



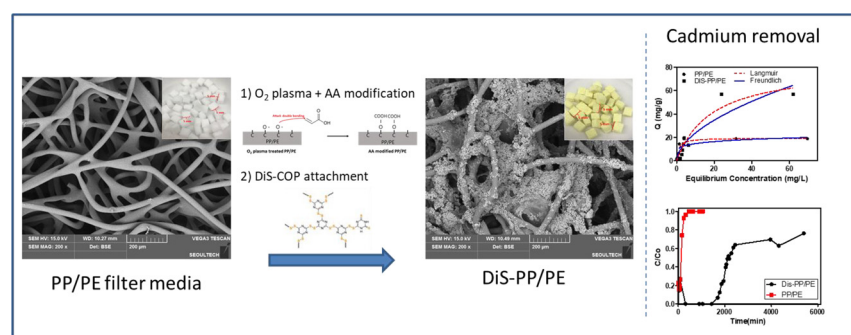
Disulfide polymer grafted polypropylene/polyethylene filter media for selective cadmium removal

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GRAPHICAL ABSTRACT



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ABSTRACT

Heavy metal pollution caused by stormwater runoff has triggered a demand for effective heavy metal sorbents. Effective heavy metal removal using conventional stormwater runoff treatment processes that employ filtration mechanisms as primary removal mechanisms is difficult. Therefore, we attempt to improve cadmium removal performance by attaching disulfide polymer (DiS-COP) containing soft bases, thiols, onto the surface of polypropylene/polyethylene (PP/PE) fiber media, which is widely used for stormwater runoff treatment. Material characterization demonstrated that DiS-COP was successfully grafted and grown on the surface of PP/PE (DiS-PP/PE). The batch and continuous flow adsorption capacities of DiS-PP/PE were 81.1 mg/g and 2.33 mg/g, respectively, which is 40 times higher than those of pristine PP/PE. Applicability of DiS-PP/PE at pH 6–8 was demonstrated, and effects of calcium and humic acid on cadmium adsorption were investigated. Calcium marginally affected cadmium adsorption, which can be explained using the Hard and soft (Lewis) acids and bases theory (HSAB), but cadmium removal efficiency decreased owing to humic acid (HA)-Cd complex formation and agglomeration in the presence of organic material. In a breakthrough test, the adsorption column exhibited complete cadmium uptake over 24 h until it reached the breakthrough point. Therefore, heavy metal adsorption performance of PP/PE was successfully enhanced by grafting DiS-COP on its surface.

1. Introduction

Owing to climate change, precipitation and its intensity are

increasing over the long term (Lenderink and van Meijgaard, 2008). In addition, the amount of rainfall discharged directly into rivers is increasing because of an increase in the impermeable area due to

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urbanization (Miller et al., 2014). The contaminants deposited on impervious surfaces are discharged with stormwater runoff, and this is a major cause of deterioration in water quality in urban areas (Zafra et al., 2017). Stormwater runoff is one of the most important nonpoint pollutant sources, especially in urban areas. Stormwater runoff collects and carries away natural and anthropogenic pollutants and eventually deposits them into lakes, rivers, wetlands, coastal waters, and groundwater. Generally, runoff is generated in irregular bases which occurs high fluctuation in quantity and quality of water.

This characteristics of stormwater make it difficult to manage the pollutants in water by using existing treatment processes. Especially, road runoff often contains heavy metals in excess of surface water quality standards (Göbel et al., 2007). Unlike organic pollutants, heavy metals are persistent and can not be decomposed by any types of natural processes such as chemical and biological mechanisms (Mousavi et al., 2018). Heavy metal accumulation is accompanied by severe health and environmental problems (Lenz and Lens, 2009). The acute toxicity and carcinogenic effects of heavy metals in aquatic environments have led to an increased interest in the treatment of stormwater runoff containing heavy metals (Genç-Fuhrman et al., 2007). Several research studies have found significant levels of heavy metals such as Cd, Cu, Pb, Ni, Cr, and Zn in urban stormwater, which poses harm to public health and the environment. Concentrations of heavy metals in stormwater runoff vary highly between locations. For example, high levels of Pb concentration was reported from the painted structure (Davis and Burns, 1999), while high levels of Cd concentration was reported from the airport site and deicing fluid (Wang et al., 2016; Ko et al., 2018a). Moreover, the source of each heavy metal was also investigated. It was reported that Cu was originated from vehicle brakes, while Pb, Cu, Cd, and Zn was attributed to building siding runoff (Davis et al., 2001). Most researches on rainfall-runoff have been conducted mainly on copper, zinc, and lead, and studies on cadmium are insufficient.

Nonpoint source pollution abatement facilities include retention ponds, buffer strips, constructed wetlands, and filtration facilities. Most stormwater filtration facilities employ granular media, such as sand (Ahn et al., 2017), gravel (Siriwardene et al., 2007), zeolite (Kim et al., 2010), and activated carbon (Sounthararajah et al., 2016). Such natural materials are easy to obtain and inexpensive, but their chemical and morphological properties are not well controlled. By contrast, synthetic polymers, such as polypropylene (PP) and polyethylene (PE), can be shaped to have various sizes and porosities. Moreover, these materials have excellent mechanical and chemical stabilities, because of which they can be used in long-term adsorption/desorption processes that employ acids or bases. Owing to these advantages, synthetic polymers have been used in various types of filtration plants, 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, their capacity to adsorb heavy metals is very limited. Hence, it is important to devise methods that can enhance the heavy metal adsorption performance of synthetic filter media.

In a previous study, we successfully developed a disulfide-linked polymer network containing a thiol group bonded to a triazine ring, which exhibited superior cadmium-removal performance (Ko et al., 2017). According to the hard and soft (Lewis) acids and bases (HSAB) theory, disulfide polymer compounds exhibit high adsorption affinity towards Lewis acid heavy metal ions in the presence of earth metals (LoPachin et al., 2012). The disulfide polymer (DiS-COP) used in this study, which is a porous network of organic molecules interconnected with covalent bonds between monomers, exhibits significant selectivity toward cadmium (Ko et al., 2018a). However, DiS-COP was synthesized in powder form, and in this form, it can induce high back-pressure in the water filtration column. Therefore, a methodology to immobilize DiS-COP on the supporting materials must be developed. In previous studies, we attempted to immobilize DiS-COP on granular activated

carbon (Ko et al., 2018b) and alginate beads (Ko et al., 2018a), but these substrates, too, have inhomogeneous properties.

