Supplementary file

Sustainable magnesium doped nanofibrillated cellulose/bentonite composites for enhanced phosphate removal: Process optimization and mechanistic insights

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Table S1 Composition of adsorbents prepared with different mass ratios of NFC, BN, and $MgCl_2$.

Adsorbents	**NFC:BN (mass ratios)**	**$MgCl_2$**
NFC_1/BN_1	1:1	0
NFC_2/BN_1	2:1	0
NFC_4/BN_1	4:1	0
NFC_1/BN_2	1:2	0
NFC_1/BN_4	1:4	0
$Mg@NFC_1/BN_1$	1:1	1.5 M

Adsorption isotherm

Adsorption isotherms were carried out at three different temperatures (298.5 K, 308.5 K, and 318.5 K) using 50 mL solutions containing different initial phosphate concentrations in the range 2, 5, 10, 20, 30, 50, 100 mg/L (typical levels found in wastewater) [1] with adsorbent dose of 1 g/L. Two isotherm models were used for the evaluation of the phosphate adsorption capacity namely Langmuir and Freundlich, isotherm models. These isotherm models were adopted to fit the experimental data.

Adsorption kinetics

The adsorption kinetics experiment was performed at different time intervals (5-120 min) to determine the equilibrium concentration. Adsorption kinetics consider the rate of adsorption and help define likely reaction/mass-transfer mechanisms. The pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models were employed to predict the adsorption kinetics mechanism. The best-fit model was selected based on the correlation coefficient (R^2) value for regression.

The equations of kinetic and isotherm models are provided in table S2:

Table S2 Kinetic and isotherm equations [2–4].

Models	**Equation**	**Parameters**
Kinetic models		
Pseudo-first-order (PFO)	$q_t = q_e(1 - e^{-K_1 t})$	q_t ($mg\ P{\cdot}g^{-1}$)is the adsorbed amount of phosphate at time t; q_e ($mg\ P{\cdot}g^{-1}$) is the adsorbed amount of phosphate at equilibrium; K_1 (min^{-1}) and K_2 ($mg{\cdot}g^{-1}{\cdot}min^{-1}$) are the rate constants of Pseudo-first-order and Pseudo-second-order respectively.
Pseudo-second-order (PSO)	$q_t = \frac{q_e^2 K_2 t}{1 + q_e K_2 t}$	
Isotherm models		
Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	q_e ($mg\ P{\cdot}g^{-1}$) is the adsorbed amount of phosphate at equilibrium; q_m ($mg\ P{\cdot}g^{-1}$) is the maximum adsorption capacity of adsorbent; C_e ($mg\ P{\cdot}L^{-1}$) is the concentration of phosphate at equilibrium; K_L ($L{\cdot}mg^{-1}$) and K_F (mg$\cdot g^{-1}$) $(L{\cdot}mg^{-1})^{1/n}$ are the adsorption constants of Langmuir and Freundlich models, respectively;

Freundlich	$q_e = K_F C_e^{1/n_F}$	n_F n is heterogeneity factor (dimensionless); R (8.314 J$\cdot mol^{-1}\cdot K$), T (298.15 K) are the universal gas constant and experimental temperature, respectively.

Adsorption thermodynamics

Thermodynamics describes the temperature dependence of the process [5]. The parameters such as standard change in Gibbs free energy (ΔG^0), enthalpy(ΔH^0) and entropy (ΔS^0) were determined with the given equations.

$$\Delta G^0 = \ -RT\ lnK_d \tag{1}$$

Where, R (8.314 J/mol/K) is the ideal gas constant, T (K) is the Kelvin temperature and K_d is the thermodynamic equilibrium constant of the adsorption process, reflecting phosphate distribution between the solid and liquid phases at equilibrium. The values of $\Delta H^0$and ΔS^0can be evaluated using Van't Hoff equation as follows

$$lnK_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{2}$$

Values of the standard changes of enthalpy (ΔH^0) and entropy (ΔS^0) are calculated by the equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{3}$$

Thus, the slope and intercept of the linear plot of ln(K_d) vs. $1/T$ can be used to determine the values of ΔH^0 and $T\Delta S^0$.

Table S3

Table S3 Thermodynamic parameters of the phosphate removal/uptake onto Mg@NFC/BN at different temperatures (298.5 K, 308.5 K and 318.5 K).

T (K)	K$_d$	ΔG^0 (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (kJ mol^{-1} K)
298.5	23.2	-7.84	-93.370	-2.865
308.5	7.16	-4.974		
318.5	2.18	-2.109		

References

1 H. Kong, W. Wang, J. Wang, G. Zhang, F. Shen, H. Jiang, Q. Li and Z. Huang, *Sep Purif Technol*, 2024, 351, 128038.

2 D. O. Omokpariola, *SSRN Electronic Journal*, DOI:10.2139/ssrn.4235196.

3 O. P. Murphy, M. Vashishtha, P. Palanisamy and K. V. Kumar, *ACS Omega*, 2023, 8, 17407–17430.

4 K. Y. Foo and B. H. Hameed, *Chemical Engineering Journal*, 2010, 156, 2–10.

5 B. Wang, H. Zhang, Z. Xu, Y. Xu, X. Hu, H. Wang, C. Wang and L. Chen, *Sep Purif Technol*, 2022, 290, 120894.