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Study on the Environmental Biological Effects of Metal Organic Framework Material MOF-74(Mg) on Pea Plants

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***Abstract*—Metal organic framework (MOF) materials are a novel porous material composed of metal ion clusters and organic ligands. Preliminary studies have shown the toxicity and potential threat of MOF materials to the environment. However, there are few reports on the plant toxicity of MOF materials, making it difficult to evaluate the harm of MOF materials to plants after entering the environment, and it is also not conducive to the development of environmental agricultural technologies related to MOF materials. This study synthesized MOF-74 material, namely MOF-74(Mg), using Mg as the metal center. This paper investigates the effect of MOF-74(Mg) on the toxicity of pea (*Pisum sativum L.*) by measuring the effects of MOF material exposure on pea biomass content and oxidative stress. The effect of MOF-74(Mg) on pea growth is limited. MOF-74(Mg) comes into direct contact with the root system during the cultivation process. The biological effect of MOF-74(Mg) on pea seedlings is dose-dependent, but MOF-74(Mg) has no significant effect on leaf quantity.**

***Index Terms*—Metal organic framework; MOF-74(Mg);Peas; Toxicity.**

INTRODUCTION

MOF materials, also known as coordination polymers, are a type of emerging porous crystalline material composed of metal ion clusters and organic compounds [1,2]. Their properties depend on the composition of the material and the structure of the material itself [3-5]. Metal organic framework MOF, as a new type of nanomaterial, is a deeply studied MOF widely used in the fields of environment, biomedicine, and other fields [6,7]. One of the most promising materials is MOF-74(Mg), also known as Mg-2(DOBDC), which is a porous crystalline material. MOF-74(Mg) is a rice shaped crystal composed of 2,5-dihydroxyterephthalic acid and coordination metal Mg^{2+}, with a unit molecular formula of $C_8H_4O_8Mg_2$ [8-10].

With the increasing application of MOF materials, toxicity research on MOF materials is also developing. MOF materials pose potential threats to plant growth and photosynthesis, and the type of MOF determines its plant toxicity [11]. The same MOF structure can be altered by altering the metal composition, which may result in different environmental impacts [12]. However, the impact of metal types on the toxicity of MOF materials has not been clearly revealed. Determining the toxicity and hazards of MOF materials is crucial for evaluating their environmental safety. Some preliminary studies investigated the toxicity of MOF-74 materials to algae, cells, and animals. For example, Fan et al. synthesized MOF-74(Cu) using hydrothermal method and studied its inhibitory effect on the growth of Pseudomonas aeruginosa. Research has found that when the concentration of MOF-74(Cu) exceeds 24 mg/L, the inhibition rate of Pseudomonas aeruginosa after 74 hours of exposure is 1%. However, the addition of MOF-74(Cu) with a concentration below 74.0 mg/L promoted the growth of algae. The inhibition of algal growth by MOF-74(Cu) is mainly attributed to the presence of hydroxyl radicals and intracellular reactive oxygen species, and the released Cu^{2+} and cell aggregation are to some extent involved [13].

The isomorphic MOF-74 material composed of different metal ions and the same ligand provides an ideal model for studying the effect of metal species on the plant toxicity of MOF materials. Plants are an important component of the ecological environment, and their photosynthesis is the material and energy foundation of the biosphere. Therefore, this article studied the plant toxicity of MOF-74(Mg) using pea plants as a model. The toxicity of MOF-74(Mg) on pea seedlings was monitored by monitoring root development, seedling quality, seedling elongation, weight gain, and oxidative stress.