In this study, we develop a methodology to graft DiS-COP on the surface of polypropylene/polyethylene fiber filter media (PP/PE). The PP/PE filter media is currently using for stormwater runoff management facilities. The porous nature of the PP/PE filter media and their low density provided advantages on operating filtration system using floating media. Many types of media have been used in stormwater filtration. However, it was reported that fibrous media are a potentially promising alternative in stormwater filtration due to high porosity and high surface area, which can lead to high solids removal efficiency, less head loss, high filtration velocity, deep bed filtration behavior by the migration of solids in the media layer (Lee et al., 2010). Moreover, it was reported that the floating media filter has several advantages compared to conventional media filtration, such as lower energy and water requirement for backwashing, small land area, lower headloss development (Al-Fatlawi and Al-Mamori, 2017). Those advantages are mainly due to that the backwash can be done entirely on gravity force and the difference in water levels. Because of these advantages, floating filter media is widely used in stormwater filtration devices. In this study, we used a PP/PE fibrous filter media; therefore, it could be expected that the advantages of fibrous filter media as well as that of floating filter media.

This surface modification is achieved using oxygen plasma and acrylic acid (AA) to provide a reaction site for the further synthesis of DiS-COP. The characteristics of DiS-COP grafted on PP/PE (DiS-PP/PE) are evaluated with Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS), thermogravimetric analysis (TGA), and elemental analysis. The cadmium adsorption performance of DiS-PP/PE was evaluated in relation to that of pristine PP/PE. The effects of pH and competitive ions were investigated as well. Finally, a continuous column experiment was conducted to verify whether DiS-PP/PE can be used in stormwater filtration devices.

2. Materials and methods

2.1. Materials

Fibrous synthetic media composed of polypropylene and polyethylene (PP/PE), which were used in this study, have a porosity of 84 % and an apparent specific gravity of 0.06. The average pore diameter was determined to be 98 μm . The PP/PE media was supplied from Ecostar co. (Korea). The size of the media was 5 mm $\times$ 5 mm $\times$ 3 mm. Acrylic acid (AA, 99 %), potassium persulfate (KPS, 98 %), and ethanol (99 %) were purchased from Samchun (Korea) and used to modify the surface of PP/PE with acrylic acid. Thionyl chloride (99 %; Samchun, Korea), dichloromethane (DCM, 99.5 %; Samchun, Korea), and 2-propanol (99.5 %; Samchun, Korea), dimethylformamide (DMF, 99.5 %; Daejung, Korea), NN-diisopropylethylamine (DIPEA, 99.0 %; Samchun, Korea), potassium iodide (KI, 99.5 %; Daejung, Korea), cysteamine (98 %; Sigma-Aldrich, USA), and trithiocyanuric acid (95 %; Sigma-Aldrich, USA) were used for grafting DiS-COP on PP/PE. Cadmium standard solution (1000 ppm; KANTO, Japan), humic acid (Sigma-Aldrich, USA), NaHCO_3 (99 %; Samchun, Korea), and CaCl_2 (96 %; Samchun, Korea) were used in the cadmium adsorption experiments.

2.2. Preparation of disulfide polymer grafted PP/PE (DiS-PP/PE)

2.2.1. Oxygen plasma and acrylic acid

The PP/PE media itself is plastic. It is inert, hydrophobic, and has low surface free energy (Wang, 2006). Oxygen plasma treatment was performed to introduce functional groups, such as hydroxyl groups or carboxyl groups, on the PP/PE surface. The surface change induced by oxygen plasma improved the hydrophilicity and adhesion of the PP/PE surface, as well as its ability to chemically react with other materials

(Lei et al., 2000). PP/PE were treated with oxygen plasma for 30 s at 50 kHz by using oxygen plasma devices (CUTE, Femto Science, Korea) (Yamada et al., 2018).

Furthermore, the acrylic acid modification was performed to convert the hydroxyl groups formed in the oxygen plasma-treated PP/PE to carboxyl groups, which would act as reaction sites for subsequent DiS-COP grafting. The overall reaction scheme was similar to that presented in our previous study on acrylic acid modification of cellulose filters (Kim et al., 2019). In brief, the polymer solution for surface modification was prepared by adding 10 mL of AA and 0.06 g of KPS to 60 mL of deionized water. Then, 0.25 g of PP/PE was added into the polymer solution. The polymer solution was then heated in a vacuum oven filled with nitrogen at 70 °C for 7 h. After the heating step, the prepared PP/PE samples were washed using a solution containing water and ethanol in a ratio of 1:1 accompanied by stirring for 24 h. The final product was denoted PP/PE-O₂+AA.

2.2.2. Disulfide polymer attachment

The procedure for grafting DiS-COP on PP/PE-O₂+AA is essentially similar to the procedure for grafting DiS-COP on granular activated carbon (Ko et al., 2018b). It was conducted in three steps, namely acyl chlorination, linear thiol attachment, and disulfide-linked polymer grafting. Firstly, acyl chlorination was realized by stirring PP/PE-O₂+AA in dichloromethane, accompanied by the gradual addition of thionyl chloride to the solution in N₂ atmosphere to prevent hydrolysis of the newly formed acyl chloride groups. The solution was mixed under reflux for 24 h at 35 °C. Subsequently, the solvent was evaporated using a rotary evaporator in 200 mbar vacuum, followed immediately by the linear thiol attachment step (PP/PE-Cl).

Thiol attachment was achieved by adding a mixture of 2 mmol of cysteamine dissolved in 180 mL of dimethylformamide to the PP/PE-Cl, followed by dropwise addition of 5.6 mmol of *N,N*-diisopropylethylamine to obtain PP/PE-SH (PP/PE-SH). After stirring for 24 h at 80 °C, the PP/PE-SH was dried in vacuum at 80 °C for 12 h and re-dispersed in 150 mL of sodium hydroxide solution with 3 mmol of trithiocyanuric acid for the final step. A strong oxidant containing excess iodine and potassium iodide was added dropwise into the mixture, and the mixture was maintained at 0 °C until it became a homogeneous solution. Then, the resulting homogenous solution was stirred overnight at room temperature. Finally, the surface-modified composite (DiS-PP/PE) was obtained and dried at 80 °C in a vacuum oven.

2.3. Characterization

The changes in the surface functional groups after the modification were analyzed with FTIR (TENSOR 27, Bruker, Germany) in the range of 400–4000 cm⁻¹. SEM-EDS (TESCAN VEGA3, Tescan Orsay Holding, Czech Republic) was used to visualize the surface modifications and to analyze the chemical composition of the synthesized material qualitatively. TGA (Discovery TGA, TA Instruments, USA) was performed to evaluate the robustness and thermal stability of the synthesized material. In addition, the composition of the material was determined using an element analyzer (Vario Macro Cube, Elementar, Germany). The porosity and pore size distribution was obtained by pore size analyzer (AutoPore IV 9500, Micromeritics, USA).

