Regulation of Ethylene Content with Metal-Organic Frameworks and Their Effect on Plant Growth

Elin Kang[1*] and Dong Kyu Park[2]

[1]*Taejeon Christian International School, 77 Yongsan 2-ro, Yuseong-gu, Daejeon 34035, Korea*
[2] *Korea Advanced Institute of Science and Technology, 291 Daehak-ro, Yuseong-gu, Daejeon 34141, Korea*
*Email: kange2019@tciscommunity.com

Abstract – Ethylene gas, Ethylene gas, a plant aging hormone, can be produced by stressed plants and can affect nearby plants. Herein the impact of the metal-organic frameworks (MOFs) on the growth of plants has been explored by measuring the chlorophyll a and b content, and stem and root lengths of plants grown in the presence of MOFs filters. The observation of the growth of the cabbage by Ethylene gas resulted in shorter stems and roots. Also, the lengths of stem and root, and the chlorophyll content of the cabbage plants were decreased in stressed cabbages. Meanwhile, the growth of the cabbage could be improved by absorbing Ethylene gas using filter papers made by pasting MOFs on PVA. These support that MOFs can capture effectively Ethylene gas, thus helping to regulate Ethylene content to ease plant growth in stressful conditions.

keywords – *MOFs Having Nanocages and Functional Organic Units, Regulation of Ethylene Content, Plant growth*

I. INTRODUCTION

Ethylene gas can be generated when fruits ripen, so that fruits such as bananas, pears, and peaches very sensitive to Ethylene gas ripe too much when placed with fruits such as apples and apricots that ripen quickly and produce a lot of Ethylene gas. Ethylene gas is also produced in stressful situations like droughts, flooding, or bacterial infections, causing plants to mature too quickly or wither. A recent report uncovered that a protein called EIN2 triggers Ethylene.[1] Thus, one must discover a novel material capable of controlling the content of Ethylene gas so that the Ethylene level is optimal for plants to grow and flourish.

Crystalline metal-organic frameworks (MOFs) have high porosity compared to other porous solids like zeolites, silicas, and carbons, which make them viable storages for gas molecules.[2-4] Also, MOFs could become potential candidates due to their having suitable nanocages or functionalized organic ligands to bond with Ethylene gas. Especially, Zr-based MOFs of MOF-867 consist of the joint $Zr_6O_4(OH)_4$ with 6 BPYDC (2,20-bipyridine-5,50-dicarboxylate) struts and UiO-67 consisting of the joint $Zr_6O_4(OH)_4$ with 6 BPDC (4,40-biphenyldicarboxylate) struts can absorb a large amounts of gas molecules compared to other MOFs. Meanwhile, the absorbance of MOF-867 and UiO-67 for a specific molecule could differ because MOF-867 have additional nitrogen atoms in its linkers that UiO-67 is void of, while they have the same nanocage size. Moreover, they are stable in the air unlike other types of MOFs, which allow to be mixed with the polymers such as PVA (polyvinyl alcohol) and applied to be designed as filter papers.

Here, we have designed three types of experiments. The first set of experiments (Fig. 1a) is to synthesize and characterize MOF-867 and UiO-67. Secondly, we discover the ability of MOF-867 and UiO-67 to absorb Ethylene, as shown in Fig. 1b. It is notable that Ethylene could be produced by stressed plants. Lastly, the effect of Ethylene, which has been used as an absorption filter (Fig. 1c), on plant growth has been explored. Also, we determine which type of MOF is more effective as the Ethylene filter.

