coatings

Electrospun Bilayer PAN/Chitosan Nanofiber Membranes Incorporated with Metal Oxide Nanoparticles for Heavy Metal Ion Adsorption

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Supplementary Materials

1. Point of Zero Charge (pH_{pzc}) for the Bilayer PAN/MO–CS Nanofiber

In this study, the determination of the pH_{pzc} for the bilayer PAN/MO–CS nanofiber mat was carried out by preparing 50 mL of 0.01M NaCl solutions in various beakers and their initial pH ($pH_{initial}$) was adjusted to different values between 3 and 10 by addition of HCl or NaOH solutions. Then, 50 mg of PAN/MO–CS nanofiber mat was added to each beaker and the final pH (pH_{final}) of the solutions was measured after 72 h. The pH_{pzc} was determined by finding the point of intersection between the $pH_{initial}$ vs. pH_{final} curve and the $pH_{initial}$ = pH_{final} line. The pH_{pzc} for our PAN/MO–CS (for both ZnO and TiO2) bilayer nanofibers in the absence of Pb(II) and Cd(II) ions was found to be very close to 7.1 as shown in Figure S1.

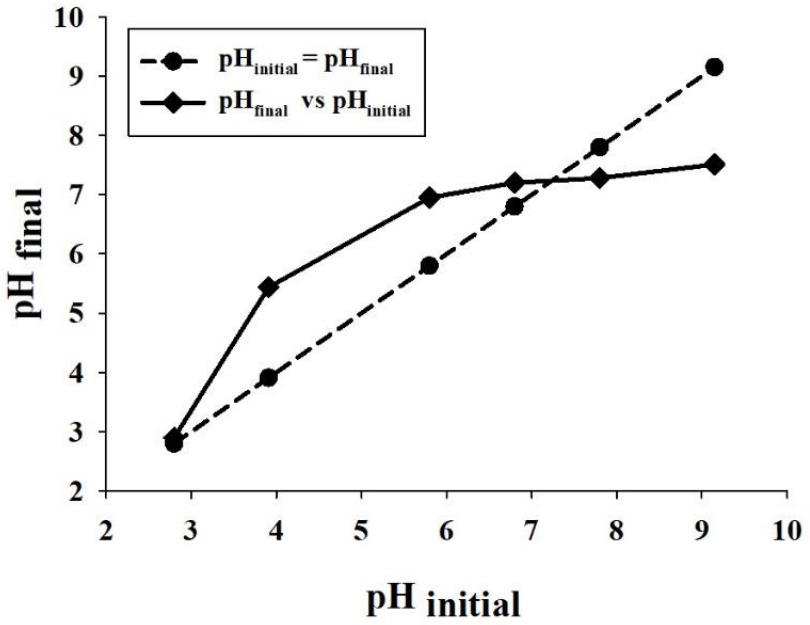


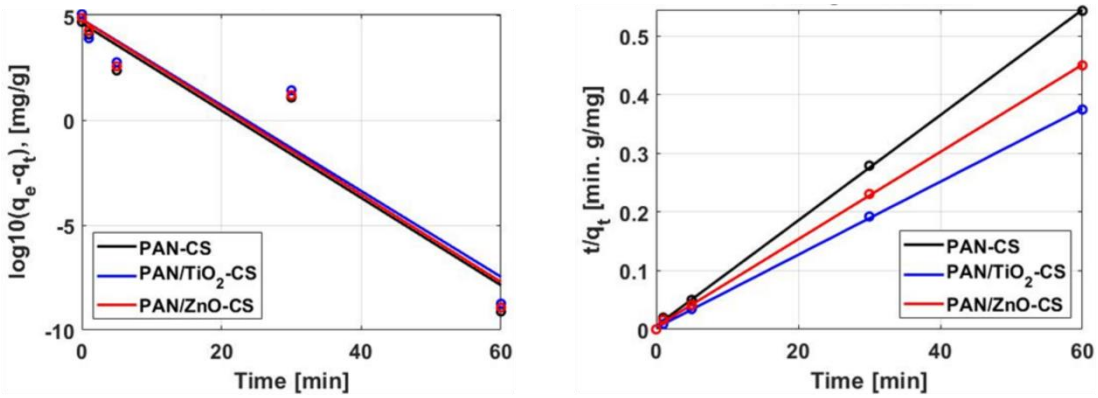
Figure S1. Point of zero charge (pH_{pzc}) of the bilayer PAN/MO–CS nanofiber mat.

