Supplementary Information

Experimental and Computational Studies of the Adsorption of Furan, Pyrrole, and Thiophene on Hydroxyapatites in a Single and Ternary Component

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Table S1. FAAS analysis conditions for quantification of Ca, Cu and Fe in the hydroxyapatites synthesized

Element	Wavelength / nm	Flame	Injection flux / (L min^{-1})	Lamp current / mA
Ca	422.7	nitrous oxide/acetylene	4.0	5.0
Cu	324.8	air/acetylene	0.9	4.0
Fe	248.3	air/acetylene	0.9	6.0

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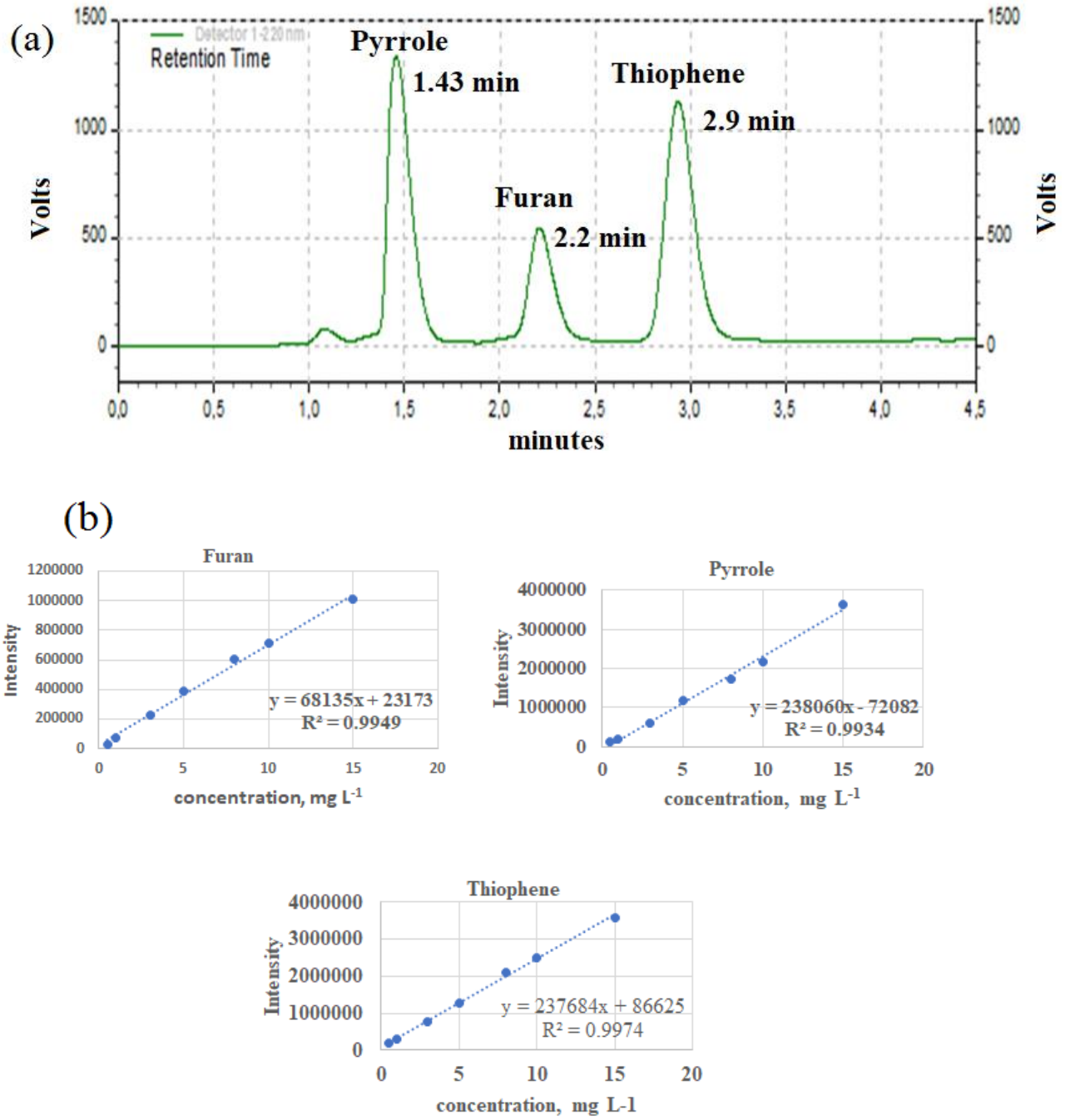

Figure S1. (a) Chromatogram obtained by injecting 10 μL of a mix of the furan, pyrrole and thiophene; (b) analytical curves to mix of the furan, pyrrole and thiophene, ranging from 0.5 to 15 mg L^{-1}, prepared from 1000 mg L^{-1} stock solution in isooctane.

