Electronic Supplementary Information

Synthesis, Characterization, and Application of a Zinc Oxide-Pyrrole-Thiophene Nanocomposite as an Efficient Adsorbent for Removal of Tetracycline

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Figure ESI-1. Molecular structures of tetracycline showing unique speciation pattern at different pH (pH range of 2 – 12).

ESI-1. **Adsorption Studies**: Influence of dissolved organic matter (DOM) on TC adsorption.

Scheme ESI-1. Equations used during the study of adsorption of TC on to ZnO-Py-Th nanocomposite.

$$\%\ desorption = \frac{amount\ of\ TC\ desorbed\ to\ desorbing\ media}{amount\ of\ TC\ adsorbed\ on\ adsorbent} \times 100 \quad \text{------ (1)} \quad [1]$$

$$Removal\ \% = \frac{C_{o-C_e}}{C_0} \times 100 \quad \text{---------- (2)} \quad [2]$$

$$q_e = \frac{(C_o - C_e)V}{m} \quad \text{---------- (3)} \quad [3]$$

$$q_t = \frac{(C_o - C_t)V}{m} \quad \text{---------- (4)} \quad [4]$$

where C_o and C_e are the initial TC concentration (mg L^{-1}) and concentration at equilibrium time respectively. q_e and q_t are adsorption capacity at equilibrium and at any time respectively. V is the volume (L) of the TC solution and m is the mass (g) of the adsorbent used.

Adsorption kinetics equations

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad \text{---------- (5)} \quad [5]$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \text{---------- (6)} \quad [6]$$

k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the pseudo-first-order & pseudo-second-order model rate constants, respectively.

Adsorption isotherm equations

Langmuir model; $q_e = \frac{q_m K_L C_e}{(1 + K_L C_e)}$ ---------- (7) [7]

Freundlich model; $q_e = K_F C_e^{1/n}$ ---------- (8) [7]

Temkin model; $q_e = Bln(AC)$ ---------- (9) [7]

Kahn model; $q_e = \frac{q_m K C_e}{(1 + K C_e)^n}$ ---------- (10) [7]

Radke-Prausniiz model; $q_e = \frac{q_{mRP} K_{RP} C_e}{(1 + K_{RP} C_e)^n}$ ---------- (11) [7]

Dubinin-Radushkevich model; $lnq_e = q_m - \beta\varepsilon^2$ ---------- (12) [8]

- where K_L (L mg^{-1}) is the Langmuir constant, which is related to adsorption and maximum adsorption capacity, q_m (mg g^{-1}) corresponding to complete monolayer coverage.
- K_F *(mg/g)* *(L/mg)$^{1/n}$* is related to the adsorption capacity of the adsorbent and *1/n* is a constant that is related to the adsorption intensity.
- *A* is the equilibrium constant of binding corresponding to the maximum energy of binding (*L mg^{-1}*) and the constant *B* is related to the heat of adsorption (*J mol^{-1}*).
- *K* is Kahn isotherm model exponent, *n* is Khan isotherm model constant, and q_m is Khan isotherm maximum adsorption capacity (*mg g^{-1}*).
- q_{mRP} is Radke-Prausnitz maximum adsorption capacity (*mg g^{-1}*), K_{RP} is Radke-Prausnitz equilibrium constant, and mRP is Radke-Prausnitz model exponent.

- q_e ($mg\,g^{-1}$) is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium; q_m ($mg\,g^{-1}$) is the maximum adsorption capacity; β ($mol^2\,kJ^{-2}$) is a constant related to the adsorption energy; and ε ($kJ\,mol^{-1}$) is the adsorption potential.

Thermodynamic equations

$$ln\ k_d = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad \text{---------- (13)} \quad [1]$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \text{---------- (14)} \quad [9]$$

where ΔG^o = standard free energy change of adsorption, R = gas constant (0.008314 kJ mol^{-1} K^{-1}), T= temperature (K).

Table ESI-1. Isotherm Data for Adsorption of TC onto the ZnO-Th-Py Nanocomposite.

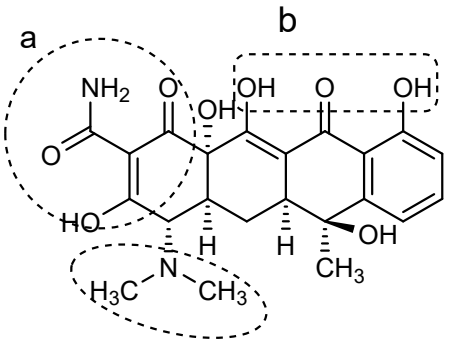
Isotherm model	Parameters	TC (Values)		
		298K	308K	318K
Langmuir	q_m *(mg/g)*	377.527 ± 0.398	404.242 ± 0.330	436.555 ± 0.293
	K_L *(L/mg)*	0.348 ± 0.003	0.373 ± 0.002	0.401 ± 0.002
	RMSE	0.387	0.274	0.222
	R^2	0.999	0.999	0.999
Freundlich	K_F $(mg^{1-1/n}\ L^{1/n}\ g^{-1})$	229.890 ± 11.334	253.13892 ± 11.70918	281.076 ± 12.220
	1/n	0.112 ± 0.013	0.10598 ± 0.01284	0.099 ± 0.01208
	RMSE	85.672	88.418	93.147
	R^2	0.900	0.901	0.900
Temkin	*A (L/g)*	252.419 ± 216.561	423.735 ± 385.986	756.492 ± 738.105
	B (J/mol)	37.801 ± 3.594	38.515 ± 3.677	39.450 ± 3.803
	RMSE	58.029	60.739	64.975
	R^2	0.995	0.995	0.996
Radke-Prausniiz	q_m	391.931 ± 1.927	253.373 ± 1211.666	281.281 ± 12.601
	K_{RP}	0.316 ± 0.004	2.42439E46 ± 1.11305E47	1.13239E45 ± 6.53376E44
	n	0.316 ± 0.004	0.894 ± 0.381	0.900 ± 0.013
	RMSE	0.046	88.423	93.151
	R^2	1.00	0.993	0.994
Kahn	q_m	58.488	414.588 ± 1.421	389.897 ± 1.731
	n	0.900	1.007 ± 0.001	1.009 ± 0.001
	R^2	0.994	1.00	1.00

