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Effects of Metal-Organic Frameworks MOF-74(Mg) on Pea Seedlings

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***Abstract*—Metal-organic framework (MOF) materials have unique structure and fantastic properties for wide applications. Pilot studies highlight the toxicity and potential threats of MOF materials to the environment. In this study, we aimed reveal the influence of metal species on the toxicity of MOF materials. MOF-74(Mg) was synthesized using nontoxic Mg as the metal center, and the phytotoxicity of MOF-74(Mg) to pea (*Pisum sativum L.*) was directly measured. MOF-74(Mg) had limited influences on the germination and growth of pea, while stimulating effect on the photosynthesis was observed at 1 mg/L and higher. MOF-74(Mg) increased the Mg contents of leaves, where Mg is an essential element for chlorophyll synthesis. Our results indicated that the environmental toxicity of MOF materials with nontoxic metal center was mostly safe to environment.**

***Index Terms*—Metal-organic framework; Metal element, Toxicity; Photosynthesis; Environmental effects**

INTRODUCTION

Metal-organic framework (MOF) materials are emerging materials with porous structures and unique properties [1]. MOF materials are composed of metal ion clusters and organic ligands to generate abundant diversities for various applications. Due to their porous structure, large surface area, abundant active sites, receptivity to functional modifications, and good stability, MOF materials have been applied in gas adsorption and separation [2], gas sensing [3], catalysis [4], water treatment [5], bioimaging [6], drug delivery [7], thermoelectric materials [8] and so on. Of particular interest, MOF materials could be used for delivery of pesticides and fertilizers in plant growth. For example, azoxystrobin loaded Fe-MIL-100 showed good fungicidal activities and provided iron micronutrient to enhance the wheat growth [9]. Fe-MOFs significantly increased the rice yield, dry mass gain, nitrogen accumulation and use efficiency. Boscalid@ZIF-67 released Boscalid at acidic pH to control citrus disease of Botrytis cinerea [10]. Wu et al. achieved the pilot scale production of Fe-MOFs with a chemical formula of $C_2H_{15}Fe_2N_2O_{18}P_3$ [11]. With their increasing applications in environment and agriculture, the release of MOF materials into environment becomes inevitable.

MOF-74 is an intensively studied MOF for gas adsorption [12], catalysis [13], battery and capacitor [14], sensing [15], and pollutant removal [16].

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Isomorphic MOF-74 materials consisting of different metal ions and the same ligand provide an ideal model to investigate the influence of metal species on the phytotoxicity of MOF materials. Herein, we synthesized MOF-74 material with nontoxic Mg as metal center, and directly compared the toxicity to pea (*Pisum sativum L.*). The influence of MOF-74(Mg) on the germination of pea seeds was measured. The toxicity of MOF-74(Mg) to pea seedlings was monitored by root development, seedling weights, and structural observations. The impact of MOF-74(Mg) on the photosynthesis was indicated by the chlorophyll content, photosynthetic rate, and chlorophyll fluorescence parameters. The metal content changes and oxidative stress were also recorded. The implications to the applications and the design of safe MOF materials are discussed.

EXPERIMENTAL

Materials preparation

MOF-74(Mg) was synthesized following the literature protocols. Briefly, $H_{12}MgN_2O_{12}$ (4.66 g) and 2,5-dihydroxyterephthalic acid (DHTA, 2.31 g) were added into 50 mL water, the pH was adjusted to 9.18 and the solution was stirred at room temperature for 6 h. After washing with methanol, the yellow solid powder was obtained by drying as MOF-74(Mg). MOF-74(Mg) was characterized by X-ray photoelectron spectroscopy (XPS, ESCALAB 250XI, Thermo-Fisher, USA), scanning electron microscopy (SEM, JSM-7500, JEOL, Japan), infrared spectroscopy (IR, Cary-600, Agilent, China) and X-ray diffraction (XRD, XD-6, Purkinje General Instrument Co. China).