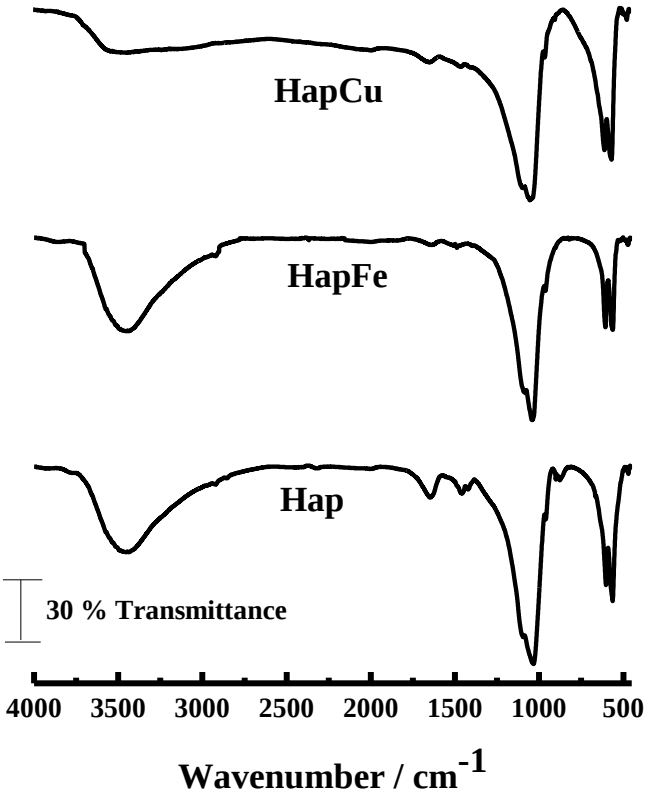

Figure S2. ATR-FTIR spectra of Hap, HapFe, and HapCu after calcination at 550 °C.

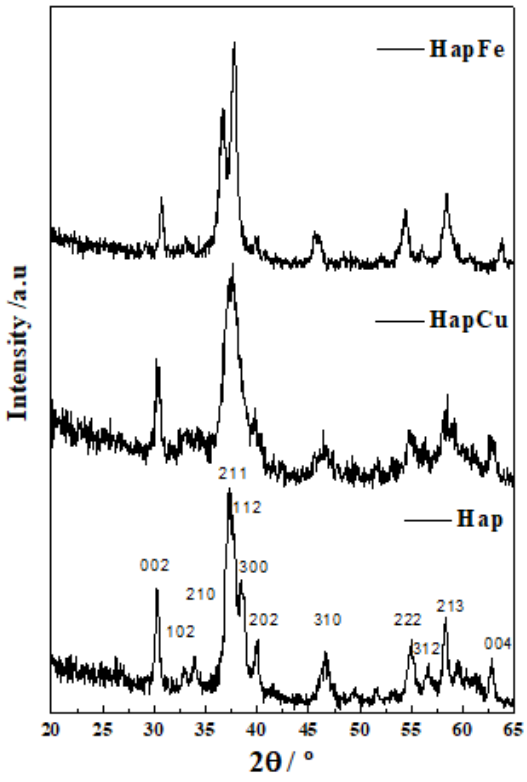

Figure S3. X-ray diffraction pattern of Hap, HapFe and HapCu after calcination at 550 °C.

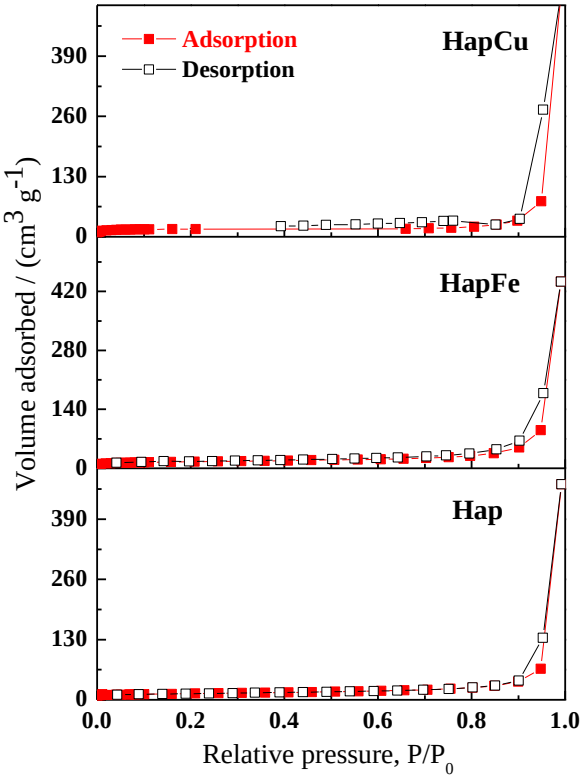

Figure S4. N_2 isotherms at 77 K of Hap, HapFe, and HapCu after calcination at 550 °C.