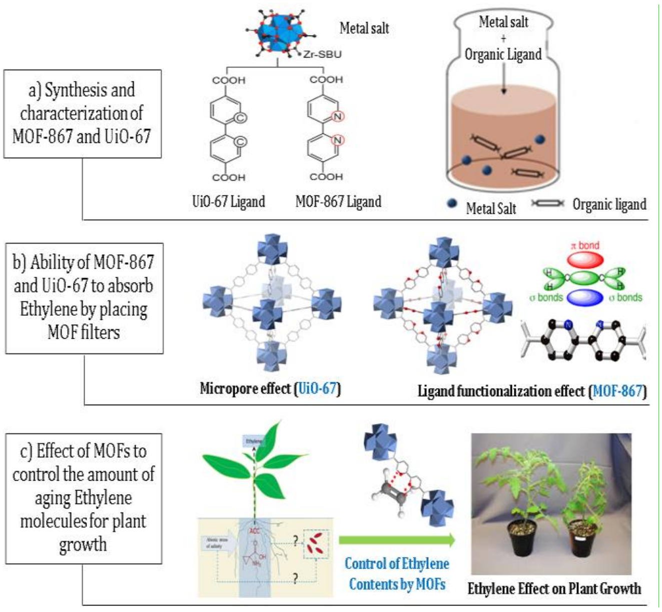

Figure 1. Schematics for sets of experiments to investigate a) the synthesis and characterization of MOFs, b) the ability of MOFs to absorb Ethylene, and c) the effect of MOFs to control the amount of aging Ethylene molecules for plant growth.

II. EXPERIMENTAL SECTION

2.1. Synthesis of MOF-867 and UiO-67

We have synthesized two different types of MOF-867 and UiO-67 with the same joint $Zr_6O_4(OH)_4$, but different functional ligands.[5] For MOF-867, zirconium chloride and acetic acid were dissolved in dimethylformamide (DMF). Simultaneously, BPYDC and triethylamine were dissolved in DMF. The solutions containing metal ions and organic linkers were combined in glass vials, which were tightly sealed and placed into an oven for 12 hrs. The white product was washed three times with DMF using a centrifuge and sonication. After the washing process, MOF-867 was immersed in methanol for 3 days, with refreshing of the methanol. Finally, MOF-867 was activated by removing the solvent in a vacuum oven. For UiO-67, all of the procedures were the same as those used for MOF-867 except that the organic linkers were exchanged with BPCD, and the reaction time was 6 hrs.

2.2. Fabrication of MOF filters absorbing Ethylene gas

5mL of PVA and 100mL of distilled water were used to create a 5% PVA paste that could be spread over plastic containers. Then, 5mL of PVA was mixed with 0.05g MOF to create a PVA+MOF paste that was also spread over plastic containers. After 20 minutes, packets of the coal containing Ethylene were placed inside the containers and any gaps were sealed to prevent Ethylene from escaping into the air.

After 4 days of Ethylene exposure, each container was placed over 25 cabbage seeds planted in 0.7% Agar. A container without any mixtures applied to the surface was set up as a control without exposure to Ethylene. However, the differences in amount of light could affect plant growth since MOF in the paste could limit the amount of light, so containers painted with PVA and MOF+PVA pastes were sealed over cabbage seeds with 1g of Ethylene gas on the side of the container. A container without any mixtures applied to the surface was set up over cabbage seeds as a control without exposure to Ethylene to track plant growth in no-stress conditions. The three variables were placed in a cabinet to prevent light exposure to plants.

Moreover, 10 leaves were clipped off from each set of plants and placed in a vial with 1mL of alcohol for 1 hour. A spectrometer was used to measure the chlorophyll content at 663nm and absorbance at 645nm. The pre-experiment has been also conducted to test if the MOF filter paper allows MOF particles to absorb Ethylene. To ensure that Ethylene gas would be able to pass the different types of filter papers to be used for the experiment, 1mL of ammonia was placed below a filter paper and a pH indicator on the top. The pH indicator changes colors within seconds, showing that gases can pass the filter.

Also, a hole was cut in each of 3 caps. One filter was painted with the MOF+PVA paste, another filter painted with the PVA paste, and the third filter wasn't painted with anything. It is notable that the coal containing Ethylene was placed on the bottom container while the cabbage seeds planted on the tops of filter papers was placed for every filter system (Fig. 2).

