

Supplementary Material

for

Investigation of the adsorptive capacity of a poly(vinyl alcohol)-based film for sodium diclofenac in aqueous media

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1. Isotherm and kinetic models evaluated

Table S1 shows the evaluated isotherm and kinetic models used to describe the adsorptive behavior of the poly(vinyl alcohol) (PVA)-based film.

Table S1. Isotherm and kinetic equations used for the analysis of DCF adsorption in PVA films.

<i>Isotherm models</i>			
Model	Equation	Constants	Reference
Langmuir	$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e}$	K_L = Langmuir adsorption constant ($L\ mg^{-1}$) q_{\max} = maximum adsorption capacity ($mg\ g^{-1}$)	[1]
Freundlich	$q_e = K_F C_e^{\frac{1}{n}}$	K_F = Freundlich adsorption capacity constant ($mg\ g^{-1}\ (mg\ L^{-1})^{-1/n}$) $1/n$ = Freundlich dimensionless adsorption intensity parameter	[2]
Temkin	$q_e = \frac{RT}{b_T} \ln(a_T C_e)$	R = universal gas constant ($8.314\ J\ mol^{-1}\ K^{-1}$) a_T = Temkin isotherm equilibrium binding constant ($L\ mg^{-1}$) b_T = Temkin isotherm constant ($J\ mol^{-1}$)	[3]
Sips	$q_e = \frac{q_{mS} K_S C_e^{\beta_S}}{1 + K_S C_e^{\beta_S}}$	q_{mS} = maximum adsorption capacity ($mg\ g^{-1}$) K_S = Sips equilibrium constant ($L\ mg^{-1}$) β_S = Sips isotherm model exponent	[4]
Redlich-Peterson	$q_e = \frac{K_{RP} C_e}{1 + \alpha_{RP} C_e^{\beta_{RP}}}$	K_{RP} = Redlich-Peterson isothermal constant ($L\ g^{-1}$) α_{RP} = Linear Redlich-Peterson constant ($(mg\ L^{-1})^{-\beta}$) β_{RP} = Exponential Redlich-Peterson constant	[5]
<i>Kinetic models</i>			
Model	Equation	Constants	Reference
PFO	$q(t) = q_e (1 - e^{-k_1 t})$	k_1 = pseudo-first order kinetic constant (min^{-1}) q_e = adsorption capacity at equilibrium ($mg\ g^{-1}$)	[6]
PSO	$q(t) = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}$	k_2 = pseudo-second order kinetic constant ($g\ mg^{-1}\ min^{-1}$) q_e = adsorption capacity at equilibrium ($mg\ g^{-1}$)	[7]

2. Investigation of interferences due to glassware cleaning method

Table S2 presents the absorbance results and corresponding DCF concentration for the blank samples from Erlenmeyer flasks washed with Extran® and neutral detergent, as well as those from pure distilled water.

Table S2. Absorbance values and corresponding DCF concentrations recorded for blank experiments samples following glassware cleaning with alkaline Extran® and neutral detergent solutions. Experimental conditions: 25 °C, 240 rpm, initial distilled water volume of 50 mL.

Sample	Absorbance (a. u.)	Corresponding DCF concentration ($mg\ L^{-1}$)
Distilled water	-0.001	- 0.03
Blank (Extran®)	0.120	3.53
Blank (neutral detergent)	0.006	0.18

The high absorbance recorded from the first blank sample suggested possible contamination in the Erlenmeyer flasks, that could be related to the presence of Extran® residuals. To address this concern, another blank experiment was performed using an Erlenmeyer that had been washed without the Extran® immersion stage, as an attempt to eliminate the interferences. Both the blank and the pure distilled water exhibited lower absorbance values, justifying the modification made to the glassware washing method.



3. Ultraviolet-visible absorption spectrum of the PVA-based film

The UV-Vis absorption spectrum of the film is presented in Figure S1. The highlighted peak at 288 nm suggests that the film's absorption occurs close to the wavelength used for DCF concentration determination (274 nm).

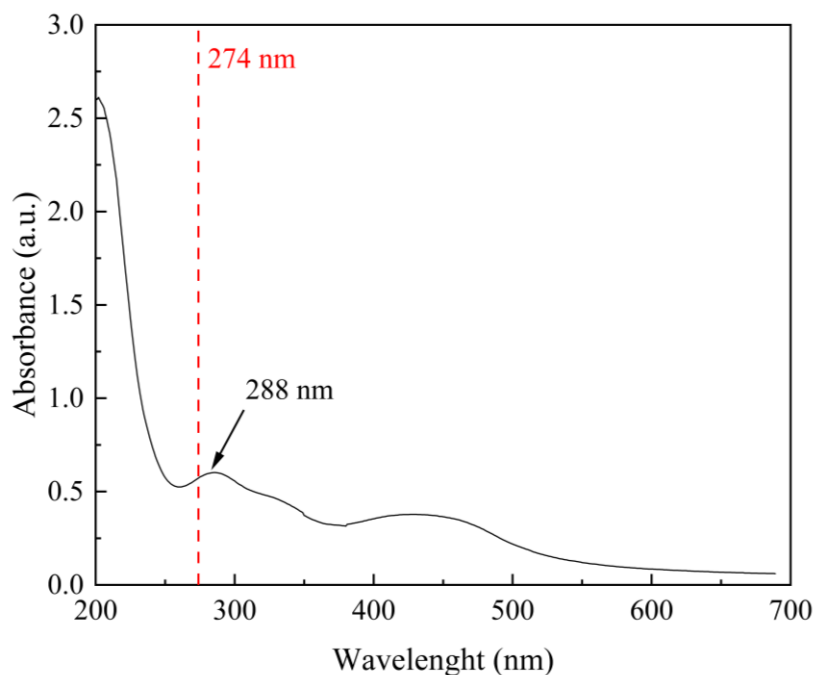


Figure S1. UV-Vis absorption spectrum of the film. Conditions: 200-690 nm, resolution of 1.0 nm.

4. Investigation of the DCF pH behavior when in contact with the PVA-based film

Table S3 presents the initial and final pH values of the DCF solution in the pH effect experiments. The pH of all samples decreases by the end of the experiment, approaching a value of 4.0. Consequently, the pH variation intensifies as the initial pH rises above 4.0.

Table S3. Initial and final pH values, along with pH variation (ΔpH), measured for DCF solutions in the adsorption experiments.

Initial pH	Final pH	ΔpH
4.15	4.04	0.11
5.18	4.16	1.02
7.06	4.20	2.86
8.18	4.30	3.88
9.11	4.37	4.74

The plot of pH variation as a function of initial pH is presented in Figure S2, where a linear behavior can be identified. Using linear regression, the initial pH value for which the corresponding pH variation equals zero is 4.05.



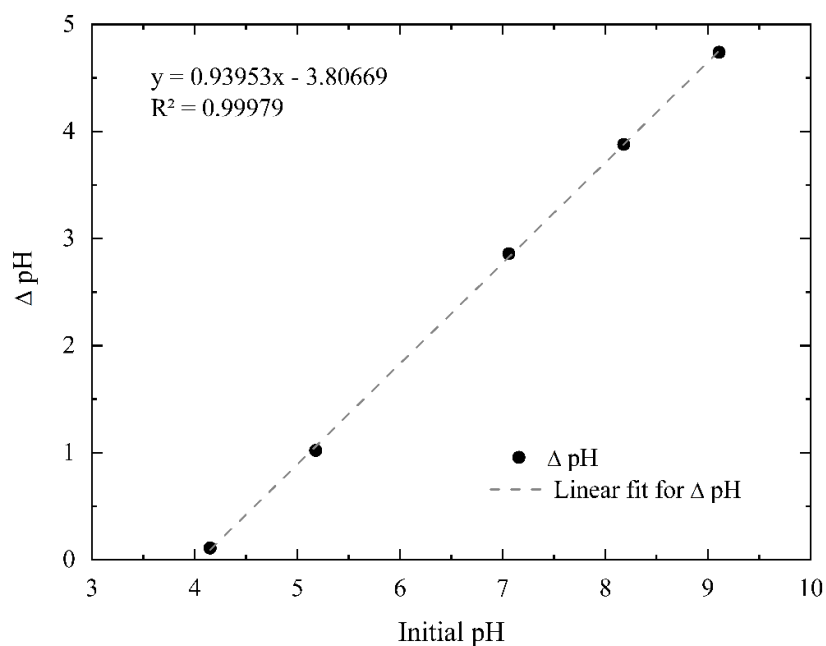


Figure S2. pH variation of the DCF solutions after the adsorption experiments with the PVA-based film as a function of the initial pH. Conditions: 25 °C, 240 rpm, initial adsorbate solution volume of 50 mL, initial DCF concentration of 10 mg L⁻¹, contact time of 240 min.

5. Parameters obtained using isotherm and kinetic models for the adsorption of DCF using the PVA-based film

The parameters obtained for the isotherm and kinetic equations are presented in Tables S4 and S5, respectively.

Table S4. Parameters obtained for equilibrium isotherms models after adjustment to the experimental data on DCF adsorption by the PVA-based film.

Model	Constants	OF	R ²
Langmuir	$q_{max} = 0.4331 \text{ mg g}^{-1}$ $K_L = 0.2504 \text{ L mg}^{-1}$	0.0339	0.9000
Freundlich	$1/n = 0.1593$ $K_F = 0.2210 \text{ mg g}^{-1} (\text{L mg}^{-1})^{1/n}$	0.0226	0.8686
Temkin	$A_t = 1.09 \times 10^{22} \text{ L mg}^{-1}$ $b_t = 4.48 \times 10^5 \text{ J mol}^{-1}$	0.0170	0.8873
Sips	$q_{mS} = 0.3803 \text{ mg g}^{-1}$ $K_s = 0.2364 \text{ L mg}^{-1}$ $\beta_s = 0.7042$	0.0400	0.8756
Redlich-Peterson	$K_{RP} = 5.741 \text{ L g}^{-1}$ $\alpha_{RP} = 5.239 (\text{mg L}^{-1})^{-\beta}$ $\beta_{RP} = 1.800$	7.748×10^{-4}	0.9767

Note: OF = objective function



Table S5. Parameters obtained for kinetic models adjusted for experimental data of DCF adsorption by the PVA-based film at initial DCF concentrations ranging from 2.5 to 10.0 mg L⁻¹

Initial DCF concentration (mg L ⁻¹)	2.5	5.0	8.5	10.0
Experimental q_e (mg g⁻¹)	0.5108	0.2456	0.2024	0.2063
<i>Pseudo-first order</i>				
Calculated q_e (mg g ⁻¹)	0.5424	0.2612	0.2357	0.2521
k_1 (min ⁻¹)	0.6738	3.5640	5.0536	0.8921
<i>OF</i>	0.00033	0.00169	0.00094	0.00219
R^2	0.9909	0.8320	0.8875	0.7792
<i>Pseudo-second order</i>				
Calculated q_e (mg g ⁻¹)	0.5403	0.2612	0.2357	0.2511
k_2 (g mg ⁻¹ min ⁻¹)	61.136	6.816 × 10 ³	8.585 × 10 ⁶	7.137 × 10 ³
<i>OF</i>	0.00037	0.00169	0.00113	0.00219
R^2	0.9897	0.8320	0.8875	0.7793

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