Physicochemical Properties And The Potential As A Phosphorus Sustained-Release Fertilizer Of MOF-74(Mg) Adsorbed Inorganic Phosphorous

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***Abstract*— The MOF-74 materials belong to a category of high-entropy metal-organic frameworks (MOFs) that are porous, hollow and composed of divalent metal ions including Mn, Fe, Mg, Co, Ni, Cu and Zn.As a new nanomaterial, MOF-74 has been extensively investigated in the fields of environment, biomedicine and so on. Phosphorus is an indispensable element for the growth and development of plants, yet many agricultural soils in the world exhibit low phosphorus utilization and may suffer from deficiency in this nutrient. In this paper, MOF-74(Mg) adsorbed inorganic phosphorous were synthesized at room temperature and characterized by X-ray diffractometer (XRD) and Fourier infrared spectroscopy (FTIR). Field emission scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were conducted on pea plant leaves sprayed with MOF-74(Mg) adsorbed inorganic phosphorus, the results showed that MOF-74(Mg) adsorbed inorganic phosphorous could be used as phosphorus sustained-release fertilizer for leaves.**

***Index Terms*— MOF-74(Mg); inorganic phosphorous; XRD; FTIR; EDS.**

I. Introduction

Metal-organic framework materials (MOFs) are new type of porous material composed of metal ion clusters and organic ligands. Due to the high porosity, large specific surface area, abundant active sites, acceptability to functional modification and adjustable stability, MOFs have a wide range of application prospects in catalysis, gas sensing, probe, sewage treatment, biomedicine and other fields[1]-[6].

Among them, MOF-74(Mg) material has an open active site in the structure and thus has better adsorption performance. For example, MOF-74(Mg) has the highest CO_2 absorption capacity among all reported MOFs, and can capture over 25% of its own weight of CO_2 from flue gas generated by power plants[7],[8].To date, there have been investigations into the modification of MOF-74 materials: (1) Post-synthetic modification method: that is, to construct determined three-dimensional MOF-74 first, and then introduce functional groups into the framework in an appropriate way, providing a roundabout scheme for the functional construction of MOF-74 [9]. (2) Impregnation method: Lawson et al. impregnated MOF with 30%, 50% and 80% ibuprofen solutions to investigate the effect of different ibuprofen solution concentrations on the drug loading of MOF-74[10].

In this paper, MOF-74(Mg) adsorbed inorganic phosphorus was prepared by impregnation method, and thephysicochemical properties were characterized. The surface morphology of MOF-74(Mg) was observed by scanning electron microscope (SEM), the composition was analyzed by energy dispersive spectrometer (EDS), the diffraction pattern was obtained by X-ray diffraction (XRD) and the surface functional groups were analyzed by Fourier transform infrared spectroscopy (FTIR).

II. EXPERIMENTAL

Material

MOF-74(Mg) was synthesized according to the literature. $Mg(NO_3)_2 \cdot 6H_2O$ (4.6592g) and DHTA (2.3114g) were added into 50mL deionized water, the pH was adjusted to 9.18, and the mixture was stirred at room temperature for 6 hours and centrifuged. The centrifuged precipitates were washed with methanol and dried, which wasMOF-74(Mg)[11]. MOF-74(Mg) was then impregnated in 0.1% potassium dihydrogen phosphate solution, and MOF-74(Mg) adsorbed inorganic phosphorus was obtained after drying.

III. RESULTS AND DISCUSSION

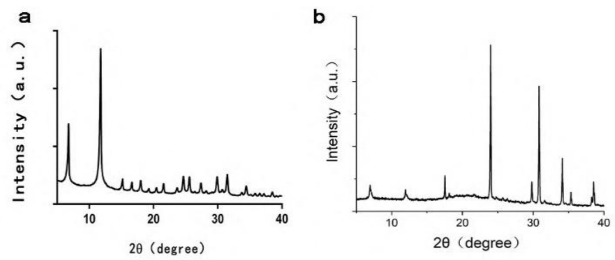

Figure 1. XRD patterns of MOF-74(Mg) (a) and MOF-74(Mg) adsorbed inorganic phosphorus (b).

In the XRD pattern, MOF-74 characteristic peaks with different intensities appeared at 2θ = 6.8° and 2θ = 11.8° (Figure1a), which was consistent with the results in the literature[12]. The characteristic peaks of MOF-74(Mg) adsorbed inorganic phosphorus appeared at 2θ of 6.8° and 11.8° belong to MOF-74(Mg), and the characteristic peaks at 2θ of 17.4°, 23.8°, 35.3° and 38.6°belong to potassium

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dihydrogen phosphate (Figure1 b).