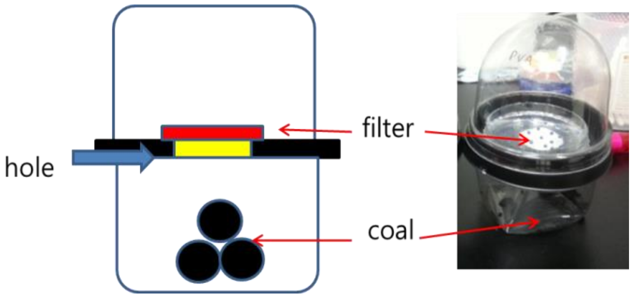

Figure 2. Filter papers over the coal containing Ethylene.

2.3. Set up to explore the effect of Ethylene content on plant growth

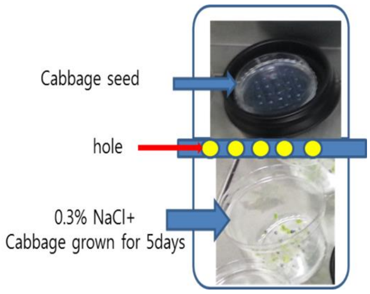

Figure 3. Set up of stressed cabbages around/below regular plants.

The experiment set up has been prepared to investigate the effect of salt stress on production of Ethylene in plants and the effect of Ethylene produced by stressed plants on the growth of surrounding plants. Multiple sets of 25 cabbage plants were planted and grown on agar for 5 days. Afterwards, 1mL of 0.3% NaCl was sprayed on some sets of cabbage plants. As shown in Fig. 3, cabbage plants were placed under a plastic cap containing 16 small holes. Then, 25 cabbage plants were placed on the top of the plastic cap and in order to ensure that Ethylene gas did not leak out, a plastic container was placed and sealed around the system. After 4 days of observing plant growth, the lengths of cabbage plants were measured by marking individual lengths of plants and a spectrometer was used to measure the chlorophyll content at 663nm and 645nm. This experiment was conducted to test if MOFs can be applied to real situations in which Ethylene is synthesized by stressed plants, where cabbage plants sprayed with NaCl was placed underneath a plastic cap with holes.

III. ESULTS AND DISCUSSION

3.1. Structures of MOF-867 and UiO-67

The low acceleration voltages (1 keV) in the gentle beam mode were used to avoid the damage on the samples during the scanning electron microscope (SEM) analysis. MOF-867 and UiO-67samples were prepared by the direct deposition of MOF/acetone dispersion (1 mg/mL) on the carbon substrate that was heated on a hot plate (70 ºC). SEM results show that MOF-867 (Fig. 4a) and UiO-67 (Fig. 4b) have the similar crystal morphologies with their average size of about 500 nm.

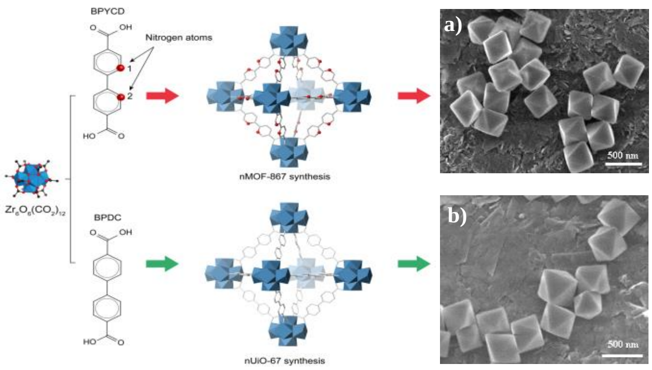

Figure 4. Synthesis moieties and SEM morphologies of a) MOF-867 and b) UiO-67. In the BPCD organic linker for MOF-867, carbon atoms were embedded in the biphenyl group while they were replaced with sp^2 N atoms at positions 1 and 2 of the BPYCD organic linker for UiO-67.

