A Study on Humidification and Absorption of Particulate Matter (PM) and Volatile Organic Compounds (VOCs) according to Alginate Gel Manufacturing Methods

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Abstract— **Alginate is a natural polymeric material derived from seaweed, and has various physical properties depending on the production method, and has low toxicity, thus is attracting attention as a new material for tissue engineering. The purpose of this study is to extend the study of alginate gel concentrated on bio-related research to utilize it as a material to solve environmental problems. Considering the gel strength and environmental friendliness, Ca2 + was selected as the gelling ion and the paper towel, which showed the best water absorption rate, was selected as the support material. Investigating the particulate matter (PM2.5, PM10) and VOC adsorption behavior of the selected ion and support, gel paper with 1% alginate solution was the most excellent in absorbability. Synergy effect with activated carbon, which is widely used as an adsorbent, was also verified, and applicability in real life was also examined through prototyping. In this study, possibility of using alginate as eco-friendly adsorbent material has been proposed, and it is expected that it will be possible to manufacture the adsorption gel with the maximum efficiency if the manufacturing method is expanded variously.**

Keywords—**Alginate Gel, Volatile Organic Compounds (VOCs), Particulate Matter (PM), Absorption, Humidification**

I. Introduction

Alginate is a natural material derived from polysaccharides that can be extracted from seaweed or sea tangle, usually in granular form such as sodium alginate or potassium alginate. The molecular formula is $(C_6H_6O_6)_n$, which is an acid in chain form, but it is weak acid due to its low ionization degree. Alginate is excellent in biocompatibility, and has a low toxicity, a low cost, and a property of easily forming a hydrogel by binding with a divalent cation. The major constituents of the alginate are D-mannuronic acid (M) and L-glutaric acid (G) (Nelson & Cretcher, 1929; Fischer & Dorfel, 1955), and Monomers of M and G form M blocks, G blocks, and MG blocks in the alginate molecule depending on the continuity. Alginate containing a large amount of G forms a gel that is stable to heat and strong but fragile, and alginate containing a large amount of M forms a weak and resilient gel. Depending on the type of divalent cations to be bonded, the ionic crosslinking structure may be changed to change the physical properties. (Lee & Mooney, 2012)

Alginate, with excellent biocompatibility and low toxicity, is a medical material that has been widely used in various fields such as tissue engineering. For example, alginate gels have been used as an artificial tissue supporter (Lee Jae Won & Lee Geun-yong, 2011), and recently, drug delivery mechanisms using alginate beads and their utilization as stem cell cultures have been actively studied. Alginate is known to adsorb and solidify radioactive materials such as cadmium, barium, copper, and manganese as well as strontium-90, and is known to be an effective means of eliminating heavy metal contamination of water resources in an environmentally friendly manner. (Jung, 2017) Yong-Bo Lin et al. (2005) reported that beads made of alginate and activated carbon adsorb well to airborne volatile organic compounds (VOCs) such as p-chlorophenol.

In this study, we propose the use of alginate gel as an environmentally friendly humidification and air purifier by studying the humidification, VOC and PM adsorption behavior of alginate gel.

II. Research Method

This study is largely divided into four parts. First, the selection of divalent cations, which are required to be robust, sustainable, and environmentally friendly. Secondly, the selection of the alginate gel support, which has to have a high adsorption and humidifying rate. Third, investigate the PM and VOC adsorption behavior according to various alginate gel production methods and selecting the production method with the best behavior. Finally, prototype is made using the selected method and it is examined for the possibility of application in an actual environment. In all experiments, 5 g, 10 g and 20 g of sodium alginate powder were dissolved in 1 L of distilled water, respectively, and 0.5%, 1% and 2% g / mL of alginate aqueous solution were prepared and used as a base material.

A. *Alginate gel formation and physical properties investigation*

The 1% alginate aqueous solution is added to an aqueous solution of Cu^{2+}, Sr^{2+}, Fe^{2+}, Ca^{2+}, Co^{2+} 1% g/mL to determine whether the gel is formed. The Young's Modulus is then calculated to measure the strength of the formed gel. To calculate the Young's modulus, form an alginate gel film, and measure the thickness, length, and width of the film using a caliper. Apply a load to one end of the film, measure the force and the stretched length using a force measuring instrument and a ruler, and substitute the following equation to calculate the

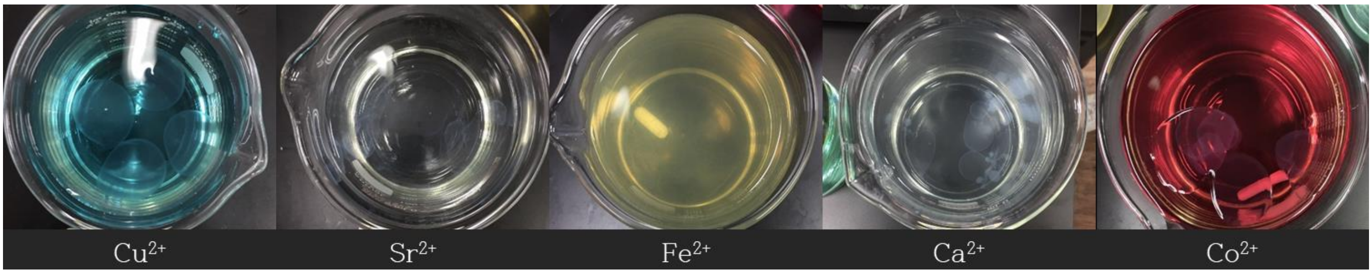

Figure 1. Experimental results on the formation of alginate gels by divalent metal cation

Young's modulus. The higher the Young's modulus, the higher the strength of the gel.

$$E \equiv \frac{\sigma(\varepsilon)}{\varepsilon} = \frac{F/A}{\Delta L/L_0} = \frac{FL_0}{A\Delta L}$$

B. *Selection of alginate gel support*

37g and 80g handmade paper (Korean traditional paper; grams represent different thickness), paper towel, filter paper, cloth, and felt were selected as candidates for the alginate gel support, and water absorption and moisture evaporation behavior were tested. Similar to the chromatographic experiment, the material is cut into 1.5 cm wide and 15 cm high, respectively, and the bottom 0.5 cm is immersed in water to measure the water absorption rate by measuring the height that the water travels up to. For the evaporation rate experiment, the papers are cut in the same dimension as that of the filter paper. After wetting each material thoroughly, it is hanged in the center of the closed acrylic bottle and the humidity increase by evaporation is measured after one hour.

