Supplementary Information (SI)

Mechanistic insights into paracetamol adsorption from water using ZnO nanoparticle-immobilized chitosan-inulin composites: Fractal kinetics, statistical physics, thermodynamic analysis, and application to real water samples

Text S1: Experimental apparatus

During the experimental studies, the solution pH was adjusted using a digital pH meter (Cyberscan pH 2100). The PCM concentration in the solution was determined with a UV-Vis spectrophotometer (Shimadzu UV-1800, Japan). Fourier transform infrared (FT-IR) spectra were recorded using a Perkin Elmer Spectrum 2 spectrometer in the range of 4000–400 cm^{-1}. Powder X-ray diffraction (XRD) analysis was performed with a Bruker AXS D8 Advance diffractometer (Germany) using Cu Kα radiation (λ = 0.154 Å) to determine the XRD pattern of the material. Surface morphology and elemental composition of the adsorbent were analyzed through scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDX) (JEOL JSM-6510LV, Japan). Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out using a Shimadzu DTG-60H thermal analyzer to assess the material's thermal stability and decomposition characteristics. Additionally, the Brunauer–Emmett–Teller (BET) surface area and porosity of the material were measured using a Micromeritics ASAP 2020 surface pore analyzer with nitrogen adsorption/desorption at 77 K.

Table S1: Independent variables and their levels used for central composite design.

Variables	**Unit**	**Factor**	**Range and level**				
			- α	**-1**	**0**	**+1**	**+α**
Contact time	(-)	**K**	12.96	-30.00	55.00	80.00	97.04
Dosage	(mg)	**L**	1.59	5.00	10.00	15.00	18.41

Initial concentration	(mg/L)	**M**	6.14	30.00	65.00	100.00	123.86

Table S2: Mathematical expressions of classical isotherm statistical physics models and its parameters

Classical isotherm	Non-linear equation	Parameters
Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	q_m,K_L and C_e
Freundlich	$q_e = K_F C_e^{1/n}$	K_F and n
Statistical physics models		
Model 1 (M_1)	$q_e = nN_o \frac{n.N_m}{1 + \left(\frac{C_{1/2}}{C_e}\right)^n} = \frac{Q_{sat}}{1 + \left(\frac{C_{1/2}}{C_e}\right)^n}$	n, N_o and N_m
Model 2 (M_2)	$q_e = \frac{n_1.N_{m1}}{1 + \left(\frac{C_1}{C}\right)^{n_1}} + \frac{n_2.N_{m2}}{1 + \left(\frac{C_2}{C}\right)^{n_2}}$	n_1, n_2,N_{m1} and N_{m2}
Model 3 (M_3)	$q_e = n.N_m \left(\frac{\left(\frac{C}{C_{1/2}}\right)^n + 2\left(\frac{C}{C_{1/2}}\right)^{2n}}{1 + \left(\frac{C}{C_{1/2}}\right)^n + \left(\frac{C}{C_{1/2}}\right)^{2n}} \right)$	n and N_m
Model 4 (M_4)	$q_e = n.N_m \left(\frac{\left(\frac{C}{C_1}\right)^n + 2\left(\frac{C}{C_1}\right)^{2n}}{1 + \left(\frac{C}{C_1}\right)^n + \left(\frac{C}{C_2}\right)^{2n}} \right)$	n and N_m

where q_e: experimental adsorption capacity(mg/g), q_m : calculated adsorption capacity (mg/g), C_e: concentration of cloxacillin in the solution phase at equilibrium(mg/L),k_L: Langmuir isotherm constant (L/mg), k_F&$\frac{1}{n}$ are Freundlich isotherm constants. N_m and n are the density of adsorption sites, occupied by adsorbate (mg/g) and number species which are adsorbed, respectively. $C_{1/2}$ and C are the concentration of acetaminophen (mg/L) at half saturation and

equilibrium concentration (mg/L), respectively. C_1 and C_2 suggested the concentration (mg/L) at half saturation of first and second adsorption sites, respectively. N_{m1} and N_{m2} are the density of first and second adsorption sites, respectively. n_1 and n_2 indicate the number of adsorbed species at first and second adsorption sites, respectively.

Table S3

Surface based kinetic studies (fractal-like kinetic models)	Mathematical expression
F-L PFO	$q_t = q_e \left[1 - \exp\left(-k_{1,0}^{'} t^{\propto}\right)\right]$
F-LPSO	$q_t = \frac{k_{2,0}^{'} q_e^2 t^{\propto}}{1 + k_{2,0}^{'} q_e t^{\propto}}$
Diffusion based kinetic model	
Intraparticle diffusion model	$q_t = k_{id} t^{1/2} + C_{id}$

In these equations $k_{1,0}^{'}\ (1/min^{\propto})$ and $k_{2,0}^{'}\ (mg/g/min^{\propto})$ express the rate coefficients of Fractal-like-PFO, Fractal-like-PSO, respectively. $\propto$ denotes fractional time index which is defined as $\propto = (1-h)$. k_{id} (mg/g $min^{-0.5}$) and C_{id} (mg/g) denotes the intraparticle diffusion rate constant and the boundary layer effect, respectively.