3.2. Ability of MOF-867 and UiO-67 to absorb Ethylene

(1) Ethylene absorbance by MOFs

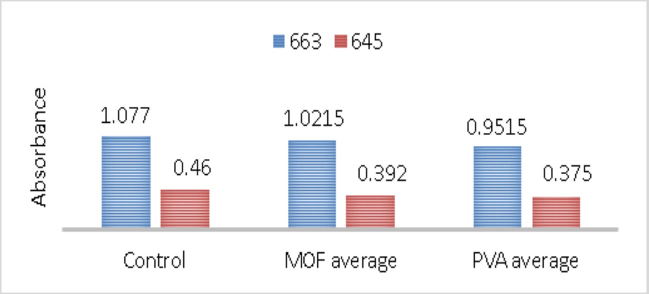

Figure 5. Averaged absorbance values by chlorophyll contents of cabbage plants (with light).

Figure 5 shows that the plants left under painted MOF/PVA paste under light have a higher chlorophyll content compared to plants left under PVA paste by 0.07A. This indicates that MOF-867 has added to the ability of the PVA paste to absorb Ethylene. The chlorophyll contents of cabbage plants without light (Fig. 6) also confirms that the plants under MOF/PVA paste have a 0.028A higher chlorophyll content than plants under PVA, but a 0.005 A lower chlorophyll content compared to control plants.

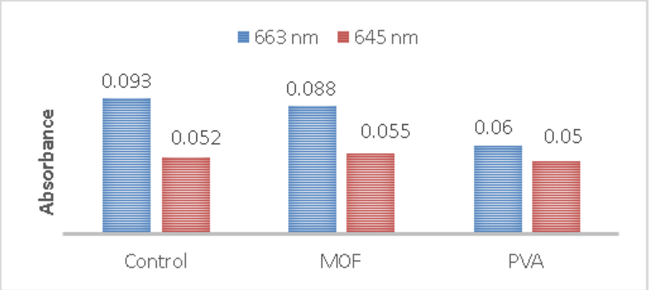

Figure 6. Averaged absorbance values by chlorophyll contents of cabbage plants (without light).

(2) Ethylene absorption by MOF filters

After applying MOF / PVA to the filter paper, the amount of charcoal containing ethylene gas was changed and it was confirmed that MOF could absorb ethylene gas.

(2.1) Changes in the growth of cabbages to 1g of charcoal absorbing Ethylene

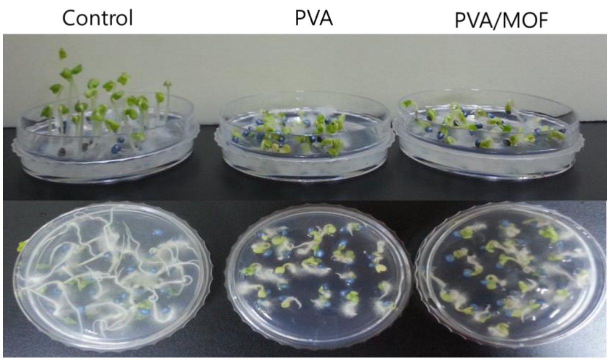

Figure 7. Changes in growth of cabbages under control, PVA, and PVA/MOF filter conditions.

When comparing the lengths of the plants, the control plants had the longest stems, but Figure 7 shows that the stem and roots of plants placed over MOF/PVA painted filter paper was slightly longer than the stem and roots of those placed over PVA painted filter paper.

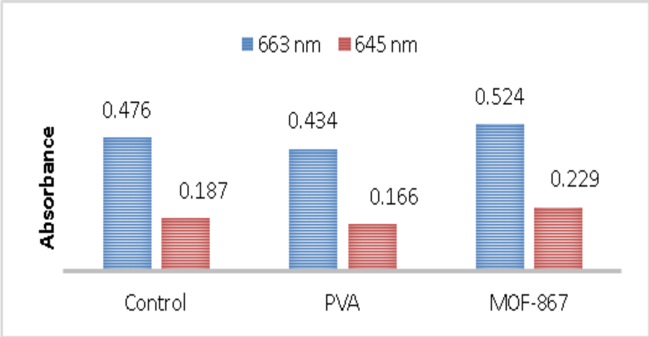

Figure 8. Averaged absorbance values by chlorophyll contents of plants exposed to light.