Seed germination

Seeds of *Pisum sativum L.* were bought from Beijing Baihe Technology Co., LTD. The modified Hoagland nutrient solution was adopted for seed germination and seedling cultivation. The modified Hoagland nutrient solution was supplemented with/without MOF-74(Mg) (0-1000 mg/L) for exposure/negative control. Pea seeds were soaked in 15% NaCl aqueous solution for sterilization, followed by rinsing in water. To estimate the impact of MOF-74(Mg) on germination, each 20 pea seeds were placed on a piece of filter paper (diameter of 11 cm) in a petri dish. The modified Hoagland nutrient solution (with/without MOF-74(Mg)) was added to moisten the filter paper. The petri dishes were placed in an incubator at 25 ℃ and relative humidity of 80% for 7 d. The seeds were checked every day for germination rate calculation. The influence of starting materials ($H_{12}MgN_2O_{12}$, $C_4H_{14}CoO_8$, DHTA) on seed germination was evaluated in the same manner.

Seeding growth

Seeds were germinated for 4 d with the modified Hoagland nutrient solution. The seedlings were collected, cultured in 100 mL beakers and exposed to MOF-74(Mg) by adding MOF-74(Mg) supplemented nutrient solution (5 seedlings/each, three parallel samples per concentration). During the incubation, the beakers were supplemented daily with nutrient solution to keep the liquid volume of 100 mL. Seedling culture was carried out under the following conditions: diurnal cycle for 12 h, sunshine intensity 2400 lx, diurnal humidity 80%/70%, diurnal temperature 25 ℃/24 ℃.

At 15 d, the root development of seedlings was recorded on a multifunctional root analyzer (LA-S, Hangzhou Wanshen Detection Technology Co., LTD., China) to obtain root length, stem length and leaf area. The roots and aboveground parts were collected, cleaned, and weighed to obtain fresh weights. The samples were further dried at 60 ℃ for 12 h and measured again to obtain dry weights. The influence of starting materials ($H_{12}MgN_2O_{12}$, DHTA) on seedling growth was evaluated in the same manner.

In order to observe the morphological changes, the small pieces of fresh roots were fixed with 2.5% glutaraldehyde solution. Negative staining was adopted for TEM analysis following our previous report. Separately, fresh root samples were fixed with formaldehyde-acetic acid-ethyl alcohol solution for paraffin sections. The slides were stained with saffrine and solid green for optical microscope observations (CAB-30PC, Chengdu, China).

Photosynthesis

The chlorophyll contents of pea leaves were assayed by a chlorophyll analyzer (SPAD-502 plus, Konica Minolta Co., Osaka, Japan) at 15 d. A portable photosynthesis system (Yaxin-1102, YaXin Liyi Technology Co., Beijing, China) was used to monitor the net photosynthetic rate, stomatal conductance, transpiration rate, and intercellular CO_2 concentration. Various chlorophyll fluorescence parameters were measured by a portable fluorometer (OPTI, Boston, MA, USA).

Bioaccumulation and oxidative stress

In order to determine the bioaccumulations of Mg^{2+} in pea seedlings, the roots, stems and leaves of peas were collected respectively. The samples were freeze-dried, ground and accurately weighed. Then, 5.0 mg of each was added with the mixture of HNO_3 and $HClO_4$ (volume ratio of 5:1) for digestion on a heating plate until the volume of digestion liquid decreased to approximate 2 mL. The digestion solution was cooled and diluted with 2% HNO_3 for the inductively coupled plasma-mass spectrometry (ICP-MS) measurements (iCAP-Qc, Thermo-Fisher Scientific, USA).

For oxidative stress measurements, root and leave samples were collected and homogenized. Five commercial kits, including catalase (CAT), total protein, malondialdehyde (MDA), glutathione (GSH), and H_2O_2, were obtained from Jiancheng Bioengineering Institute, Nanjing, China. The measurements were performed following the recommended protocols from the manufacturer (http://www.njjcbio.com/).

RESULTS AND DISCUSSION

Toxicity of MOF-74(Mg) to pea seedlings

In our experiments, a wide concentration range of 0.1-1000 mg/L was tested, because there were no data on the phytotoxicity of MOF-74(Mg) available in the literature. The wide concentration range could provide the toxicity thresholds to cover non-toxic to highly toxic doses. First, the germination of pea beans was monitored upon the exposure to MOF-74(Mg). There was no significant inhibition of germination rate in the presence of MOF-74(Mg) even at 1000 mg/L. Previously, we found that MOF-199 increased the germination potentials. The promoted seed germination of sorghum and switchgrass by graphene and carbon nanotubes (CNTs). The mixture of starting materials without forming particulates did not stimulate the germination (data not shown). The micro-sizes of MOF-74(Mg) was not suitable for seed coat penetration.