Also, investigate the difference in water evaporation behavior when applying alginate gel. In order to make the alginate gel paper, first, the support material is submerged in a 1% aqueous alginate solution for about 30 seconds to sufficiently absorb the solution, which is then submerged in a 1% cationic solution for about one minute to form a gel. The support on which the thin gel is formed is dried for about 30 minutes to wait for the reaction to cease completely and to remove excess water. The moisture evaporation rate of the 1% alginate gel paper formed is measured in the same manner as in the above experiment, and the most suitable support for the gel is finally selected.

C. *Investigation of PM and VOC adsorption behavior*

Alginate gel paper is prepared by using the selected divalent metal cation and support, and PM (Particulate Matter) and VOC adsorption behavior are investigated. First, the adsorption behavior is observed using gel papers formed with 0.5%, 1%, and 2% alginate aqueous solution to investigate the differences in adsorption behavior of different alginate aqueous solution concentrations. In order to test the adsorption behavior of alginate paper of different thicknesses, gel thickness is adjusted by repeating the alginate forming process by coating 1% alginate aqueous solution and metal cation aqueous solution several times to prepare multiple layers of gel films. 16 sheets of alginate gel papers are prepared, and four sheets are attached to each of the four sides of a cube made of acrylic resin to prepare the adsorption experiments.

In the present study, the tobacco smoke was injected into the acrylic bottle for about 1 second to establish the micro dust environment. The PM adsorption trend is observed every 10 minutes through a PM meter placed at the center. The use of isopropyl alcohol (IPA), which is known to be a VOC that is comparatively less hazardous to the human body than other VOCs. A little amount of IPA that is put on the tip of toothpick is set into the acrylic cube. Then, the tube is sealed and the adsorption behavior is measured every 10 minutes using a VOC analyzer. After the 1% gel paper is thoroughly dried, PM and VOC adsorption experiment using alginate gels that were re-supplied with water is executed to test the possibility of reusing the alginate gel paper.

Finally, in order to investigate the synergistic effect of activated carbon and alginate gel paper, firstly, activated carbon with a suitable size for the experiment is selected by investigating the PM and VOC adsorption behavior of different particle sizes of activated carbon. After the adsorption of the selected activated carbon on the 1% alginate gel paper, the adsorption behavior of the PM and VOC was observed.

D. *Field application review*

A simple prototype is fabricated by using the final adopted manufacturing method. The prototype is tested for VOC and PM adsorption in a 2.3m by 2m by 2.3m room to observe whether or not the PM and VOC are adsorbed in the actual environment.

III. RESULTS

A. *Determination of formation and strength of divalent cationic alginate gel*

1% alginate solution was added to Cu^{2+}, Sr^{2+}, Fe^{2+}, Ca^{2+}, and Co^{2+} 1% g / mL aqueous solutions. The results showed that the gel was formed in divalent cation solutions other than the Fe^{2+}solution as shown in Fig 1. In the case of Fe ions, alginate gel is able to form when in the trivalent cation state, but formation of the ion bridging structure at the divalent cation state is very slow and weak and thus is known that formation of the alginate gel is difficult (Narayanan et al., 2012), which was observed in the above experiment. (Fig. 1)

The Young's modulus was measured in the order of Cu^{2+}, Ca^{2+}, Sr^{2+}, and Co^{2+}. (Fig. 2) Cu^{2+} formed the strongest alginate gel, but it, as a heavy metal ion, can cause pollution problems when exposed to the environment. Using Cu^{2+} ions did not meet the purpose of this study of proposing an environmentally friendly method of humidification and air purification. Therefore, the Ca^{2+} ion, which has a lower Young's modulus,

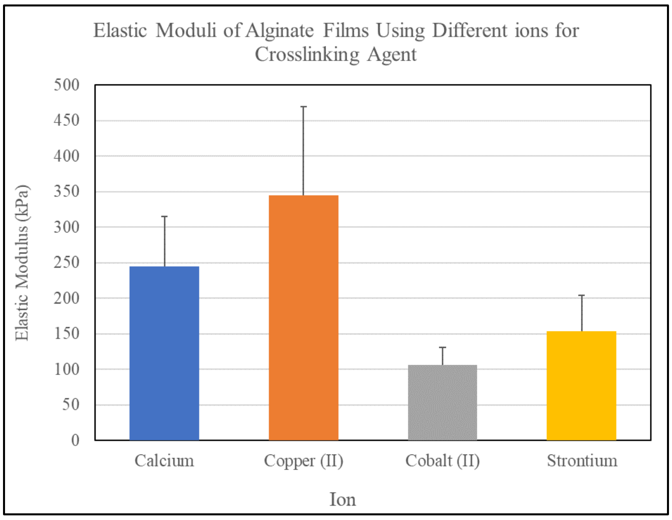

Figure 2. Strength measurements of alginate gels according to the type of divalent cations

but is found in organisms and has less environmental pollution, was adopted as the gel forming ion of this study.

B. Selection of alginate gel support

As the support, we selected 37 g handmade paper, 80 g handmade paper, paper towel, filter paper, cloth, and felt as candidates. For the water adsorption rate test, the height of water of both 37g handmade paper and paper towel rose to about 12 cm. The 80g handmade paper absorbed about 11cm of water, and filter paper, cloth, and felt showed low water absorption rate with a risen height of less than 8cm. (Fig. 3). In the water evaporation experiment, the increase of humidity in all materials was uniformly average of 24.2%, thus the evaporation rate of different materials were not significantly different.