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EXPERIMENTAL

Synthesis of materials

The synthesis of MOF-74(Mg) was carried out based on literature synthesis methods [14]. MOF-74(Mg) synthesis: accurately weigh 4.6592 g of Mg $(NO_3)_2·6H_2O$ and 2.3114 g of 2,5-dihydroxyterephthalic acid (DHTA) and add them to 50 mL of water. Adjust the pH of the mixture to 9.18 by adding sodium hydroxide particles and stirring at room temperature for 6 hours. After stopping the reaction, separate the mixture by centrifugation at 10000 rpm for 10 minutes. Wash with methanol to clear the supernatant. Finally, dry the obtained solid in an oven at 80 ℃ for 12 hours to obtain yellow solid powder.

Pea seedling cultivation

Using improved Hoagland nutrient solution for seed germination and seedling cultivation. Place filter paper (select a medium speed filter paper with a diameter of 11 cm) in each culture dish, add a mixed solution of MOF-74 material and Hoagland nutrient solution with a concentration gradient of 0-1000 mg/L. Add 5 mL of culture mixture to each culture dish to moisten the filter paper. After the filter paper is completely soaked, pour out the excess culture mixture solution. A total of 6 concentrations were set, with 3 parallel samples for each concentration. Place 20 selected seeds in each culture dish, place the dish in the incubator, set the day/night temperature to 25 ℃/24 ℃, the day/night relative humidity to 70%/80%, and the day/night light intensity to 2400 Lx/0 Lx for 7 days of cultivation.

Plant growth evaluation and toxicity testing methods

Analyze seedlings on a multifunctional root system analyzer to obtain data on root and stem length as well as leaf area. Cut the plant into roots and stems, clean the sample and weigh it after removing surface moisture to obtain the fresh weight of the plant; Dry the plants in a 60 ℃ oven for 12 hours and weigh them again to obtain their dry weight. Total protein, glutathione (GSH), malondialdehyde (MDA), catalase (CAT), and H_2O_2 were tested using standard test kits, strictly following the manufacturer's recommended protocol for measuring oxidative stress.

RESULTS AND DISCUSSION

Characterization of MOF-74(Mg)

The SEM image shows that MOF-74(Mg) is a grain like crystal (Figure 1) (The length is 1.1 ± 0.2 μm; The width is 0.7 ± 0.1 μm). They are aggregates of small particles rather than tightly packed crystals, similar to the results of literature [14].

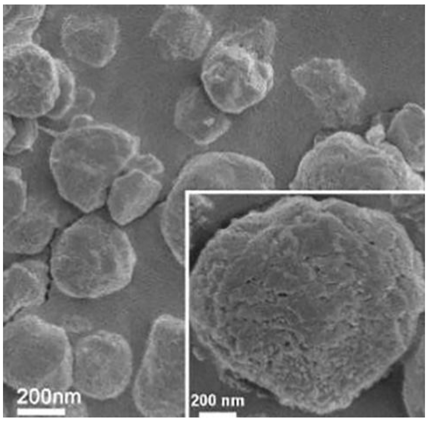

Figure 1SEM image of MOF-74(Mg).

Toxic effects of MOF-74(Mg) on the growth of pea seedlings

MOF-74(Mg) is in direct contact with the root system during cultivation. Analysis of root growth showed that the biological effects of MOF-74(Mg) on pea seedlings were dose-dependent (Figure 2b). MOF-74(Mg) at 10 mg/L significantly stimulated root length (123 ± 19% in the control group), and further increases in concentration resulted in a decrease in root length. The number of roots of MOF-74(Mg) increased significantly at 100 mg/L and 1000 mg/L (Figure 2a). Thus, the overall fresh weight of the roots did not change after exposure to MOF-74(Mg) (Figure 2b). MOF-74(Mg) had no significant effect on the number of leaves. At a concentration of MOF-74(Mg) of 1000 mg/L, the above-ground length decreased only (72 ± 10% of the control group). The influence of seedling length was mainly reflected in the change of dry weight, and MOF-74(Mg) did not affect the fresh weight and dry weight of pea seedlings (Figure 2b). The effect of MOF-74(Mg) on the growth of root seedlings was more obvious than that of above-ground seedlings, which may be due to the direct contact of MOF-74(Mg) with the root of seedlings.

