

Selective adsorption of Sr(II) from aqueous solution by

Na₃FePO₄CO₃: Experimental and DFT studies

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Text S1. Adsorption performance parameters

The adsorptive interaction between Sr^{2+} and NFPC was quantified by determining the adsorbate removal rates (R , %), distribution coefficients (K_d , $\text{mL}\cdot\text{g}^{-1}$), and adsorption capacities at specific time intervals (Q_t , $\text{mg}\cdot\text{g}^{-1}$) and equilibrium (Q_e , $\text{mg}\cdot\text{g}^{-1}$).

$$R = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$K_d = \frac{(C_0 - C_e)V}{mC_e} \quad (2)$$

$$Q_t = \frac{(C_0 - C_t)V}{m} \quad (3)$$

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (4)$$

Where C_0 ($\text{mg}\cdot\text{L}^{-1}$) and C_e ($\text{mg}\cdot\text{L}^{-1}$) are the initial and equilibrium concentrations of adsorbates, respectively; V (mL) is the solution volume; m (mg) is the weight of adsorbent. Generally, a K_d value exceeding $5000 \text{ mL}\cdot\text{g}^{-1}$ indicates good adsorbate/adsorbent affinity; C_t ($\text{mg}\cdot\text{L}^{-1}$) is the Sr^{2+} concentration after interaction with NFPC for a set duration.

Text S2. Adsorption model

S2.1 Adsorption kinetics models

We applied the Lagergren pseudo-first order [47], pseudo-second order [48], Elovich [49], Boyd [50], and Weber-Morris [51] models to decipher the adsorption mechanism to our experimental data.

Pseudo-first order model:

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \quad (5)$$

Pseudo-second order model:

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \quad (6)$$

$$h = K_2 Q_e^2 \quad (7)$$

$$t_{1/2} = \frac{1}{K_2 Q_e} \quad (8)$$

Elovich model:

$$Q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (9)$$

Where Q_e ($\text{mg}\cdot\text{g}^{-1}$) and Q_t ($\text{mg}\cdot\text{g}^{-1}$) are the adsorption capacity at equilibrium and time t (min), respectively; K_1 (min^{-1}) and K_2 ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$) are the pseudo-first-order and pseudo-second-order kinetic rate constant, respectively; h ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$) is the initial adsorption rate; $t_{1/2}$ (min) is the time to reach half of the adsorption equilibrium; α ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$) and β ($\text{mg}\cdot\text{g}^{-1}$) are the initial elovich rate constant and desorption elovich rate constant, respectively.

Boyd model:

$$B_t = K_B t + I_B \quad (10)$$

$$B_t = -0.4977 - \ln\left(1 - \frac{Q_t}{Q_e}\right) \quad (11)$$

Weber-Morris model:

$$Q_t = I_W + K_W t^{1/2} \quad (12)$$

Where B_t is the function of Q_t/Q_e , K_B (min) and I_B are the constant and intercept of the Boyd model, respectively; K_W ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1/2}$) and I_W are the diffusion rate constant and intercept of the Weber-Morris model, respectively.

S2.2 Adsorption isotherm models

The adsorption isotherms were interpreted using the Langmuir [52,53], Freundlich [54], Dubinin-Radushkevich (D-R) [55], and Temkin [56] models, respectively:

Langmuir model:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_L Q_m} \quad (13)$$

$$R_L = \frac{1}{1 + K_L C_0} \quad (14)$$

Freundlich model:

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (15)$$

D-R model:

$$\ln Q_e = \ln Q_{DR} - K_{DR} \varepsilon^2 \quad (16)$$

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (17)$$

$$E = \frac{1}{\sqrt{2K_{DR}}} \quad (18)$$

Temkin model:

$$Q_e = \beta_T \ln K_T + \beta_T \ln C_e \quad (19)$$

Where C_e ($\text{mg} \cdot \text{L}^{-1}$) is the concentration at adsorption equilibrium; Q_m ($\text{mg} \cdot \text{g}^{-1}$) and Q_{DR} ($\text{mg} \cdot \text{g}^{-1}$) are the maximum adsorption capacity predicted by the Langmuir model and D-R model, respectively; K_L ($\text{L} \cdot \text{mg}^{-1}$), K_F ($\text{mg}^{1-1/n} \cdot \text{g}^{-1} \cdot \text{L}^{1/n}$), K_{DR} ($\text{mol}^2 \cdot \text{kJ}^{-2}$) and K_T ($\text{kJ} \cdot \text{mol}^{-1}$) are the equilibrium constant of Langmuir isotherm model, Freundlich isotherm model, D-R isotherm model and Temkin isotherm model, respectively; The separation coefficient (R_L , dimensionless) provides insight into adsorption favorability, with R_L values between 0 and 1 indicating favorable adsorption, and values above 1 suggesting unfavorable conditions; n is the Freundlich intensity parameter; ε ($\text{J} \cdot \text{mol}^{-1}$) is the Polanyi potential; R ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) is the gas constant; T (K) is the Kelvin temperature; E ($\text{kJ} \cdot \text{mol}^{-1}$) is the mean adsorption energy, which distinguishes between chemisorption ($E > 8$) and physisorption ($E < 8$); β_T ($\text{L} \cdot \text{mg}^{-1}$) is the Temkin constant.