2.4. Cadmium adsorption batch test

2.4.1. Adsorption kinetics

The adsorption kinetics of cadmium were evaluated by conducting a batch test with an initial cadmium concentration of 5 mg/L. First, 50 mL of 5 mg/L cadmium solution mixed with 3 mM of NaHCO₃ buffer was placed in conical centrifuge tubes, and the pH of this solution was adjusted to 8 by adding 0.1 M HCl and 0.1 M NaOH. Then, 10 mg of DiS-PP/PE was added to the solution, and the solution was sampled at 2, 10, 60, 240, 1080, 1440 min, while the conical tubes were

continuously stirred by using a vertical stirrer operated at 20 rpm. At the aforementioned time intervals, 1.5 mL of the solution was sampled, and acidified with 1% HNO₃. The cadmium concentrations of the filtrates were determined using an atomic absorption spectrophotometer (Elemental SOLAAR M6 AAS, USA).

The adsorption kinetics were evaluated by applying the following pseudo first-order (Eq. 1) and pseudo second-order kinetic equations (Eq. 2) (Ko et al., 2017).

$$q_t = q_e(1 - e^{-k_1 t}) \quad (1)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (2)$$

where q_t is the quantity adsorbed at time t (mg/g), q_e is the equilibrium concentration (mg/g), k_1 is the first-order rate constant (1/min), and k_2 is the second-order rate constant (g/mg min).

2.4.2. Adsorption isotherm

The adsorption isotherms were determined using different cadmium concentrations and different DiS-PP/PE doses. The tests were conducted by following the procedure described in section 2.4.1, but the sampling intervals were changed to 0 h and 24 h. Cadmium concentrations were determined as described in section 2.4.1.

Adsorption isotherm data were fitted using the Langmuir (Eq. 3) and the Freundlich (Eq. 4) isotherms (Foo and Hameed, 2010).

$$q_e = q_m \frac{a_L C_e}{1 + a_L C_e} \quad (3)$$

$$q_e = K_F C_e^{1/n} \quad (4)$$

where q_e is the quantity of adsorbate adsorbed per unit weight of solid adsorbent, q_m the maximum adsorption capacity of the adsorbent (mg/g), C_e the equilibrium concentration of the adsorbate in solution (mg/L), and a_L the Langmuir affinity constant. K_F and $1/n$ are constants indicating the adsorption capacity and adsorption intensity, respectively.

2.4.3. Effect of pH

It was reported that the pH of rainwater runoff in urban areas fluctuates within the range of 6–8 (Jeng et al., 2005). The effect of pH (6–8) on cadmium adsorption onto DiS-PP/PE was scrutinized by following the experimental procedure described in section 2.4.2. The initial cadmium concentration and DiS-PP/PE dosage were set to 10 mg/L and 0.2 g/L, respectively. The pH was adjusted to the desired level by adding 0.1 M HCl and 0.1 M NaOH. A sample was taken at 24 h, and its cadmium concentration was determined as described in section 2.4.1.

2.4.4. Competitive adsorption with calcium and humic acid

The effects of calcium ions and humic acid were evaluated using the experimental procedure described in section 2.4.2. Representatively, calcium ions were selected for cations, and humic acids were selected for organics because those compounds were commonly detected in stormwater runoff (Zhang et al., 2013; Rangsvik and Jekel, 2005a). The initial cadmium concentration and DiS-PP/PE dosage were set to 10 mg/L and 0.2 g/L, respectively. Calcium and humic acid were added to achieve initial concentrations of 10–100 mg/L. The solution pH was adjusted to 8. A sample was taken at 24 h, and its cadmium concentration was determined as described in section 2.4.1.

2.5. Regeneration

The following experiment was conducted to evaluate whether the DiS-PP/PE adsorbing cadmium ions are recyclable. The adsorbent was added into a 5 mg/L cadmium solution at a concentration of 1 g/L, and the adsorbent was separated from the solution after achieving the adsorption equilibrium. The regeneration was performed by 0.05 M HNO₃

solution. After cadmium was eluted from the spect adsorbent, cadmium adsorption experiments were conducted under the same conditions using the regenerated adsorbent. Regeneration and adsorption were carried out three times. The initial pH of all experiments was set to 8, and the reaction time for adsorption and desorption was 24 h, respectively.

2.6. Column experiment

The adsorption column consisted of a Pyrex glass tube having an inner diameter of 2 cm and a height of 20 cm (Fig. 2). Sea sand was used to create inert filling layers, and DiS-PP/PE was placed between the sand layers (the thickness of the DiS-PP/PE layer: 5 cm). The flow rate of the cadmium solution was controlled to 0.5 mL/min by using a peristaltic pump, leading to an empty bed contact time of 31.4 min. The initial cadmium concentration was set to 0.5 mg/L, and the solution pH was adjusted to 8. Samples were frequently collected using a fraction collector.

3. Results and discussion

3.1. DiS-PP/PE characterization

3.1.1. The functional group of DiS-PP/PE

Changes in functional groups during DiS-PP/PE synthesis were evaluated by analyzing the FTIR spectra of pristine PP/PE, PP/PE-O₂, PP/PE-AA, PP/PE-O₂ + AA and DiS-PP/PE, as shown in Fig. 3. Pure PP/PE (blue line) exhibited major peaks at 2700–2900 cm⁻¹ and 1430–1470 cm⁻¹, which correspond to CH groups and methyl groups, respectively (–Zhang et al., 2016); these peaks were attributed to the chemical structures of PP and PE.

PP/PE-O₂, O₂ plasma irradiated PP/PE, did not show any significant change in FTIR spectra. It is well known that the O₂ plasma can attach an oxygen functional group temporarily. On the other hand, PP/PE-AA, acrylic acid treated PP/PE, showed a slight increase of peak at 1700–1750 cm⁻¹, and this peak was considered a C=O bond in the carboxyl (–COOH) functional group formed during acrylic acid synthesis (Kim et al., 2019).

PP/PE-O₂ + AA, acrylic acid treated PP/PE after O₂ plasma irradiation, exhibited a clear peak at 1700–1750 cm⁻¹. In addition, the peaks at 1050–1225 cm⁻¹ and 1200–1400 cm⁻¹, which correspond to C–O and O–H binding, respectively, were considered a functional group grafted owing to the effects of acrylic acid and oxygen plasma (Gao et al., 2019). In these results, it could be seen that the combination of oxygen plasma and acrylic acid showed a synergistic effect. Oxygen plasma generated hydroxyl groups on the surface of the media to activate the surface, and then acrylic acid was synthesized on the surface.

In the case of DiS-PP/PE (green line), the intensity of the C=O peak was lower than that in the case of PP/PE-AA, indicating that the carboxyl group acted as a reaction point for DiS–COP synthesis, as presented in Fig. 1. The FTIR spectra exhibited a peak in the range of 2899–3136 cm⁻¹, which corresponded to N–H stretching in triazine groups. The three strong peaks at 1466, 1230, 825 cm⁻¹ corresponded to aromatic trithiol stretching in the polymer, reflecting the formation of a disulfide polymer. The peak at 1119 cm⁻¹ represented C=S stretching in DiS–COP (Ko et al., 2017).

