

Improved adsorption performance of heavy metals by surface modification of polypropylene/polyethylene media through oxygen plasma and acrylic acid

Jeongmin Hong¹, Seungwoo Lee², Dongah Ko³, Eunmi Gwon⁴ and Yuhoon Hwang^{*1}

¹Department of Environmental Engineering, Seoul National University of Science and Technology, Seoul 01811, Korea

²Department of Fine Chemistry, Seoul National University of Science and Technology, Seoul 01811, Korea

³Innovation Centre Denmark, Seoul 04637, Korea

⁴ECOSTAR Co., Ltd., Gyeonggi-do 16295, Korea

(Received November 8, 2019, Revised January 3, 2020, Accepted January 27, 2020)

Abstract. Industrialization and modern developments have led to an influx of toxic heavy metals into the aquatic environment, and the accumulation of heavy metals has serious adverse effects on humans. Among the various heavy metal treatment methods, adsorption is very useful and frequently used. Plastic materials, such as polypropylene and polyethylene, have been widely used as filter media due to their mechanical and chemical stability. However, the surface of plastic material is inert and therefore the adsorption capability of heavy metals is very limited. In this study, granular media and fiber media composed of polypropylene and polyethylene are used, and the surface modification was conducted in order to increase adsorption capability toward heavy metals. Oxygen plasma generated hydroxyl groups on the surface of the media to activate the surface, and then acrylic acid was synthesized on the surface. The grafted carboxyl group was confirmed by FT-IR and SEM. Heavy metal adsorption capability of pristine and surface modified adsorbents was also evaluated. Overall, heavy metal adsorption capability was increased by surface modification due to electrostatic interaction between the carboxyl groups and heavy metal ions. Fibrous PP/PE showed lower improvement compared to granular PP media because pore blockage occurred by the surface modification step, thereby inhibiting mass transfer.

Keywords: Polypropylene, polyethylene, oxygen plasma, acrylic acid, heavy metals

1. Introduction

Industrialization and modernization of society have adverse effects such as air, water, and soil pollution. Notably, the influx of toxic heavy metals into the aquatic environment is one of the main issues in environmental management. Heavy metals are a group of trace elements, i.e., metals and metalloids with an atomic density greater than $4 \pm 1 \text{ g/cm}^3$, such as Cu, Zn, Hg, Cd, Pb, Sn, Fe, Mn, Ag, Cr, Co, Ni, As, Al, etc. Unlike organic pollutants, heavy metals do not decompose naturally by chemical or biological processes (MoU.S.A.vi *et al.* 2018). The accumulation of heavy metals is accompanied by severe health and environmental problems (Lenz and Lens 2009). Accordingly, techniques for heavy metal removal should be investigated.

Various techniques are available for the treatment of heavy metals such as chemical precipitation, membrane filtration, adsorption, ion exchange, and photocatalysis (Wang 2005, Sharma *et al.* 2018). Among them, adsorption appears to have the most significant impact on transport, toxicity, and biological availability of heavy metals (especially at trace amounts) in aqueous media and it is also easy to operate and cost-effective (Jawed *et al.* 2020). The most commonly used adsorbents to remove heavy metals

includes sand, zeolites, and activated carbon. Such natural materials have the advantage of being easy to obtain and inexpensive, but also have the disadvantage that their properties are inhomogeneous. On the contrary, synthetic polymers, such as polypropylene (PP) and polyethylene (PE), can be shaped with various sizes and porosities. These materials also have excellent mechanical and chemical stability; long term operation of an adsorption/desorption process using acid/base thus would be possible. Due to these advantages, synthetic polymers have been used in various types of filters, such as sewage treatment plants and nonpoint pollution reduction facilities (Go *et al.* 2019, Yang *et al.* 2016). However, plastics themselves are inert to most chemicals under standard conditions and therefore the adsorption capability of heavy metals is very limited.

In this study, the surface of polypropylene granular media (PP) and polypropylene/polyethylene fiber filter media (PP/PE) was modified to enhance the adsorption capacity for heavy metals. The surface modification was performed by using oxygen plasma and acrylic acid (AA). The oxygen plasma helps to graft oxygen-containing functional groups on the surface of PP or PP/PE media. A further grafting reaction using acrylic acid polymerization was then carried out. The oxygen-containing functional groups formed by oxygen plasma were subsequently used as reaction sites for acrylic acid polymerization. FTIR and SEM analyses were performed in order to track the changes in surface modification steps. Moreover, the heavy metal removal efficiency was also evaluated.

*Corresponding author, Ph.D.
E-mail: yhhwang@seoultech.ac.kr



Fig. 1 (a) PP (b) PP/PE

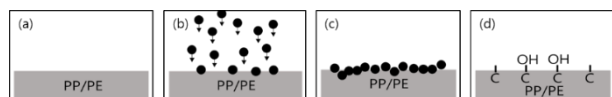


Fig. 2 Schematic illustration of the surface modification process using oxygen plasma. (a) pristine PP/PE, (b) plasma treatment, (c) after plasma treatment, (d) result of plasma treatment

2. Material and methods

2.1 Materials

Two types of media were used in this study, granular PP media and fibrous PP/PE media. Polypropylene granular media (PP) have a non-porous spherical shape with a diameter of about 2–3 mm (Fig. 1 (a)). The fibrous synthetic media composed of polypropylene and polyethylene (PP/PE) have a porosity of 92%. In order to improve the performance of the media, a uniform size of 3–4 mm was used (Fig. 1 (b)).

Acrylic acid (AA; 99%), potassium persulfate (KPS; 98%), and ethanol (99%) were purchased from Samchun (Korea) and used for surface modification. The heavy metal stock solution was purchased from KANTO (Japan) and pH buffer of NaHCO_3 was purchased from Duksan (Korea).

2.2 Surface modification of PP and PP/PE

2.2.1 Oxygen plasma

The material is plastic, which is inert and hydrophobic and has low surface free energy. (Wang 2006) With oxygen plasma, the hydrophilicity of PP and PP/PE can be improved by inducing a surface change, and adhesion is improved on the surface of the sheaf, enabling it to be combined with other materials (Lei *et al.* 2000). Oxygen plasma devices (FEMTO SCIENCE, CUTE) were used, and PP and PP/PE materials were treated by oxygen plasma for 30 seconds at 50 kHz (Yamada *et al.* 2018). The surface modification process is illustrated in Fig. 2.

2.2.2 Acrylic acid modification

Acrylic acid modification is a type of radical polymerization. In this study, potassium persulfate (KPS) was used to convert the hydroxyl groups formed in the oxygen plasma-treated PP/PE material to a radical state (Smuleac *et al.* 2010). The AA monomer was then added in order to combine with the radical state and then further polymerization could occur, as illustrated in Fig. 3 (Wi *et al.* 2019).

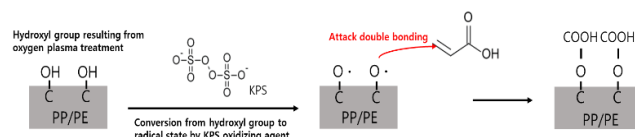


Fig. 3 Reaction mechanism of PP/PE (PP) with acrylic acid

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. Next, 0.25 g of the PP and PP/PE materials was respectively 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 and PP/PE samples were then washed with a solution of water and ethanol at a ratio of 1: 1 with stirring for 24 hours. The final products were denoted as PP-AA and PP/PE-AA.

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, Japan) was used to visualize surface modifications as well as to analyze the chemical composition qualitatively.

2.4 Evaluation of heavy metals adsorption capacity

A heavy metal adsorption test was performed to evaluate the overall adsorption capacity of PP-AA and PP/PE-AA together with pristine PP and PP/PE as a test control.

Three kinds of heavy metals, Fe, Mn, and Cd, were selected as model heavy metals. In order to simply determine whether the material is adsorbed, the following concentrations were set. Heavy metal solutions with 8 mg/L concentration and a pH range of 8–9 were prepared with 3 mM NaHCO_3 solution. The concentration of the adsorbent was 10 g/L. At a given time interval, the supernatant was collected, and the sample was filtered with a PES syringe filter. The concentration of heavy metals in the sample was measured using an atomic absorption spectrometer (Thermo Fisher Scientific, Elemental SOLAAR M6 AAS, U.S.A.).