Table S4: Nonlinear Langmuir and Freundlich isotherm parameters and error values

Isotherm	**Temp.** (K)	**Parameters (Linear)**					
		q_{m*} (mg /g)	K_L (L/mg)		R^2	**Error Functions** RMSD	χ^2
Langmuir	298	287.538	1.627		0.9996	6.149	0.004
	308	282.189	2.248		0.9997	6.147	0.003
	318	279.171	3.753		0.9996	6.083	0.002
		q_{m*} (mg /g)	n	K_F			
Freundlich	298	269.54	2.525	53.92	0.9268	16.425	3.065
	308	265.48	2.023	49.59	0.9528	13.293	1.939
	318	262.89	1.955	46.28	0.9922	9.399	0.949

* The experimental values of adsorption capacity (q_e) for acetaminophen are 287.15 mg/g, 281.98 and 280.078 mg/g at 298, 308 and 318 K, respectively.

Table S5: Mathematical expressions of statistical physics models with R^2 and SSE for fitting of experimental date for the adsorption of acetaminophen onto

Models	Temp (K)	Parameters		
		R^2	χ^2	RMSD
Model 1 (M_1)	298	0.9897	2.197	14.132
	308	0.9908	1.7635	16.332
	318	0.9946	1.141	13.328
Model 2 (M_2)	298	0.9998	0.066	1.905
	308	0.9997	0.037	1.587
	318	0.9999	0.031	1.721
Model 3 (M_3)	298	0.9925	6.764	26.656
	308	0.9698	5.675	26.282
	318	0.9809	3.371	21.436
Model 4 (M_4)	298	0.9895	18.635	38.783
	308	0.9498	12.966	33.335
	318	0.9299	7.2337	9.399

Table S6. Diffusion based kinetic parameters and regression coefficients obtained by linear regression analysis for the adsorption of PCM onto ZnO/Cs-In.

Kinetic model		Parameters	Concentration (mg/L)		
			95	115	195
Intra-particle diffusion model	I	C_{id}	-167.47	-199.21	-202.73
		K_{id} (mg/g.min$^{1/2}$)	57.813	71.119	74.703
		R^2	0.9992	0.9995	0.9999
	II	C_{id}	94.546	150.39	170.54
		K_{id} (mg/g.min$^{1/2}$)	16.729	15.659	15.603
		R^2	0.9998	0.9996	0.9994

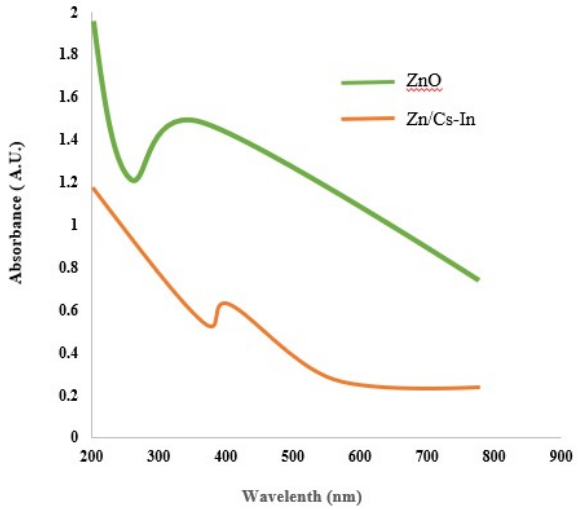

Fig. S1: Uv-visible absorption spectra of ZnO nanoparticles and the ZnO/CS-In nanocomposite