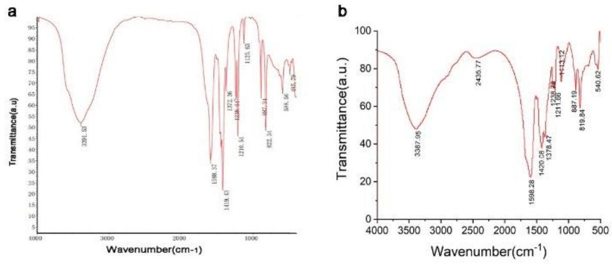
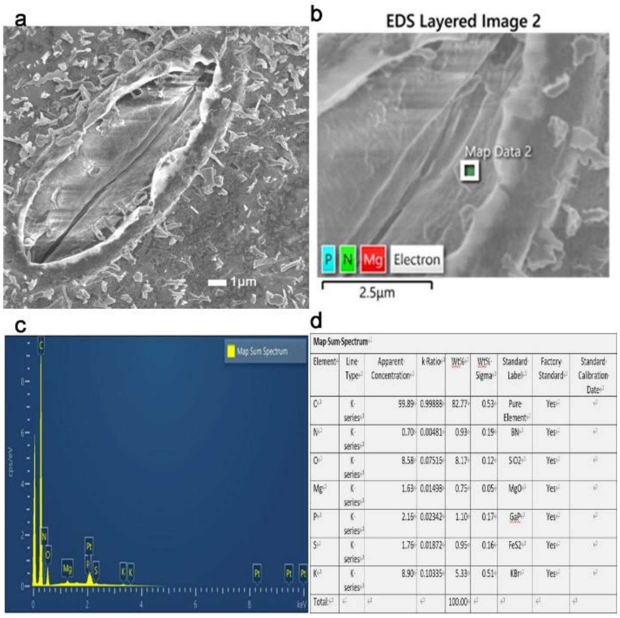


Figure 2. FTIR spectra of MOF-74(Mg) (a) and MOF-74(Mg) adsorbed inorganic phosphorus (b).

Bands near 3391 cm^{-1}(Figure 2a) represent O-H tensile vibrations of the hydroxyl group, which can be attributed to the large amount of water absorbed in the porous material. The absorption peak at 1588 cm^{-1} was attributed to the C=O of the benzene ring in the organic ligand DHTA. The bands at 1419 and 1372 cm^{-1} can be attributed to C=C vibrations of the benzene ring skeleton and also indicate the presence of organic ligands in the resulting structure. The weak absorption peak at 1238 cm^{-1} is due to the stretching vibration of the phenol-based C-O band. The band at 1210 cm^{-1} corresponds to the -C-H stretch. The vibration and absorption peaks at 887 cm^{-1} and 822 cm^{-1}can be attributed to the C-H bending vibration of the benzene ring. In addition, two absorption peaks corresponding to Mg-O vibrations appear at 588 cm^{-1} and 485 cm^{-1}(Figure2a). The stretching peak at 1238 cm^{-1} and the bending peak at 819 cm^{-1} and 887 cm^{-1} were the characteristic peaks of phosphate after immersion of potassium dihydrogen phosphate. The vibration peak at 1113cm^{-1} is the vibration peak of P-O bond, which proves the existence of potassium dihydrogen phosphate (Figure2b).

To evaluate the potential as an inorganic phosphorus sustained-release fertilizer, SEM and EDS analyses were conducted on pea plant leaves sprayed with MOF-74(Mg) adsorbed inorganic phosphorus.



Map Sum Spectrum								
Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Standard Label	Factory Standard	Standard Calibration Date
C	K series	99.89	0.99888	82.77	0.53	Pure Element	Yes	
N	K series	0.70	0.00481	0.93	0.19	BN	Yes	
O	K series	8.58	0.07515	8.17	0.12	SiO2	Yes	
Mg	K series	1.63	0.01498	0.75	0.05	MgO	Yes	
P	K series	2.16	0.02342	1.10	0.17	GaP	Yes	
S	K series	1.76	0.01872	0.95	0.16	FeS2	Yes	
K	K series	8.90	0.10335	5.33	0.51	KBr	Yes	
Total:				100.00				

Figure 3. SEM image (a) and EDS image (b) of MOF-74(Mg) adsorbed inorganic phosphorus; (c) Mapping nuclear spectrum; (d) Mapping nuclear spectroscopy table.

Fig. 3a shows SEM image of pea plant leaves sprayed with MOF-74(Mg)adsorbed inorganic phosphorus. According to Fig. 3a, the pore size of the leaves reaches the micron level, and MOF-74(Mg) can enter the leaves through the physical pore channels. The nuclear spectrum drawing and the nuclear spectrum table are belonging to the map in Fig. 3b, the proportion of C, O, Mg, P and K is 82.77%, 8.17%, 0.75%, 1.10% and 5.33%, respectively (Figure 3c and d).The results show that inorganic phosphorus is sprayed on the leaves with MOF-74(Mg), which also confirmed the potential of MOF-74(Mg) adsorbed inorganic phosphorus as a phosphorus slow-release fertilizer.