Next, whether coating the paper with the alginate gel made a significant difference in the water evaporation rate was tested for (Fig. 4). Alginate gels, each having a thickness of 0.5 mm, were coated on paper towels, filter papers, and handmade papers, and the same procedure as in the water evaporation experiment above was executed. The results showed that there was no significant difference in the evaporation rate when the gel film was coated onto the papers.

Unless the presence of the alginate gel causes a major interference in the supplying of water, it would be appropriate to select an alginate support with excellent water absorption so that the alginate gel can always be maintained in a moist state. Although the handmade paper is structurally compact and stiff, thus would be advantageous in maintaining a certain shape, but it is disadvantageous in that it is not economical and accessible compared to a paper towel, which has a similar water absorption rate to the handmade paper. Therefore, in this study,

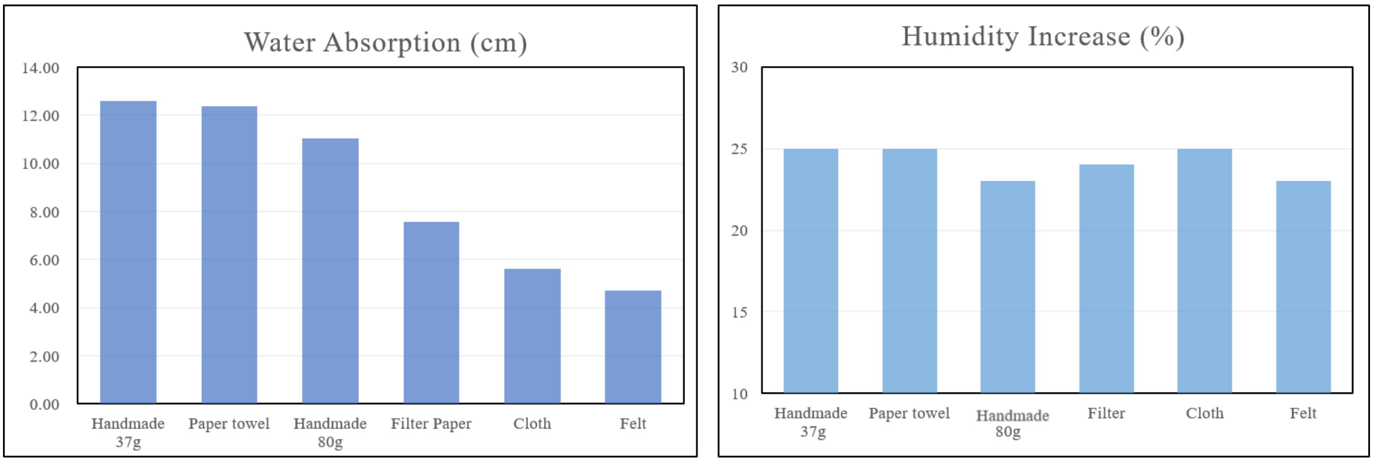

Figure 3. (Left) Water absorption rate experiment result, (Right) Evaporation rate experiment results

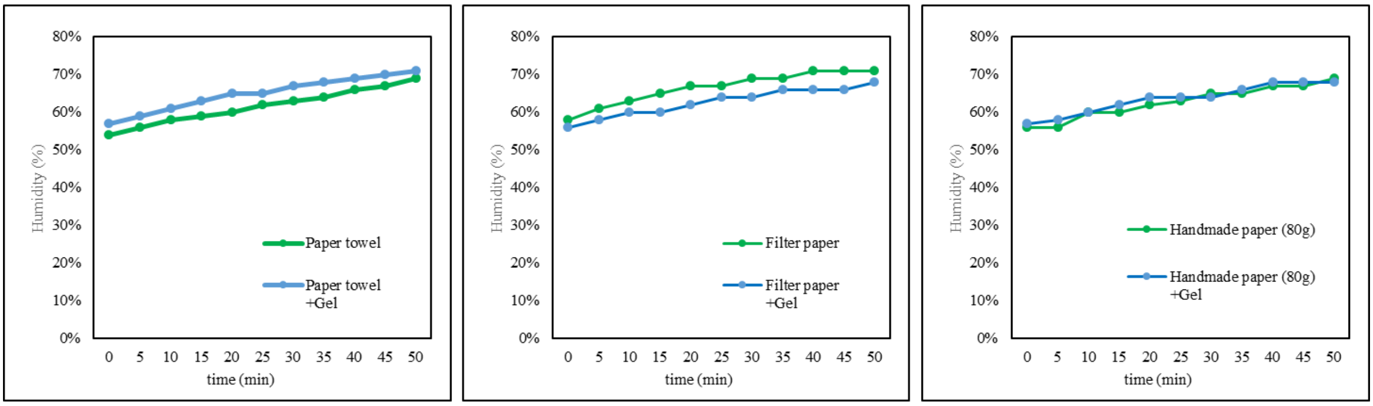

Figure 4. (From the left) the gel applied to the paper towel, the gel applied to the filter paper, the gel applied to 80 g of pure paper evaporation rate comparison result

