Separation of microplastics from water using superhydrophobic silane-coupling-agent-modified geopolymer foam

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ABSTRACT

Microplastics are a topical environmental problem that requires urgent solutions. They are ubiquitously present in various wastewaters and are discharged into aquatic environments because of difficulties in their removal. In this study, a novel filtration medium, superhydrophobic geopolymer foam, was prepared and investigated for the separation of microplastics from water. The foam was prepared using metakaolin, sodium silicate, sodium hydroxide, hydrogen peroxide, and Triton X-100 surfactant as raw materials and superhydrophobized with a silane coupling agent, triethoxy(octyl)silane. The purpose of the superhydrophobization was to improve the attachment of hydrophobic microplastic particles to the foam surface via chemical interactions. The modified geopolymer foam exhibited a water contact angle of 152°, and the presence of octyl chains on its surface was confirmed using Fourier transform infrared and X-ray photoelectron spectroscopies. When applied as a filter, the modified foam separated 53-63-µm sized polyethylene microspheres with ~99 % removal efficiency, and no change in its separation efficiency was observed for ~200 bed volumes of treated water. A comparison with an unmodified foam filter confirmed that the removal mechanism was not based on physical separation at higher flow rates, because the performance of the unmodified foam began to degrade after treating ~5 bed volumes of wastewater. The performance of the modified foam was also validated with laundry washing effluents (particle size of microplastics varied roughly within 2–2000 µm), achieving ~84 % separation efficiency for ~50 bed volumes of wastewater. This study provides proof of concept of using superhydrophobic geopolymers as efficient, easy-to-prepare, and potentially low-cost separation media for microplastics from water effluents.

1. Introduction

The global production of plastics was estimated to be 391 million metric tons in 2021 [1]. A significant fraction of this amount ends up in the aquatic environment, where weathering eventually degrades plastic items into microplastics (MPs, particles with a diameter between 1 µm and 5 mm) and subsequently nanoplastics (NPs, particles with a diameter between 1 nm and 1 µm) [2]. Some important direct discharge sources of MPs/NPs include industrial and municipal wastewater and tire or bitumen wear [3–7]. It has been estimated that approximately 2.3 million tons of plastic waste float in oceans [8].

Conventional wastewater treatment processes (such as coagulation and flocculation) can separate more than 90 % of the MPs in raw wastewater [9–11]. However, the amount of MPs in treated wastewater

has been estimated to be on the order of 10^{11}–10^{12} particles per day from a single wastewater treatment plant (WWTP) [12,13]. The estimated MP/NP amounts are highly uncertain, especially when data from different measurements are combined [14]. The presence of MPs is ecotoxicologically alarming because most fish are contaminated by them in the areas affected by WWTPs [15,16]. MP ingestion can have several negative impacts on aquatic organisms, including a reduction in growth rate, difficulty in digestion, and intestinal abrasion [17]. MPs can also adsorb persistent organic pollutants, pathogenic microbes, and toxic metals on their surfaces, acting as carriers of these pollutants into aquatic organisms and releasing them into the digestive system [18].

To improve wastewater treatment for MP separation, various approaches are studied. For instance, conventional pressure-driven membrane separation processes, such as microfiltration, ultrafiltration, or

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nanofiltration, have been demonstrated to remove up to 100 % of MPs from water [19–21]. However, membrane filtration is unlikely to be a universal solution to MP pollution due to the commonly occurring issues of fouling and high costs [9]. MPs can also be separated by gravity-driven filtration, such as deep sand filters or multimedia filters using biochar, zeolite, or sand as the filtration media [22–26], where the unit cost of treated water can be ~60 % lower than that in microfiltration or ultrafiltration [27]. The separation of MPs by sand filtration is a simple and cost-effective method with efficiency between 74 % and 97 %. However, its effectiveness in separating small MP particles remains unclear [28]. Research has shown that biochar-based filtration methods have successfully separated over 95 % of MPs [22] but the regeneration or reuse of biochar used as filtration media is difficult [29]. Natural zeolites with an average size of 3 mm have been investigated as filter media for separating MPs; however, separation efficiency of less than 50 % has been achieved [30]. The separation capability of zeolite particles was reported to improve by hydrophobizing their surface using hexadecylpyridinium bromide: this modification enabled the removal of granular polyethylene (PE, 10 μm in size) and fibrous polyamide (100 μm in size) particles from water with efficiency exceeding 96 %, which is nearly twice as efficient as unmodified zeolite [30].

In this study, geopolymers (zeolite-like amorphous alkali-metal aluminosilicates [31]) are evaluated as novel materials for the separation of MPs for the first time. They are simpler to prepare and have potentially lower cost and environmental impacts than competing materials, such as synthetic zeolites or activated carbon [32–34]. Furthermore, unlike zeolites, geopolymers can be easily formulated to contain macropores (i.e., pore sizes > 0.05 μm), which is important for the efficient separation of NPs/MPs. The preparation of geopolymers typically occurs by mixing an aluminosilicate precursor (such as metakaolin) with a solution of alkali metal silicate at (near) ambient temperature [35]. With the use of additives (such as foaming agents or surfactants) and advanced manufacturing methods, geopolymers can be easily prepared into membrane disks, granules, solid foams, or three-dimensional printed lattices with desired porosity [36–45].

However, geopolymer surfaces are hydrophilic, which is not optimal for the separation of hydrophobic NP/MP particles. One method for transforming geopolymers into (super)hydrophobic materials is the use of silane coupling agents (i.e., $X\text{-}(CH_2)_n\text{-}Si\text{-}(OR)_3$, where X represents a functional group and OR denotes a hydrolyzable alkyl group) [46]. Successful modification of geopolymers with for example (3-aminopropyl)triethoxysilane or [3-(2,3-Epoxypropoxy)-propyl]-trimethoxysilane has been reported [47–49]. Here, the surface silanol or aluminol (i.e., Si-OH or Al-OH) groups of the geopolymer react with the silane coupling agent and form an organic layer on the geopolymer surface [47]. Existing studies have mainly focused on construction material applications to obtain water-repellent properties and avoid efflorescence (i.e., the formation of carbonate salt deposits on the geopolymer surface) [47–49]. However, geopolymers modified with silane coupling agents have not been investigated for water treatment applications, which is an obvious research gap.

In this study, we hypothesize that (super)hydrophobization of geopolymer foam would improve its interaction with hydrophobic MP particles, leading to the attachment of MPs on the geopolymer surface. Developing cost-effective and sustainable filtration media for MPs, especially of small particle size ranges ($\leq$ 100 μm), would be an important step forward in the management of MPs in different wastewater effluents. The objectives of this study are to (i) modify geopolymer foam with a silane coupling agent, triethoxy(octyl)silane, (ii) confirm the success of the modification with infrared spectroscopy, water contact angle measurements, and X-ray photoelectron spectroscopy, and (iii) compare modified and unmodified foams at various flow rates to separate MPs from synthetic wastewater containing polyethylene microspheres (53–63 μm) and laundry effluent containing fibers (approximately 2–2000 μm). The results demonstrate that the obtained superhydrophobic geopolymer is a potentially efficient, easy-to-prepare,

and low-cost separation medium for MPs from water effluents.

2. Materials and methods

2.1. Chemicals and materials

The raw materials for the geopolymer were metakaolin (MK, BASF, Germany, more details are available in **Table S1**), sodium silicate solution (Merck, Germany, molar $SiO_2/Na_2O \approx 3.5$, water content of ~65 %), and NaOH pellets (VWR, Germany). H_2O_2 (VWR, Belgium, 30 %) and a Triton X-100 solution (VWR, France, 100 %) were used as a foaming agent and surfactant, respectively. CH_3COOH (0.1 M) diluted from glacial acetic acid (100 %, Merck, Germany) was used to neutralize the residual alkalinity of the geopolymer before its modification. A triethoxy(octyl)silane solution (Merck, USA, 97 %) was used to modify the geopolymer surface.

MP microspheres of PE (Cospheric, the USA, 53-63 μm) were used to prepare model wastewater. Furthermore, to obtain laundry washing effluent, three 100 % polyester blankets (Kotikulta, Tokmanni, Finland) were washed at 30 °C for 56 min in a washing machine (Electrolux PERFECTCARE 700) using detergent powder (OMO Sensitive, Unilever, Finland), and the rinsing effluent was collected.

2.2. Preparation of geopolymer

An alkali activator solution was prepared by mixing a sodium silicate solution with NaOH pellets in a weight ratio of 6.69:1.00 overnight to obtain a molar ratio of $SiO_2/Na_2O \approx 1.2$. Geopolymer foam was prepared according to a previous study [50] where the detailed of characterization of morphology and pore size distribution of the foam is reported. In the preparation process, MK and the alkali activator solution were mixed in a weight ratio of 1.00:1.36 with a high shear mixer (IKA Eurostar 20) using 3,000 rpm mixing speed for 4 min. Then, H_2O_2 (1.28 wt% of MK) and Triton X-100 (3.06×10^{-4} wt% of MK) were added, and mixing was continued for an additional 2 min at 3000 rpm. The formed paste was cast in an acrylic plastic column mold (10.2 cm height and 4.3 cm inner diameter) closed from one end. The mold was then placed in a plastic bag and cured in an oven at 60 °C for 4 h. It was ensured that no MP contamination was released from the plastic column mold during the MP separation experiments by investigating water filtered through the foam using an optical microscope (Olympus DSX10-UZH) based on the color and shape of the particles.