3. Results and discussion

3.1 Change of surface functional groups

An FT-IR analysis was conducted to investigate the change of surface functional groups through surface modification. The results of the analysis of the PP (blue line) and the PP-AA (red line) modified with acrylic acid using FT-IR are shown in Fig. 4 (a), PP/PE (blue line) and PP/PE-AA (red line) are shown in Fig. 4 (b).

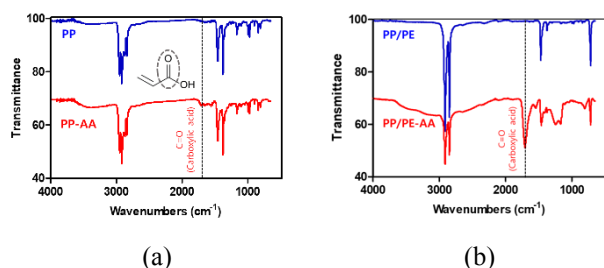


Fig. 4 Surface functional group analysis using FT-IR (a) PP-AA (b) PP/PE-AA

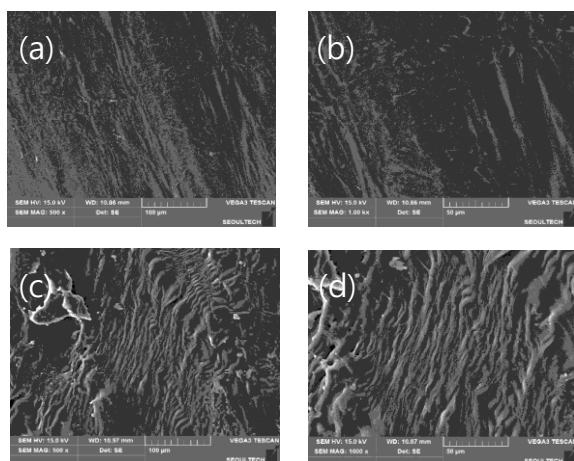


Fig. 5 SEM images of (a, b) PP, (c, d) PP-AA

The pristine PP and PP/PE showed major peaks at 2700–2900 cm^{-1} and 1430–1470 cm^{-1} , which represent the C–H group and the methyl groups, respectively. These peaks were also found in the sample after surface modification; it could therefore be confirmed that the overall structure was not changed.

However, the surface-modified samples in Figs. 4 (a) and (b) both showed a new peak at 1700–1750 cm^{-1} , and this new peak is considered to be a C=O bond in the carboxyl (–COOH) functional group formed by acrylic acid synthesis. In addition, the peak at 1050–1225 cm^{-1} shown in the PP/PE-AA is considered to be a functional group produced by the effect of acrylic acid and oxygen plasma with a C–O group. Therefore, it was confirmed that acrylic acid was successfully formed on the PP and the PP/PE surface.

3.2 Morphology of modified PP and PP/PE

Figure 5 showed the morphologies of pristine PP and PP-AA. The smooth surface was observed for pristine PP (Fig. 5 (a), (b)). On the other hand, in the case of PP-AA (Fig. 5 (c), (d)), it was possible to identify rough surfaces that were not previously observed in pristine PP. This change appeared evenly throughout the PP, and it is the result of the acrylic acid formation on the surface.

The morphological change through surface modification was monitored by SEM. Figure 6 shows the morphologies of pristine PP/PE and PP/PE-AA. The pristine PP/PE media showed typical non-woven filters with irregularly entangled fiber strands consisting of polypropylene and polyethylene

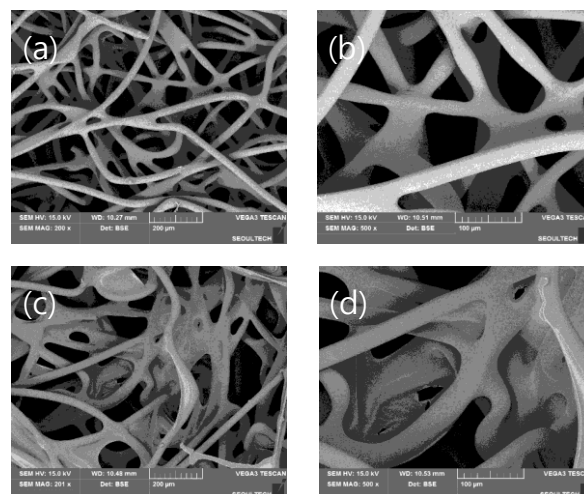


Fig. 6 SEM images of (a, b) PP/PE, (c, d) PP/PE-AA

(Figs. 6 (a) and (b)). Moreover, large voids between the fibers could be seen. In contrast, a thin layer of poly-acrylic acid was found on the surface of PP/PE-AA, and some pore blockage was also observed. As a result, the overall porosity was reduced, and the surface area could be expected to be reduced.

3.3 Heavy metal adsorption evaluation

In order to evaluate the adsorption performance improvement by surface modification, adsorption experiments were performed with selected heavy metals: Fe, Mn, and Cd. Figure 7 shows the results of heavy metal adsorption by pristine and surface modified media.

The adsorption performance improvement for PP-AA is shown in Fig. 7 (a). The removal efficiency of pure PP (white bar) was almost zero for all three heavy metals tested. On the other hand, PP-AA (gray bar) showed a Fe removal rate of 81%, an Mn removal rate of 32%, and a Cd removal rate of 94%.

The white bar in Fig. 7 (b) is the results of adsorption of pure PP/PE, and the gray bar is the results of modified PP/PE-AA. The pristine PP/PE showed removal efficiency of 74%, 28%, and 65% for Fe, Mn, and Cd, respectively. After the surface modification, the adsorption performance increased by about 12% for Fe and up to 29% for Cd, but the improvement of adsorption was not significant for Mn.

Even though the degree of increase was different for PP and PP/PE, it was clear that the adsorption performance was improved by surface modification using oxygen plasma and acrylic acid. The increased adsorption efficiency could be explained by the change of surface functional groups. Similar results have been reported for carbon-based materials, such as activated carbon, graphene, and carbon nanotubes (Bohli, 2017, Atieh, 2010, Zhao *et al.* 2011). The carboxylic acid groups were successfully formed on activated carbon or graphene by strong acid treatment, and these functionalized carbon materials showed better metal adsorption capacity due to the surface complexation between carboxylic acid groups and metal ions. The results from our study were consistent with previous reports

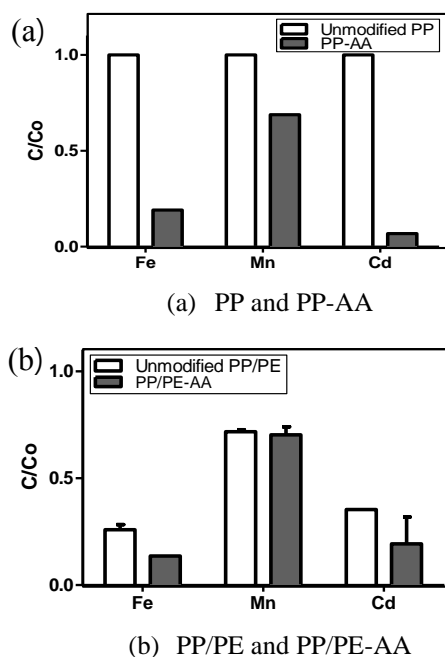


Fig. 7 Comparison of heavy metal (Fe, Mn, Cd) adsorption efficiency (metal concentration 8 ppm, absorbent dosage 10 g/L, pH 8-9)

regarding the surface functionalization of carbon-based materials.

On the other hand, the acid treatment for generating carboxylic acid groups did not work for PP or PE materials; the oxygen plasma and acrylic acid techniques reported in this study thus could be useful techniques for grafting carboxylic acid groups.

PP granular media showed more significant adsorption efficiency increased compared to PP/PE fiber media. Even though the same functionalization technique was applied for both media, the enhancement of adsorption efficiency was not similar. This is due to the different morphology of the two media, which affects the water permeability.

3.4 Adsorbed iron distribution

After the iron adsorption experiment using PP-AA and PP/PE-AA, the recovered material was denoted as Fe-PP-

Table 1 EDS element analysis of Fe-PP-AA and Fe-PP/PE-AA

Weight%	C	O	Na	Cl	Fe
Fe-PP-AA	75.99	12.97	1.29	1.24	8.51
Fe-PP/PE-AA	78.47	14.76	0.87	-	5.90

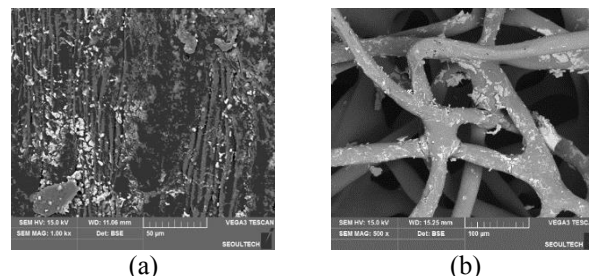


Fig. 8 SEM image of (a) Fe-PP-AA (b) Fe-PP/PE-AA

AA, Fe-PP/PE-AA, and observed using SEM and EDS. In the case of Fe-PP-AA (Fig. 8 (a)), it was confirmed that the material showing a crystalline form was irregularly attached to the uneven surface of PP-AA. Fe-PP/PE-AA (Fig. 8 (b)) also showed similar results in the SEM image.

The elemental analysis results obtained by EDS are presented in Table 1. In both Fe-PP-AA and Fe-PP/PE-AA, oxygen was detected at a high rate of about 13-15%, which is the result of carboxylic acid group formation through surface modification. Iron was also detected in both cases, indicating adsorption of iron on the media.

As described in section 3.3, the low improvement of PP/PE-AA is due to the change of permeability and specific surface area. In order to confirm the change of permeability, the adsorbed metal distribution in the media was monitored by EDS mapping (Fig. 9).

In the case of Fe-PP-AA, EDS mapping was conducted for the surface because it is not a porous medium. It was confirmed that iron was uniformly detected throughout the material surface. On the other hand, cross-sectional EDS mapping was performed for Fe-PP/PE-AA. Since Fe-PP/PE-AA is a porous medium, the permeability change can alter the overall adsorption behavior. As shown in Fig. 9, most of the iron was attached to the outside of the PP/PE-AA media, while almost no iron was detected inside of

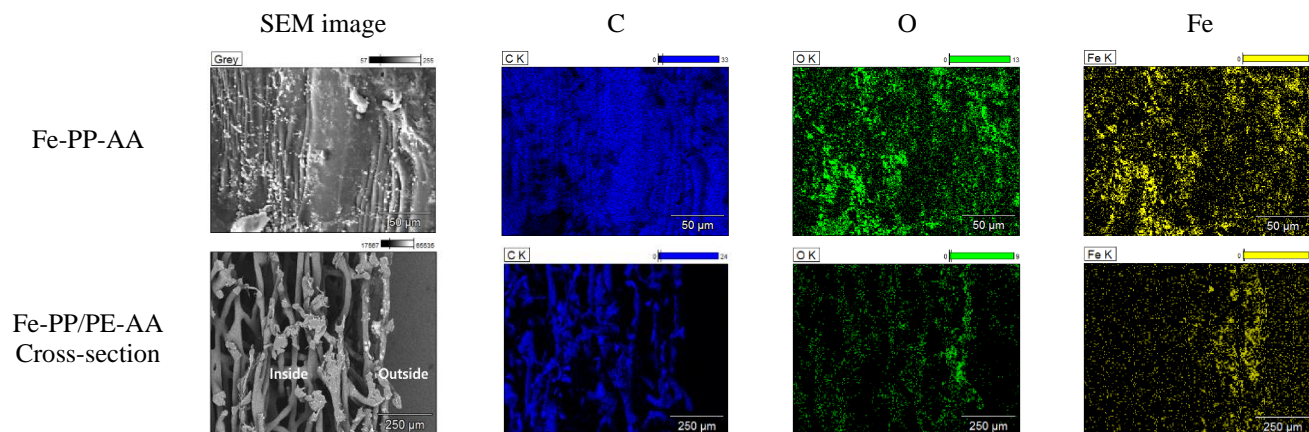


Fig. 9 EDS mapping of C, O, and Fe for Fe-PP-AA and Fe-PP/PE-AA Cross

the media. This result is consistent with the decreased porosity of PP/PE-AA monitored by SEM, as presented in Figs. 5 (c) and (d).

Overall, the results proved that the surface modification method using oxygen plasma and acrylic acid successfully functionalized carboxylic acid groups on the surface of plastic media. However, the surface modification method can also alter porosity and permeability, which can inhibit mass transfer of dissolved heavy metals. Serious consideration of this issue is thus necessary in the case of porous media.

4. Conclusion

In this study, the surface of plastic media was modified using oxygen plasma and acrylic acid in order to improve the performance of heavy metal adsorption.

- A surface modification process combining oxygen plasma treatment for hydroxyl group generation and acrylic acid polymerization for carboxyl group formation was successfully developed.

- Overall, the heavy metal adsorption efficiency of surface-modified media, PP-AA and PP/PE-AA, was enhanced compared to that of pristine media, and this was due to the interaction between carboxylic acid groups and metal ions.

- The improvement of the adsorption efficiency of PP/PE-AA was much less than that of PP-AA. This may be due to changes in permeability and specific surface area, as shown in SEM and EDS mapping images.

- The developed surface modification process is a versatile and straightforward method to enhance the overall filtration performance of commercially available polymeric filter media.

Acknowledgments

The present study was funded by the Seoul Green Environment Center (SGEC) in South Korea.

References

- Atieh, M. A., Bakather, O. Y., Tawabini, B., Al-Tawabini, B., Bukhari, A. A., Abuilaiwi, F. A., *et al.* (2010), "Effect of carboxylic functional group functionalized on carbon nanotubes surface on the removal of lead from water", *Bioinorg. Chem. Appl.*, 603978. <http://dx.doi.org/10.1155/2010/603978>.
- Bohli, T., Ouederni, A. and Villares U.S.A., I. (2017), "Simultaneous adsorption behavior of heavy metals onto microporous olive stones activated carbon: Analysis of metal interactions", *Euro-Mediterr. J. Environ. Integr.*, **2**(1), 19. <https://doi.org/10.1007/s41207-017-0030-0>.
- Genç-Fuhrman, H., Mikkelsen, P.S. and Ledin, A. (2007), "Simultaneous removal of As, Cd, Cr, Cu, Ni and Zn from stormwater: experimental comparison of 11 different sorbents", *Water Res.*, **41**, 591-602. <https://doi.org/10.1016/j.watres.2006.10.024>.
- Go, Y.S., Seo, Y.G., Lee, P.E., Hwang, Y., Kim, B. and Lee, T.J. (2019), "Pollutant removals according to media type at the filtration unit with the circulation of suspended media", *J. Korean Soc. Environ. Eng.*, **41**(5), 257-264.