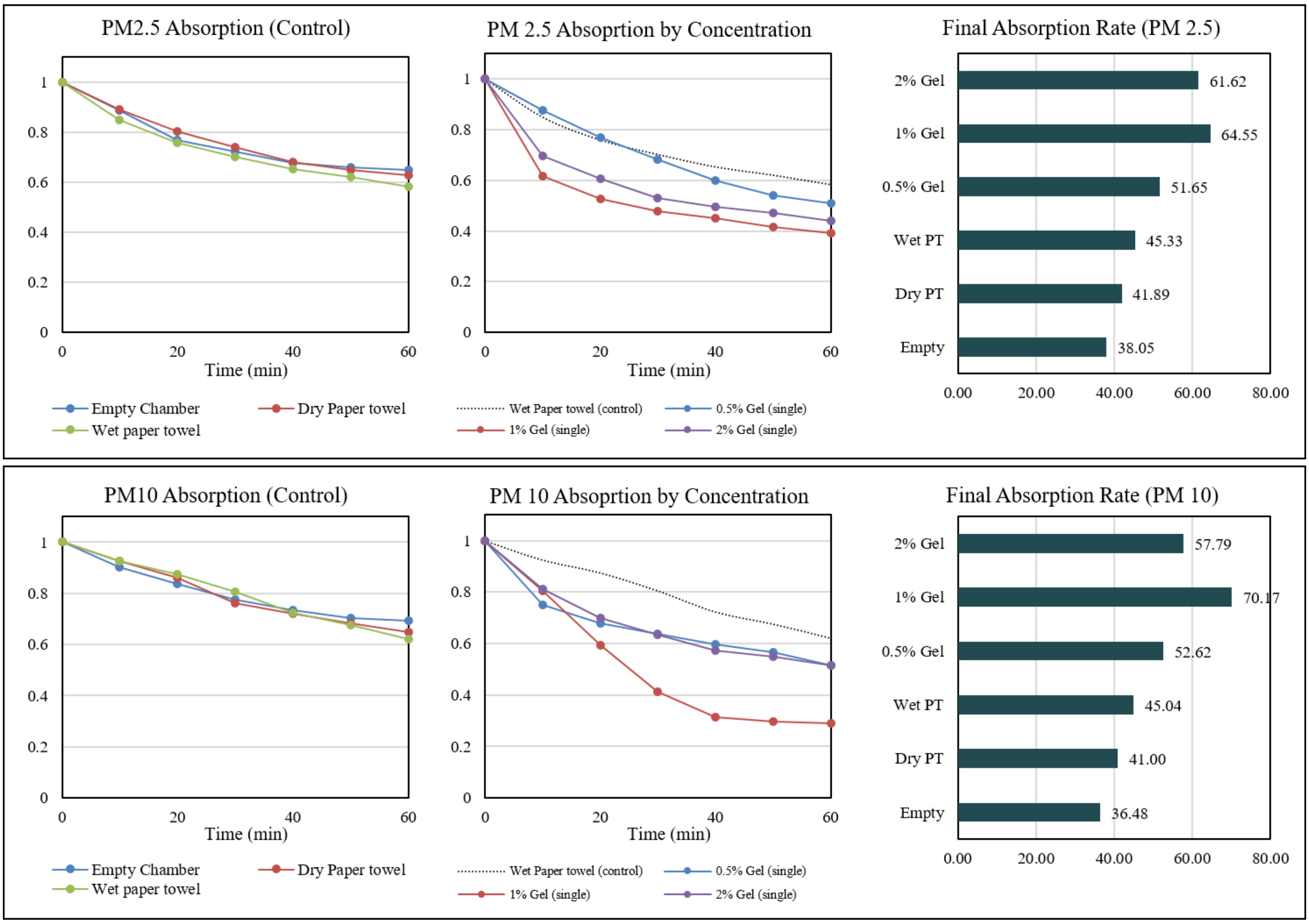

Figure 5. (Top) Comparison of PM2.5 adsorption and final adsorption by production concentration, (Bottom) Comparison of PM10 adsorption and final adsorption by production concentration

the paper towel, which can be obtained easily and is inexpensive was selected as the gel paper support.

C. Investigation of PM adsorption behavior of gel paper

In the control group without any treatment in the acrylic bottle, the PM concentration naturally decreased by about 40% after 70 minutes. This is probably due to PM adsorbed on the walls and floor because of the static electricity of the acrylic material. The results of experiments using paper towels coated with alginate gel showed a significantly higher PM adsorption rate than the control experiment, which means that the alginate gel can adsorb a significant amount of PM.

Gel made using 1% alginate solution exhibited the most favorable adsorption rate for both PM2.5 and PM10, and for PM10, the adsorption rate was about 70% or more. (Fig. 5). In case of gel made using 0.5% alginate solution, it is speculated that the pores of the net structure are too large to capture the PM particles. In case of the 2% alginate solution, the gel polymerization reaction occurs too much, which compactly covers the surface of the paper towel, resulting in a reduction in the surface area capable of capturing PM.

In the case of varying the thickness of the alginate gel membrane, there was a slight difference in the adsorption progress, but no significant difference was found in the final adsorption rate. (Fig. 6) This is probably due to the fact that the PM adsorption occurs mainly on the surface of the alginate gel, and that the PM particles does not penetrate into a deep portion. In addition, when the alginate gel was dried, it was found that the PM adsorption rate was reduced by about 25%. It is assumed that the adsorption rate decreases as the amount of PM trapped by the surface tension of the water decreases.

D. Investigation of VOC adsorption behavior of gel paper

Alginate gels were able to adsorb VOCs known to cause sick house syndrome. Isopropyl alcohols (IPA) with low toxicity among VOCs were selected as our target VOC. Unlike PM, the IPA concentration did not decrease naturally in empty acrylic chambers. This means that the electrostatic property of the acrylic tube is independent of VOC adsorption.