Table S2. Kinetics and isotherm models

Isotherm model	Equation	Reference
Langmuir	$q_e = \frac{q_{máx} K_L C_e}{1 + K_L C_e}$	1
Freundlich	$q_e = K_f C_e^{1/n}$	2
Sips	$q_e = \frac{q_{máx}\, b C_e^n}{1 + b C_e^n}$	3
Kinetic model	**Equation**	
Pseudo-first order	$q_t = q_e(1 - e^{-k_1 t})$	4-7
Pseudo-second order	$q_t = \frac{t}{\frac{1}{k_2 q_e^2} + \frac{t}{q_e}}$	8
Intraparticle diffusion	$q_t = k_{int}\sqrt{t}$	9

For isotherms models, the parameter qt (mg g^{-1}) is the adsorption amount; Ce (mg L^{-1}) is the concentration of the adsorbates in solution at equilibrium; qe (mg g^{-1}) is the adsorption capacity, q_{max} (mg g^{-1}) is the maximum adsorption capacity, K_L (L g^{-1}) is the Langmuir constant related to the adsorption temperature. K_f and n are constant and exponent Freundlich, respectively, n in range of 1 < n < 10 indicates a favorable adsorption. For Sips isotherm b and n

are constant Sips and the heterogeneity degree. In the kinetic equations, the parameters k_1, k_2 and k_{int} are the first order, second order and intraparticle diffusion (mmol g $min^{-1/2}$) rate constants, respectively, Table 1.

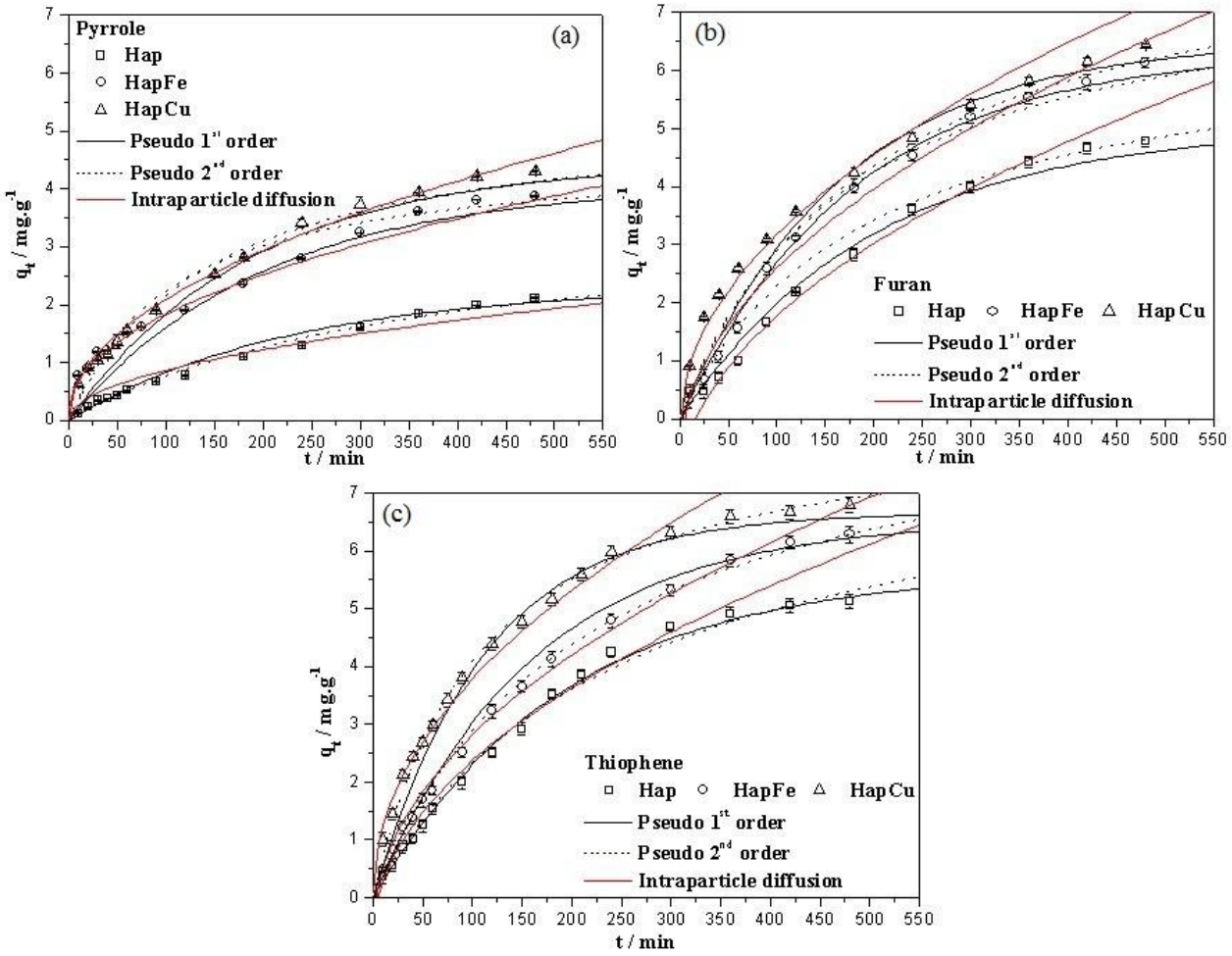

Figure S5. Kinetic plots of (a) pyrrole, (b) furan and (c) thiophene on hydroxyapatites in single component system at 298 K and C_0 = 50 mg L^{-1}.