2. Comparison of the Kinetic Model Parameters Obtained from Linear Least Square Method and Nonlinear Optimization Method

The kinetics of the adsorption behavior are usually represented by the pseudo-first-order (PFO) and pseudo-second-order (PSO) models [1–4]. The kinetic parameters (i.e., k_1, k_2, and q_e) in the PFO and PSO models can be obtained by fitting the following linear forms (see Figure S2):

$$\mathbf{log(\, q_e - q_t) = log(\, q_e) - \frac{k_1\, t}{2.303}} \quad (1)$$

$$\mathbf{\frac{t}{q_t} = \frac{1}{k_2\, q_e^2} + \frac{1}{q_e} t} \quad (2)$$



(a) (b)

Figure S2. Linear fitting of (**a**) the PFO and (**b**) PSO models for the adsorption of Cd(II) onto PAN–CS and PAN/MO–CS nanofiber mats.

In this linear fitting, the ability of the model to fit the experimental data is usually evaluated using the value of the correlation coefficient (R^2). The other method to get the kinetic parameters is to apply the nonlinear optimization technique in the following forms of the PFO and PSO models:

$$\mathbf{q_t = q_e\left(1 - e^{-k_1\, t}\right)} \quad (3)$$

$$\mathbf{q_t = \frac{q_e^2\, k_2\, t}{1 + k_2\, q_e\, t}} \quad (4)$$

To compare the performance of the above two methods (linear fitting and nonlinear optimization) to get the kinetic parameters and adequately describe adsorption kinetic experimental data, we use the mean absolute adsorption error (MAAE), defined as

$$\mathrm{MAAE} = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{(q_t)_i^{exp} - (q_t)_i^{model}}{q_e^{exp}}\right| \text{ x } 100\ \% \quad (5)$$

where q_e^{exp} denotes the experimental equilibrium adsorption capacity, and $(q_t)_i^{exp}$ and $(q_t)_i^{model}$ denote the values of the adsorption capacity at time t from the experimental and kinetic model, respectively. For brevity, we show here only the results of the adsorption of Cd(II), and similar trends were obtained for the adsorption of Pb(II). Table S1 compares the kinetics parameters of the PSO model obtained by linear fitting and nonlinear optimization methods. Although the values of R^2 are very high (>0.999) for the linear fitting, the mean absolute errors (MAAE) are lower than those

obtained by the nonlinear optimization method. The predicted equilibrium adsorption capacities (q_e^{model}) for the two methods are very close to the experimental values.

Table S1. Comparison of kinetics parameters of the PSO model for the adsorption of Cd(II) obtained by linear fitting and nonlinear optimization methods.

Adsorbents	q_e^{exp} (mg/g)	Kinetic Parameters Using Linear Fitting				Kinetic Parameters Using Nonlinear Optimization		
		k_2 (1/min)	q_e^{model} (mg/g)	R^2	MAAE %	k_2 (1/min)	q_e^{model} (mg/g)	MAAE %
PAN–CS	110.5	0.0134	115.35	0.999	3.59	0.0078	114.0	2.53
PAN/TiO2–CS	160.1	0.0148	161.56	0.999	1.32	0.0136	159.2	0.66
PAN/ZnO–CS	133.3	0.0115	138.36	0.999	3.42	0.0067	137.4	2.31