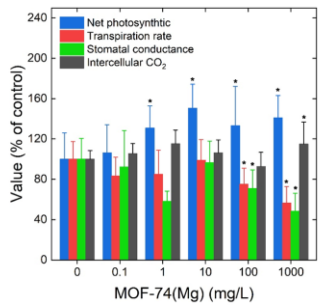

Figure 1 Influences of MOF-74(Mg) on the photosynthesis of leaves (n=3). * $p < 0.05$ compared with the control group.

When seedling roots were serious damaged, the photosynthesis might be disturbed through direct or indirect effect. MOF-74(Mg) did not alter the chlorophyll contents of leaves. There were meaningful increases of net photosynthetic rates in MOF-74(Mg) groups at 1-1000 mg/L (Fig. 1). In particular, the net photosynthetic rate increased to 150±23% of the control, while the other parameters kept normal. Consistent with the disruption of xylem vessels at high concentration, MOF-74(Mg) led to the decreases of transpiration rate and stomatal conductance at 100 and 1000 mg/L. The intracellular CO_2 increased at 1000 mg/L, which might be due to the lack of stomatal conductance to breathe out CO_2. MOF-199 stimulated the photosynthesis at 10 and 100 mg/L, but the net photosynthetic rate decreased to normal level at 1000 mg/L. MOF-199 lowered the leaf areas rather than decreasing the net photosynthetic rate to affect the total photosynthesis. MOF materials decreased the chlorophyll contents of green algae C. reinhardtii at 4 h and the chlorophyll contents recovered at 24 h. ZIF-8 showed inhibition to chlorophyll content of C. vulgaris, but ZIF-67 did not. ZIF-8 had more influence on photosynthesis gene than ZIF-67. These results suggested that MOF materials affected photosynthesis depending on the type of MOF materials.

Chlorophyll fluorescence is a powerful method for studying photosynthetic pathways. The O-J-I-P chlorophyll fluorescence transients were recorded in a typical four-step

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process. In the Fv/Fm mode, Fm and F0 are the initial recorded data points. Fv/Fm represents the maximum mass photon yield of primary photochemistry, and Fv/F0 is another way of expressing Fv/Fm, which makes it easier to distinguish between different data sets. The variation trends of Fv/Fm and Fv/F0 roughly reflected the stress degree of plants. MOF-74(Mg) had no significantly stress effect on the potential activity of chlorophyll PS II in pea leaves, because no changes in Fv/F0 and Fv/Fm (Fig. 2a). There was no significant change in PI value in the exposure group of MOF-74(Mg) at all concentrations, indicating that MOF-74(Mg) had no negative effect on the activity of chlorophyll PS II system in leaves (Fig. 2b). Although the M0 of MOF-74(Mg) did not change significantly, the M0 of MOF-74(Mg) at high concentrations showed a downward trend, indicating that the electron transport efficiency of PS II was accelerated (Fig. 2b). At 100 mg/L, RC/CSm was slightly stimulated by MOF-74(Mg), indicating that MOF-74(Mg) had a slight promoting effect on RC/CSm of chlorophyll PS II in leaves at 100 mg/L concentration (Fig. 2b).

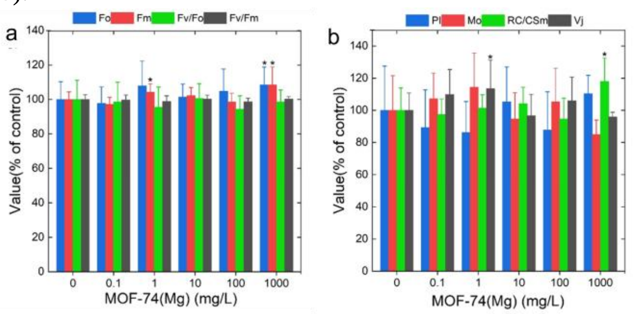

Figure 2 Chlorophyll fluorescence of leaves after the exposure to MOF-74(Mg) (n=3). (a) Chlorophyll fluorescence parameters of Fv/Fm mode for MOF-74(Mg); (b) Chlorophyll fluorescence parameters of OJIP mode for MOF-74(Mg). * *p* <0.05 compared with the control group.