The alginate gel papers showed a significantly higher IPA adsorption rate than the control. In the case of 0.5% gel, IPA was rapidly adsorbed at first, but the adsorption efficiency decreased rapidly with time and the final adsorption rate was lower than that of 1% and 2% gel. (Fig. 7). The adsorption rate was reversed after 40 minutes, which is thought to occur because the net structure of the 0.5% alginate gel surface gets

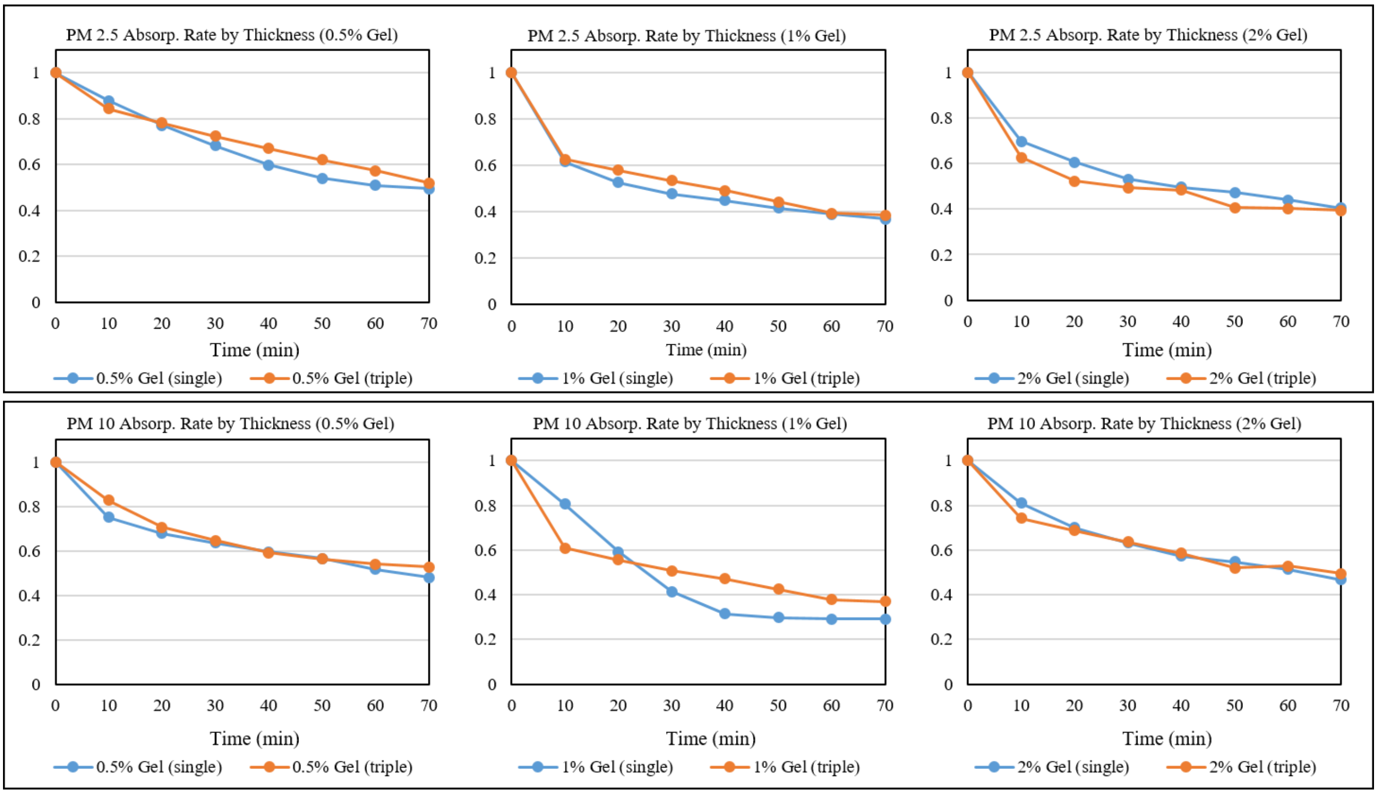

Figure 6. When the thickness is varied, (Top) PM 2.5 Adsorption (Bottom) PM 10 Adsorption

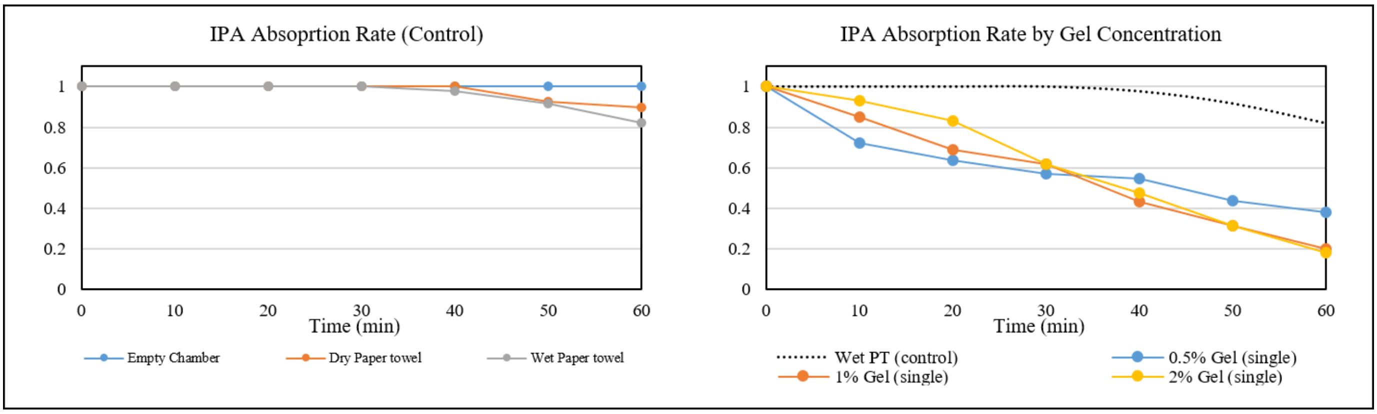

Figure 7. IPA adsorption trend and final adsorption rate by alginate concentration