3.1.2. Morphology of DiS-PP/PE

The morphological changes resulting from DiS–COP grafting were observed using photographs and SEM-EDS. Fig. 4 highlights the visual changes in DiS-PP/PE. Pristine PP/PE was initially white, and its color changed to yellow owing to the grafting of DiS–COP.

Fig. 5 shows SEM images of pristine PP/PE, PP/PE-O₂ + AA, and DiS-PP/PE. Pristine PP/PE appeared similar to typical non-woven filters with irregularly entangled fiber strands consisting of polypropylene and polyethylene (Fig. 5 (a)). By contrast, a thin layer of poly-acrylic acid

was formed on the surface of PP/PE-O₂ + AA, and a few pore blockages were observed as well (Fig. 5 (b)). In the case of DiS-PP/PE (Fig. 5 (c)), DiS–COP particles were attached to the fiber network. The pores blocked with acrylic acid disappeared, and DiS–COP particles adhered to the region in which the acrylic acid layer was located. In the process of polymer synthesis, the carboxyl group of acrylic acid acted as a reaction site, and acrylic acid itself dissolved and disappeared.

3.1.3. TGA analysis

TGA was conducted to determine the thermal stability and the DiS–COP content of the synthesized material (Fig. 6). The weights of both PP/PE and DiS-PP/PE decreased by 98–99 % as the temperature increased from 40 °C to 900 °C, which is consistent with the chemical natures of PP and PE. An apparent difference between PP/PE and DiS-PP/PE was observed in the temperature range of 250–350 °C, which was ascribed to polymer thermal degradation. DiS-PP/PE exhibited weight loss before PP/PE, and the weight difference was approximately 5.4 %. Therefore, we concluded that the DiS–COP content in DiS-PP/PE was 5.4 %.

3.2. Adsorption kinetics and isotherm of DiS-PP/PE

3.2.1. Adsorption kinetics

Adsorption kinetic experiments were performed to investigate cadmium adsorption kinetics on the adsorption material, as shown in Fig. 7 (a). The adsorption efficiencies of DiS-PP/PE and PP/PE within 24 h differed significantly. DiS-PP/PE removed 70 % of the total cadmium. By contrast, PP/PE removed only 33 % of the total cadmium. This indicates the high adsorption performance of DiS-PP/PE. The removal data were used for kinetics fitting according to pseudo first-order kinetics (Eq. (1)) and pseudo second-order kinetics. Both kinetics models exhibited good fits with the data, as indicated by the respective correlation coefficients. Within 32 min of contact time, half of the initial cadmium was adsorbed onto DiS-PP/PE at a loading of 0.2 g/L. This result indicated the high adsorption tendency of DiS-PP/PE compared to that of PP/PE in terms of removal capacity and removal kinetics. The kinetic constants were considerably higher than those reported in a similar study conducted using granular activated carbon as the supporting material. The DiS–COP-grafted granular activated carbon (DiS-AC) exhibited a half-life of 53 min with a loading of 2 g/L and an initial cadmium concentration of 0.2 mg/L (Ko et al., 2018b). The fast kinetics obtained in DiS-PP/PE was due to overall structural differences between PP/PE and GAC. The GAC was well known to have microporous nature, while the PP/PE has a large pore size produced by its fibrous structure. The average pore size of PP/PE and GAC was 98 μm and 15.6 nm, respectively. The porosity of PP/PE, 84 %, was also much higher than that of GAC, 24 %. The large size pore allowed faster mass transfer than microporous GAC; therefore, high kinetic could be expected. In addition, rapid cadmium adsorption occurred for 60 min, followed by gradual adsorption, and adsorption equilibrium was reached after 24 h. Based on these results, we set the duration of the isothermal adsorption experiment in this study to 24 h.

3.2.2. Adsorption isotherm

The Langmuir and Freundlich isotherms were fitted onto the cadmium adsorption plots of PP/PE and DiS-PP/PE (Fig. 7(b)). The parameters, along with the correlation coefficients, are listed in Table 1. The Langmuir isotherm yielded a superior fit than the Freundlich isotherm, which indicated that monolayer adsorption through chemical interactions was the primary adsorption mechanism. The maximum adsorption capacity of DiS-PP/PE was calculated to be 81.1 mg/g, which was approximately 4.1 times higher than that of PP/PE (19.6 mg/L). Moreover, the obtained Q_m was higher than the values reported in previous studies. The maximum adsorption capacity of the DiS–COP-embedded alginate beads (DiS-algi) was 22.4 mg/g (Ko et al., 2018a), and the reported Q_m values of commercial carbonaceous materials (activated