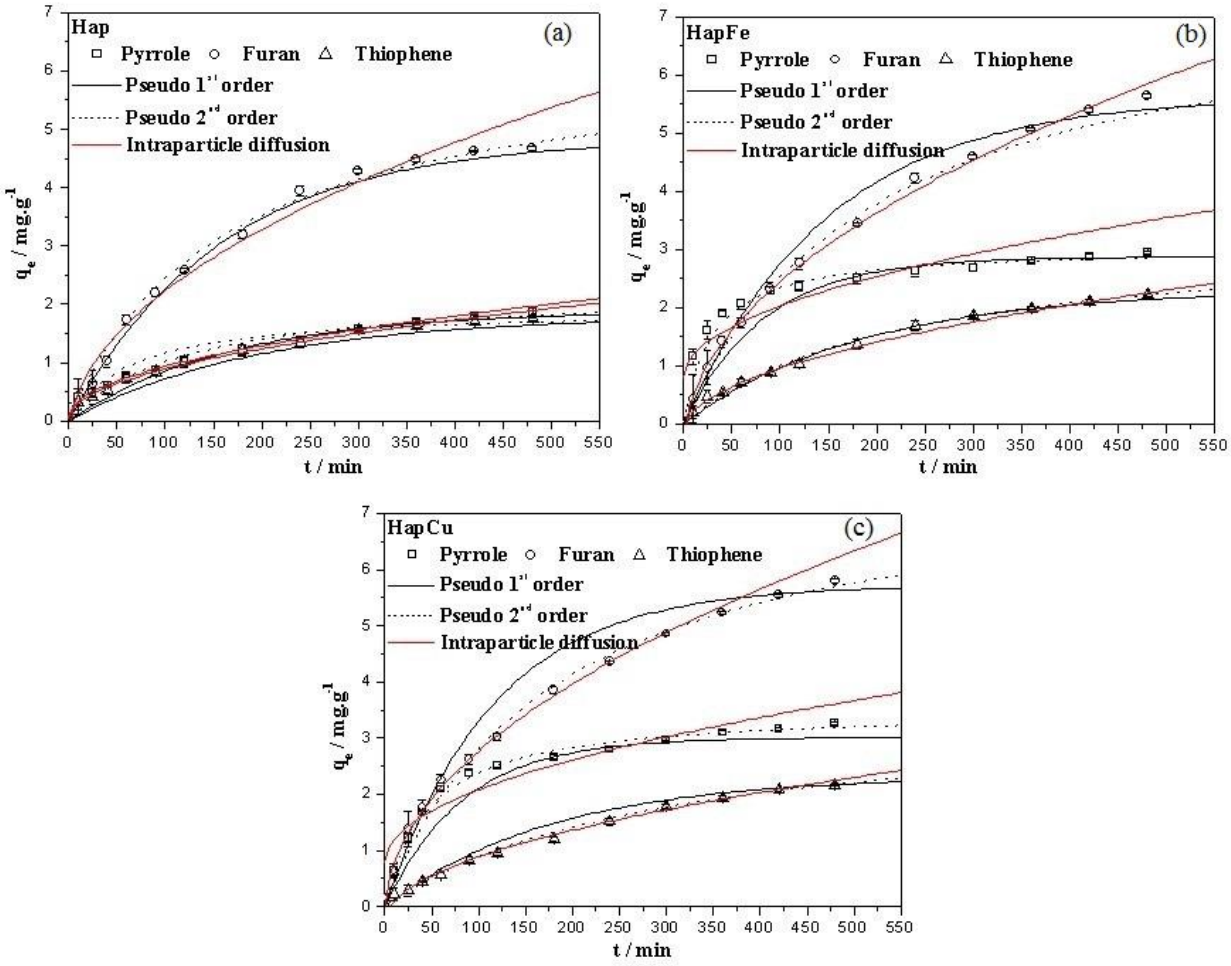

Figure S6. Kinetic plots for (a) pyrrole, (b) furan and (c) thiophene on hydroxyapatites in ternary component system at 298 K and C_0 = 50 mg L^{-1}.