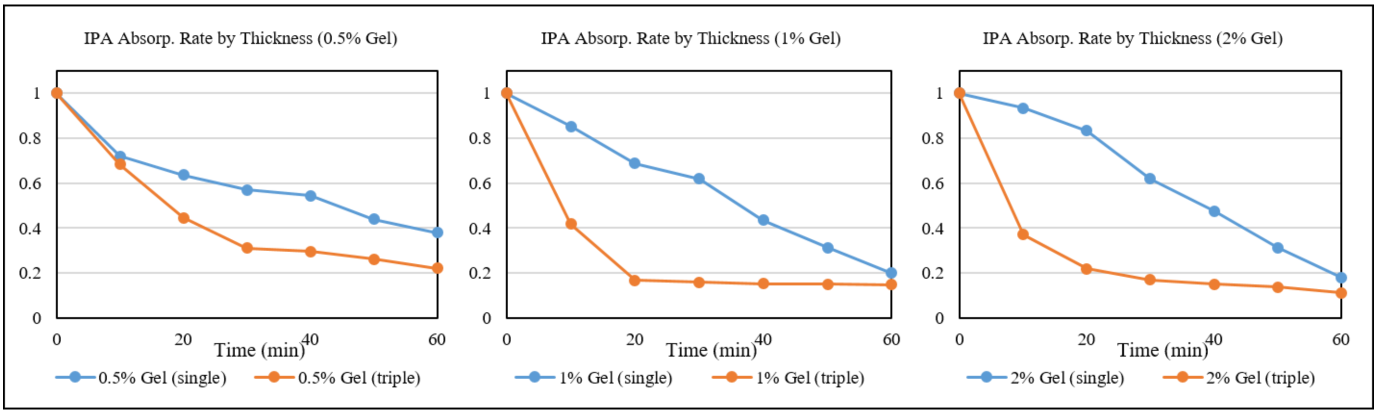

Figure 8. IPA adsorption trend by alginate gel thickness

rapidly saturated. Alginate 1% gel and 2% gel showed no significant difference in adsorption ratio and final adsorption ratio. This is interpreted that the influence of the density of the net on the gel surface on the IPA adsorption mechanism decreases from a certain concentration.

As a result of examining the adsorption change with different thicknesses, it was confirmed that the thicker the more the final adsorption was for 0.5% alginate gel. However, for 1% gel and 2% gel, the final adsorption rate was not significantly different. (Fig. 8) In case of 3 layers of thickness, IPA was rapidly adsorbed in the early stage, and the efficiency was rapidly decreased with time, showing an overall exponential adsorption trend. In the case of 1 layer, a linear adsorption trend was shown at a constant rate. As a result, it is regarded that the thickness of the gel in terms of IPA adsorption does not significantly affects the final adsorption rate because the adsorption mechanism occurs mainly on the surface of the gel.

Finally, 1% gel was proved to be excellent in PM and VOC adsorption. In case of 2% gel, the adsorption efficiency of VOC was good, but there was no significant difference from 1% gel and the adsorption rate of PM was even low. Depending on the thickness of the gel, the overall trend of VOC adsorption was different, but there was no significant difference in the final adsorption rate. Therefore, considering economic efficiency and production efficiency, using 1% alginate aqueous solution to prepare one layered gel papers is the most favorable production method in terms of PM and VOC adsorption.

E. *Confirmation of gel paper reusability*

When the alginate gel paper was dried and then regenerated by supplying water again, the difference in VOC and PM adsorption rate was observed. When moisture was supplied to the dried gel paper, the original volume and texture were recovered. (Fig. 9)

In the case of the PM adsorption rate, the efficiency decreased by about 20%, compared to the initial use, at the first reuse. It is considered that the efficiency decreased because the PM adsorbed on the alginate gel net structure was not removed in the drying process. In the case of second reuse PM adsorption efficiency was not significantly decreased. In the case of VOC adsorption, the adsorption efficiency did not decrease significantly even after first and second reuse. This is presumably due to volatilization of all VOCs during the drying process. Therefore, it is considered that there is no problem in terms of efficiency even when the alginate gel paper is reused many times, and it is thought that the reusability is an economical advantage when practically used.

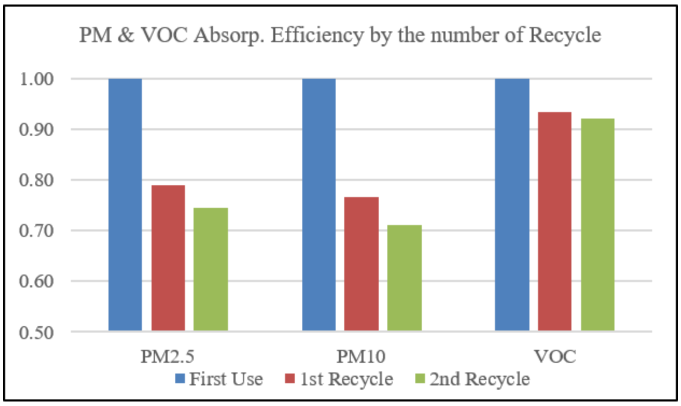

Figure 9. Identification of gel paper reusability and comparison of fine dust and VOC adsorption rate

F. *Confirmation of adsorption synergy with activated carbon*

It was confirmed that the adsorption power of PM and VOC of an alginate gel was enhanced by attaching activated carbon, which is widely used as a common adsorbent. First, using the viscosity of the alginate gel, the activated carbon was attached to the gel surface, and then the activated carbon was observed to stick on the surface of the gel stably. Activated carbon is divided into thin activated carbon (14×25) and coarse activated carbon (30×80) depending on the mesh size.