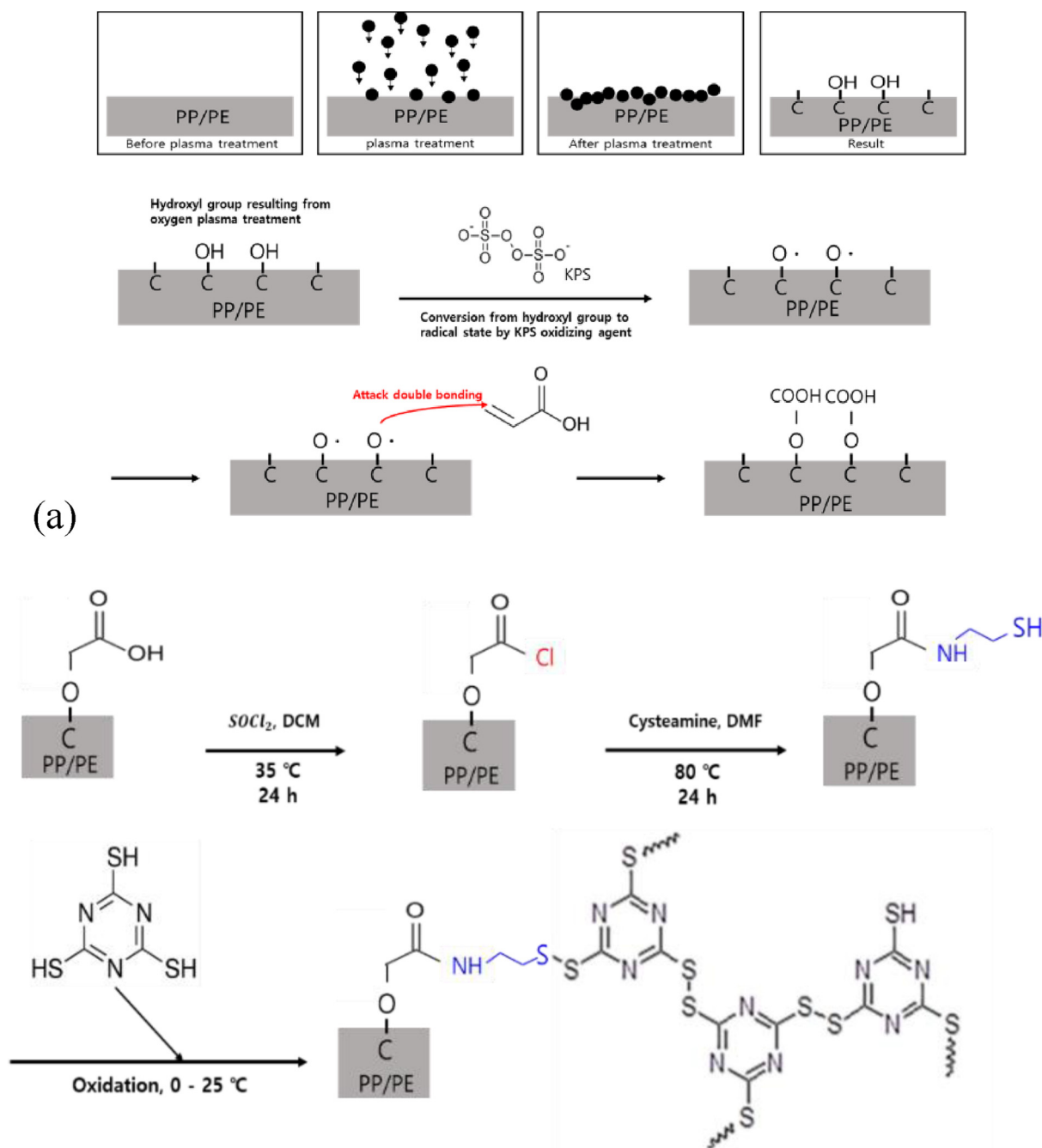


Fig. 1. (a) Scheme of oxygen plasma and acrylic acid modification, and (b) scheme of disulfide polymer attachment.

carbon, coal, or coconut shell) were 0.215–11.98 mg/g (Genç-Fuhrman et al., 2007; Ko et al., 2017; Wasewar et al., 2010; Bhattacharya Arun and Venkobachar, 1984). These results confirmed that the DiS-PP/PE synthesized in this study offers superior cadmium adsorption performance than the existing materials.

3.2.3. Adsorption mechanism

Additionally, the FTIR analysis was conducted for spent DiS-PP/PE in order to investigate the reaction mechanism. The FTIR spectra of new and spent DiS-PP/PE are presented in Fig. 8 (a). The peak located at 1119, 1230, 1466 cm^{-1} , indicating C=S stretching as well as aromatic trithiol stretching, was decreased after cadmium adsorption. This result clearly showed the cadmium was chemically bound to the disulfide and dangling thiols in the polymer. SEM/EDS analysis was also conducted to the distribution of Cd after adsorption test (Fig. 8 (b)). The EDS

mapping image showed that cadmium was detected in the same spot where sulfur was detected.

The overall batch test results, including isotherm and kinetic tests, DiS-PP/PE showed superior adsorption performance compared to pristine PP/PE. It is due to the disulfide and dangling thiols in the polymer, which has a high affinity to attract soft acid metal ions, cadmium, based on HSAB theory (LoPachin et al., 2012). Moreover, the strong coordination capability of backbone structure $\text{C}_3\text{N}_3\text{S}_3$ with transition metal ions explains the exceptional adsorption ability of DiS-PP/PE (Zhuang et al., 2015). The morphological analysis results support the interaction between the disulfide functional group and cadmium.

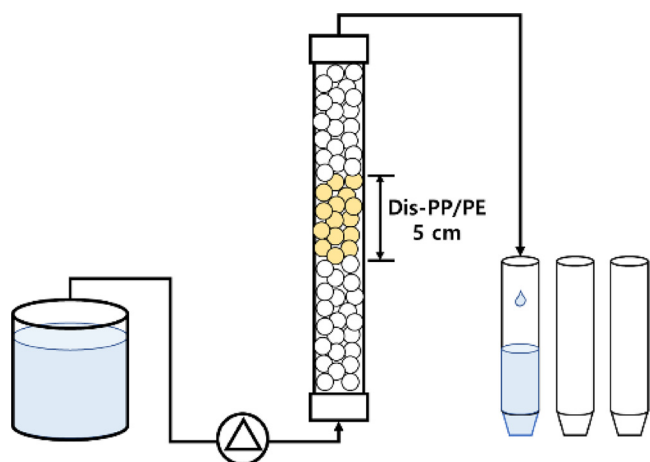


Fig. 2. Schematic diagram of the experimental setup used for continuous cadmium adsorption on DiS-PP/PE.

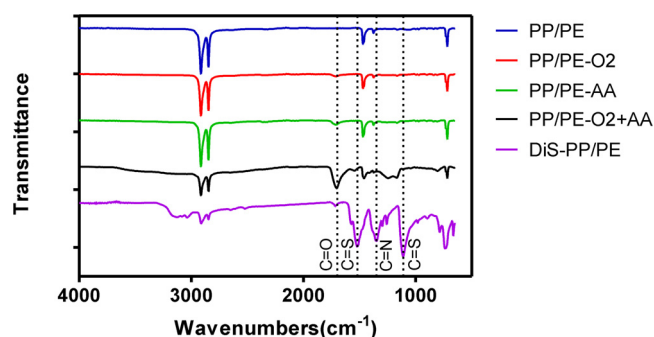


Fig. 3. Surface functional group analysis of PP/PE (blue line), PP/PE-O₂ (red line), PP/PE-AA (green line), PP/PE-O₂+AA (black line), and DiS-PP/PE (purple line) by using Fourier transform infrared spectroscopy.

3.3. Effects of pH and competitive ions

The effects of pH on cadmium adsorption and active adsorption sites are shown in Fig. 9(a). The percentages of cadmium removal at the initial cadmium concentration of 10 mg/L were 66.7 %, 66.7 %, and 95.6 % at pH 6, 7, and 8, respectively. pH 8 was found to be the most conducive condition for cadmium adsorption, and at this pH, the cadmium removal rate was approximately 30 % higher than that at other pH values. DiS-COP exhibited the lowest zeta potential of -32.4 to -33.7 mV at pH 6–8 (Ko et al., 2017). Therefore, it can be expected to have a higher cadmium adsorption efficiency under these pH

conditions. Moreover, the highest cadmium adsorption performance was reported at pH 8. At lower pH values, significant competition between H⁺ and metal cations for the binding site was observed, which decreases adsorption efficiency (Genç-Fuhrman et al., 2016). Notably, the pH of stormwater runoff from urban areas fluctuates within the range of 6–8 (Jeng et al., 2005).

Other major cations, such as calcium and magnesium, competes for sorption with cadmium, thus reducing the efficiency of the adsorbent for heavy metal binding in many types of wastewaters (Uwamariya et al., 2016). In this light, to enhance the adsorption efficiency for cadmium in real treatment applications, a sorbent must not only have sufficient adsorption capacity and fast adsorption kinetics but also high selectivity for the target metal ions. Therefore, selective metal adsorption studies in the presence of competitive cations were conducted to demonstrate the selectivity of DiS-PP/PE.

In this study, we investigated the inhibitory effect of competitors on cadmium adsorption. Calcium and humic acid were selected as one of the most abundant divalent cations and a model organic matter, respectively. Both materials have been reported to be commonly present in stormwater (Zhang et al., 2013; Rangsvik and Jekel, 2005a). Fig. 9(b) exhibits the inhibitory effects of calcium and humic acid at different concentrations on cadmium adsorption.

When only cadmium was present in the water, its removal rate was approximately 95.2 %, and a high cadmium removal rate (81 %) was maintained when calcium was added at the concentrations of 10 and 100 mg/L. This result can be explained using the HSAB theory. DiS-COP is a soft base material that has a strong affinity toward soft acidic materials, such as cadmium (Ko et al., 2017). These soft materials have higher polarizability, because of which electron distortion tends to contribute more to affinity. However, calcium is known to be a hard acidic material (Pearson, 1968). Therefore, high selectivity toward cadmium was maintained.

By contrast, a significant decrease in the removal rate was observed when the humic acid was added. Cadmium removal decreased to 52.0 % with the addition of humic acid at the concentration of 10 mg/L, and it further decreased to 4.1 % with the addition of humic acid at the concentration of 100 mg/L. It has been reported that the organic materials can interfere with cadmium removal through the formation of HA-Cd complexes at pH 3.5–8 (Genç-Fuhrman et al., 2016; Park et al., 2017). At low concentrations of organic materials, HA-Cd complexes are adsorbed on the adsorbent as monomers, but as the concentration of organic matter increases, the HA-Cd monomers are likely to aggregate and precipitate (Rangsvik and Jekel, 2005b).

3.4. Regeneration

The spent DiS-PP/PE was regenerated using 0.05 M HNO₃, and the cadmium adsorption efficiency after regeneration was evaluated

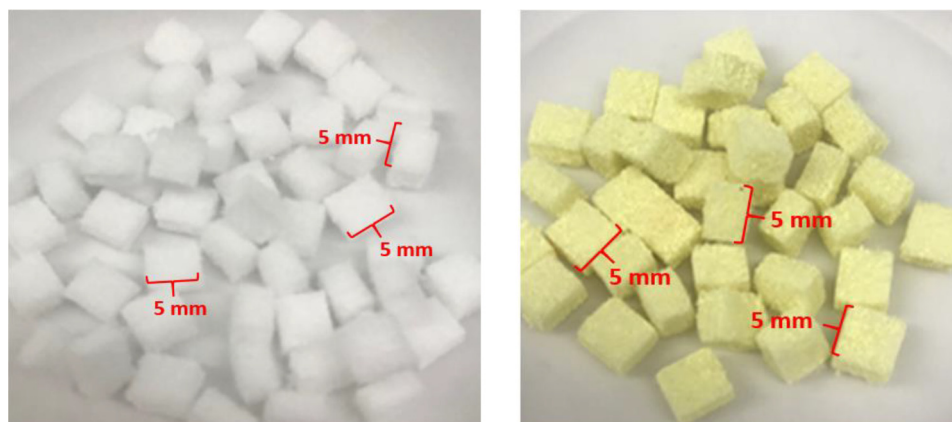


Fig. 4. PP/PE fiber media (left), and DiS-PP/PE fiber media (right).



Fig. 5. SEM images of (a) PP/PE, (b) PP/PE-AA, and (c) DiS-PP/PE.

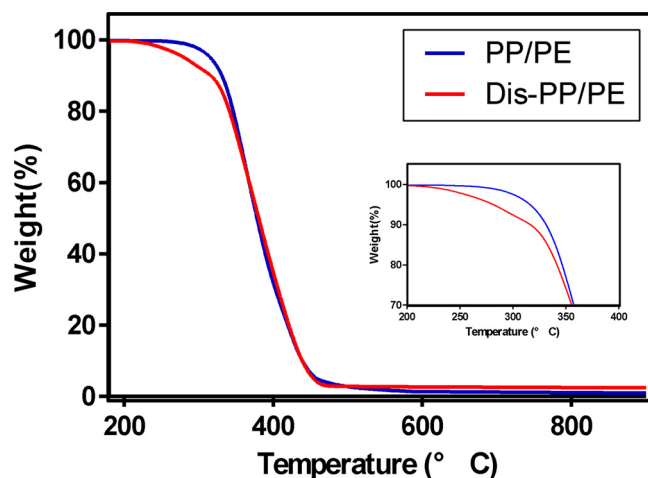


Fig. 6. TGA results of PP/PE and DiS-PP/PE.

(Fig. 10). New DiS-PP/PE showed 95 % removal efficiency, while the removal efficiency was slightly decreased after regeneration. However, around 84 % of removal efficiency was obtained after three times of regeneration, which proved the reusability of DiS-PP/PE. The physical morphology of DiS-PP/PE was also not observed. The use of HNO_3 as a regeneration agent was proved to be effective, due to the effective dissolution of attached cadmium by ion exchange with H^+ ion (Ghasemi et al., 2017).

3.5. Column test

A continuous adsorption experiment involving DiS-PP/PE was conducted to evaluate the practical applicability of DiS-COP as a water filtration material for cadmium adsorption. The initial cadmium concentration was set to 0.5 mg/L, and the flow rate was set to 0.5 mL/min, resulting in an empty bed contact time of 31.4 min.

In the case of pristine PP/PE, the cadmium concentration in the effluent increased rapidly immediately after the commencement of column operation, and cadmium removal reached 0% after only 4 h of column operation (Fig. 11). By contrast, in the case of DiS-PP/PE, almost complete cadmium removal was achieved in the first 24 h of column operation. Thereafter, the effluent concentration increase gradually, and at the end of the column operation (90 h), the cadmium removal efficiency was approximately 24 %.

The quantity of cadmium adsorbed during column operation was calculated based on the area above the adsorption curve. The quantities adsorbed with DiS-PP/PE and PP/PE were 2.33 Cd mg/g and 0.096 Cd mg/g, respectively, which indicates that the cadmium adsorption capacity of DiS-PP/PE was 24 times higher than that of pristine PP/PE.