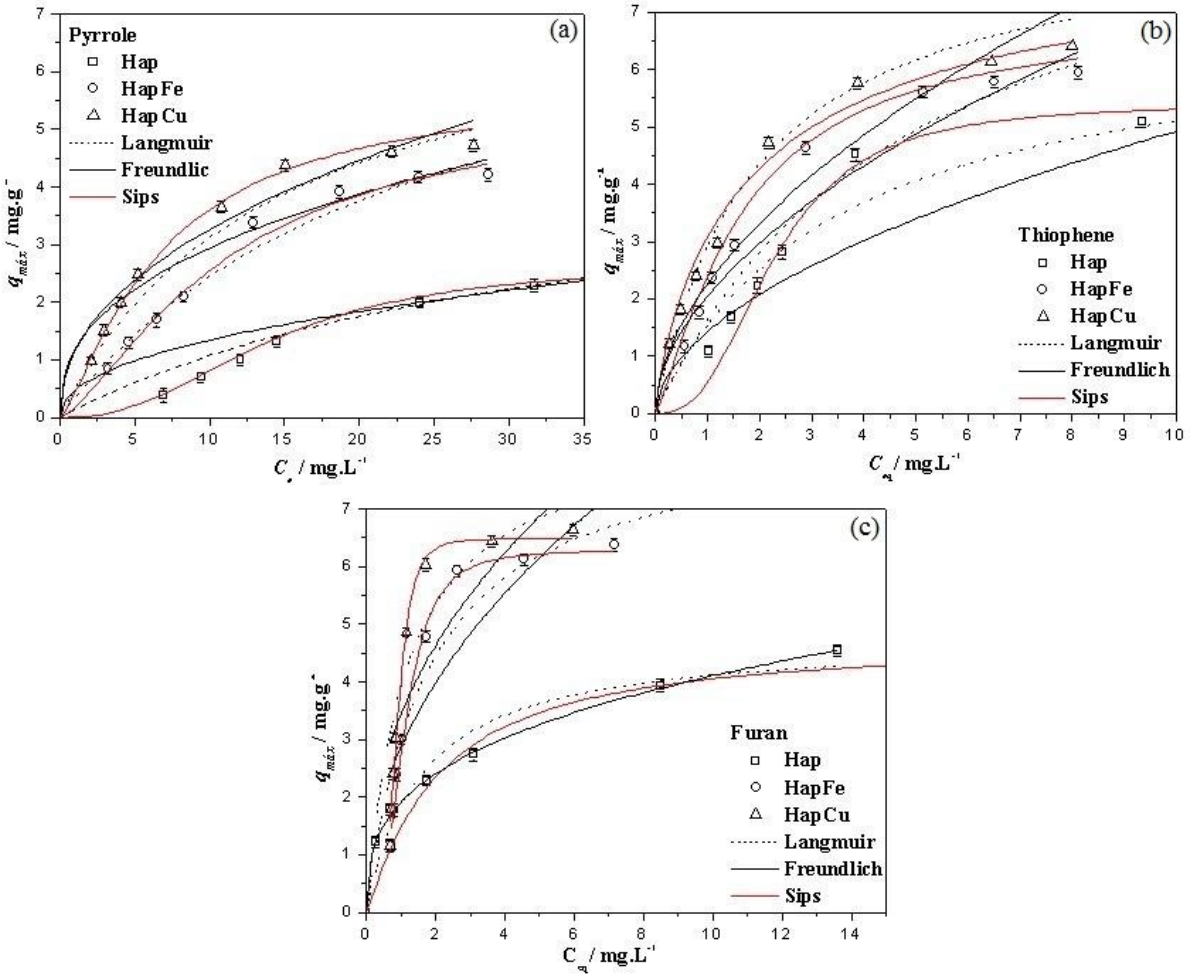

Figure S7. Adsorption isotherms of (a) pyrrole, (b) thiophene and (c) furan onto adsorbents Hap, HapFe and HapCu, in single component system.