Moreover, chlorophyll contents a and b (Fig. 8) are shown for plants placed over 1g of Ethylene filtered by a regular filter, PVA paste filter, and MOF-867/PVA filter. The plants placed over the MOF-867/PVA filter had the highest absorbance and chlorophyll content, exceeding the chlorophyll contents of plants placed over a regular filter and PVA painted filter by 0.048A and 0.09 A, respectively.

(2.2) Changes in the growth of cabbages to 0.5g of charcoal absorbing Ethylene

As a result of this experiment, it was difficult to observe the growth of cabbage plants due to the high amount of charcoal absorbed by ethylene. UiO-67 was also mixed with PVA in combination with MOF-867. After one week, the growth length and beak of the cabbage were observed, and stem and root lengths of plants on MOF-867/PVA and UiO-67/PVA filters are found to be longer than plants placed on regular or PVA filter, with the stem and root lengths of plants placed on MOF-867/PVA being slightly longer than the those of plants placed on UiO-67/PVA filter. The plants that were not placed over the Ethylene had low chlorophyll content, but this can be attributed to long stems and roots, which implies that plant growth is hindered by Ethylene. Therefore, it was confirmed that MOF-867 and UiO-67 absorbed Ethylene and produced healthier plants, with MOF-867 being a little more effective.

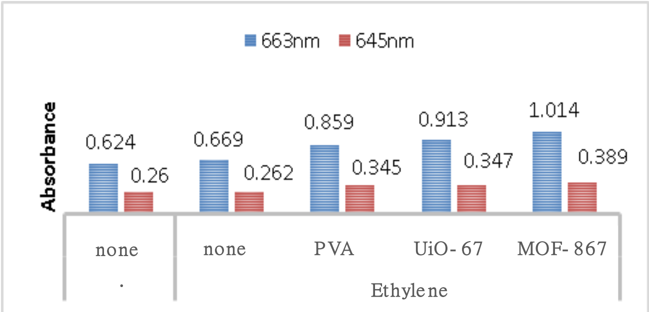

Figure 9. Average absorbance values by chlorophyll contents of plants over 0.5 g of filtered Ethylene.

The chlorophyll absorbance of the cabbage (Fig. 9) shows that the absorbance and chlorophyll content of plants on MOF-867/PVA filter over 0.5g of Ethylene is the highest out of all other sets of plants. The chlorophyll content of plants on UiO-67/PVA filter was also greater than plants on PVA and regular filter by 0.19A and 0.244A, respectively.

(2.3) Changes in the growth of cabbages to 0.1g of charcoal absorbing Ethylene

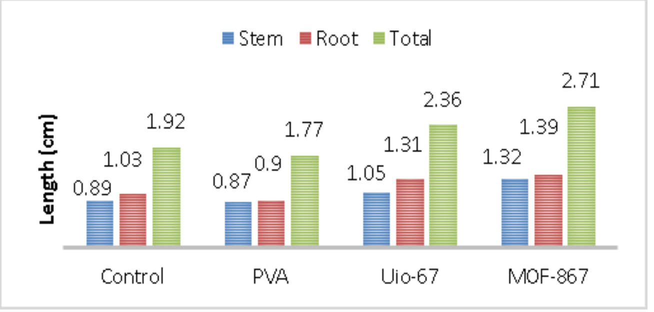

Figure 10. Average lengths of plants over 0.1 g of filtered Ethylene.

After replacing 0.5 g of charcoal with 0.1 g, the amount of Ethylene gas was further reduced and then the absorption effect on MOF-867 and UiO-67 was observed again. At first, we have measured the growth of the cabbage. As shown in Figure 10, the total length of plants placed over MOF-867 filter paper is found to be 0.94 cm and 0.79 cm greater than plants placed on PVA filter and regular filter paper respectively. Therefore, it is confirmed that MOF-867 has absorbed Ethylene effectively and greatly prevented Ethylene from hindering plant growth. UiO-67 was less effective, but reasonable prevented the over-abundance of Ethylene.