2.3. Geopolymer modification with silane coupling agent

Two types of geopolymer samples were prepared for modification using a silane coupling agent: pieces with dimensions of 20 × 20 × 5 mm (m = 2.85 ± 0.10 g) and foam samples with dimensions of 10.2 cm height, 4.3 cm diameter, and volume of ~ 148 cm^3 (m = 63 ± 2 g). The samples were neutralized with 2 L of acetic acid (0.1 M). To perform the modification using the silane coupling agent, the pieces were dipped in a 97 % triethoxy(octyl)silane solution (20 mL) and left standing overnight ($\approx$ 16 h) at 22 °C. The foam was modified by pumping 80 mL of the 97 % triethoxy(octyl)silane solution through it for 2 h at a flow rate of 10 mL/min and leaving the foam saturated with the solution standing overnight. After modification, 500 mL of ultrapure water was pumped through the foam.

2.4. Characterization of modified geopolymer

Hydrophobicity was assessed by measuring the contact angle of a water droplet on the geopolymer surface, both modified and unmodified, using a drop shape analyzer (DSA25, KRÜSS). A droplet volume of 2 μL was used, and three measurements were taken to obtain an average value.

Fourier transform infrared (FTIR) spectra were recorded for the

pulverized sample of modified and unmodified foam with a resolution of 2 cm^{-1} within the $450–4000 \text{ cm}^{-1}$ range using the Bruker VERTEX 80v instrument.

X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Fisher Scientific ESCALAB 250Xi XPS System. The modified foam sample was washed with ultrapure water and dried at 80 °C before analysis. The samples (pieces of foam) were annealed in vacuum at 100 °C–200 °C for 2 h. Avantage software (Thermo Avantage, version 5.9925) was used for data analysis and peak fitting.

2.5. Particle size distribution

The particle size distribution of MPs (PE) was measured using a Beckman Coulter 13320XR particle size analyzer via laser diffraction. The Fraunhofer model was used to interpret the data [51]. Isopropanol was used as the dispersion medium. The data were taken as an average of three measurements, and the particle size distribution graphs for MPs are shown in Fig. S1 (supplementary materials).

2.6. MP separation experiments

A stock solution of 1000 mg/L of PE (i.e., 13 million MP particles per L) was prepared in ultrapure water (Milli-Q Ultrapure Water System, Millipore). To disperse the MPs in water, 2–3 drops of detergent TK140 (TEKNON, UK) were added and stirred continuously at 300 rpm. The detergent was added to reduce the surface tension of water to suspend MPs in water but the added amount of detergent did not render the MPs hydrophilic. The stock solution was diluted to 5 mg/L (i.e., 65,000 MP particles per L) of PE in ultrapure water and used in the experiment. The pH of the solution was ~7.0. The dimensions of the foams inside the filters employed in the separation experiments were 10.2 cm height, 4.3 cm diameter that is volume of $\sim148 \text{ cm}^3$ (mass of 63 ± 2 g). In the MP separation experiments involving the model solutions, the following factors were investigated: (1) comparison of unmodified and modified foam (flow rates of 3 and 5 mL/min) for the treatment of 450 mL of model water; (2) effect of flow rate using the modified foam (flow rates of 3–10 mL/min) for the treatment of 450 mL of model water; (3) performance of modified geopolymer foam in the separation of MPs for the

treatment of 30 L (~200 bed volumes) of model water. The duration of the longer experiment was 100 h. The empty bed contact time (EBCT) corresponding to flow rates 3, 5, 7, and 10 mL/min are approximately 50, 30, 20, and 15 min, respectively. The EBCT was calculated from the ratio of the volume of empty bed and flow rate. Water collected from the foam column outlet was filtered through 0.45 μm cellulose acetate membranes (diameter of 47 mm, Merck), and the MP amount was quantified by imaging the whole filter paper area with an optical microscope (Nikon SMZ1500, Japan). To cover the imaging of whole filter paper, minimum 8 spots of the filter paper were imaged. For the quantification of MP separation efficiency, an average of two separate filtration assays and measurements was used.

In the experiment involving laundry wastewater, the wastewater was pumped through modified and unmodified foam at a flow rate of 5 mL/min. Similarly, as with the model solutions, laundry wastewater was continuously stirred at 300 rpm during the experiment, and samples were collected from the outlet of the foam column. The experiment was conducted to treat ~7 L of laundry wastewater (i.e., ~48 bed volumes). The collected samples were filtered and quantified similarly as above using an Olympus DSX10-UZH microscope (Japan). The experimental setup for MP separation is schematically shown in Fig. 1.

3. Results and discussion

3.1. Confirmation of the modification of geopolymer with silane coupling agent

3.1.1. FTIR

The FTIR spectra of both the unmodified and modified geopolymer samples are shown in Fig. 2. Both spectra contained the typical features of a geopolymer structure: 3436 cm^{-1} (stretching vibrations of surface OH groups), 1641 cm^{-1} (bending vibrations of embedded H_2O molecules), 880 and $1390–1461 \text{ cm}^{-1}$ (stretching vibrations of carbonates), and 1000 cm^{-1} (stretching vibrations of Si–O–Si or Al–O–Si bonds) [46,47,52,53]. In addition, the modified geopolymer contained features that were absent from the unmodified geopolymer: three absorption bands in the range of $2860–2965 \text{ cm}^{-1}$, which are associated with the C–H bond stretching in the $–CH_2$ and $–CH_3$ groups of the alkyl chain of
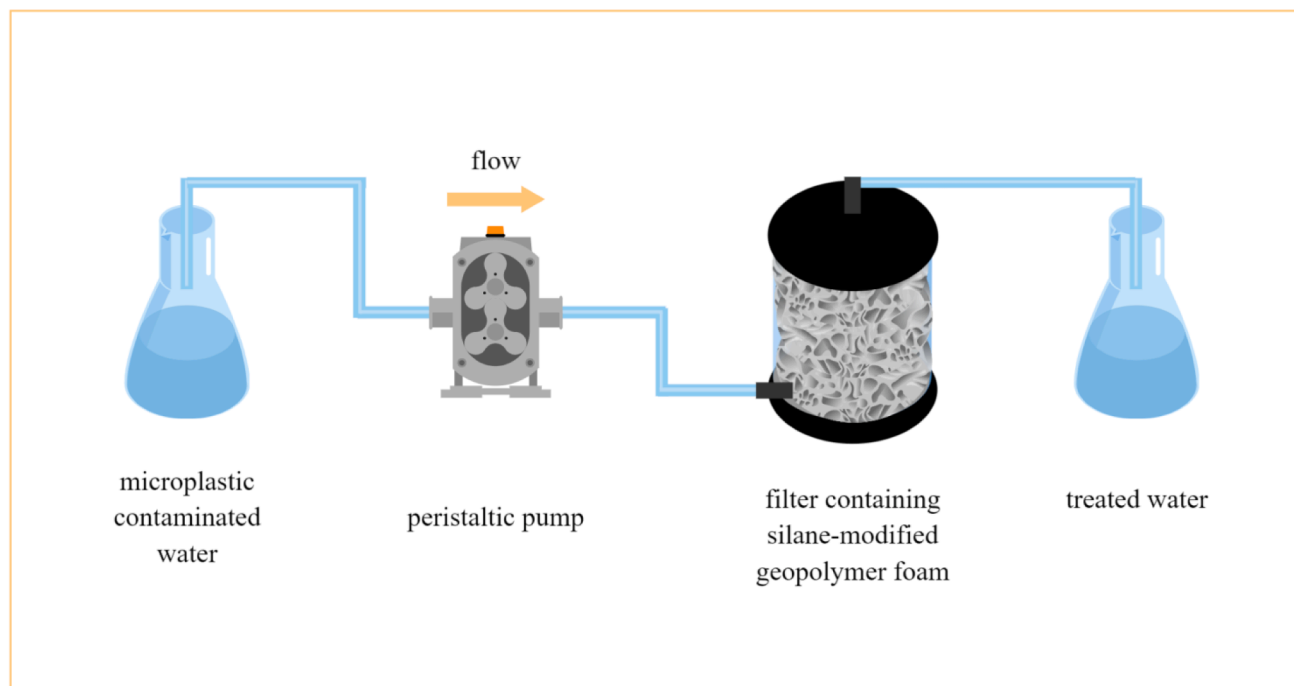