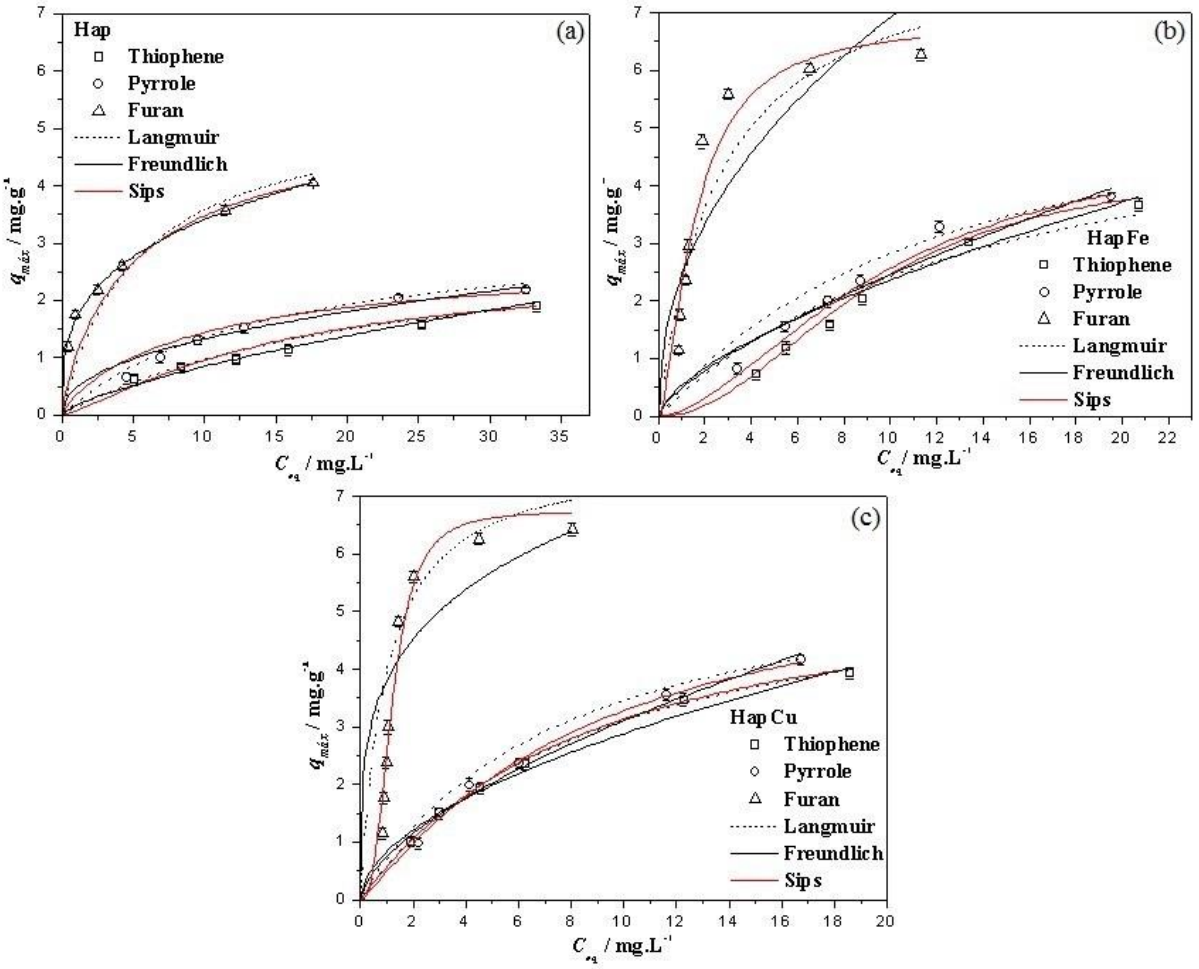

Figure S8. Adsorption isotherms of thiophene, pyrrole and furan on adsorbents (a) Hap, (b) HapFe and (c) HapCu in ternary component systems.