- <https://doi.org/10.4491/KSEE.2019.41.5.257>.
- Jawed, A., Saxena, V. and Pandey, L.M. (2020), "Engineered nanomaterials and their surface functionalization for the removal of heavy metals: A review", *J. Water Process Eng.*, **33**, 101009. <https://doi.org/10.1016/j.jwpe.2019.101009>.
- Ko, D., Lee, J.S., Patel, H.A., Jakobsen, M.H., Hwang, Y., Yavuz, C.T., Hansen, H.C.B. and Andersen, H.R. (2017), "Selective removal of heavy metal ions by disulfide linked polymer networks", *J. Hazard. Mater.*, **332**, 140-148. <https://doi.org/10.1016/j.jhazmat.2017.03.007>.
- Lei, J., Gao, J., Zhou, R., Zhang, B. and Wang, J. (2000), "Photografting of acrylic acid on high density polyethylene powder in vapour phase", *Polym. Int.*, **49**(11), 1492-1495. [https://doi.org/10.1002/1097-0126\(200011\)49:11<1492::AID-PI538>3.0.CO;2-Q](https://doi.org/10.1002/1097-0126(200011)49:11<1492::AID-PI538>3.0.CO;2-Q).
- Lenz, M. and Lens, P.N.L. (2009), "The essential toxin: The changing perception of selenium in environmental sciences", *Sci. Tot. Environ.*, **407**, 3620-3633. <https://doi.org/10.1016/j.scitotenv.2008.07.056>.
- Lim, J.H., Stolzenbach, K.D. and Schiff, K.C. (2005), "Contribution of trace metals from atmospheric deposition to stormwater runoff in a small impervious urban catchment", *Water Res.*, **39**, 3929-3937. <https://doi.org/10.1016/j.watres.2005.07.003>.
- MoU.S.A.vi, S.J., Parvini, M. and Ghorbani, M. (2018), "Adsorption of heavy metals (Cu²⁺ and Zn²⁺) on novel bifunctional ordered mesoporous silica: Optimization by response surface methodology", *J. Taiwan Inst. Chem. E.*, **84**, 123-141. <https://doi.org/10.1016/j.jtice.2018.01.010>.
- Sharma, S., Tiwari, S., Hasan, A., Saxena, V. and Pandey, L.M. (2018), "Recent advances in conventional and contemporary methods for remediation of heavy metal-contaminated soils", *3 Biotech.*, **8**(4), 216. <https://doi.org/10.1007/s13205-018-1237-8>.
- Siriwardene, N.R., Deletic, A. and Fletcher, T.D. (2007), "Clogging of stormwater gravel infiltration systems and filters: Insights from a laboratory study", *Water Res.*, **41**, 1433-1440. <https://doi.org/10.1016/j.watres.2006.12.040>.
- Smuleac, V., Bachas, L. and Bhattacharyya, D. (2010), "Aqueous-phase synthesis of PAA in PVDF membrane pores for nanoparticle synthesis and dichlorobiphenyl degradation", *J. Membrane Sci.*, **346**(2), 310-317. <https://doi.org/10.1016/j.memsci.2009.09.052>.
- Wang, H. (2006), "Improving the adhesion of polyethylene by UV grafting", *J. Adhes.*, **82**(7), 731-745. <https://doi.org/10.1080/00218460600775815>.
- Wang, L.K., Hung, Y. and Shammass, N.K. (2005), *Physicochemical Treatment Processes*, Volume 3, Humana Press, New Delhi, India.
- Wi, H., Kim, H., Oh, D., Bae, S. and Hwang, Y. (2019), "Surface modification of poly(vinyl alcohol) sponge by acrylic acid to immobilize prussian blue for selective adsorption of aqueous cesium", *Chemosphere*, **226**, 173-182. <https://doi.org/10.1016/j.chemosphere.2019.03.101>.
- Yamada, K., Tachi, M. and Kimura, Y. (2018), "Improvement of adhesive strength of poly (tetrafluoroethylene) plates through oxygen plasma treatment and subsequent photografting of methacrylic acid", *Int. J. Mater. Sci. Appl.*, **7**(1), 18. <https://doi.org/10.11648/j.ijmsa.20180701.14>.
- Yang, S.H., Lee, M.J., Gwon, E.M. and Lee, J. (2016), "Analysis of characteristic of filtration pilot plant for combined sewer overflows treatment", *J. Korean Soc. Urban Environ.*, **16**(5), 503-509.
- Zhao, G., Li, J., Ren, X., Chen, C. and Wang, X. (2011), "Few-layered graphene oxide nanosheets as superior sorbents for heavy metal ion pollution management", *Environ. Sci. Technol.*, **45**(24), 10454-10462. <https://doi.org/10.1021/es203439v>.