Fig. 1. Schematic diagram of experimental setup for MP separation using silane coupling agent-modified geopolymer foam.
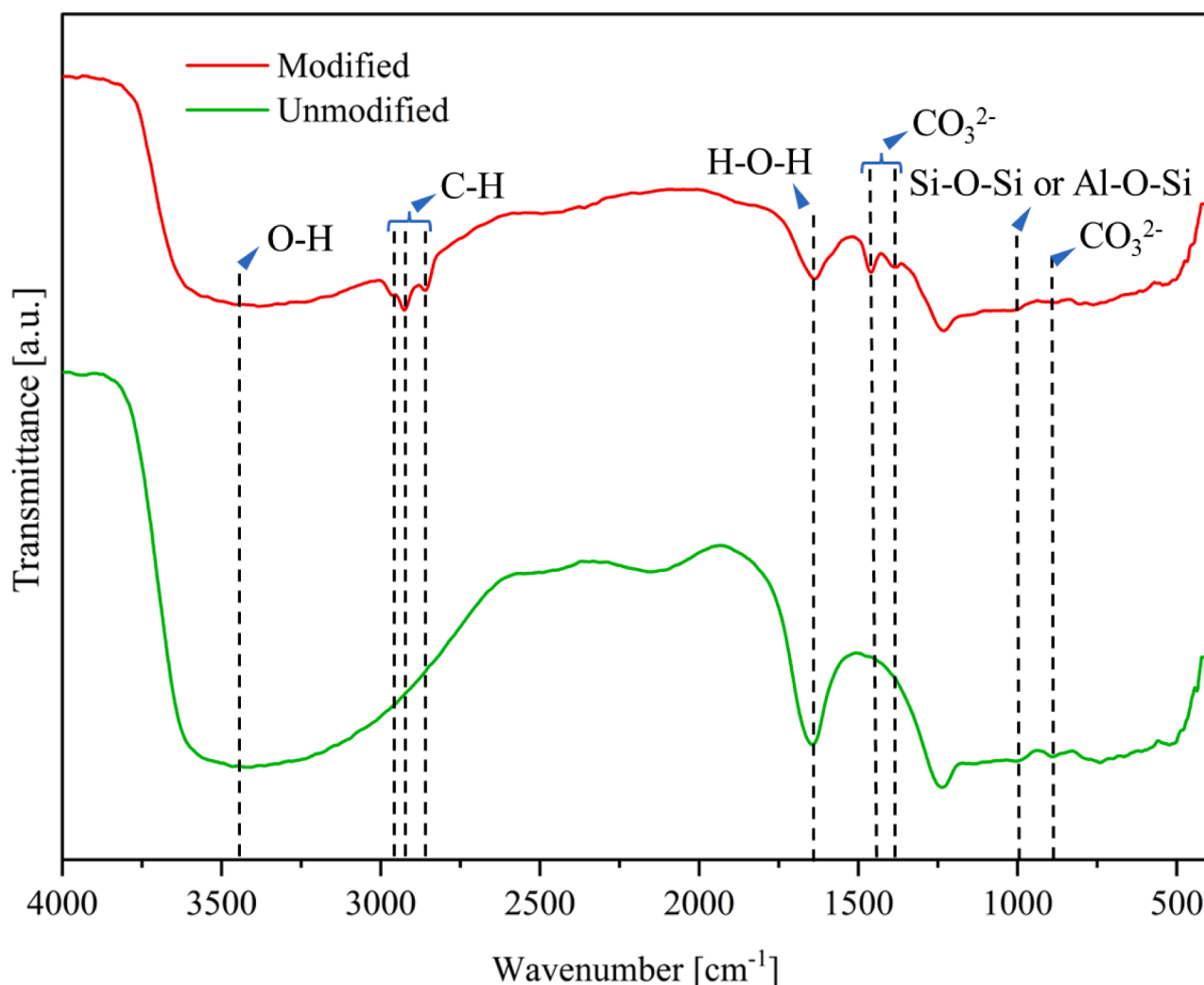
Fig. 2. FTIR spectra of modified and unmodified geopolymers.

the silane coupling agent [54]. Thus, the FTIR analysis confirmed the successful introduction of carbon chains to the surface.

3.1.2. Water contact angle

To characterize the hydrophobicity of the modified and unmodified geopolymers, the contact angle of a water droplet on their surfaces was measured (Fig. 3). For the modified geopolymer surface, the average water contact angle was approximately 152°, which is classified as superhydrophobic (i.e., the water contact angle $\geq 150°$). In contrast, the water contact angle of the unmodified geopolymer surface could not be recorded because the water droplet was immediately absorbed by the material, indicating a highly hydrophilic nature. Thus, also this result confirms the successful introduction of the hydrophobic alkyl chains of the silane coupling agent to the geopolymer surface.

3.1.3. XPS

The XPS spectra for the analysis of the composition and chemical state of the surfaces (1-10 nm) of the modified and unmodified geopolymers are shown in Fig. 4 (more detailed data are available in **Table S2**). The identification of the peak positions of C is crucial for confirming the successful introduction of alkyl chains to the surface. Comparing Fig. 4(a) and (b), the intensity of the C 1s peak in the modified geopolymer was greater than that in the unmodified geopolymer, suggesting an increased surface concentration of C after the modification. Two peaks were identified at higher binding energies in

both the modified and unmodified geopolymers, which indicated the presence of C=O, C–O, and O–C=O in carbonates [55]. Their presence is likely related to the surface reacting with CO_2 from the atmosphere. The peak at approximately 283.8 eV in the modified geopolymer can be associated with Si–C, whereas the peaks at approximately 284.8 and 285.0 eV can be associated with C–H and C–C. The presence of these groups (especially Si-C) indicated a successful integration of alkyl chains from the silane coupling agent to the geopolymer surface [56,57]. Thus, the XPS results supported the FTIR results (Fig. 2). The presence of the Si–C group in the modified geopolymer was also observable from the Si 2p spectrum at around 101 eV with a low intensity. The surface hydroxyl group (silanol group) and carbonate group could be identified in both the modified and unmodified geopolymers; however, the intensity of both has decreased after modification [46,58]. This decrease could be explained by the dehydration condensation reaction of the surface hydroxyl group with the ethoxy group from the silane coupling agent.

When the surface silanol groups react with the silane coupling agent, they are converted into Si–O–Si and a new layer of Si–C is formed (see Fig. 5 for a schematic presentation of the reaction mechanism of the geopolymer surface reacting with the silane coupling agent). The surface concentration of carbon on the modified surface was 34.6 atomic-%, which was almost three times higher than that on the unmodified surface. This result also indicated that alkyl groups were introduced to the surface. The surface concentrations of Si and O on the modified geopolymer surface were 15.6 and 41.0 atomic %, respectively, which were
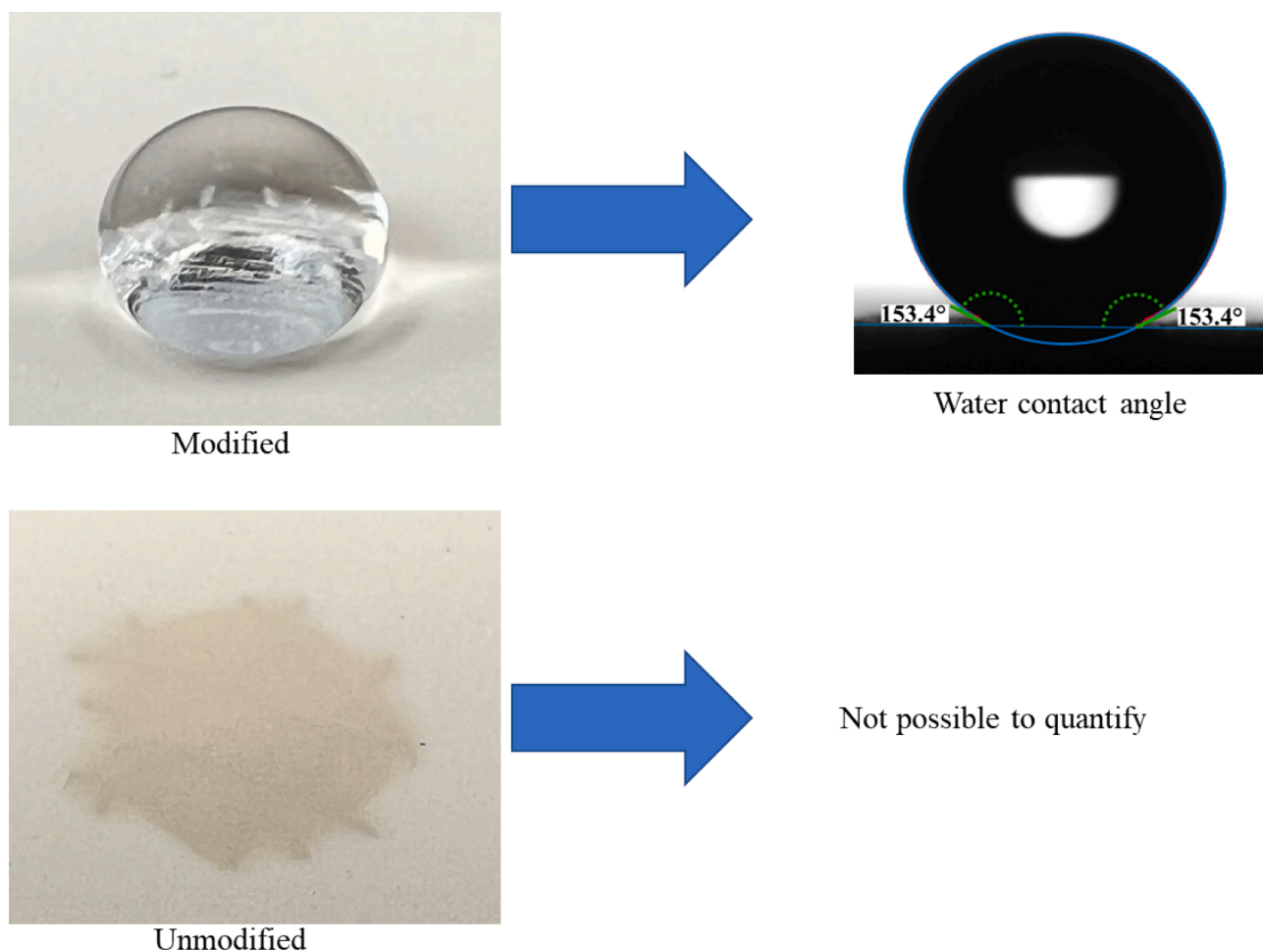
Fig. 3. Comparison of water contact angle on modified and unmodified geopolymer surfaces.

0.9 and 15.7 %-units lower than those on the unmodified geopolymer surface. These changes also reflected the introduction of carbon chains to the surface (i.e., decreasing the proportion of Si and O).

3.2. Separation of MPs using geopolymer foam

3.2.1. Comparison of MP separation using modified and unmodified geopolymer foams

The separation of PE, one of the most common MPs in aquatic environments and representing the size of MPs typically found in the effluent of WWTPs (i.e., 59-63 μm) [59], using the modified and unmodified geopolymer foams was compared (Fig. 6). Both the modified and unmodified foams exhibited similar separation performance (>99 %) at a flow rate of 3 mL/min, as shown in Fig. 6(a). Since both foams had a similar performance under these conditions, it is likely that there was also a physical separation mechanism for MP removal taking place (i.e., trapping of MPs inside the pores). The pore size distribution of the foams varied approximately within 25-1500 μm (as shown in Fig. 6d); thus, some of the PE microspheres (sizes 53-63 μm, Fig. 6c) could be removed via physical separation.

However, when the flow rate was increased to 5 mL/min, there was a clear difference in the MP separation capability between the modified and unmodified foams, as shown in Fig. 6b. Here, the super-hydrophobicity of the modified foam likely enhanced the attraction and subsequent retention of hydrophobic PE microspheres. A similar observation was reported earlier for MP removal by using super-hydrophobic materials [60,61]. The separation capability of the modified foam remained at ~99 %, whereas the efficiency of the unmodified foam decreased to ~84 % during the experiment. This decrease could be explained by the hydrophilic nature of the unmodified foam, where high-flow rate water flushes away PE particles attached to the pores and there is less time for PE microspheres to be trapped inside the pore structure of the unmodified foam. This result also indicated that physical separation played only a minor role at higher flow rates, because the separation capacity of a physical filtration medium should increase over time because of the accumulation of MP particles in the foam, further decreasing the pore openings. Similar observations (i.e., a decrease in the separation efficiency with increasing flow rate), were made for hydrophobic zeolite filter media (modified with hexadecylpyridinium bromide) in the separation of spherical PE MPs [30].

The attraction between the PE particles and the modified foam surface was also visually confirmed through a video recorded using an optical microscope (see the video files attached to this article). Here, no attachment of PE microspheres occurred on the unmodified surface, whereas a clear attraction was observed between the PE microspheres and the modified surface. Thus, the unmodified geopolymer foam could be useful only for the separation of MPs at low water flow rates, which is likely not feasible in most real-world wastewater treatment scenarios.

3.2.2. Effect of flow rate on MP separation using modified geopolymer foam

The PE microsphere separation efficiency of the modified geopolymer foam was investigated at different flow rates (3–10 mL/min), resulting in contact times representative of the practical requirement for a filter [24,25]. The results are shown in Fig. 7. As the flow rate increased to 10 mL/min, separation efficiency decreased by ~4.5 %-units. The decreased separation efficiency was likely caused by the
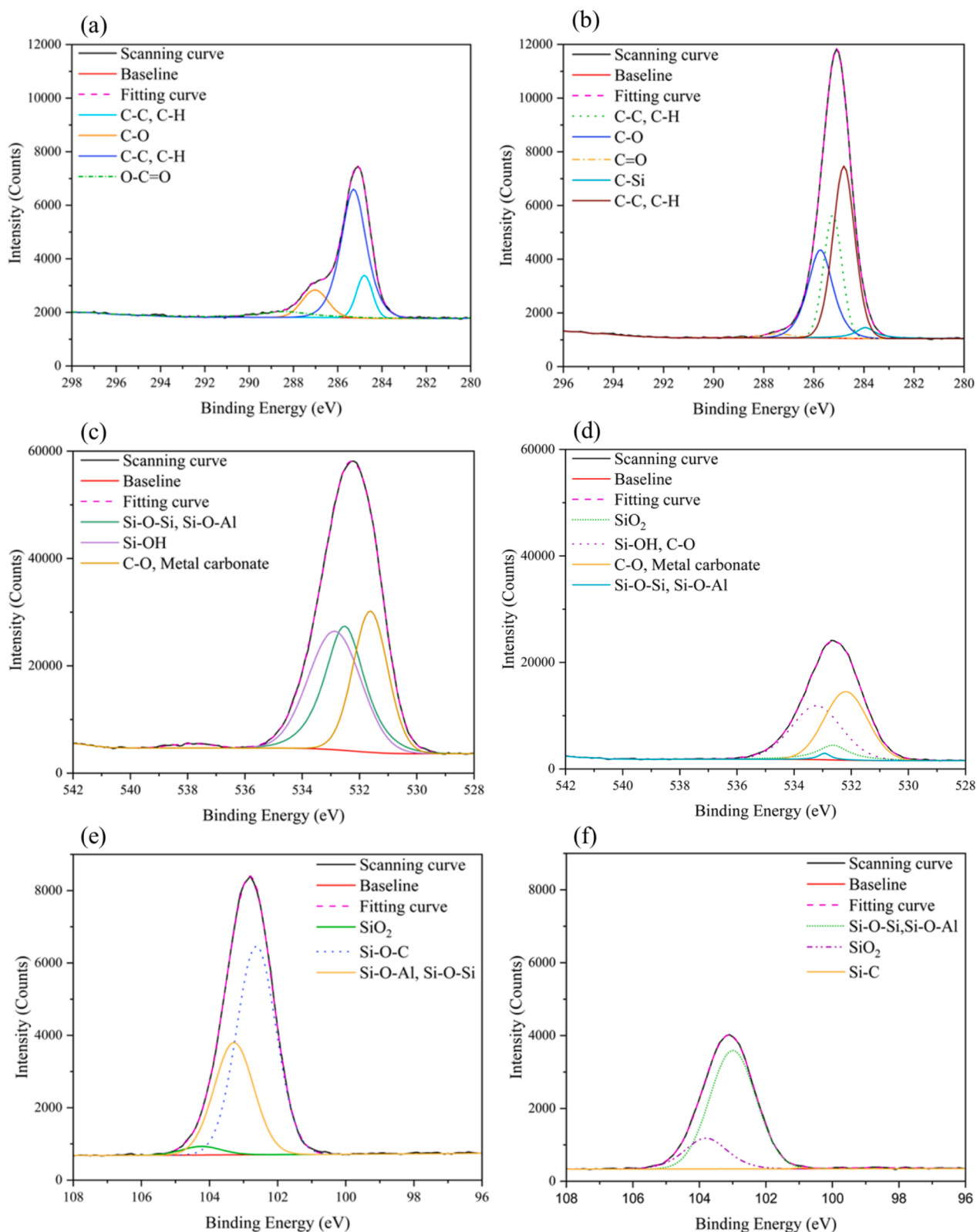
Fig. 4. (a) C 1s spectra of unmodified geopolymer; (b) C 1s spectra of modified geopolymer, (c) O 1s spectra of unmodified geopolymer; (d) O 1s spectra of modified geopolymer; (e) Si 2p spectra of unmodified geopolymer; (f) Si 2p spectra of modified geopolymer.

higher shear stress of water as the flow rate increased, which partially overcame the attraction between the hydrophobic surface and the PE microspheres. These findings were consistent with those of previous research, which has demonstrated the successful removal of PE particles using hydrophobic zeolites for the treatment of 500 mL of model water