IV. CONCLUSION

MOF-74(Mg) adsorbed inorganic phosphorus was successfully preparedby impregnation method. The size of the prepared MOF-74(Mg) particles wassignificantly smaller than the pore diameter of pea leaves. XRD and FTIR were used to obtain the diffraction patterns and the groups and structures of MOF-74(Mg) adsorbed inorganic phosphorus. The composition and proportion of elements were determined by SEM and EDS. The above results proved that inorganic phosphorus was successfully adsorbed on MOF-74(Mg) material, which proved that MOF-74(Mg) adsorbed inorganic phosphorus had the potential as a phosphorus sustained-release fertilizer.

REFERENCES

[1] Liu C, Wang J, Wan JJ,et al. MOF-on-MOF hybrids: synthesis and applications[J]. Coordination Chemistry Reviews, 2021, 432: 213743.

[2] Chen L. Z, Gong Q B, Chen Z. Preparation and application of ultra-thin two dimensional MOF nanomaterials[J]. Progress in Chemistry, 2021, 33: 1280-1292.

[3] Zhang R, Lu L H, Chang Y Y, et al. Gas sensing based on metal-organic frameworks: concepts, functions, and developments[J]. J Hazard Mater, 2022, 429: 128321.

[4] Han W. G, Huang X S, Lu G X, et al. Research progresses in the preparation of Co-based catalyst derived from Co-MOFs and application in the catalytic oxidation reaction[J]. Catal SurvAsia, 2019, 23: 64-89.

[5] Lu Y N, Young D. Coordination polymers for n-type thermoelectric applications[J]. Dalton Trans, 2020, 49: 7644-7657.

[6] Jahan I, Islam M A, Rupam T H, et al. Enhanced water sorption onto bimetallic MOF-801 for energy conversion applications[J]. Sustainable Materials and Technologies, 2022, 32: 00442.

[7] Howe J D, Morelock C R, JiaoY, et al. Understanding structure, metal distribution, and water adsorption in mixed-metal MOF-74[J]. Journal of Physical Chemistry C, 2017, 121: 627-635.

[8] Wang MT, Wang D K, Li Z H. Self-assembly of CPO-27-Mg/TiO2 nanocomposite with enhanced performance for photocatalytic CO_2 reduction[J]. Applied Catalysis B-Environmental, 2016, 183: 47-52.

[9] Ge Y M, Wang K, Li H L, et al. An Mg-MOFs based multifunctional medicine for the treatment of osteoporotic pain[J]. Materials Science & Engineering C-Materials for Biological Applications, 2021, 129: 112386.

[10] Lawson S, Newport K, Schueddig K, et al. Optimizing ibuprofen concentration for rapid pharmacokinetics on biocompatible zinc-based MOF-74 and UTSA-74[J]. Materials Science and Engineering C-Materials for Biological Applications, 2020, 117: 111336.

[11] Garzon-Tovar L, Carne-Sanchez A, Carbonell C, et al. Optimised room temperature, water-based synthesis of CPO-27-M metal-organic frameworks with high space-time yields[J]. J Mater Chem A, 2015, 3 (41): 20819-20826.

[12] Haque E, Jhung SH. Synthesis of isostructural metal-organic frameworks, CPO-27s, with ultrasound, microwave, and conventional

heating: Effect of synthesis methods and metal ions[J]. Chemical Engineering Journal, 2011, 173 (3): 866-872.

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Phytotoxicity of metal-organic frameworks MOF-74(Mg) and MOF-74(Co) to pea seedlings: Importance of metal species (under review)

(1) Phytotoxicity of VO2 nanoparticles with different sizes to pea seedlings. Ecotoxicology and Environmental Safety, 2022. 242, 113885. Qun Li, **Ruonan Hu**, Zhang Chen , Lingyun Chen, Jiahao Zhang, Xian Wu, Jia-Bei Li, Yanfeng Gao, Sheng-Tao Yang*, Haifang Wang*。(SCI，IF=7.129)

(2) Magnetic Fe_3O_4/TiO_2/graphene sponge for the adsorption of methylene blue in aqueous solution. DIAMOND AND RELATED MATERIALS, 2022.123.108811. Tusunniyaze Maimaiti , **Ruonan Hu,** Huahui Yuan, Chengzhuang Liang, Fangshi Liu, Qun Li, Suke Lan, Baowei Yu, Sheng-Tao Yang*(SCI）

(3) Toxicity and activity inhibition of metal-organic framework MOF-199 to nitrogen-fixing bacterium Azotobacter vinelandii . Science of The Total Environment, 813: 151912. Bowei Ouyang, Fangshi Liu, Chengzhuang Liang, Jianhao Zhang, **Ruonan Hu**, Huahui Yuan, & Shengtao Yang (2022). (SCI，IF=10.753)

Photo: