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Enhanced heavy metal adsorption by the surface grafted polyethylene/polypropylene fiber filter using oxygen plasma and acrylic acid

Jeongmin Hong[1)], Seungwoo Lee[2)] and Yuhoon Hwang[1)*]

1) Department of Environmental Engineering, Seoul National University of Science and Technology, Seoul 01811, Korea
2) Department of Fine Chemistry, Seoul National University of Science and Technology, Seoul 01811, Korea
[*] *yhhwang@seoultech.ac.kr*

ABSTRACT

The various kinds of contaminants can be accumulated on the road surface, and it can be discharged as non-point source pollution when the rainfall comes. However, it was found that the efficiency of removing the dissolved contaminants in existing non-point source pollution control device using filtration as the primary process is insufficient. Therefore, the countermeasure to minimize the discharge of dissolved contaminants into surface water stream should be considered. In this study, we functionalize the existing filter material in order to provide adsorption capacity. The polyethylene/polypropylene (PE/PP) fiber filter material was treated by oxygen plasma. The PE/PP filter material itself was very inert, so the heavy metal adsorption was not so significant. The oxygen plasma help to graft oxygen-containing functional groups on the surface of PE/PP filter material. Then, further grafting reaction using acrylic acid polymerization was taken place. The oxygen-containing functional groups formed by oxygen plasma was then used as reaction place for acrylic acid polymerization. FTIR and SEM analysis were performed in order to track the change in surface modification steps. Moreover, the organic contaminant and heavy metal removal efficiency in different pH region were evaluated.

1. INTRODUCTION

As the development of urbanization and industrialization accelerated land development and the area of impervious floors such as roads and parking lots increased, the effect of water quality on rivers and lakes caused by nonpoint pollution sources has also increased. Contaminants released along with rainfall in nonpoint sources are challenging to collect and process, and they enter the river directly without any special treatment, thereby polluting the water quality and disturbing the water ecosystem.

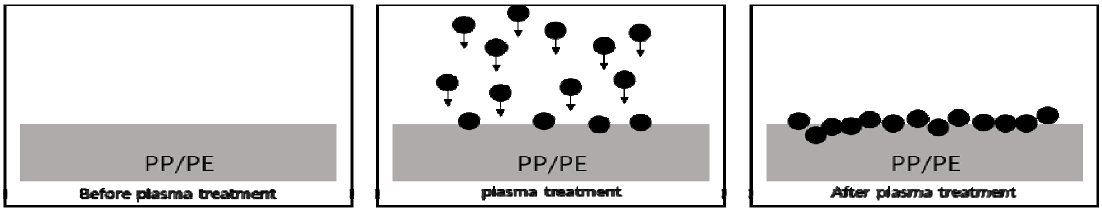
Several types of non-point source pollution control devices have been applied in order to reduce the potential risk of pollutants. Filtration was the most common process used in the non-point source pollution control device. Polymeric materials such as polypropylene (PP) and polyethylene (PE) have been applied in the form of granules or filters, but there has been no mechanism for removing dissolved materials other than filtration of suspended materials. Therefore, in this study, it is aimed to develop a material capable of adsorbing and removing dissolved substances through simple surface treatment on such filter materials.

In this study, surface modification of PP/PE fiber filter material was performed by using oxygen plasma and acrylic acid (AA) to improve the performance of materials used in existing nonpoint pollution abatement facilities and water treatment facilities. The PE/PP filter material itself was very inert, so the heavy metal adsorption was not so significant. The oxygen plasma help to graft oxygen-containing functional groups on the surface of PE/PP filter material. Then, further grafting reaction using acrylic acid polymerization was taken place. The oxygen-containing functional groups formed by oxygen plasma was then used as reaction place for acrylic acid polymerization. FTIR and SEM analysis were performed in order to track the change in surface modification steps. Moreover, the organic contaminant and heavy metal removal efficiency in different pH region were evaluated.

2. METHOD

2.1 Oxygen plasma treatment

The material used in this study was a fibrous filter material, which is already widely used as a filter material in the field of non-point source pollution control device. It was prepared by thermal fusion of polypropylene and polyethylene, which is inert, hydrophobic, and has a low surface free energy (Wang, 2006). With oxygen plasma, the hydrophilicity of PP/PE material could be improved through induction of surface change, and adhesion is improved on the surface of the sheaf, enabling it to be combined with other materials (Lei, 2000). Oxygen plasma devices (FEMTO SCIENCE, CUTE) were used, and PP/PE material was treated by oxygen plasma for 30 seconds at 50 KHz (Yamada, 2018). The surface change process can be described in Figure 1.



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ig. 1 Scheme of surface change process using oxygen plasma

2.2 Acrylic acid polymerization

Acrylic acid modification is a type of radical polymerization. In this study, potassium persulfate (KPS) was used to convert the hydroxyl group formed in the oxygen plasma treated PP/PE material to a radical state (Smuleac, 2010). Then, AA monomer was added in order to combine with the radical state; then further polymerization could occur as described in Fig. 2 (Wi, 2019).

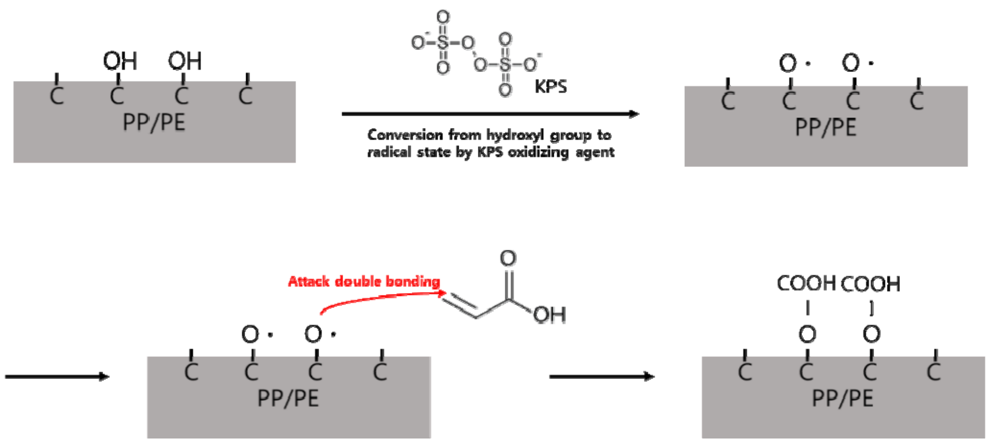

Fig. 2 Surface modification mechanism

The polymer solution for surface modification was prepared by adding 10 mL of AA and 0.06 g of KPS in 60 mL of DI water. 0.25 g of the PP/PE material was then added into the polymer solution. The polymer solution was then heated in a vacuum oven filled with nitrogen at 70°C for seven hours. After the heating step, the prepared PP/PE was then washed with a solution of water and ethanol at a ratio of 1: 1 with stirring for 24 hours. The final product was named as O_2 PP/PE-KPSAA.

2.3 Characterization

The effect of functionalization was evaluated by monitoring the changes in the functional groups on the surface using Fourier-transform infrared spectroscopy (FTIR, TENSOR27, and Bruker, Germany) recorded in the 400–4000 cm^{-1} region. A scanning electron microscope with energy dispersed spectroscopy (SEM/EDS, JSM-6700F, JEOL, and Japan) was used to visualize surface modifications as well as to analyze the chemical composition qualitatively.

2.4 Evaluation of methylene blue adsorption capacity

The adsorption test was performed to evaluate the overall adsorption capacity of O_2 PP/PE-KPSAA together with pristine PP/PE as a test control. Methylene blue was selected as model organic contaminant while manganese was selected as model heavy metal. 1 g of the PP/PEs was mixed with 50 mL of methylene blue or manganese solution with 5 mg/L of initial concentration. The pH of the solution was not adjusted, and the solution was continuously shaken at 303 K for 24 h in an agitator. The concentration of methylene blue was measured with UV-Vis spectroscopy (Libra S22, BioChrom Ltd., USA) while atomic absorption spectroscopy was used for determination of manganese ion concentration.

3. RESULT AND DISCUSSION

3.1 Grafting degree

The following equation (1) used to calculate the degree of grafting after the modification step (Lei, 2000). All materials were dried in a 24-hour oven before measuring the grafting rate.

$$\text{Grafting degree} = (W_t - W_0)/W_0 * 100\ \% \qquad \cdots\cdots\cdots\cdots(1)$$

W_t and W_0 represent the weight after and before the modification of PP/PE material. The weight before surface modification was about 0.01 g, and the weight after surface modification is 0.013 g, which showed about 30% increased mass. The increased mass was considered as the mass of grafted acrylic acid on the filter surface.