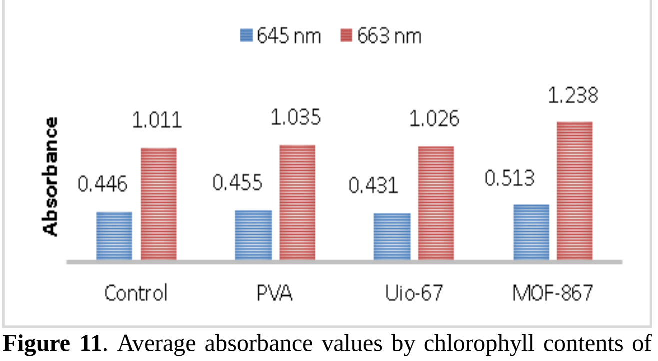

Figure 11. Average absorbance values by chlorophyll contents of plants over 0.1 g of filtered Ethylene.

The measurements of chlorophyll contents (Fig. 11) demonstrates that the chlorophyll content a of plants placed on MOF-867 painted filter paper is the greatest out of all the other variables, especially 0.203 A compared to PVA painted filter paper. However, the chlorophyll content of plants placed on UiO-67 painted filter paper is found to be greater than that of plants placed on regular filter paper but lower than that of plants placed on PVA filter paper. This may be attributed to the long length of the stems and roots of plants placed on UiO-67 filter paper, since chlorophyll content tends to decrease as the length of the plant increases.

3.3. The effect of MOF-867 and Uio-67 to control Ethylene contents for plant growth

Ethylene gas was generated when the plant was stressed and it was confirmed that the gas affected the environment.

(1) Effect of Stress for underneath and overhead plants

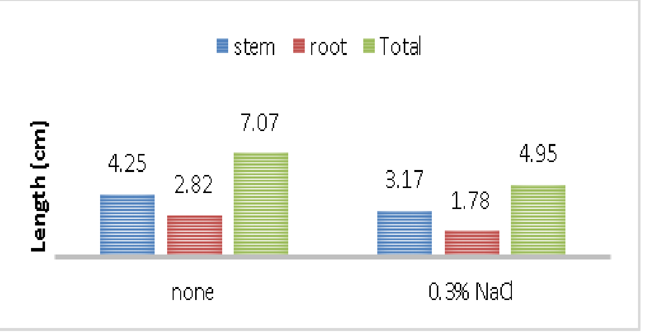

Figure 12. Average lengths of plants subjected to NaCl and light stress.

The growth of the cabbage was observed after 0.3% NaCl solution treatment to stress the cabbage. Figures 12 shows that the plant without NaCl stress is clearly longer than the plant subjected to NaCl stress when viewing the photo. Figure 12 supports further that both the length of the stem and root of the plants without NaCl are longer than that of plants subjected to NaCl stress and on average, the plants without NaCl stress have a 2.12 cm greater total length, which indicates that the NaCl stress deters plant growth.

To determine if Ethylene was released from the stressed cabbage, the cabbages with 0.3% NaCl were placed on the bottom and the other plants were placed on their top. After that, the growth of the plants has been observed.

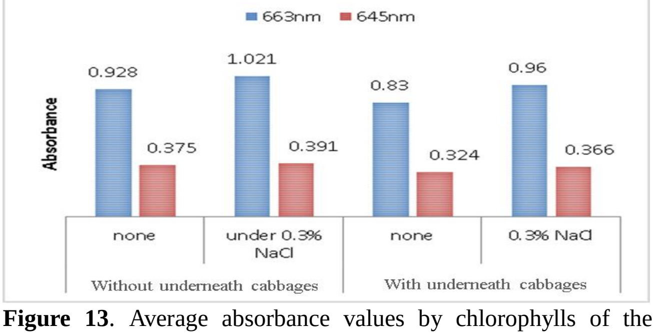

Figure 13. Average absorbance values by chlorophylls of the overhead plants depending on NaCl stress and ethylene-producing underneath cabbages.