with an initial number of particles 1×10^6 per L and a flow rate of 3-7 mL/min [30]. Even at decreased efficiency of 95.5 % (i.e., when operated at a flow rate of 10 mL/min), the modified geopolymer foam could still steadily separate approximately 62,000 MP particles per L of water. The estimated number of MPs in wastewater may vary between 1 and
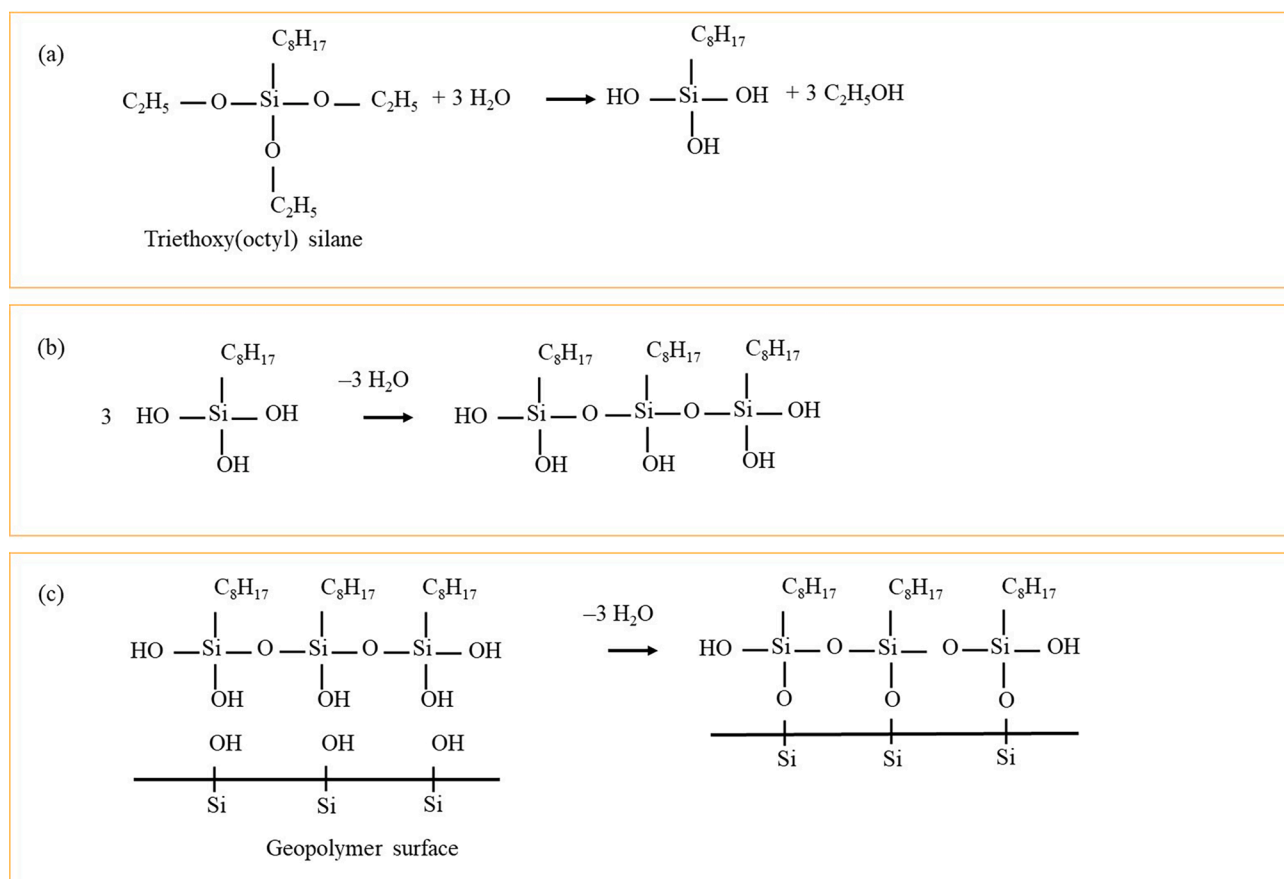
Fig. 5. Schematic presentation of the reaction mechanism of geopolymer surface with triethoxy(octyl) silane: (a) hydrolysis, (b) polymerization, and (c) reaction with the surface hydroxyl groups of geopolymer.
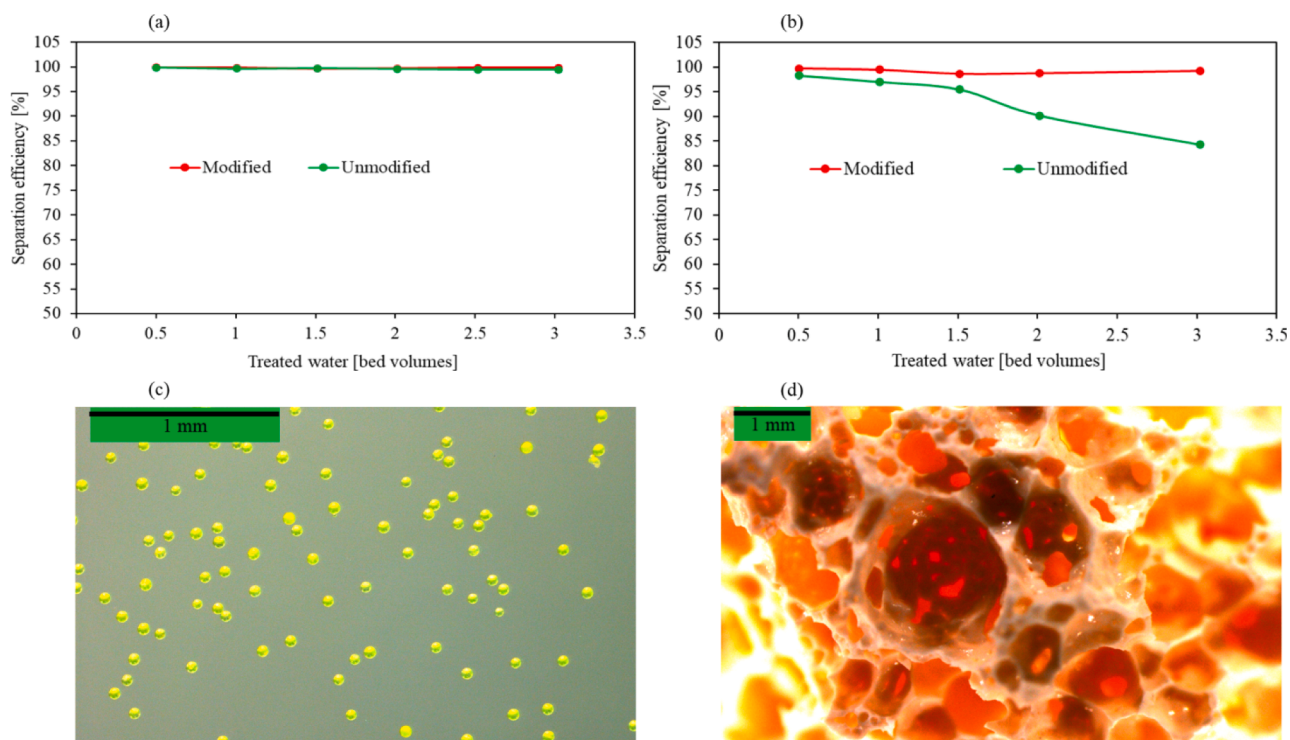

Fig. 6. Comparison of PE microsphere (59-63 μm) separation efficiency of modified and unmodified geopolymer foams at different flow rates. (a) 3 mL/min (EBCT ≈ 50 min), and (b) 5 mL/min (EBCT ≈ 30 min). During the experiment, 450 mL of water containing 5 mg/L of PE microspheres was treated. The appearance of (c) PE microspheres and (d) geopolymer foam was imaged using an optical microscope.
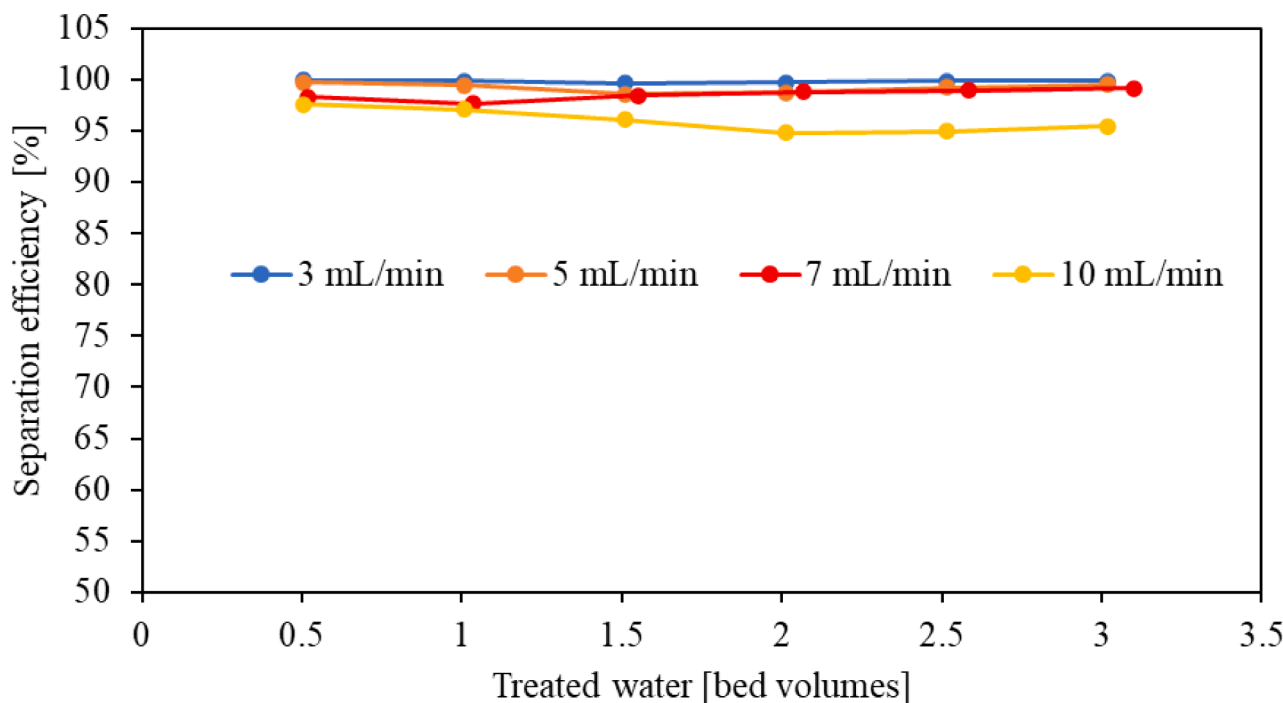
Fig. 7. Effect of different flow rates on PE microsphere (59-63 μm) separation efficiency using modified geopolymer foam.

10,000 per L depending on the location [15,20]. Considering this range, the modified geopolymer foam exhibited a remarkable separation performance. A flow rate of 5 mL/min (EBCT ≈ 30 min) was selected for further experiments.

