**Supporting Information**

**Studies on the removal of phosphate in water through adsorption using a novel Zn-MOF and its derived materials**

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**1.1. Materials and chemicals**

All chemicals and solvents were commercially available and used as received without purification. Propanedioic acid (98%) was purchased from Jiuding Chemical. 5-Amino-1H-tetrazole (98%) and zinc acetate dihydrate (98%) were purchased from Macklin. Ammonium molybdate, Vitamin C, L-Antimony Potassium Tartrate and Sulfuric acid (GR) were purchased from XiLong Scientific. Ultrapure water was prepared by the laboratory.

PHS-3C precision pH meter, Nicolect Nexus 470 FT-IR infrared spectrometer, JMS-6380LV scanning electron microscope, X-ray powder diffractometer, ZS90 Zeta Potentiometer, X-ray single crystal diffractometer, NETZSCH TG209, and X-ray photoelectron spectrometer were used in the experiment.

**1.2. Scheme and characterization of adsorption experiment**

1.2.1 Optimal modification selection

To choose the better material from the carbonized material in this paper, experiments were carried out with phosphate concentrations of 10-400 mg/L which was extracted 15 mL and poured in 100 mL centrifuge tubes with 0.020 g different carbonized material, while the speed of the shaker was 200 rap/min for 12 h at the temperature of 25 oC (Wang, et al., 2020) . Then the date of equilibrium adsorption capacity (qe) were compared.

To comfirm the phosphate concentration in sample, ammonium molybdate spectrophotometry (GB11893-89) was used.

1.2.2 Selection of experimental conditions

To explore the effect of pH, experiments were carried out with phosphate concentrations of 50 mg/L, which was extracted 15 mL and poured in 100 mL centrifuge tubes with 0.020 g of Zn-MOF-500, while the pH of the initial phosphate solution was adjusted to 3±0.1, 5±0.1, 7±0.1, 9±0.1, 11±0.1 and the original pH, using 6 mol/L NaOH and HCl solution (Wang, et al., 2020) . To explore the effect of dosing amount, these experiments was simulated with the experiments about the pH, the difference were dosing amount and the pH which was the best pH whose qe was better (Wang, et al., 2020) . All of these experiments were implemented in the shaker ZD-88 whose speed was 200 rap/min for 12 h at the temperature of 25oC.

The removal efficiency was calculated from Eq.(1) and equilibrium adsorption capacity (qe)was calculated from Eq.(2) as expressed below (Karthikeyan, Meenakshi, 2021) :

(1)

where *C*0 (mg/L) and *C*e (mg/L) were the initial and equilibrium concentration of the phosphate in the solution (Karthikeyan, Meenakshi, 2021) .

The equilibrium adsorption capacity (qe) was calculated using Eq.(2) (Nuryadin, et al., 2021).

(2)

where *C*0 (mg/L) and *C*e (mg/L) were the initial and equilibrium concentration of the phosphate in the solution, *V* (L) was the volume of the phosphate solution, and *m* (g) was the mass of the added adsorbent.

1.2.3 Adsorption isotherm and adsorption kinetics

The experiment of adsorption isotherm was simulated with the one of choosing the better material. To further study the adsorption, the model of adsorption isotherms developed by Langmuir and Freundlich was used, that described the relationship between the adsorption of phosphate on Zn-MOF and Zn-MOF-500 (Hassan, et al., 2020). The Langmuir model was expressed by following nonlinear equation (Hassan, et al., 2020):

(3)

where *qmax* (mg/g) was the theoretical maximum adsorption capacity calculated by the Langmuir adsorption isotherm model, and *B* (L/mg) was the Langmuir adsorption constant which was related to the adsorption bonding energy (Hassan, et al., 2020).

Here, the Freundlich model could be expressed as Hassan, et al., 2020)

(4)

where *KF* was the Freundlich constant related to the adsorption capacity of material, and the 1/n represented the intensity of adsorption (Hassan, et al., 2020).