Figure 13 shows the effect of ethylene-producing underneath cabbages and NaCl stress on the overhead plants. The graph shows the stem and root lengths of the overhead plants placed in 1) 0.7% Agar, 2) 0.7% Agar with 0.3% NaCl, 3) over the underneath cabbage plants planted in Agar, and 4) over the underneath cabbage plants planted in Agar sprayed with 0.3% NaCl. Chlorophyll content a, which is abundant in a healthy plant, is shown to be lower for the overhead plants placed over the stressed plants. This implies that Ethylene molecules produced from the stressed cabbage plants hindered the growth of the overhead plants. The plants placed over the underneath cabbage plants with no stress conditions have longer stems and root lengths than the plants placed over the cabbage plants subjected to NaCl. Therefore, greater Ethylene production from plants under stress can deter the growth of surrounding plants.

(2) Effect of MOFs on regulating Ethylene gas synthesized by plants

(2.1) Changes in the growth of cabbages and its surrounding cabbages under light and fungal stress

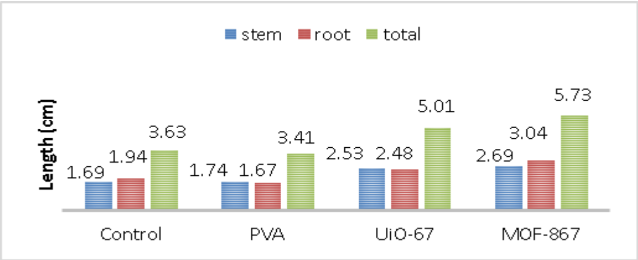

Figure 14. Average lengths of plants subjected to bacteria and light stress.

For plants affected by bacteria and light stress, Figure 14 shows that the plants placed on MOF-867 and UiO-67 filters had the greatest total lengths of 5.73 cm and 5.01 cm, respectively, and the plants placed on the regular and PVA filters had significantly lower total lengths. However, according to Figure 15, the chlorophyll content ratio for plants placed on UiO-67 filter was lower than 1 and the lowest compared to those of plants placed on other types of filters. This is likely to have been caused by the long plant lengths of plants placed on the UiO-67 filter. While UiO-67 did not prove to be extremely effective at filtering Ethylene in this experiment, MOF-867 proved to be very effective because it had a high chlorophyll content ratio of around 1.20, close to the highest chlorophyll content ratio, which the plants on the PVA filter displayed.

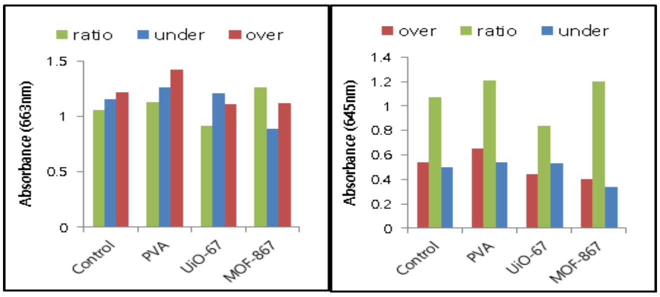

Figure 15. Average chlorophyll contents (663 nm and 645 nm) for plants exposed to the filtered Ethylene from the plants subjected to light and bacteria stress.

(2.2) Changes in growth of cabbages and surrounding cabbages under light and NaCl stress

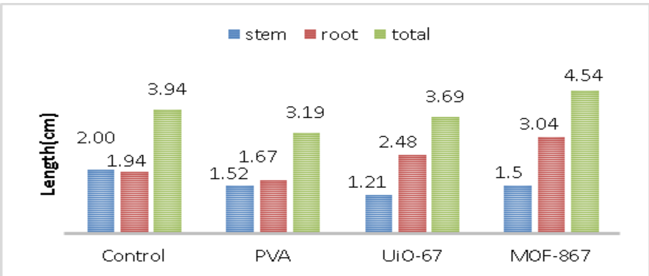

Figure 16. Average lengths of the plants subject to NaCl and light stress.

When comparing the different types of filters: regular, PVA, UiO-67, and MOF-867, for plants affected by NaCl and light stress, the plants placed on the regular filter had the highest total plant length of 4.54 cm, while the those placed on the UiO-67 and MOF-867 filters had a higher plant length than plants placed on the PVA filter (Fig. 16).