3.2.3. Long-term MP separation experiment

The performance of a filtration medium in the long-term impacts its cost-efficiency, sustainability, and adoption by the industry. The separation performance of PE microspheres using the modified geopolymer foam was investigated with 30 L (or ~200 bed volumes) of model water spiked with MPs (5 mg/L with approximately 1.95 million MPs) at a flow rate of 5 mL/min (Fig. 8). Similarly, as shown in Fig. 7, the separation efficiency initially decreased and then gradually increased, which may indicate a built-up of a filter cake consisting of the separated PE particles. At the end of the experiment (i.e., after the treatment of ~200 bed volumes of water), the separation performance remained above 99 % and ~1.9 million PE microspheres were separated, demonstrating excellent efficiency compared with that of existing MP separation methods based on sand and hydrophobic zeolite-based filtration methods [30,62]. Notably, no pressure drop after the filter (i.e., the need
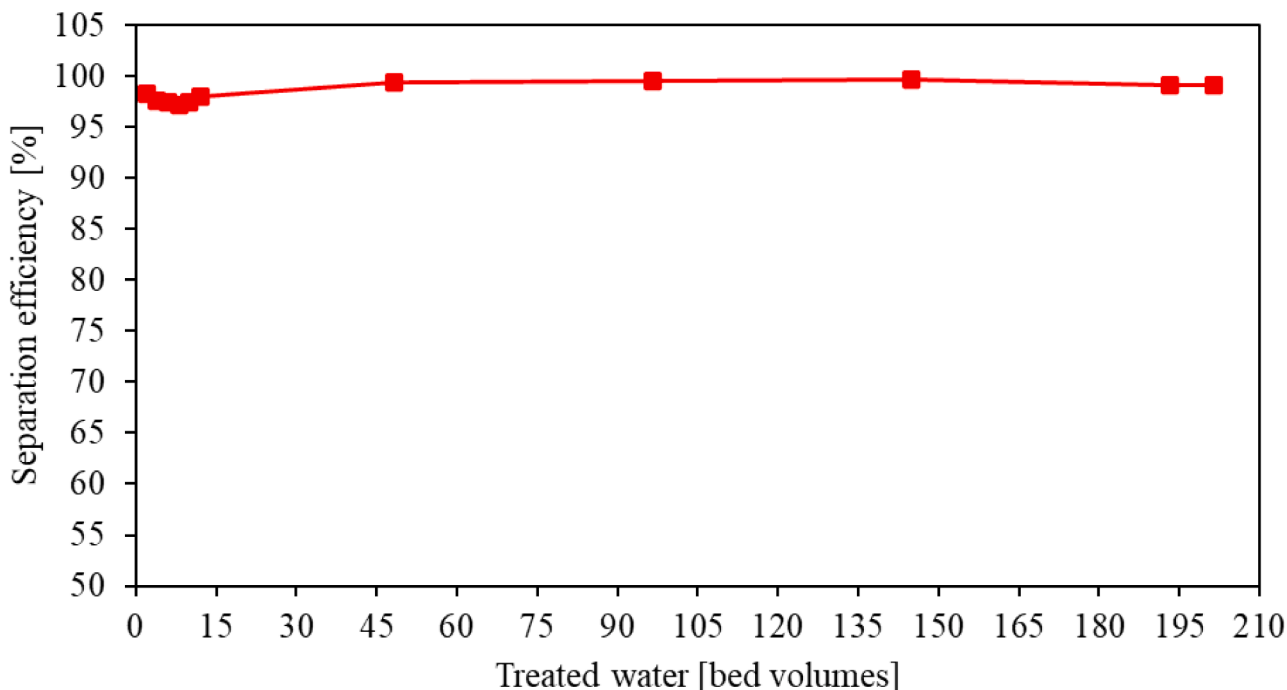

Fig. 8. PE microsphere (59-63 μm) separation efficiency of modified geopolymer foam over extended time.

to increase the speed of the pump to maintain a constant flowrate) was observed during the long-term experiment, which also indicated that the main mechanism of MP removal was not likely a physical separation. Moreover, it indicated that there was no blocking of the pores after the separation of MP particles for long-term. During this long-term experiment, no physical change of the modified foam (i.e., mechanical disintegration) was observed which confirms the practical durability of the foam in this application.

3.2.4. Separation of MPs from laundry wastewater

Washing synthetic clothes generates a large number of MPs (typically in the form of fibers). More than 0.7 million MP particles can be released from a typical wash of 6 kg of clothes [63] even though washing conditions, such as the use of softeners, can reduce the release of fibers [64]. The separation efficiency of the modified and unmodified foams was compared for the treatment of 48 bed volumes of laundry wastewater containing ~9000 MPs per L with a size ranging from approximately 2 μm to 2 mm (Fig. 9a). Similar to the model solutions containing PE microspheres, a clear difference between the modified and unmodified foams was observed. After the treatment of 48 bed volumes of laundry

wastewater, the separation efficiency of the modified foam was 84 %, whereas the separation efficiency of the unmodified foam decreased to 52 %. This difference was again likely due to the enhanced interaction between MPs (fibers) and the superhydrophobic geopolymer surface. The largest MP size found in the untreated laundry wastewater was ~2 mm, whereas the largest MP sizes found in the treated water were ~550 μm and ~76 μm when using the unmodified and modified geopolymer foams, respectively. This result indicated that surface modification enabled the separation of smaller particles or fibers compared with the unmodified foam. Larger MPs ($\geq$ 550 μm) were captured by both foam materials. The microscope images of the fiber particles on the modified geopolymer foam surface are shown in Fig. 9b. Larger MPs were retained in the pores of the geopolymer foam whereas the smaller fibers were trapped to the material surface without clear localization to the pores.

3.3. Mechanism of MP separation by geopolymer foam

The proposed mechanism involved in the separation of MPs by modified and unmodified foam can be seen in Fig. 10. By treating the geopolymer foam with a silane coupling agent, its surface changes from
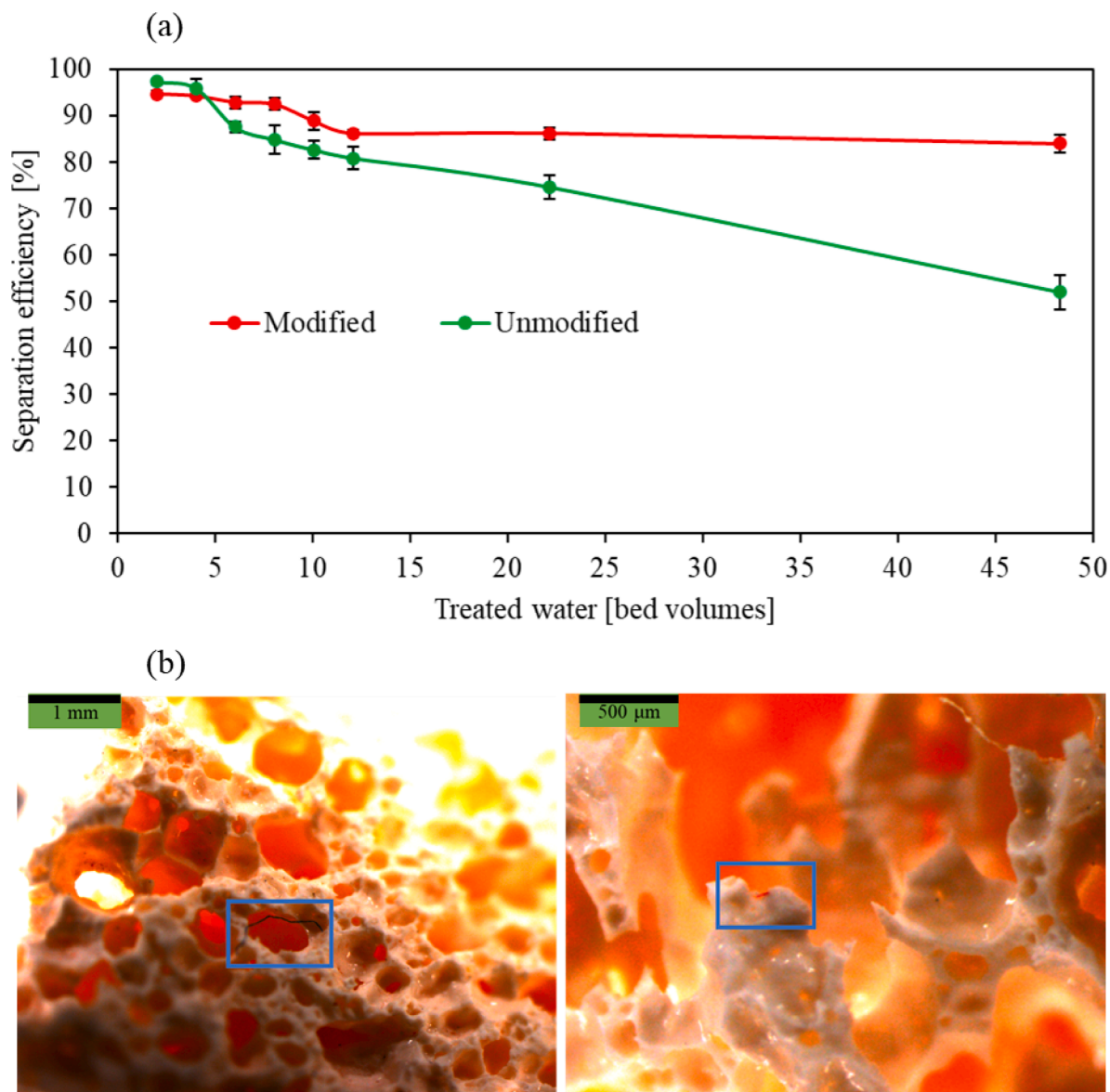