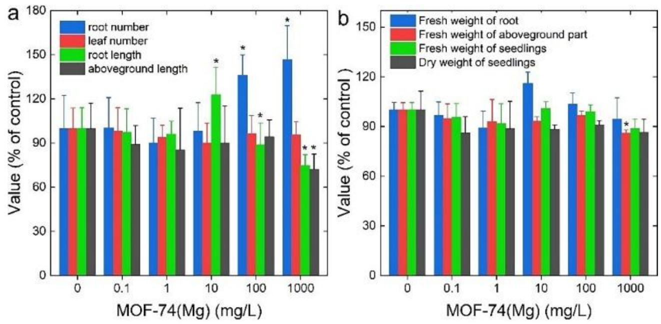

Figure 2 Effect of MOF-74(Mg) on the biomass content of peas. (a) MOF-74(Mg) number of planted pea roots, number of leaves, root length, length of above-ground part; (b) Biomass content of MOF-74(Mg) planted peas.

Toxicological mechanism of MOF-74(Mg) on pea seedlings

Reactive oxygen species (ROS), initially thought to be the only disruptive agent in living organisms, were later found to also play a positive role [15]. The imbalance between the production and elimination of ROS has certain consequences for cellular physiology, known as "oxidative stress". Oxidative stress is a widely recognized mechanism through which foreign organisms produce negative effects [16]. Oxidative stress is also a widely observed heterologous biological mechanisms [16]. Low concentrations of MOF-74(Mg) caused mild oxidative stress, and CAT levels increased and MDA levels changed at 1 mg/L (Figure 3a). H_2O_2 concentration increased significantly at 1000 mg/L, reaching 173 ± 7% of the control, and oxidative stress was aggravated. Oxidative stress in the roots appeared to be more severe (Figure 3b), with CAT levels increasing to 189 ± 5% of the control at 10 mg/L. When MOF-74(Mg) concentration was 1000 mg/L, CAT was 137 ± 23% of the control group, H_2O_2 was 132 ± 20% of the control group, MDA was 90 ± 28% of the control group, GSH was 104 ± 17% of the control group. Our oxidative stress results are very consistent with toxicological evaluations of MOF materials [17].

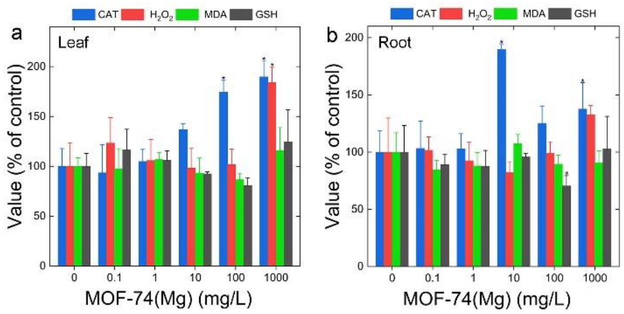

Figure 3 Toxicological mechanism of MOF-74(Mg) on pea seedlings (n = 5). (a) Oxidative stress in MOF-74(Mg) leaves; (b) Oxidative stress of MOF-74(Mg) roots.

CONCLUSION

In this chapter, MOF-74 materials were synthesized with Mg as the metal center, and the key effects of metal types on environmental toxicity of MOF materials were revealed. The central metal ion of MOF-74(Mg) is non-toxic metal Mg, and MOF-74(Mg) has limited effect on pea growth. MOF-74 is directly in contact with roots during cultivation. The biological effect of MOF-74 on pea seedlings is dose-dependent, but MOF-74(Mg) has no significant effect on the number of leaves. Therefore, when designing MOF materials, the environmental risks that may be brought by metal elements should be fully considered, and non-toxic metals can be preferred to achieve a similar frame structure with higher safety. This study has certain guiding significance for the environmental safety evaluation and safety application of MOF materials.

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