Toxicological mechanisms of MOF-74(Mg) to pea seedlings

Although we did not observe the accumulations of MOF-74(Mg) particulates in pea roots, there might be changes of Mg contents in pea seedlings due to the release of metal ions from MOF-74(Mg). Thus, we measured the Mg contents of MOF-74(Mg) exposed seedlings (Fig. 3). The changes of Mg contents were moderate, because it is an essential macroelements for plants and there was abundant Mg^{2+} in the modified Hoagland nutrient solution. Even at the highest concentration of 1000 mg/L, the root Mg content increased from 3386±234 μg/g (control) to 5583±50 μg/g, equaling to an increase of 65%. The stem Mg content increased 38% and the leaf Mg content increased 97%. Thus, when MOF materials enter the environment, the first issue should be considered is the metal bioaccumulations.

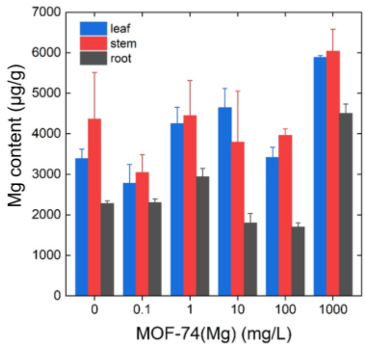

Figure 3 Metal uptakes by pea seedlings after the exposure to MOF-74 (n=3). (a) Mg contents after exposure to MOF-74(Mg); (b) Co contents after exposure to MOF-74(Co). * *p* <0.05 compared with the control group.

Oxidative stress is a well-recognized mechanism for the negative effects of exogenous organisms. The changes of metal contents would very likely induce oxidative stress to organisms. Especially, those metal elements with variable valent are good candidates of redox reaction. Oxidative stress is also a widely observed toxicological mechanism for xenobiotics. Slight oxidative stress was induced by MOF-74(Mg) at low concentrations as indicated by the increase of CAT level and changes of MDA level (Fig. 4a). The oxidative stress became serious at 1000 mg/L, because the H_2O_2 largely increased to 223±7% of the control. The oxidative stress seemed more serious in root (Fig. 4b), where CAT level increased to 197±5% of the control at 10 mg/L. At 1000 mg/L of MOF-74(Mg), the CAT level was 156±23% of the control, the H_2O_2 level was 137±20% of the control, the MDA level was 65±28% of the control, and the level of GSH was 114±17% of the control. Our results of oxidative stress were well consistent with the toxicological evaluations of MOF materials.

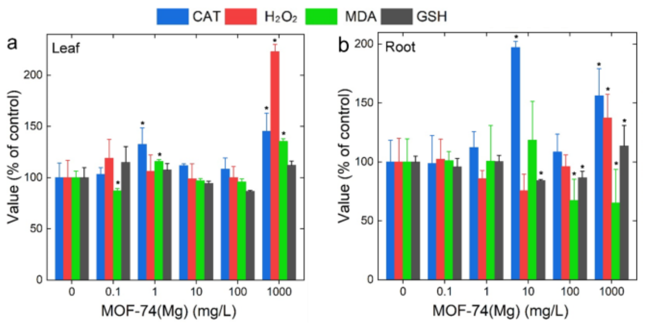

Figure 4 Oxidative stress of leaves (a) and roots (b) after the exposure to MOF-74(Mg) (n=3). * *p* <0.05 compared with the control group.

CONCLUSION

In summary, two MOF-74 materials were synthesized with Mg as the metal centers to reveal the importance of metal species on the environmental toxicity of MOF materials. MOF-74(Mg) was composed by nontoxic metal Mg and showed stimulating effects on the net photosynthesis rates of leaves. MOF-74(Mg) had no significant inhibition on the growth and photosynthesis of pea seedlings. The exposure to MOF-74(Mg) did not lead to significant uptakes of Mg in pea leaves, which aroused oxidative damage there and affected the acceptor side of photosynthesis system II. Our results suggested that metal element should be fully considered when designing MOF materials to avoid environmental risks. Nontoxic metals are preferred to achieve similar framework structure with higher safety. It is hoped that our study would benefit the environmental safety evaluations and safe applications of MOF materials.

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