3.2 FT-IR Results

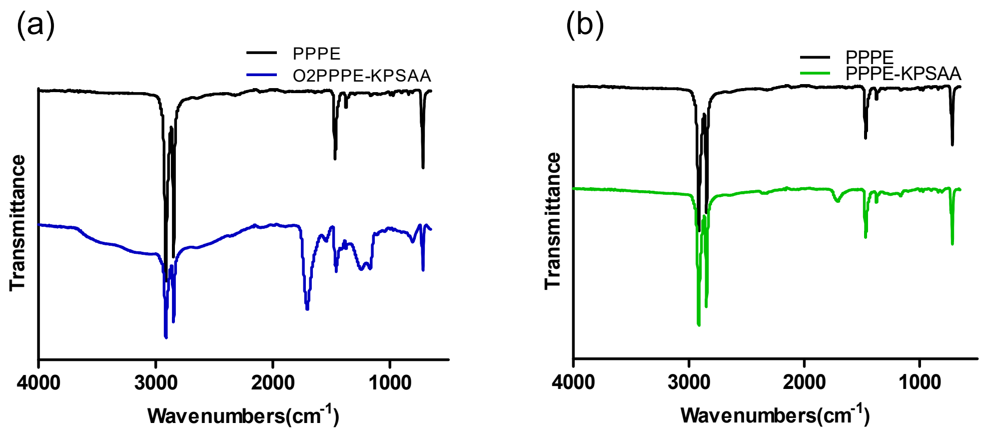

Fig. 3 (a) FT-IR spectra of pristine PP/PE (black, above) and O2 PP/PE-KPSAA (blue, below), (b) FT-IR spectra of pristine PP/PE (black, above) and PP/PE-KPSAA (green, below)

Fig. 3 (a) is the result of an analysis of pristine PP/PE and O_2 PP/PE-KPSAA using FT-IR. The pristine PP/PE showed major peaks at 2900-2700 cm^{-1} and 1440-1320 cm^{-1}, which represent the -CH group. However, a sharp peak appears at 1750-1700 cm^{-1}, which is C=O stretching of the carboxyl group. This result confirmed that the carboxylic acid groups were successfully generated by surface modification.

We also have analyzed PP/PE-KPSAA in order to confirm the effect of oxygen plasma. The PP/PE-KPSAA was prepared by acrylic acid polymerization without prior oxygen plasma treatment. The weak C=O stretching of the carboxyl group could be detected, but the intensity was much lower than O2 PP/PE-KPSAA. In this result, the effect of oxygen plasma on the surface activation, such as hydroxyl group formation, was successfully revealed.

3.3 Methylene Blue adsorption result

The methylene blue adsorption test was conducted to evaluate the adsorption performance of O_2 PP/PE-KPSAA compared to pristine PP/PE. Fig. 4 showed the color and morphology after the adsorption test. The more dark blue color was observed in Fig. 4(b), which is the O_2 PP/PE-KPSAA. The remaining methylene blue in the solution was also measured by UV-Vis, then the methylene blue removal efficiency of pristine PP/PE and O_2 PP/PE-KPSAA was 21.9% and 63.1%, respectively. The overall removal efficiency was increased almost four times, which could be explained as the advantage of surface modification.

(a) (b)

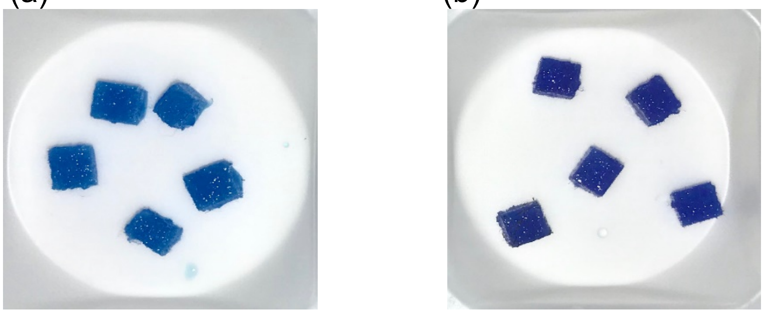

Fig. 4 The pictures of materials after adsorption, (a) pristine PP/PE, (b) O_2 PP/PE-KPSAA

4. Conclusion

In this study, we modified the commercially available PP/PE fiber filter media in order to enhance adsorption capacity for dissolved contaminants. The surface modification process combining the oxygen plasma treatment for hydroxyl group generation and the acrylic acid polymerization for carboxyl group formation was successfully developed in this study. By the surface modification process, the inert, hydrophobic PP/PE could be modified as hydrophilic O_2 PP/PE-KPSAA. The change of surface functional group was monitored by FT-IR. The adsorption capacity toward organic contaminant, methylene blue, was enhanced four times by the surface modification. ,The developed surface modification process is versatile and straightforward method to enhance overall filtration performance of commercially available polymeric filter media.

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