3. Dubinin-Radushkevich isotherm

The Dubinin-Radushkevich equation [5] is defined as

$$q_e = q_{DR}\ e^{-k_{DR}\ \epsilon^2} \tag{6}$$

$$\epsilon = R\ T\ \ln\left(1 + \frac{1}{C_e}\right) \tag{7}$$

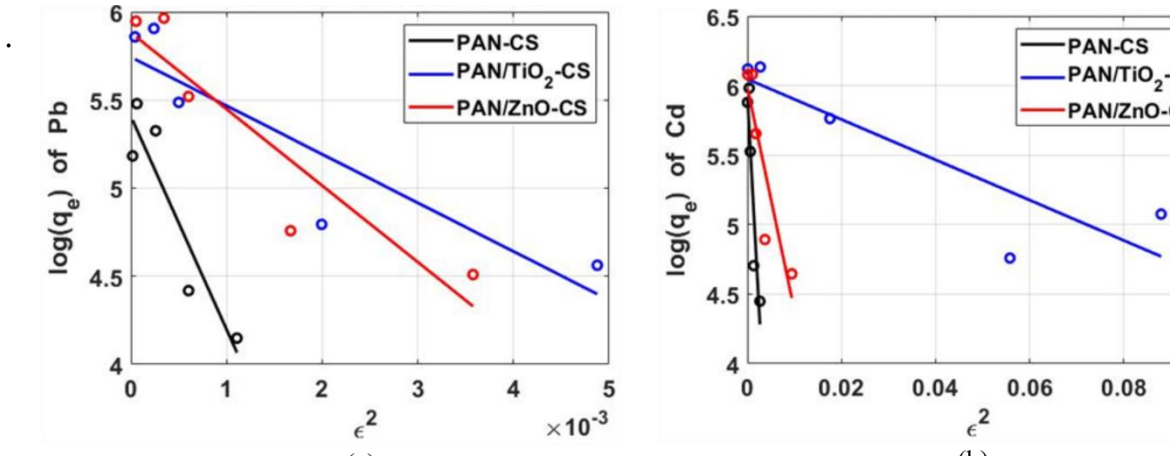
where k_{DR} (mol2/kJ2) is a constant related to the sorption energy, q_{DR} (mg/g) is the adsorption capacity, ϵ is the Polanyi potential, R is the gas constant, and T is the temperature in Kelvin. The linearized form is given by

$$\ln q_e = \ln q_{DR} - \ k_{DR}\ \epsilon^2 \tag{8}$$

A plot of $\ln q_e$ against ϵ^2 is used to extract the parameters q_{DR} and k_{DR}. Once these parameters are obtained, the mean adsorption energy E (kJ/mol) is calculated as:

$$E = \frac{1}{\sqrt{2\ k_{DR}}} \tag{9}$$

Figure S3 and Table S2 show the fitting and the values of the parameters, respectively, for the adsorption of Pb(II) and Cd(II) by the bilayer nanofiber mats developed in this work. The coefficient of determination R2 for the fitting was approximately 0.85 for most adsorbent materials.



(a) (b)

Figure S3. Fitting of the Dubinin-Radushkevich model for the adsorption of Pb(II) (**a**) and Cd(II) (**b**) onto PAN-CS and PAN/MO–CS nanofiber mats.

Table S2. Parameters of the Dubinin-Radushkevich equation and the mean adsorption energy E for the adsorption of Pb(II) and Cd(II) by PAN-CS and PAN/MO-CS nanofibers.

Adsorbents	Adsorption of Pb(II)				Adsorption of Cd(II)			
	k_{DR} (mol2/kJ 2)	q_{DR} (mg/g)	R^2	E (kJ/mol)	k_{DR} (mol2/kJ 2)	q_{DR} (mg/g)	R^2	E (kJ/mol)
PAN–CS	0.0008	222.9	0.86	13.62	0.0016	377.2	0.85	12.81
PAN/TiO2–CS	0.0036	312.1	0.83	11.71	0.0689	422.6	0.80	4.65
PAN/ZnO–CS	0.0023	358.5	0.85	14.72	0.0062	399.5	0.83	8.93

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