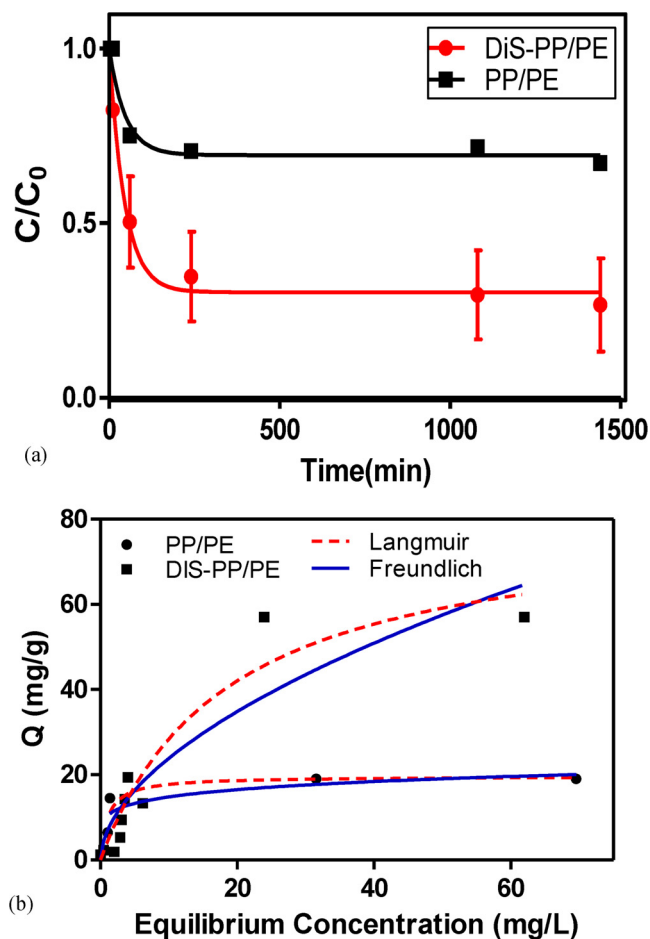


Fig. 7. (a) Kinetics of cadmium adsorption on PP/PE and DiS-PP/PE (initial Cd concentration = 5 mg/L, quantity of adsorbent = 0.2 g/L, and pH 8), (b) Adsorption isotherm experiment of cadmium with PP/PE and DiS-PP/PE as fitted using the Langmuir isotherm and Freundlich isotherm (quantity of adsorbent = 0.2 g/L and pH 8).

4. Conclusions

In this study, as a method for controlling heavy metals in storm-water runoff, the fiber media (PP/PE) used in nonpoint pollution abatement facilities was modified with DiS-COP. PP/PE was first treated with oxygen plasma and acrylic acid to activate its surface. Subsequently, DiS-COP was successfully grafted onto the surface-treated PP/PE-AA. Physical and chemical characterizations of the synthesized material confirmed that DiS-COP was successfully grafted

Table 1

Results of adsorption isotherm experiments of (a) PP/PE and (b) DiS-PP/PE fitted using Langmuir isotherm and Freundlich isotherm.

	Langmuir isotherm			Freundlich isotherm		
	Q_m (mg/g)	a_L (L/mg)	R^2	k_F (g/mg min)	$1/n$ (mg/g)	R^2
PP/PE	19.61	0.966	0.7835	10.3	0.157	0.6999
DiS-PP/PE	81.11	0.054	0.9255	6.76	0.547	0.8589

and grown on the surface of PP/PE, and the quantity of DiS-COP attached was approximately 5 wt.%.

The cadmium adsorption tests conducted in this study indicated that DiS-COP exhibited a cadmium adsorption capacity of 81.1 mg/g, which is 4.1 times higher than that of pristine PP/PE. Furthermore, half of the cadmium ions were removed in less than 30 min at the sorbent loading of 0.2 g/L. Additionally, the effects of pH and competitor ions were evaluated. As a result, the applicability of DiS-PP/PE in the pH range of 6–8 was demonstrated. Calcium had a minor effect on cadmium adsorption owing to the high affinity between DiS-COP and cadmium, which can be explained using the HSAB theory. However, in the presence of organic material (humic acid), the cadmium removal

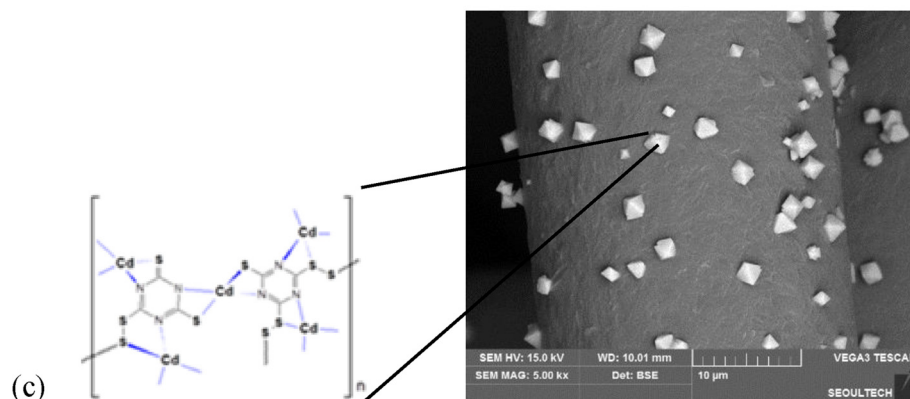
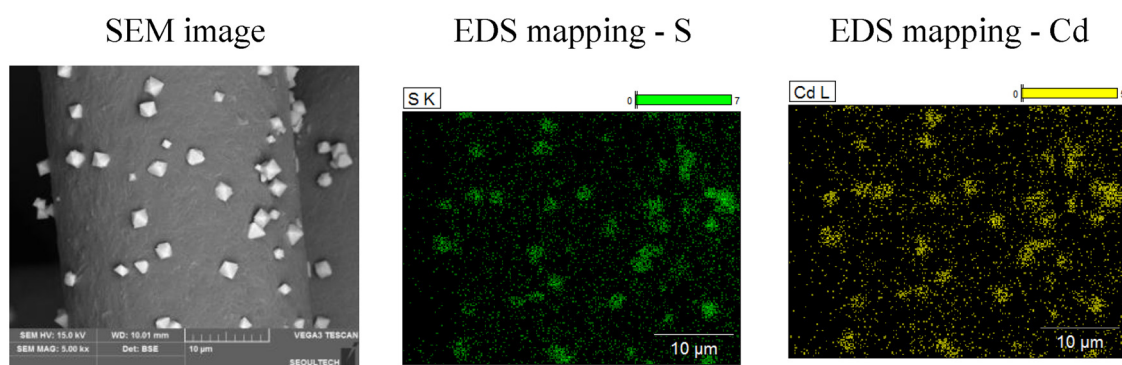
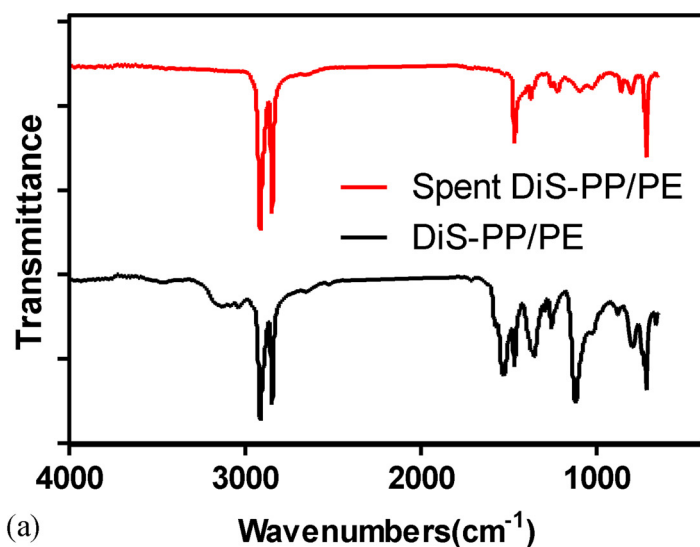