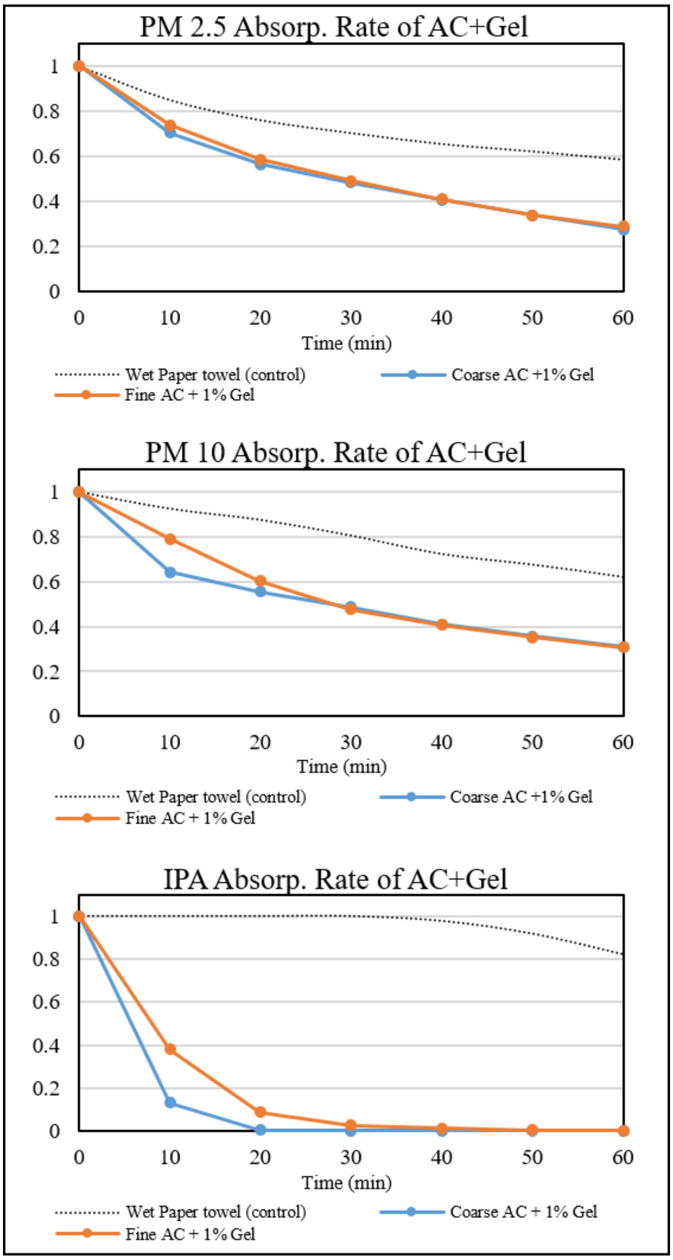

Figure 10. Synergy effect of activated carbon and alginate gel. PM and VOC adsorption trend of activated carbon gel paper

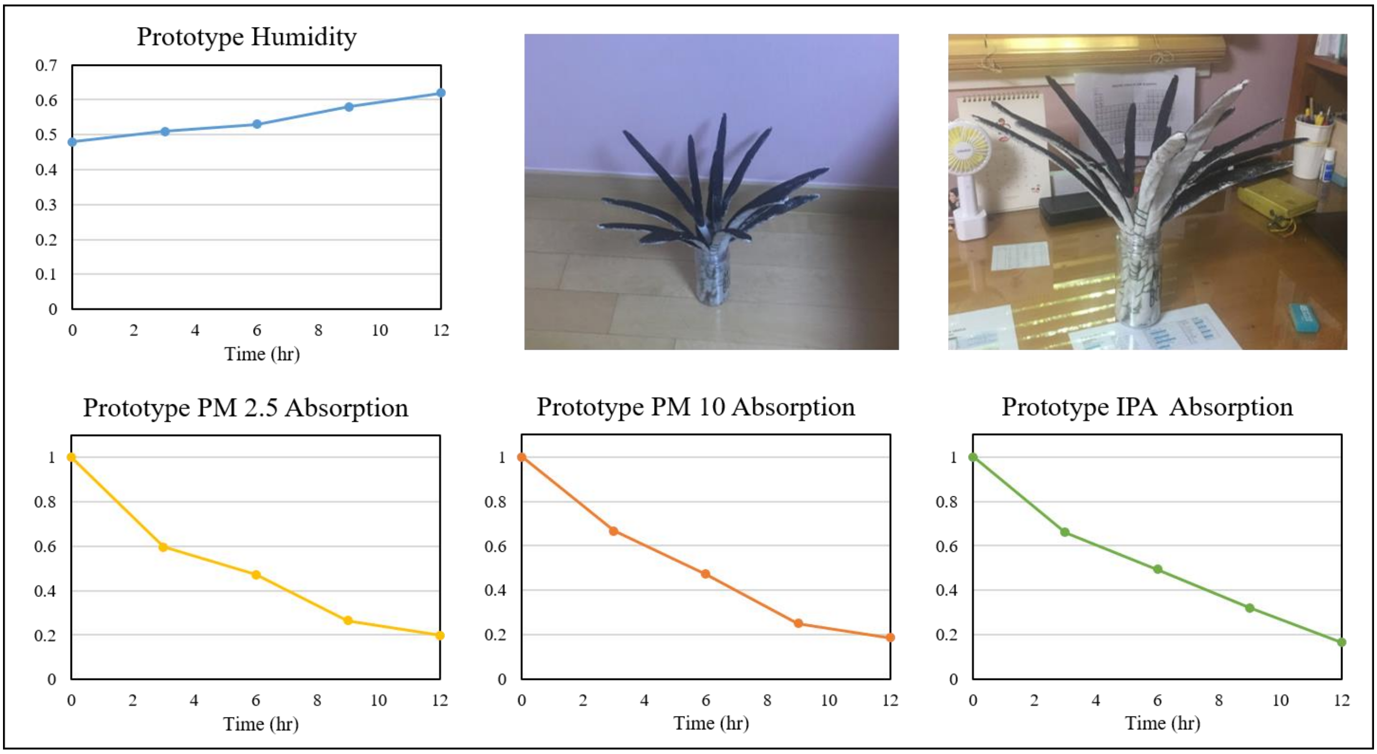

Figure 11. Survey of prototype, adsorption performance, and humidification performance using activated carbon gel paper

When activated carbon and alginate gel were used together, it was confirmed that the adsorption rate of PM and IPA greatly improved. (Fig. 10) Adsorption efficiency increased by about 15% when compared with alginate gel paper, and IPA showed adsorption rate close to 100%. However, it is expected that the thin activated carbon is more likely to be attached to the gel paper than the coarse activated carbon, thus increasing the adsorption surface area.