Table ESI-2. Kinetic Parameters for Removal of TC by nanocomposite, ZnO-Py-Th

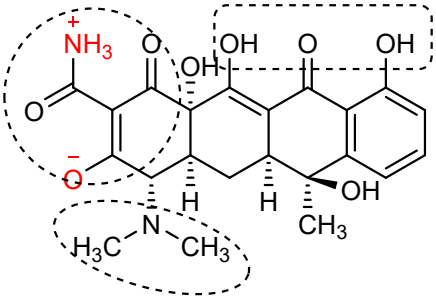
Adsorbent	Pseudo-first order				Pseudo-second-order	
ZnO-Py-Th C_o (mg/L)	k_1 (min^{-1})	$q_{e\ (cal.)}$ (mg/g)	R^2	k_2 (g mg^{-1} min^{-1})	$q_{e\ (cal.)}$ (mg/g)	R^2
50 ppm	0.018	158	1.00	0.00167	257.50	0.98
60 ppm	0.013	199.32	1.00	0.0057	284.90	0.99
70 ppm	0.009	251.18	1.00	0.020	306.74	0.99
80 ppm	0.0046	316.22	1.00	0.0027	357.14	0.97
90 ppm	0.0036	416.82	1.00	0.0022	390.62	0.97

Table ESI-3. Values of Thermodynamic Parameters of Adsorption of TC onto the Nanocomposite, ZnO-Py-Th

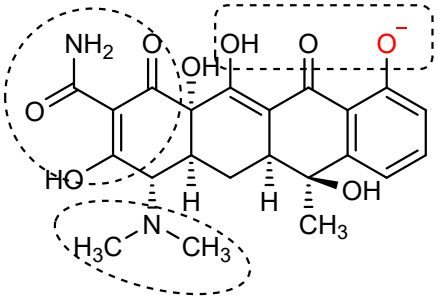
Conc.	Thermodynamic Parameters				
			ΔG° ($kJ\ mol^{-1}$)		
ppm	**ΔH°** ($kJ\ mol^{-1}$)	**ΔS°** ($kJ\ mol^{-1}\ K^{-1}$)	**298K**	**308K**	**318K**
50	- 18.66	0.077	- 4.28	- 5.05	- 5.82
60	- 19.49	0.086	- 6.13	- 6.99	- 7.58
70	- 20.32	0.094	- 7.69	- 8.32	- 9.52
80	- 21.20	0.102	- 9.11	- 10.13	- 11.15
90	- 22.11	0.108	- 10.07	- 11.15	- 12.23



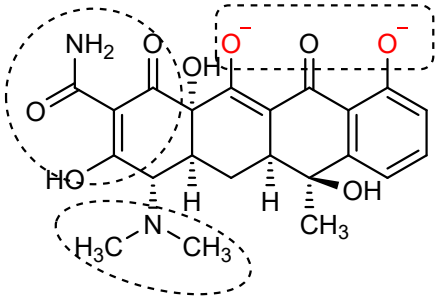
Neutral molecule (TC)



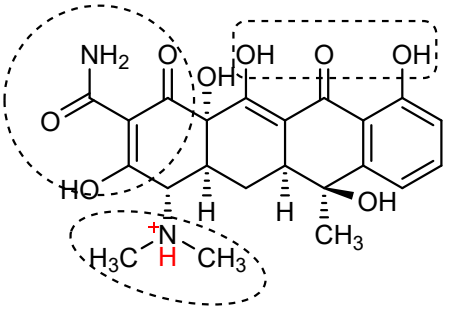
Zwitterion ($H_2TC^{\pm}$)



Monovalent anion (H_2TC^{-})



Divalent anion (HTC^{-2})



Cation (H_3TC^{+})

Figure ESI-1. Molecular structures of tetracycline showing unique speciation pattern at different pH (pH range of 2 – 12).

ESI-1. Adsorption Studies

Influence of dissolved organic matter (DOM) on TC adsorption

Dissolved organic matter (DOM), a significant component of wastewater, is a complex heterogeneous mixture of organic compounds including humic acid, tryptophan and protein-like organic matter etc., which may limit the adsorption of pharmaceuticals by blocking the pores on the adsorbent (ZnO-Py-Th) surface or by direct competition for the adsorption sites[10]. Additionally, research has demonstrated that many antibiotics, including tetracycline (TCs) antibiotics, can form ternary complexes with DOM through functional groups (such as aldehyde group, carbonyl group, and hydrogen bond), which can impact the adsorption of antibiotics[11]. Complexation of tetracycline with dissolved organic matter (DOM) in aqueous solution could alter the adsorption of tetracycline to adsorbent material (ZnO-Py-Th), thereby declining the adsorption capacity of TC over the adsorbent[12,13]. The magnitude of the inhibition is related to the amount of DOM adsorbed and tetracycline affinity for the DOM. As a result, the influence of DOM with various molecular weights on the adsorption of antibiotics is also very significant. In order to evaluate the impact of DOM on the adsorption of TC onto the adsorbent ZnO-Py-Th, fulvic acid (FA) was selected as a typical DOM and 1 mg/L antibiotics was chosen. Interestingly, it was observed that the introduction of FA (2 -10 mg/L) did not significantly change the adsorption of TC.

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