Fig. 8. (a) FTIR spectra of new and spent DiS-PP/PE, (b) SEM-EDS mapping images of spent DiS-PP/PE, (c) Scheme of cadmium adsorption by DiS-PP/PE.

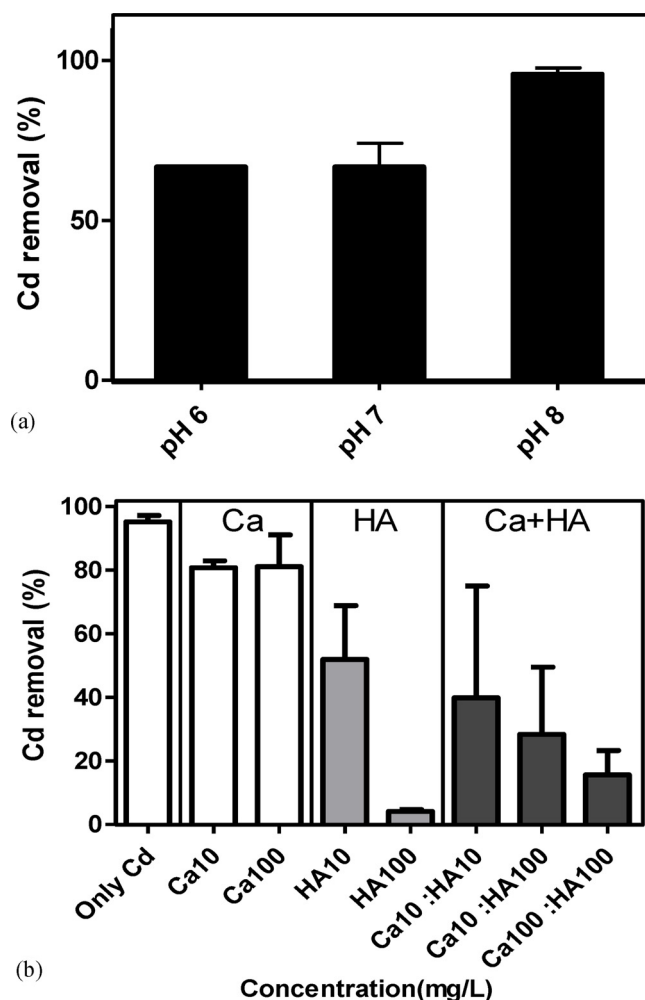


Fig. 9. (a) Cadmium adsorption experiment results of DiS-PP/PE (initial Cd concentration = 10 mg/L, quantity of adsorbent = 0.2 g/L, and pH 8), (b) evaluation of cadmium adsorption in the presence of calcium ion and humic acid (initial Cd concentration = 10 mg/L, quantity of adsorbent = 0.2 g/L, and pH 8).

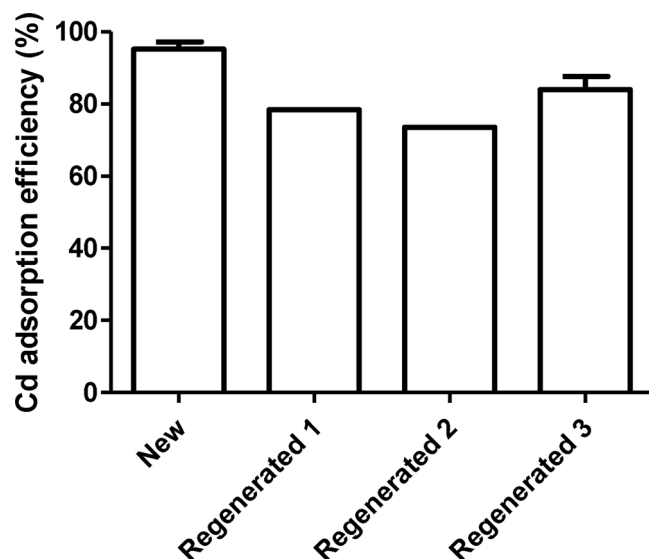


Fig. 10. Regeneration evaluation of DiS-PP/PE (initial Cd concentration = 5 mg/L, quantity of adsorbent = 1 g/L, and pH 8, desorption solution = 0.05 M HNO_3).

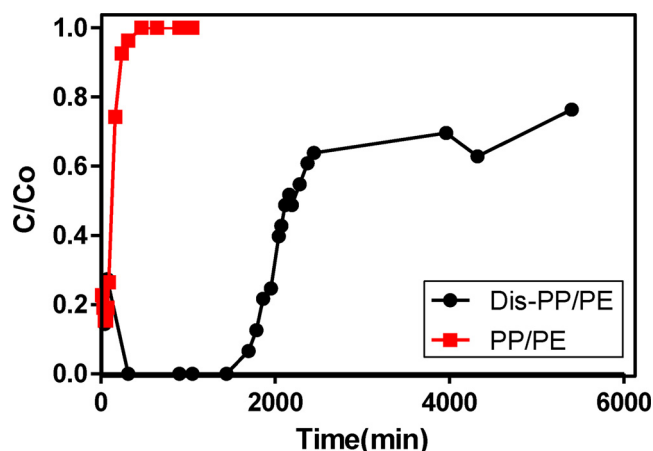


Fig. 11. Results of DiS-PP/PE continuous adsorption experiment (initial Cd concentration = 0.5 mg/L, quantity of adsorbent = 0.5 g, pH 8, and flow rate = 0.5 mL/min).

efficiency decreased owing to HA-Cd complex formation and agglomeration. Finally, continuous column experiments confirmed the rapid kinetics of DiS-PP/PE and its 24 times higher cadmium adsorption capacity than that of PP/PE. In conclusion, the heavy metal adsorption performance of plastic-based filter material (PP/PE) was successfully improved by grafting DiS-COP on its surface.

CRediT authorship contribution statement

Jeongmin Hong: Investigation, Writing - original draft. **Dongah Ko:** Methodology, Supervision. **Yuhoon Hwang:** Conceptualization, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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