The experiment of adsorption kinetics was simulation with the one of exploring the effect of dosing amount, differently, in this experiment, time was variable. To quantitatively analyzed the kinetics of the adsorption, plots of qt versus time were further analyzed using the pseudo first order, second order rate, and Weber Morris Intra-Particle Diffusion model (Lin, et al., 2015; Lian, et al., 2021). The equations of Pseudo-First-order (Eq.(5)), Pseudo-Second-order (Eq.(6)) and Weber Morris Intra-Particle Diffusion model (Eq.(7)) were shown below:

(5)

(6)

(7)

when t=0, qt=0, and t=t, qt=qt, Eq.(5) could change to Eq.(8).

(8)

where *qt* and *qe* were adsorption capactity at moments t (h) and equilibrium. *k1* and *k2* were kinetic constant (Wang, et al., 2020). *kp* was Internal diffusivity constant, and C constants related to the thickness of the boundary layer (Lian, et al., 2021).

1.2.4 Regeneration of adsorbents

In this study, the experiments were carried out with phosphate concentrations of 100 mg/L, while the pH of the initial phosphate solution was adjusted to 3±0.1 for Zn-MOF-500 and 7±0.1 for Zn-MOF at the temperature of 25oC in a beaker with 0.7 g material (Wang, et al., 2020), and then put into the shaker whose speed is 200 rap/min for 12 h. The experiment of desorption was using 0.1 mol/L NaCl solution whose pH was 7.0±0.1 for 5 h. The experiment of regeneration was 6 times.

1.2.5 Characterization experiment

FT–IR spectra were recorded as KBr pellets from 4000 to 400 cm-1 on a Nicolect Nexus 470 FT-IR infrared spectrometer (Zhang, et al., 2021).

The surface area of the material was analyzed using Brunauer-Emmett-Teller (BET) N2 adsorption-desorption isotherm by the surface analyzer (Micromeritics ASAP 2460 Version 3.01) (He, et al., 2020) .

X-ray photoelectron spectroscopy (XPS) measurements were performed using a Mono Al Kα source, operated at 12 kV and the analysis was performed at a pressure below 5 × 10−9 mbar on a Thermo Scientific K-Alpha. The analysis of the XPS spectra was performed with Avantage 5.9922 software (Liu, et al., 2019).

The X-ray diffraction (XRD) spectra were obtained using a PANalytical X’Pert3 powder diffractometer from 5° to 50° (Zhang, et al., 2021).

The thermogravimetry analyzer (TGA) was recorded from room temperature to 800 ℃ under air condition on a NETZSCH TG209 with a speed of 10℃/min.

The X-ray single crystal structures were determined on a SuperNova (Single source at offset, Eos) diffractometer (Zhang, et al., 2021).

The ZATE potential of the adsorbent was recorded in pH=1-12 on ZS90 ZATE Potentiometer.

1.2.6 Calculation

Visual MINTEQ 3.1 was used to calculate the concentration of phosphate in different pH. The simulation date of XRD was calculation by Mercury 3.1. The coordination configuration was calculated by shape 2.1.

Table S1 Crystal data and structures refinement for Zn-MOF

|  |  |
| --- | --- |
| Complex | Zn-MOF |
| Formula | C8H12N10O10Zn3 |
| *Fw* | 302.19 |
| Crystal system | Monoclinic |
| Space group | *I*2/*a* |
| *a* (Å) | 11.7936 (5) |
| *b* (Å) | 13.9051 (6) |
| *c* (Å) | 11.1436 (5) |
| *α* (°) | 90 |
| *β* (°) | 94.211 (4) |
| *γ* (°) | 90 |
| *V* (Å3) | 1822.52 (14) |
| *F*(000) | 1200 |
| *Z* | 4 |
| *D*x (g cm–3) | 2.203 |
| *μ* (mm–1) | 4.00 |
| *θ* range (°) | 3.9-28.7 |
| Ref. meas. / indep. | 6347, 2160 |
| Obs. ref.[*I* > 2*σ* (*I*)] | 1971 |
| *R*int | 0.028 |
| *R*1 [*I* ≥ 2*σ* (*I*)] a | 0.030 |
| *ωR*2(all data)b | 0.0775 |
| Goof | 1.10 |
| Δ*ρ*(max, min) (e Å-3) | 0.66, -1.02 |

a *R*1 = Σ||*F*o| – |*F*c||/Σ|*F*o|. b *wR*2 =[Σ*w*(|*F*o2|–|*F*c2|)2/Σ*w*(|*F*o2|)2]1/2