G. Examination of applicability in real environment through prototyping

Three prototypes of activated charcoal gel paper adsorbent possessing an orchid shape were fabricated, and the performance was measured by observing for about 12 hours in a room environment with 2.3 m, 2 m, and 2.3 m height. (Fig. 11) As a result, the humidity increased about 12%, and the concentration of PM and VOC decreased about 80%. This suggests that the activated carbon - gel paper proposed in this study exhibits sufficient adsorption of harmful substances and humidification performance and is likely to be an idea product in the future.

IV. Conclusion and Discussion

In this study, humidification effect, PM and the VOC adsorption ability of a natural material alginate were measured, and an eco-friendly prototype which works as an air cleaner and a humidifier was manufactured.

First, paper towel coated with one layer of alginate gel was not much different from the conventional paper humidifiers in terms of how it absorbed water and humidified it into air. However, since the alginate gel itself is weak in its ability to support and absorb moisture, a paper-like support such as a paper towel can be used to maintain the durability and the continuous water supply capability. Though hanji(Korean paper) showed a somewhat higher ability to absorb and evaporate moisture than paper towels, it is considered better to use paper towels considering the economic efficiency and accessibility. However, it is also a good idea to use hanji if necessary.

The adsorption capacity of PM of alginate was highest when water was sufficiently supplied, and when the gel was dried, the adsorption capacity of PM was decreased. This is because, due to the nature of the alginate gel, the volume increases when the gel has a large amount of water, thereby increasing the surface area of the microporous structure and increasing the viscosity of the gel. When the gel is dried, the volume is reduced, and the surface area of the microporous structure is decreased, which seems to be the reason of the decrease of adsorption capacity. That is, since the adsorption performance is ensured together with the alginate gel in an environment in which water is sufficiently supplied, it is appropriate to devise methods for utilizing the alginate gel as a humidifier simultaneously with air purification.

Also, when the concentration was varied, it was confirmed that the PM adsorption effect was more excellent in the 1% alginate gel. This suggests that if the alginate concentration gets overly high, the alginate gel structure gets denser and smoother, resulting in a more smaller adsorption surface area than the 1% alginate gel. When the thickness and amount of the alginate gel were increased by one, two or three alginate gel layers, the PM adsorption performance was not significantly different. This is because the adsorption of PM mostly occurs on the surface of the gel, and therefore, it is considered that the adsorption effect of PM can be exhibited with a single layer of alginate gel alone. In order to confirm this, there was an attempt to take an electron microscope (SEM) photograph, but in order to take a SEM, it had to be dried, and it was difficult to confirm the net structure of the gel adsorbed by the PM. In future studies, it is necessary to take an electron microscope photograph in an environment that is not dry to check whether the PM is trapped in the alginate microporous structure.

IPA, which is used as a solvent, was used to confirm the VOC adsorption ability of the alginate gel. The IPA adsorption performance of the alginate gel was more than 80%, which was much better than expected. It is considered that the hydrophilic alginate gel adsorbs well by hydrogen bonding with the hydroxyl group (-OH) of IPA. 1% gel showed more favorable adsorption performance than 0.5% alginate gel, and there was no significant difference in adsorption performance between 1% gel and 2% gel. It was found that the thickness of the gel also did not significantly affect the IPA adsorption performance, which means that if the gel net structure has a certain density or more, there is no significant effect on the IPA adsorption mechanism, and that adsorption occurs only on the gel surface. However, in order to expand further research, it is necessary to conduct adsorption performance tests on other VOCs. In particular, in the case of benzene, toluene, and xylene, which are hydrophobic VOCs, adsorption performance is expected to be insufficient due to the hydrophilicity of alginate. Therefore, in order to secure various practicalities, further research on the synergy effect with activated carbon should be conducted.

As a result of confirming the possibility of reusing the alginate gel, the adsorption efficiency was not significantly decreased even after several times of use. The adsorption performance was not significantly decreased even after repeated reuse after the initial reuse, but the reusability of VOC did not cause a great decrease in adsorption performance. Therefore, it can be confirmed that the alginate gel is an adsorbent capable of ensuring both economical efficiency and environment friendliness because it can be reused not once. Environmentally friendly air cleaners and humidifiers made of alginate gel are expected to be able to be recycled several times simply by rinsing out dust and harmful substances on the surface. Even if the main material is discarded because it is an alginate gel and paper, there is no great burden on the environment. Above all, it is a feature of alginate gel that it can look like air cleaning effect with humidification function. It is expected to save socioeconomic costs because it is composed of materials that can consume a lot of energy and can be easily manufactured at home instead of high cost air cleaner and humidifier.

Finally, in this study, it was confirmed through synergy effect experiment with activated carbon that the alginate gel adsorbent can improve its efficiency by adding a simple process to the production method thus extending the utilization plan. As mentioned above, studies about the synergistic effect with activated carbon can be suggested in order to procure the adsorption performance to the overall VOC having various physical properties. In addition, by studying the kind of VOC adsorbed only by the alginate gel without the activated carbon, the utilization method can be considered as a substitute adsorbent for the harmful substances. Particularly, activated carbon is most widely used for the study of PM and VOC adsorption. However, large amounts of greenhouse gases are emitted during the manufacturing process and the environmental cost is not cheap at all. In contrast, since the alginate gel is a naturally derived substance, it can be manufactured simply by a simple polymerization reaction. Therefore, it is expected that the environment problem of the activated carbon manufacturing process can be solved if a utilization method to replace the activated carbon is devised.

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