S2.3 Adsorption thermodynamics models

Thermodynamic parameters, including the Gibbs free energy change (ΔG^0 , $\text{kJ} \cdot \text{mol}^{-1}$), entropy change (ΔS^0 , $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), and enthalpy change (ΔH^0 , $\text{kJ} \cdot \text{mol}^{-1}$), were calculated to understand temperature's impact on the adsorption process [57].

$$\ln K_d^0 = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (20)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (21)$$

$$K_d^0 = K_d \times \frac{C^0}{Q^0} \quad (22)$$

Where R ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) is the gas constant; T (K) is the Kelvin temperature; K_d^0 is the dimensionless equilibrium constant; C^0 and Q^0 are the standard states of solution in liquid and solid, respectively. According to IUPAC regulations, C^0 is $1 \text{ mol}\cdot\text{L}^{-1}$. When the adsorbate is not a gas, we suggest Q^0 is set to $1 \text{ mol}\cdot\text{kg}^{-1}$.

Text S3. DFT calculation

Our DFT calculations utilized the CP2K code, employing a hybrid Gaussian and plane-wave basis set approach. Core electrons were modeled using the norm-conserving Goedecker-Teter-Hutter pseudopotentials. The valence electron wavefunctions were expanded in a double-zeta basis set augmented with polarization functions, further complemented by an auxiliary plane-wave basis set with an energy cutoff threshold set at 400 eV. The generalized gradient approximation exchange-correlation functional by Perdew, Burke, and Ernzerhof (PBE) was selected for our simulations. Each configuration was optimized using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm, with self-consistent field (SCF) convergence criteria set to 1.0×10^{-6} au. To account for the long-range van der Waals dispersion interactions, we integrated the DFT-D3 scheme, with an empirical dispersion correction, into the energies derived from the exchange-correlation functional. Furthermore, the self-consistent continuum solvation (SCCS) model, calibrated with a dielectric constant of 78.54, was engaged to replicate the aqueous solvent environment pertinent to the Sr^{2+} adsorption process.

The binding energy (BE) between NFPC and the Sr^{2+} ion was computed employing the following equation:

$$BE = E_{\text{Sr}^{2+}/\text{NFPC}} - E_{\text{NFPC}} - E_{\text{Sr}^{2+}} \quad (22)$$

Where $E_{\text{Sr}^{2+}/\text{NFPC}}$ and E_{NFPC} represent the total energies of the NFPC with and without the adsorption of the Sr^{2+} ion, respectively. $E_{\text{Sr}^{2+}}$ is the total energy of the Sr^{2+} ion. As this equation dictates, a negative BE indicates a stable adsorption complex.

Table S1 Partial kinetic parameters of the Sr²⁺ adsorption by NFPC.

Adsorbate	Pseudo-first-order model		Pseudo-second-order model				Elovich model	
	Q_e (mg·g ⁻¹)	K_1 (min ⁻¹)	Q_e (mg·g ⁻¹)	K_2 (g·mg ⁻¹ ·min ⁻¹)	H (mg·g ⁻¹ ·min ⁻¹)	$t_{1/2}$ (min)	A (mg·g ⁻¹ ·min ⁻¹)	β (g·mg ⁻¹)
Sr ²⁺	1.94	2.70E-2	12.58	4.41E-3	0.67	18.04	475.99	1.02

Table S2 Fitting parameters obtained by Boyd model and Weber-Morris models.

Adsorbate	Boyd model		Weber-Morris model	
	K_B (min ⁻¹)	I_B	K_W (mg·g ⁻¹ ·min ^{-0.5})	I_W (mg·g ⁻¹)
Sr ²⁺	6.73E-2	0.13	4.41E-2	11.66

Table S3 Fitting parameters obtained by adsorption isotherm models.

Adsorbate	Langmuir		Freundlich		D-R			Temkin	
	Q_m (mg·g ⁻¹)	K_L (L·mg ⁻¹)	K_F ((mg·g ⁻¹)· (L·mg ⁻¹) ^{1/n})	N ..	Q_{DR} (mg·g ⁻¹)	K_{DR} (mol ² ·KJ ⁻²)	E (KJ·mol ⁻¹)	β_T (L·mg ⁻¹)	K_T (KJ·mol ⁻¹)
Sr ²⁺	63.48	0.16	24.97	6.82	2.61	1.99E-3	15.82	8.65	11.86

Table S4 Fitting parameters obtained by adsorption thermodynamic models.

Adsorbent/Adsorbate	T	K_d^0	ΔH^0	ΔS^0	ΔG^0
	(K)		(kJ·mol ⁻¹)	(J·mol ⁻¹ ·K ⁻¹)	(kJ·mol ⁻¹)
NFPC /Sr ²⁺	303	1.01	-121.38	-39.92	-109.28
	313	0.87			-108.89
	323	0.75			-108.49