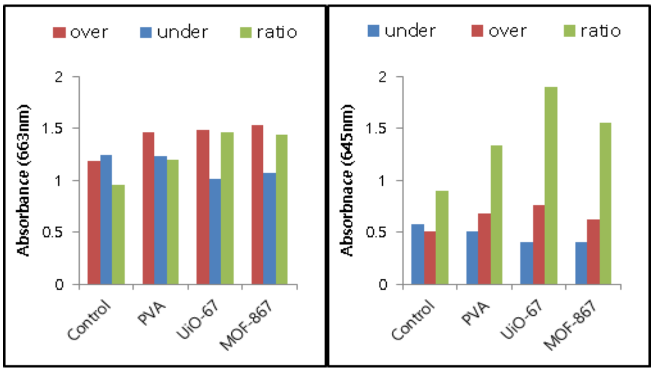

Figure 17. Average chlorophyll contents (663 nm and 645 nm) ratio of plants exposed to filtered Ethylene from the plants subjected to NaCl and light stress.

Figure 17 also clarifies that the chlorophyll content level ratios of plants over MOF-867 and UiO-67 were higher. Since the ratio compares the chlorophyll content of overhead plants to underneath plants, this indicates MOF-867 and UiO-67 was relatively efficient in filtering out Ethylene so that there was a big gap between the chlorophyll content level of plants which synthesized the Ethylene and plants that were affected by the Ethylene production. Also, because the plants on the MOF-867 and UiO-67 filters had chlorophyll content ratios greater than 1, the chlorophyll level of plants affected by the Ethylene is higher than the plants that emitted the Ethylene.

IV. CONCLUSION

We reported that the growth of plants could be improved by absorbing Ethylene gas using MOFs as the filter papers, where MOF filters have been fabricated using the 5% PVA (polyvinyl alcohol) 1 mL pasted with two kinds of MOFs. Ethylene gas produced when plants are stressed can be captured into nanocages of MOFs. Moreover, the ratios of chlorophyll in stressed cabbages and their surrounding plants prove that MOF having nitrogen in its ligands was more effective in absorbing Ethylene gas than that having no nitrogen in its ligands. Consequently, these results demonstrate that the use of suitable nanocages and functional organic ligand units in MOFs can be used to tailor the damage of surrounding plants by stressed plants attributed to their unique capability for absorption of Ethylene gas and that they could be also applied to fruits aged by Ethylene gas for controlling the aging speed. As one plant is stressed by external factors such as pests, moisture and light stress, Ethylene gas can affect normal plants. In these situations, this work could give a real solution to overcome the problems relating to plant growth by Ethylene gas. It is possible to solve the problem that the stressed crop affects other crops with a filter such as an air cleaner to purify the air using MOFs.

ACKNOWLEDGMENT

We appreciate for support of experimental instruments and facilities at Taejeon Christian International School and Korea Advanced Institute of Science and Technology.

AUTHOR CONTRIBUTIONS

Elin Kang designed and performed the research for the effects of MOFs on plant growth. Dong Kyu Park helped conduct SEM measurements. Elin Kang wrote the manuscript on discussion with Dong Kyu Park.

REFERENCES

[1] Joyce, Kim. "What Fruits Shouldn't Be Stored Next to Each Other?", LIVESTRONG.COM, Leaf Group, 2015.

[2] Qiao, Hong, et al. Processing and subcellular trafficking of ER-tethered EIN2 control response to ethylene gas. *Science* 338, 6105, 2012, pp. 390-393.

[3] Furukawa, Hiroyasu, et al. The chemistry and applications of metal-organic frameworks. Science 341, 6149, 2013, p.1230444.

[4] Bai, Yan, et al. Zr-based metal–organic frameworks: design, synthesis, structure, and applications. Chemical Society Reviews 45, 8, 2016, pp. 2327-2367.

[5] Christopher, Trickett et. al. The chemistry of metal–organic frameworks for CO_2 capture, regeneration and conversion, Nature Reviews Materials, 2, 17045, 2017. pp 1-16.