0.441
24	5	25	0.02	0.02	0.054	0.035	0.089
25	5	10	0.16	0.30	0.235	0.584	0.819
26	5	25	0.16	0.16	0.336	0.278	0.614
27	10	25	0.16	0.02	0.374	0.020	0.394

Table S3.- Values of the parameters of the Langmuir, Freundlich and Prausnitz-Radke adsorption isotherm models in the individual adsorption process of SMX and MNZ on GAC at 25°C and pH 7.

Molécula	*pH*	*Langmuir*				*Freundlich*				*Prausnitz-Radke*				
		q_m	K	R^2	%	K	n	R^2	%D	a	B	β	R^2	*%D
		mmol g^{-1}	L $mmol^{-1}$		D	$Mmol^{/1/n}L^{1/n}/g$				L g^{-1}	L^{β} $mmol^{-\beta}$			
SMX	7	1.611	9.062	0.990	2.9	1.051	6.971	0.939	7.2	10.333	7.257	1.303	0.998	5.0
MNZ	7	1.103	9.721	0.984	9.3	1.632	2.884	0.895	15.3	51.798	47.252	0.938	0.984	6.1

*** Values obtained from the following equation:**

$$\%D = \left(\frac{1}{N}\sum_{i=1}^{N}\left|\frac{q_{i,exp} - q_{i,pred}}{q_{i,exp}}\right|\right) \times 100\%$$

Where:

%D is the percentage deviation.
$q_{i,exp}$ is the experimental mass of pharmaceutical adsorbed at equilibrium in mmol g^{-1}
$q_{i,pred}$ is the mass of pharmaceutical adsorbed predicted with the adsorption isotherm in mmol g^{-1}.
N represents the number of experiments

Table S4. ANOVA for the Surface quadratic model of q_{SMX}

Source	Sum of squares	df	Mean square	F value	Prob > F
Model	1.06	7	0.15	57.55	< 0.0001
pH	0.020	1	0.020	7.48	0.0131
T	1.12×10^{-03}	1	1.12×10^{-03}	0.43	0.5213
[SMX]	0.82	1	0.82	314.26	< 0.0001
pH * [SMX]	0.021	1	0.021	8.04	0.0106
pH^2	9.15×10^{-03}	1	9.15×10^{-03}	3.49	0.0772
T^2	0.011	1	0.011	4.27	0.0527
$[SMX]^2$	0.15	1	0.15	55.49	< 0.0001
Residual	0.050	19	2.62×10^{-03}		
Lack of fit	0.039	17	2.28×10^{-03}	0.41	0.8802
Pure error	0.011	2	5.50×10^{-03}		
Total	1.11	26			

Table S5. ANOVA for the Surface quadratic model of q_{MNZ}

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	0.810	5	0.162	54.026	< 0.0001
pH	0.0430	1	0.0430	14.372	0.0011
[MNZ]	0.673	1	0.673	224.688	< 0.0001
[SMX]	0.0328	1	0.0328	10.947	0.0033
pH * [MNZ]	0.0206	1	0.0206	6.870	0.0160
pH^2	0.0254	1	0.0254	8.492	0.0083
Residual	0.0629	21	0.00230		
Lack of Fit	0.0590	19	0.00310	1.574	0.459
Pure Error	0.00394	2	0.00197		
Total	0.873	26			

Table S6. ANOVA for the Surface quadratic model of q_{total}.

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	1.202	6	0.200	10.948	< 0.0001
pH	0.00357	1	0.00357	0.195	0.663
[MNZ]	0.655	1	0.655	35.782	< 0.0001
[SMX]	0.225	1	0.225	12.279	0.0022
pH * [SMX]	0.0917	1	0.0917	5.012	0.0367
pH^2	0.137	1	0.137	7.483	0.0127
$[SMX]^2$	0.166	1	0.166	9.075	0.0069
Residual	0.366	20	0.0183		
Lack of Fit	0.329	18	0.0183	0.997	0.613
Pure Error	0.0367	2	0.0183		
Total	1.568	26			

Table S7. Adsorption energies (E_{ads}) of SMX and MNZ n the oxygenated carbonaceous surface.

Structures	**E_{ads}(kcal mol^{-1})**		
Monocomponent system	**SMX [0]**	**SMX [-]**	**MNZ**
Ether - NH	-2.59	--	--
Ether - NH_2	-1.48	--	--
Ether π-π	-0.28	3.38	-0.60
Ether - OH	--	--	3.05
Semiquinone - NH	-7.65	--	--
Semiquinone - NH_2	-10.00	--	--
Semiquinone π-π	-1.32	-1,20	-6.01
Semiquinone - OH	--	--	-6.55
Carboxylic-protonated - NH_2	-0.66	--	--
Carboxylic-protonated π-π	-3.19	-3.21	0.05
Carboxylic-protonated - OH	--	--	-0.37
Carboxylic-protonated – NO		-62.86*	
Carboxylic-protonated – SO_2		-42.26*	
Phenol-protonated	0.27		
Phenol-protonated π-π		0.02	0.40
Carboxylic-protonated – NO		-44.08*	
Carboxylic-protonated – SO_2		-44.05*	

*H^+ transfer to SO_2 group in SMX molecule.