Supporting information

Surface-Cleaned Hydroxyapatite Nanowires for Aqueous Copper Ion Removal: Performance, Adsorption Mechanisms and Membrane Filtration Application

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Detailed Procedures for Adsorption Kinetic Models

The adsorption kinetic data were analyzed using both the pseudo-first-order and pseudo-second-order models.

Non-Linear Pseudo-First-Order Kinetic Model

1. Model Equation:

The integral form of the pseudo-first-order (Lagergren) model is expressed as:

$$q_t = q_e(1 - e^{-k_1 t})$$

where:

- q_t is the amount of adsorbate adsorbed at time t (mg g^{-1}),
- q_e is the calculated adsorption capacity at equilibrium (mg g^{-1}),
- k_1 is the pseudo-first-order rate constant (min^{-1}),
- t is the contact time (min).

2. Detailed Fitting Steps:

a. Data Preparation: Prepare a two-column data set in your graphing/analysis software. Column A contains the independent variable, time (t, in minutes). Column B contains the dependent variable, the adsorption capacity at time t (q_t, in mg g^{-1}).

b. Define the Model: Access the non-linear curve fitting tool (e.g., in OriginPro, select Analysis > Fitting > Nonlinear Curve Fit). Create a new function and define the above equation. Name the function "PseudoFirstOrder".

c. Set Parameters: Assign the variables and parameters as follows:

- Independent Variable: t
- Dependent Variable: qt
- Parameters: qe and k1

d. Initial Parameter Estimates: Provide initial guesses for the parameters to help the fitting algorithm converge. A reasonable initial guess for qe can be the experimentally observed $q_{e,exp}$ value. For k1, an initial guess of 0.01 to 0.1 is often a good starting point.

e. Perform the Fit: Execute the iterative fitting process. The software will use an algorithm (e.g., Levenberg-Marquardt) to find the values of q_e and k_1 that minimize the sum of squared residuals between the experimental q_t data and the model curve.

f. Output and Validation: The fitting result will provide the best-fit values for q_e and k_1, along with their standard errors. The goodness of fit is typically evaluated using

the coefficient of determination (R^2) and the adjusted R^2. The fitted curve should be visually compared to the experimental data points to ensure a good match across the entire time range.

Linear Pseudo-Second-Order Kinetic Model

1. Model Equation:

The linearized form of the pseudo-second-order model is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

where:

- q_t is the amount of adsorbate adsorbed at time t (mg g^{-1}),
- q_e is the calculated adsorption capacity at equilibrium (mg g^{-1}),
- k_2 is the pseudo-second-order rate constant (g mg^{-1} min^{-1}),
- t is the contact time (min).

2. Detailed Fitting Steps:

a. Data Transformation: Prepare a new data set for linear regression. Calculate a new Y-value, t/q_t, for each corresponding time point (t).

b. Data Preparation: Create a two-column data set for the linear plot. Column A contains the independent variable, time (t). Column B contains the new dependent variable, t/q_t (with units of min g mg^{-1}).

c. Perform Linear Regression: Perform a standard linear regression on the transformed data (t vs. t/q_t) using the software's linear fitting tool (e.g., Analysis > Fitting > Linear Fit). The model for the regression is a straight line: $y = A + Bx$, where $y = t/q_t$ and $x = t$.

d. Extract Parameters: The slope and intercept of the best-fit line are used to calculate the kinetic parameters:

- The slope of the line is equal to $1/q_e$.

$$\text{Slope} = \frac{1}{q_e} \Rightarrow q_e = \frac{1}{\text{Slope}}$$

- The intercept of the line is equal to $1/(k_2 q_e^2)$.

$$\text{Intercept} = \frac{1}{k_2 q_e^2} \Rightarrow k_2 = \frac{1}{\text{Intercept} \times q_e^2}$$

e. Goodness of Fit: The goodness of fit for the linear model is evaluated by the coefficient of determination (R^2) of the linear regression of t vs. t/q_t.

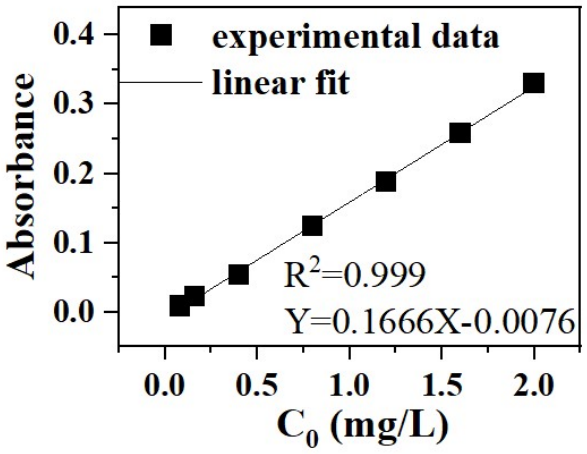

Figure S1. Standard curve showing the linear relationship between copper ion concentration and absorbance (pH = 5.5). The regression equation was Y = 0.1666X - 0.0076 with a correlation coefficient (R^2) of 0.999.

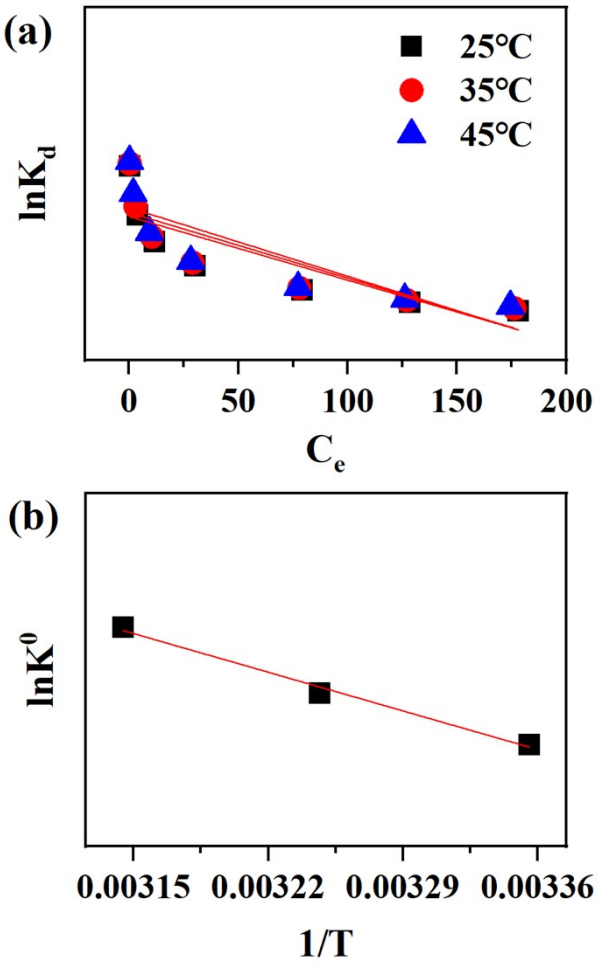

Figure S2. Linear fitting of thermodynamic parameters for copper ion adsorption: (a) plots of $\ln K_d$ versus C_e; (b) plots of $\ln K^0$ versus 1/T for sample ET-70. Experimental conditions: initial copper ion concentration = 10–200 mg/L, adsorbent dose = 0.4 g/L, temperature = 25°C, and pH = 5.5.

Table S1 The content changes of calcium and phosphorus elements in ET-70 before and after the adsorption of copper ions

Sample	Species	BE (eV)	Percent (%)
ET-70	Ca 2p	346.00	37.80
	P 2p	131.91	28.20
ET-70-Cu	Ca 2p	346.12	31.97
	P 2p	132.11	26.70