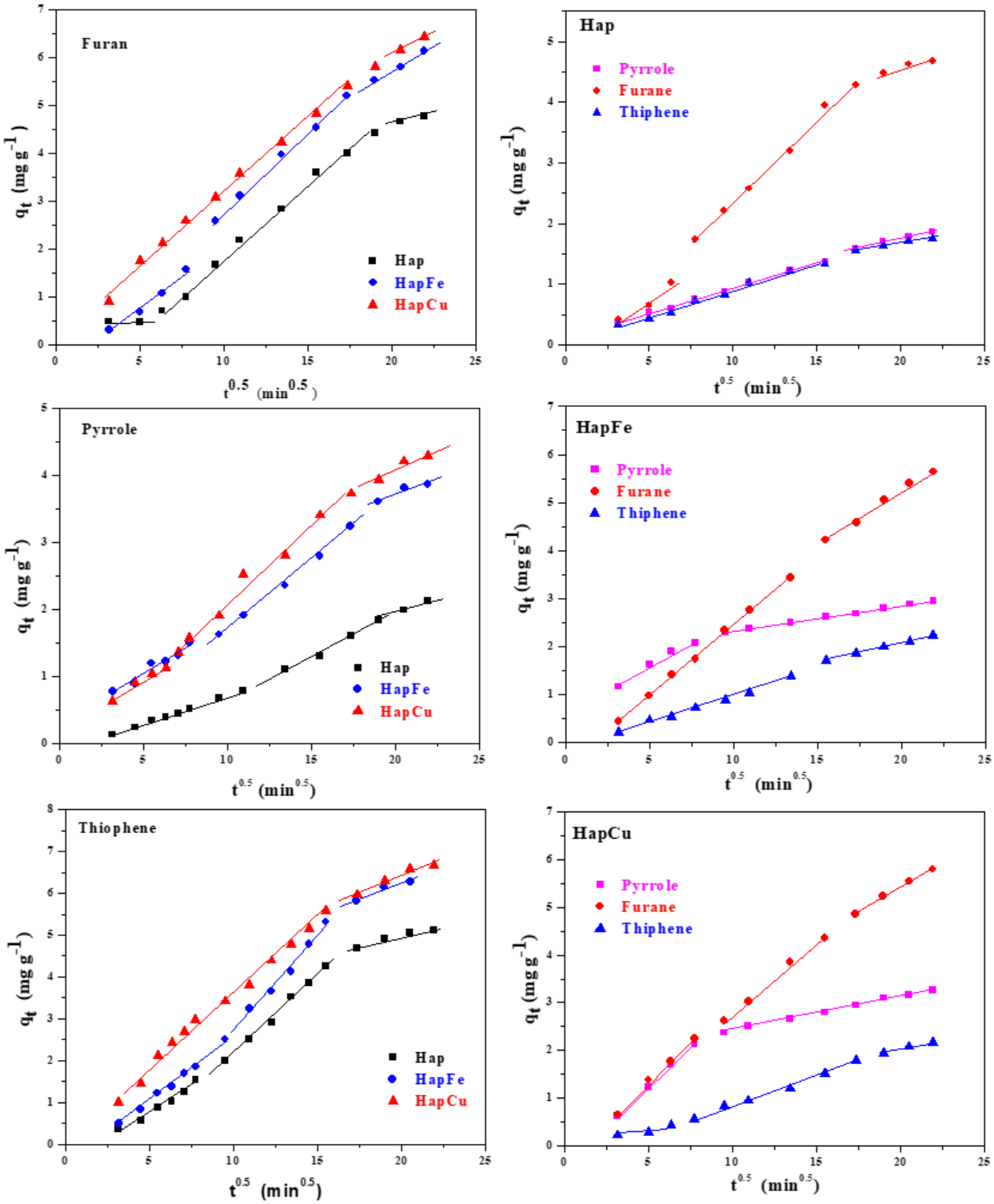

Figure S9. Intraparticle diffusion plots to thiophene, pyrrole and furan on synthesized hydroxyapatites in single and ternary component systems.

Table S3. Isotherm parameters to single and ternary system to the pyrrole, furan and thiophene adsorbate on the hydroxyapatites

System	Adsorbent	Adsorbate	$q_{max(exp)}$ / (mg g^{-1})	Langmuir				Sips				
				q_{max} / (mg g^{-1})	K_L / (mg L^{-1})	SSRE	R^2	q_{max} / (mg g^{-1})	b	n_s	SSRE	R^2
Single	Hap	thiophene	5.42 ± 0.11	6.85	0.29	0.07	0.939	5.41	0.113	2.61	0.00	0.991
		furan	4.55 ± 0.094	4.87	0.63	0.01	0.939	4.75	0.450	1.12	0.00	0.987
		pyrrole	2.45 ± 0.10	4.77	0.03	0.90	0.969	2.69	0.002	2.40	0.01	0.994
	HapFe	thiophene	6.38 ± 0.10	9.88	0.20	0.30	0.989	7.01	0.690	1.73	0.01	0.992
		furan	5.95 ± 0.11	8.38	0.56	0.17	0.979	6.29	0.761	1.44	0.00	0.986
		pyrrole	4.21 ± 0.11	8.12	0.04	0.86	0.989	5.57	0.032	1.31	0.10	0.989
	HapCu	thiophene	6.64 ± 0.094	8.55	0.52	0.08	0.949	6.61	1.161	3.10	0.00	0.991
		furan	6.41 ± 0.010	8.44	0.86	0.10	0.979	6.49	1.050	1.54	0.00	0.985
		pyrrole	4.72 ± 0.098	7.57	0.07	0.36	0.989	5.82	0.081	1.31	0.05	0.991
Ternary	Hap	furan	4.05 ± 0.053	5.46	0.19	0.12	0.978	5.51	0.427	0.62	0.13	0.982
		pyrrole	2.18 ± 0.084	3.31	0.07	0.26	0.987	2.94	0.057	1.15	0.12	0.993
		thiophene	1.89 ± 0.054	3.20	0.04	0.48	0.988	2.61	0.036	1.17	0.14	0.957
	HapFe	furan	6.27 ± 0.079	8.32	0.38	0.11	0.927	6.76	0.363	2.49	0.01	0.972
		pyrrole	3.81 ± 0.11	6.34	0.08	0.44	0.939	5.01	0.027	1.62	0.10	0.991
		thiophene	3.66 ± 0.10	5.93	0.07	0.38	0.909	4.46	0.009	2.09	0.05	0.996
	HapCu	furan	6.42 ± 0.095	7.76	1.05	0.04	0.905	6.80	0.536	2.71	0.00	0.974
		pyrrole	4.16 ± 0.098	6.11	0.13	0.22	0.997	6.08	0.086	1.14	0.21	0.994
		thiophene	3.92 ± 0.11	5.98	0.11	0.27	0.958	5.84	0.108	1.01	0.24	0.998

$q_{max(exp)}$: experimental maximum adsorption capacity; q_{max}: maximum adsorption capacity; K_L: Langmuir constant related to the adsorption temperature; SSRE: sum of squares of relative error; R^2: coefficient of determination; b is the Sips constant and ns is the heterogeneity degree.