Table S2 Selected bond lengths (Å) and angles (°) for Zn-MOF

|  |  |  |  |
| --- | --- | --- | --- |
| Zn1-O2i | 2.088 (2) | Zn1-O2 | 2.088 (2) |
| Zn1-O3i | 2.045 (2) | Zn1-O3 | 2.045 (2) |
| Zn1-N3ii | 2.158 (2) | Zn1-N3iii | 2.158 (2) |
| Zn2-O2iv | 1.977 (2) | Zn2-O4 | 1.948 (2) |
| Zn2-N4v | 2.023 (2) | Zn2-N1 | 2.006 (2) |
| O2-Zn1-O2i | 179.96 (9) | C4-O2-Zn2vi | 115.6 (2) |
| O2i-Zn1-N3iii | 95.36 (8) | C2-O3-Zn1 | 124.5 (2) |
| O2-Zn1-N3iii | 84.61 (8) | C2-O4-Zn2 | 119.9 (2) |
| O2-Zn1-N3ii | 95.36 (8) | N4-N3-Zn1vii | 123.1 (2) |
| O2i-Zn1-N3ii | 84.61 (7) | N2-N3-Zn1vii | 126.1 (2) |
| O3i-Zn1-O2i | 88.24 (7) | O3-Zn1-O2 | 88.24 (7) |
| N3-N4-Zn2viii | 116.1 (2) | O3i-Zn1-O2 | 91.79 (7) |
| C1-N4-Zn2viii | 136.3 (2) | O3-Zn1-O2i | 91.79 (7) |
| O3-Zn1-O3i | 96.5 (1) | N2-N1-Zn2 | 123.7 (2) |
| O3i-Zn1-N3ii | 170.51 (8) | C1-N1-Zn2 | 129.6 (2) |
| O3i-Zn1-N3iii | 89.93 (8) | O3-Zn1-N3iii | 170.51 (8) |
| O3-Zn1-N3iii | 89.93 (8) | N3iii-Zn1-N3ii | 84.6 (1) |
| O2iv-Zn2-N4v | 93.83 (8) | O2iv-Zn2-N1 | 110.24 (9) |
| O4-Zn2-O2iv | 127.78 (8) | O4-Zn2-N4v | 111.61 (9) |
| O4-Zn2-N1 | 94.77 (9) | N1-Zn2-N4v | 121.17 (9) |
| Zn2vi-O2-Zn1 | 118.09 (8) | C4-O2-Zn1 | 125.7 (2) |

Symmetry codes: (i) -x+3/2, y, -z-2; (ii) -x+2, y, -z+3/2; (iii) x-1/2, y-1/2, z+1/2; (iv) x+1/2, -y+1, z; (v) x, -y+3/2, z+1/2; (vi) x-1/2, -y+1, z; (vii) x+1/2, y+1/2, z; (viii) x, -y+3/2, z-1/2.

Table S3 SHAPE data of Zn-MOF

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Complex | Metal | Vertices | Code | Label | Shape | Symmetry | Energy |
| Zn-MOF | Zn1 | 6 | 1 | HP-6 | Hexagon | D6h | 32.187 |
| 2 | PPY-6 | Pentagonal pyramid | C5v | 26.238 |
| 3 | OC-6 | Octahedron | Oh | 0.423 |
| 4 | TPR-6 | Trigonal prism | D3h | 12.777 |
| 5 | JPPY-5 | Johnson pentagonal pyramid (J2) | C5v | 29.898 |
| Zn2 | 4 | 1 | SP-4 | Square | D4h | 22.381 |
| 2 | T-4 | Tetrahedron | Td | 2.307 |
| 3 | SS-4 | Seesaw or sawhorse‡  (cis-divacant octahedron) | C2v | 6.087 |
| 4 | vTBPY-4 | Vacant trigonal bipyramid | C3v | 5.483 |

‡ A regular polyhedron with one or two vertices removed.