Fig. 9. (a) Comparison of MP (fiber) separation from laundry wastewater using modified and unmodified geopolymer foams at flow rate of 5 mL/min. (b) Separated fiber on the modified geopolymer foam surface as imaged with optical microscope.
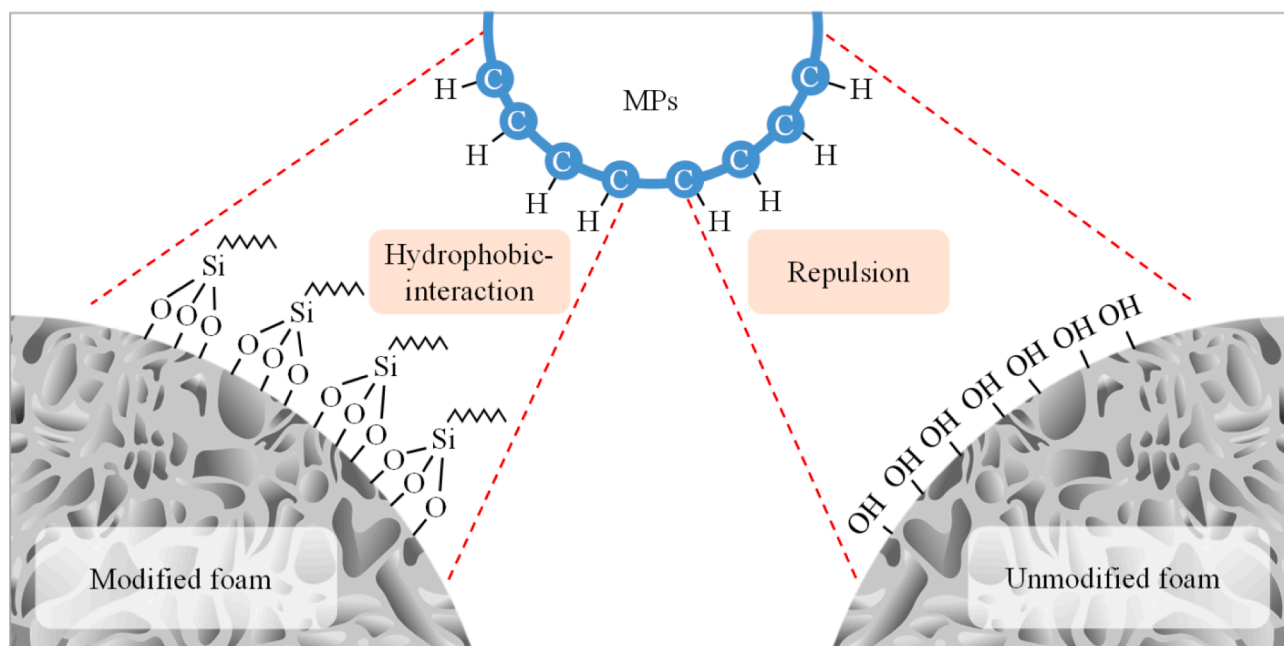
Fig. 10. Separation mechanism of MPs using modified and unmodified geopolymer foam.

hydrophilic to hydrophobic as depicted in Fig. 3. This modification allows for a hydrophobic-hydrophobic interaction between the MPs and the modified foam. Conversely, the hydrophilic nature of unmodified geopolymer foam results in repulsion towards hydrophobic MPs. Furthermore, both modified and unmodified foams employ physical separation mechanisms such as trapping within their pores [22,30].

3.4. Comparison of this study with the literature

The separation of MPs using silane coupling agent-modified geopolymer foam was compared with other materials and methods reported in the literature (Table 1). The separation efficiency obtained in this study is higher or comparable to that of existing methods and materials, which indicates the feasibility of using superhydrophobic geopolymer foam in the separation of MPs from water. However, this comparison with other studies is not straightforward because the experimental conditions and parameters (e.g., amount and size of MPs, design of the experimental setup, and type of water being studied) affect the results.

4. Conclusions

In this study, geopolymer foam modified with triethoxy(octyl)silane was investigated for the separation of MPs from water. The investigated MPs were representative of particles typically found in effluents from WWTPs in terms of their sizes (< 300 μm). The modified geopolymer was superhydrophobic (water contact angle $\approx 152°$) and had alkyl groups on its surface, as confirmed by water contact angle measurements, XPS, and FTIR analyses. It was observed that both the modified and unmodified foams were effective in physically separating MPs (PE, 53–63 μm) from water at low flow rates (3 mL/min). However, when the flow rate was increased to ≥ 5 mL/min, the enhanced interaction between the superhydrophobic foam and hydrophobic MP particles caused the modified foam to clearly outperform the unmodified foam. It was verified that ~200 bed volumes of water could be treated with more than 99 % MP separation capacity. Moreover, the modified foam was effective in the separation of MPs (microfibers) from laundry wastewater. The size of MPs observed in laundry wastewater ranged between 2 μm and 2 mm. After the treatment of 48 bed volumes of laundry wastewater, the separation efficiency of the unmodified and modified

Table 1
Comparison of MP separation or removal using different materials and filtration methods.

Separation or removal method	Materials	Size of MPs [μm]	Type of water	Initial concentration (MPs/L)	Removal efficiency (%)	Reference
Column filtration	Sand, biochar	10	Model water	1.6×10^8	> 95	[22]
Rapid sand filtration	Sand, gravel	20–100	Secondary wastewater	0.7	97	[62]
Rapid sand filtration	Silica Sand	> 200	Model water	256–588	85–97	[26]
Rapid sand filtration	Sand	> 200	Municipal wastewater	1.08	75	[65]
Dissolved air flotation	N/A	20–100	Secondary wastewater	2	95	[62]
Membrane bioreactor	Ultrafiltration membrane	20–100	Primary wastewater	6.9	100	[62]
Filtration	Surfactant-modified zeolite	10 and 100	Model water	1.0×10^6	> 96	[30]
Filtration	Surfactant-modified zeolite	5–100	Municipal	468–546	> 96	[30]
Filtration	Geopolymer foam modified with silane coupling agent	53–63	Model water	6.5×10^4	> 97	current study
Filtration	Geopolymer foam modified with silane coupling agent	2–2000	Laundry wastewater	9000	> 84	current study

geopolymer foams was 52 % and 84 %, respectively. The modified geopolymer foam was more effective in the separation of smaller MPs than the unmodified geopolymer foam without silane coupling agent modification. The largest MPs in the treated water were ~550 μm and ~76 μm when using the unmodified and modified geopolymer foams, respectively. This result indicates that surface modification enables the effective separation of smaller MPs compared with the unmodified foam.

MPs in aquatic environments, such as lakes or oceans, can be introduced from municipal and industrial wastewater. Separation of MPs at their sources, i.e., industrial or municipal WWTPs, before their migration to the aquatic environment can prevent or reduce MP pollution. Based on the preliminary results of this study, geopolymer foam modified with a silane coupling agent could be used as a component of tertiary wastewater treatment or other at-source separation. Modified geopolymer materials, for example, in granular form could be used in a multimedia filter instead of sand, or small foam filters could be installed, for example, at the outlet of laundry washing machines. After saturation with MPs, the geopolymer foam can be disposed via incineration or could be regenerated by thermal treatment, microbial/enzymatic degradation of MPs, or backwashing with water or other suitable solvents [66,67]. However, this needs to be investigated in the future. Geopolymer foams can retain their integrity after thermal regeneration, as reported in earlier studies [36,39]. After thermal regeneration, foams could be potentially reused by reapplying silane coupling agent modification. After its lifetime, the geopolymer materials could be recycled by pulverizing and potentially using again as a raw material for alkali activation. Furthermore, the future research topics include studying smaller MPs than the size of 53–63 μm, determining the maximum MP separation capacity of the modified geopolymer foam filter until its complete saturation, and optimization of pore size and porosity of the foam by varying amount of foaming agent (i.e., changes in pore size and porosity can improve the performance of the foam in the wastewater treatment [68]).

CRediT authorship contribution statement

M.A.H. Bhuyan: Conceptualization, Data curation, Methodology, Investigation, Validation, Writing – original draft, Visualization. **R. Busquets:** Supervision, Writing – review & editing. **L.C. Campos:** Supervision, Writing – review & editing. **T. Luukkonen:** Funding acquisition, Project administration, Supervision, 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.

Data availability

Data will be made available on request.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2024.126709.

References

[1] Plastic production worldwide 2021, Statista (2023). https://www.statista.com/statistics/282732/global-production-of-plastics-since-1950/ (accessed August 9, 2023).

[2] J.P.G.L. Frias, R. Nash, Microplastics: finding a consensus on the definition, Mar. Pollut. Bull. 138 (2019) 145–147, https://doi.org/10.1016/j.marpolbul.2018.11.022.

[3] M. Lares, M.C. Ncibi, M. Sillanpää, M. Sillanpää, Occurrence, identification and removal of microplastic particles and fibers in conventional activated sludge process and advanced MBR technology, Water Res. 133 (2018) 236–246, https://doi.org/10.1016/j.watres.2018.01.049.

[4] X. Zhang, J. Chen, J. Li, The removal of microplastics in the wastewater treatment process and their potential impact on anaerobic digestion due to pollutants association, Chemosphere. 251 (2020) 126360, https://doi.org/10.1016/j.chemosphere.2020.126360.

[5] H. Deng, Z. He, Interactions of sodium chloride solution and calcium silicate hydrate with different calcium to silicon ratios: A molecular dynamics study, Constr. Build. Mater. 268 (2021) 121067, https://doi.org/10.1016/j.conbuildmat.2020.121067.

[6] E. Winquist, M. Vahvaselkä, M. Vuola, P. Sainio. Traffic microplastic – solutions to mitigate the problem: FanpLESStic-sea project report, Natural Resources Institute Finland, 2021. https://jukuri.luke.fi/handle/10024/547717.

[7] L.O. Goehler, R.B. Moruzzi, F. Tomazini da Conceição, A.A.C. Júnior, L.G. Speranza, R. Busquets, L.C. Campos, Relevance of tyre wear particles to the total content of microplastics transported by runoff in a high-imperviousness and intense vehicle traffic urban area, Environ. Pollution. 314 (2022) 120200, https://doi.org/10.1016/j.envpol.2022.120200.

[8] M. Eriksen, W. Cowger, L.M. Erdle, S. Coffin, P. Villarrubia-Gómez, C.J. Moore, E.J. Carpenter, R.H. Day, M. Thiel, C. Wilcox, A growing plastic smog, now estimated to be over 170 trillion plastic particles afloat in the world's oceans—Urgent solutions required, PloS One 18 (2023) e0281596, https://doi.org/10.1371/journal.pone.0281596.

[9] B. Ma, W. Xue, C. Hu, H. Liu, J. Qu, L. Li, Characteristics of microplastic removal via coagulation and ultrafiltration during drinking water treatment, Chem. Eng. J. 359 (2019) 159–167, https://doi.org/10.1016/j.cej.2018.11.155.