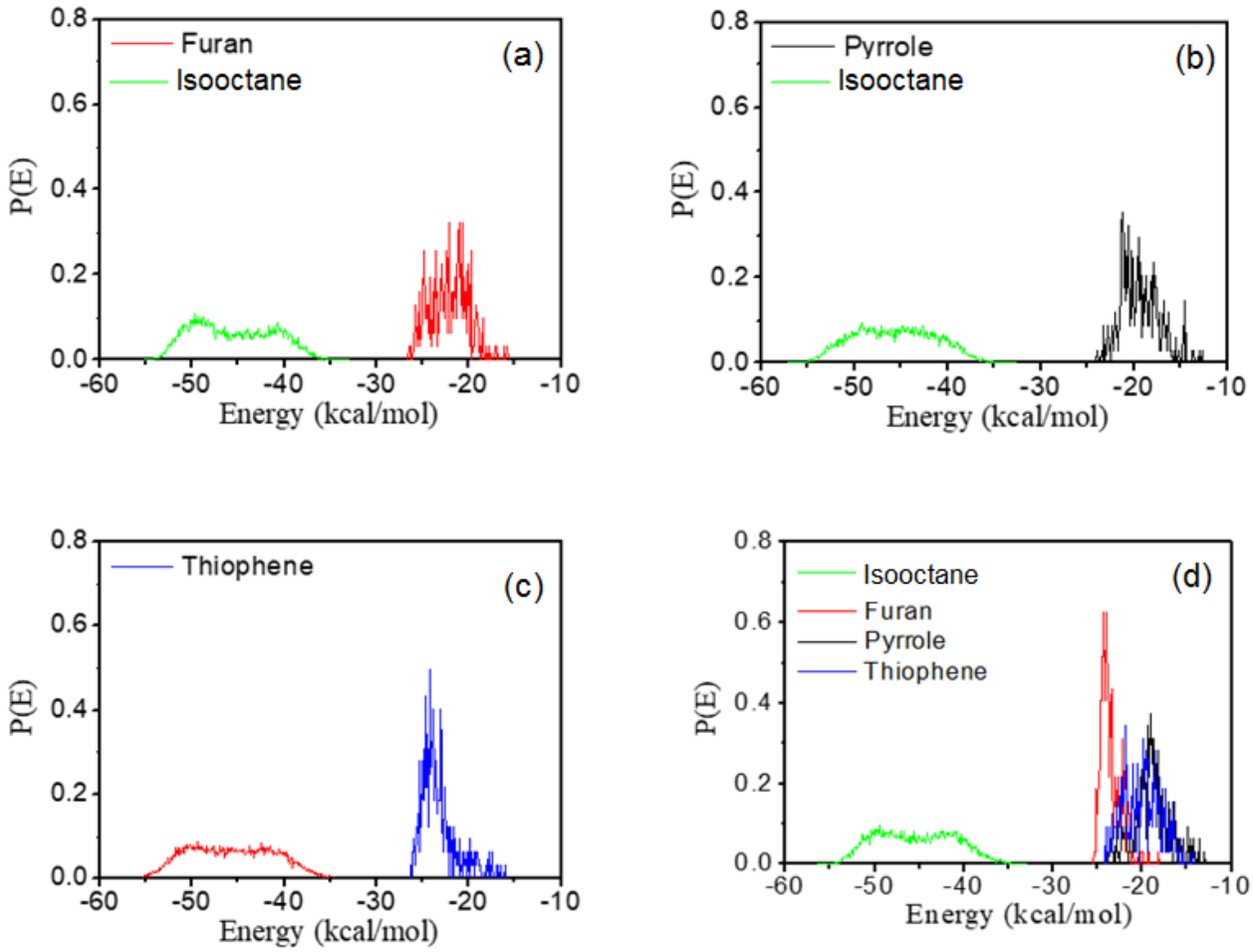

Figure S10. Distribution plots Monte Carlo adsorption energies for Fur (a), Pyr (b), and Thi (c) in the single and ternary (d) component systems in presence of the isooctane solvent by using the Dreiding force field.

References

1. Langmuir, I.; *J. Am. Chem. Soc.* **1916**, *38*, 2221.
2. Foo, K. Y.; Hameed, B. H.; *Chem. Eng. J.* **2010**, *156*, 2.
3. Sips, R.; *J. Chem. Phys.* **1948**, *16*, 490.
4. Ho, Y. S.; Mckay, G.; *Process Saf. Environ. Prot.* **1998**, *76*, 332.
5. Ho, Y. S.; Mckay, G.; *Process Saf. Environ. Prot.* **1998**, *76*, 183.
6. Ho, Y. S.; Mckay, G.; *Can. J. Chem. Eng.* **1998**, *76*, 822.
7. Ho, Y. S.; Mckay, G.; *Chem. Eng. J.* **1998**, *70*, 115.
8. Ho, Y. S.; Mckay, G.; *Process Biochem*. **1999**, *34*, 451.
9. Weber, W. J.; Morris, J. C.; *J. Sanit. Eng. Div., Am. Soc. Civ. Eng.* **1963**, *89*, 31.

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