Fig. S1 FTIR spectra of Zn-MOF



Fig. S2 (a, b) Zn1 and Zn2 coordination patterns; (c, d, e) Zn-MOF stacking diagram in specific directions, a, b, c directions (cyan is zinc, red is oxygen, blue is nitrogen, gray is carbon, light gray is hydrogen, and yellow is false Atoms, delete solvent molecules in the pores);



Fig. S3 XRD spactra of Zn-MOF

Table S4 Distribution of various forms of phosphate in water at different temperatures

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| T/K | pH | PO43-/% | HPO42-/% | H2PO4-/% | H3PO4/% |
| 288.15 | 3 |  |  | 89.022 | 10.972 |
| 5 |  | 0.619 | 99.256 | 0.125 |
| 7 |  | 38.665 | 61.334 |  |
| 9 | 0.037 | 98.422 | 1.541 |  |
| 11 | 3.711 | 96.274 | 0.015 |  |
| 298.15 | 3 |  |  | 87.958 | 12.036 |
| 5 |  | 0.646 | 99.216 | 0.138 |
| 7 |  | 39.687 | 60.312 |  |
| 9 | 0.045 | 98.478 | 1.477 |  |
| 11 | 4.691 | 95.296 | 0.014 |  |
| 308.15 | 3 |  |  | 86.884 | 13.110 |
| 5 |  | 0.672 | 99.176 | 0.152 |
| 7 |  | 40.652 | 59.347 |  |
| 9 | 0.055 | 98.526 | 1.419 |  |
| 11 | 5.937 | 94.050 | 0.013 |  |



Fig. S4 Adsorption kinetics of phosphate onto (a) Zn-MOF and (b) Zn-MOF-500 fitted by Weber Morris Intra-Particle Diffusion model in different temperature



Fig. S5 Recyclability test of Zn-MOF and Zn-MOF-500 in water at 25 oC



Fig. S6 Nitrogen adsorption-desorption isotherm and pore size distribution of Zn-MOF (a,b) and Zn-MOF-500(c,d)



Fig. S7 TGA of (a) Zn-MOF and (b) Zn-MOF-500



Fig. S8 Comparison of XPS P2p of the (a) **Zn-MOF-P** and (b) **Zn-MOF-500-P**



Fig. S9 SEM images of **Zn-MOF-500** before the adsorption of phosphate under 20000 times



Fig. S10 The EDS energy spectrum of the (a) Zn-MOF, (b) Zn-MOF-500, (c) Zn-MOF-P and (d) Zn-MOF-500-P under three thousand times

Table S5 EDS Energy Spectrum Data Sheet

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Complexes | Element | Line type | Apparent concentration | k ratio | Wt% | Wt% Sigma | Standard sample label | Manufacturer standard |
| Zn-MOF-P | C | K | 5.94 | 0.05944 | 7.24 | 0.76 | C Vit | yes |
| N | K | 47.02 | 0.08371 | 7.04 | 0.82 | BN | yes |
| O | K | 159.22 | 0.53579 | 33.76 | 0.83 | SiO2 | yes |
| P | K | 48.12 | 0.26912 | 9.40 | 0.72 | GaP | yes |
| Zn | L | 82.99 | 0.82995 | 42.55 | 0.95 | Zn | yes |
| Total： |  |  |  | 100.00 |  |  |  |
| Zn-MOF-500-P | C | K | 8.45 | 0.08455 | 10.92 | 0.85 | C Vit | yes |
| N | K | 26.67 | 0.04749 | 4.46 | 0.82 | BN | yes |
| O | K | 83.49 | 0.28095 | 18.79 | 0.64 | SiO2 | yes |
| P | K | 5.23 | 0.02926 | 1.08 | 0.58 | GaP | yes |
| Zn | L | 125.95 | 1.25945 | 64.74 | 1.09 | Zn | yes |
| Total： |  |  |  | 100.00 |  |  |  |

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