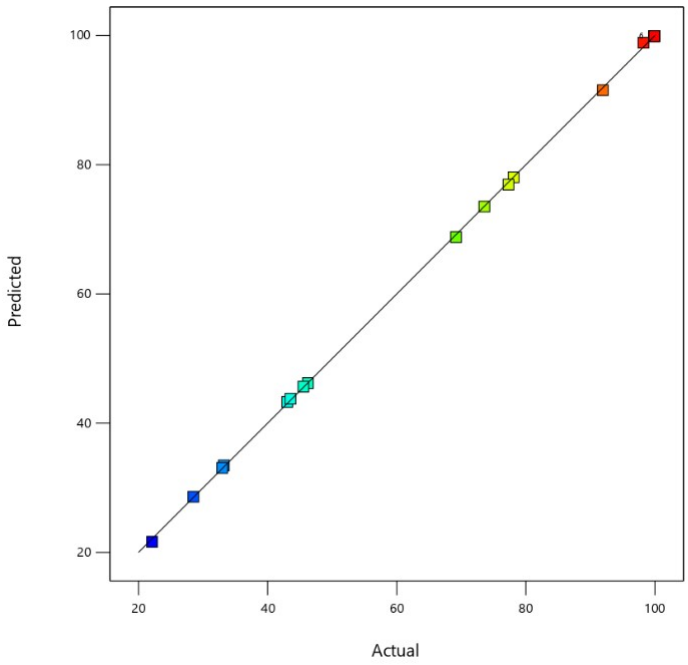

Fig S2: Predicted versus actual plot.

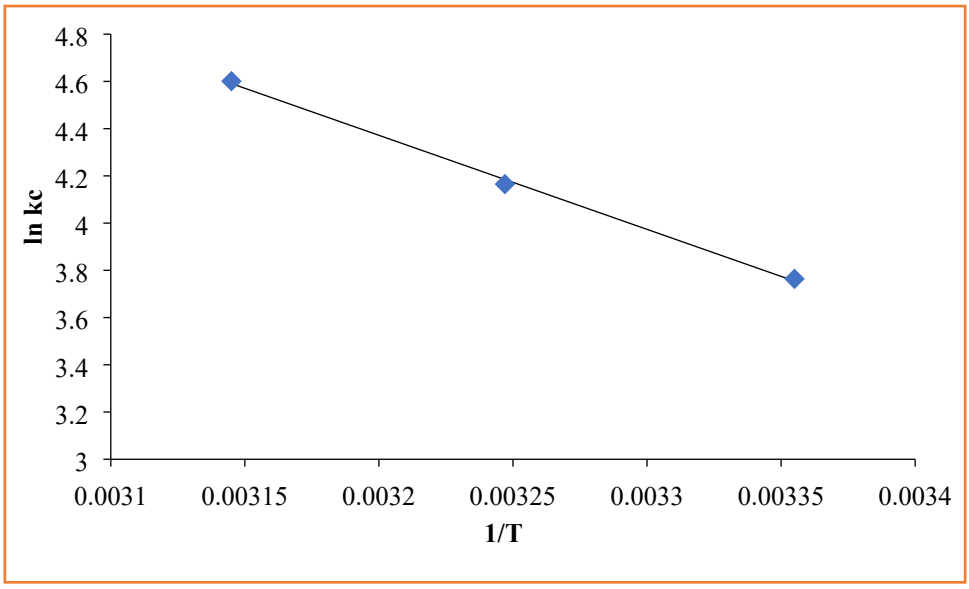

Fig. S3: Van't Hoff plot for determining thermodynamic parameters of PCM adsorption onto ZnO/Cs-In

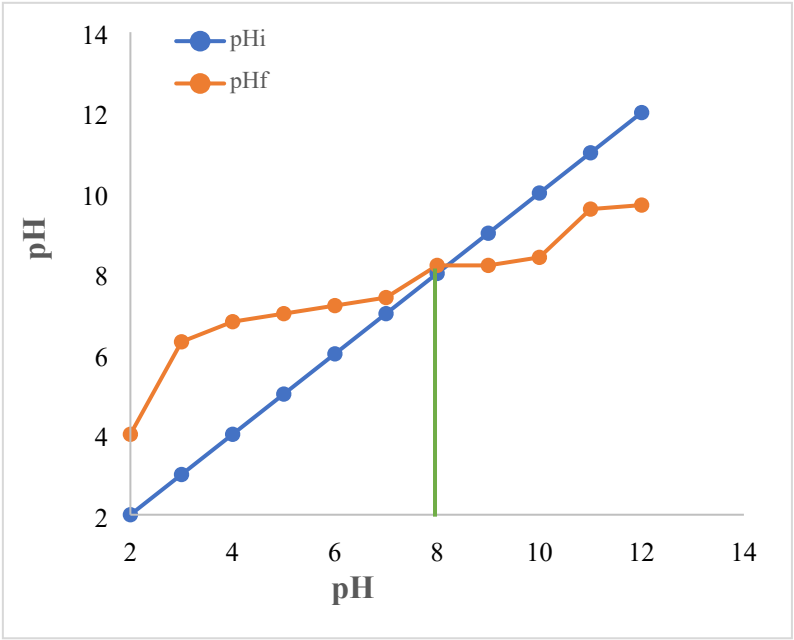

Fig. S4: Point of zero charge pH_{pzc} of the ZnO/Cs-In, determined by the pH drift method