[10] B. Ma, W. Xue, Y. Ding, C. Hu, H. Liu, J. Qu, Removal characteristics of microplastics by Fe-based coagulants during drinking water treatment, J. Environ. Sci. 78 (2019) 267–275, https://doi.org/10.1016/j.jes.2018.10.006.

[11] C. Li, R. Busquets, R.B. Moruzzi, L.C. Campos, Preliminary study on low-density polystyrene microplastics bead removal from drinking water by coagulation-flocculation and sedimentation, J. Water Process Eng. 44 (2021) 102346, https://doi.org/10.1016/j.jwpe.2021.102346.

[12] C. Schmidt, R. Kumar, S. Yang, O. Büttner, Microplastic particle emission from wastewater treatment plant effluents into river networks in Germany: loads, spatial patterns of concentrations and potential toxicity, Sci. Total Environ. 737 (2020) 139544, https://doi.org/10.1016/j.scitotenv.2020.139544.

[13] K. Conley, A. Clum, J. Deepe, H. Lane, B. Beckingham, Wastewater treatment plants as a source of microplastics to an urban estuary: removal efficiencies and loading per capita over one year, Water Research X. 3 (2019) 100030, https://doi.org/10.1016/j.wroa.2019.100030.

[14] M. Pletz, Ingested microplastics: do humans eat one credit card per week? J. Hazardous Mater. Lett. 3 (2022) 100071 https://doi.org/10.1016/j.hazl.2022.100071.

[15] J. Sun, X. Dai, Q. Wang, M.C.M. van Loosdrecht, B.-J. Ni, Microplastics in wastewater treatment plants: detection, occurrence and removal, Water Res. 152 (2019) 21–37, https://doi.org/10.1016/j.watres.2018.12.050.

[16] C.J. Thiele, M.D. Hudson, A.E. Russell, M. Saluveer, G. Sidaoui-Haddad, Microplastics in fish and fishmeal: an emerging environmental challenge? Sci Rep. 11 (2021) 2045, https://doi.org/10.1038/s41598-021-81499-8.

[17] M. Shen, Y. Zhang, Y. Zhu, B. Song, G. Zeng, D. Hu, X. Wen, X. Ren, Recent advances in toxicological research of nanoplastics in the environment: a review, Environ. Pollut. 252 (2019) 511–521, https://doi.org/10.1016/j.envpol.2019.05.102.

[18] I. Ali, T. Ding, C. Peng, I. Naz, H. Sun, J. Li, J. Liu, Micro- and nanoplastics in wastewater treatment plants: occurrence, removal, fate, impacts and remediation technologies – a critical review, Chem. Eng. J. 423 (2021) 130205, https://doi.org/10.1016/j.cej.2021.130205.

[19] S. Ziajahromi, P.A. Neale, L. Rintoul, F.D.L. Leusch, Wastewater treatment plants as a pathway for microplastics: development of a new approach to sample wastewater-based microplastics, Water Res. 112 (2017) 93–99, https://doi.org/10.1016/j.watres.2017.01.042.

[20] M. Shen, B. Song, Y. Zhu, G. Zeng, Y. Zhang, Y. Yang, X. Wen, M. Chen, H. Yi, Removal of microplastics via drinking water treatment: Current knowledge and future directions, Chemosphere. 251 (2020) 126612, https://doi.org/10.1016/j.chemosphere.2020.126612.

[21] C. Akarsu, H. Kumbur, A.E. Kideys, Removal of microplastics from wastewater through electrocoagulation-electroflotation and membrane filtration processes, Water Sci. Technol. 84 (2021) 1648–1662, https://doi.org/10.2166/wst.2021.356.

[22] Z. Wang, M. Sedighi, A. Lea-Langton, Filtration of microplastic spheres by biochar: removal efficiency and immobilisation mechanisms, Water Res. 184 (2020) 116165, https://doi.org/10.1016/j.watres.2020.116165.

[23] V. Siipola, S. Pflugmacher, H. Romar, L. Wendling, P. Koukkari, Low-cost biochar adsorbents for water purification including microplastics removal, Appl. Sci. 10 (2020) 788, https://doi.org/10.3390/app10030788.

[24] M. Umar, C. Singdahl-Larsen, S.B. Ranneklev, Microplastics removal from a plastic recycling industrial wastewater using sand filtration, Water. 15 (2023) 896, https://doi.org/10.3390/w15050896.

[25] L. Hsieh, L. He, M. Zhang, W. Lv, K. Yang, M. Tong, Addition of biochar as thin preamble layer into sand filtration columns could improve the microplastics removal from water, Water Res. 221 (2022) 118783, https://doi.org/10.1016/j.watres.2022.118783.

[26] E. Sembiring, M. Fajar, M. Handajani, Performance of rapid sand filter – single media to remove microplastics, Water Supply. 21 (2021) 2273–2284, https://doi.org/10.2166/ws.2021.060.

[27] V.K. Gupta, I. Ali, T.A. Saleh, A. Nayak, S. Agarwal, Chemical treatment technologies for waste-water recycling—an overview, RSC Adv. 2 (2012) 6380–6388, https://doi.org/10.1039/C2RA20340E.

[28] M. Vahvaselkä, E. Winquist. Existing and emerging technologies for microplastics removal: Review report of the FanpLESStic-sea project, Natural Resources Institute Finland, Helsinki, 2021. https://jukuri.luke.fi/handle/10024/547999.

[29] M. Tong, L. He, H. Rong, M. Li, H. Kim, Transport behaviors of plastic particles in saturated quartz sand without and with biochar/Fe$_3$O$_4$-biochar amendment, Water Res. 169 (2020) 115284, https://doi.org/10.1016/j.watres.2019.115284.

[30] M. Shen, T. Hu, W. Huang, B. Song, G. Zeng, Y. Zhang, Removal of microplastics from wastewater with aluminosilicate filter media and their surfactant-modified products: performance, mechanism and utilization, Chem. Eng. J. 421 (2021) 129918, https://doi.org/10.1016/j.cej.2021.129918.

[31] A. Campanile, B. Liguori, C. Ferone, D. Caputo, L. Gigli, P. Aprea, From geopolymers to zeolites: synthesis and characterization of foamed FAU-X monoliths, Microporous Mesoporous Mater. 349 (2023) 112426, https://doi.org/10.1016/j.micromeso.2022.112426.

[32] T. Luukkonen, J. Yliniemi, H. Sreenivasan, K. Ohenoja, M. Finnilä, G. Franchin, P. Colombo, Ag- or Cu-modified geopolymer filters for water treatment manufactured by 3D printing, direct foaming, or granulation, Sci Rep. 10 (2020) 7233, https://doi.org/10.1038/s41598-020-64228-5.

[33] M. Abdulkareem, J. Havukainen, M. Horttanainen, 17 - Environmental performance of alkali-activated materials in environmental technology applications, in: T. Luukkonen (Ed.), Alkali-Activated Materials in Environmental Technology Applications, Woodhead Publishing, 2022, pp. 383–405, https://doi.org/10.1016/B978-0-323-88438-9.00017-X.

[34] A.A. Natsheh, A. Gray, T. Luukkonen, 18 - Drivers and barriers for productization of alkali-activated materials in environmental technology, in: T. Luukkonen (Ed.), Alkali-Activated Materials in Environmental Technology Applications, Woodhead Publishing, 2022, pp. 407–426, https://doi.org/10.1016/B978-0-323-88438-9.00008-9.

[35] C. Bai, P. Colombo, Processing, properties and applications of highly porous geopolymers: a review, Ceram. Int. 44 (2018) 16103–16118, https://doi.org/10.1016/j.ceramint.2018.05.219.

[36] R.M. Novais, G. Ascensão, D.M. Tobaldi, M.P. Seabra, J.A. Labrincha, Biomass fly ash geopolymer monoliths for effective methylene blue removal from wastewaters, J. Clean. Prod. 171 (2018) 783–794, https://doi.org/10.1016/j.jclepro.2017.10.078.

[37] R.M. Novais, J. Carvalheiras, M.P. Seabra, R.C. Pullar, J.A. Labrincha, Highly efficient lead extraction from aqueous solutions using inorganic polymer foams derived from biomass fly ash and metakaolin, J. Environ. Management. 272 (2020) 111049, https://doi.org/10.1016/j.jenvman.2020.111049.

[38] C. Bai, P. Colombo, High-porosity geopolymer membrane supports by peroxide route with the addition of egg white as surfactant, Ceram. Int. 43 (2017) 2267–2273, https://doi.org/10.1016/j.ceramint.2016.10.205.

[39] M.A.H. Bhuyan, R.K. Gebre, M.A.J. Finnilä, M. Illikainen, T. Luukkonen, Preparation of filter by alkali activation of blast furnace slag and its application for dye removal, J. Environ. Chem. Eng. 10 (2022) 107051, https://doi.org/10.1016/j.jece.2021.107051.

[40] T. Luukkonen, M. Bhuyan, A.-M. Hokajärvi, T. Pitkänen, I.T. Miettinen, Water disinfection with geopolymer–bentonite composite foam containing silver nanoparticles, Mater. Lett. 311 (2022) 131636, https://doi.org/10.1016/j.matlet.2021.131636.

[41] F.J. Humberto Tommasini Vieira Ramos, M. de F. Vieira Marques, V. de Oliveira Aguiar, F.E. Jorge, Performance of geopolymer foams of blast furnace slag covered with poly(lactic acid) for wastewater treatment, Ceram. Int. 48 (2022) 732–743, https://doi.org/10.1016/j.ceramint.2021.09.153.

[42] G. Franchin, J. Pesonen, T. Luukkonen, C. Bai, P. Scanferla, R. Botti, S. Carturan, M. Innocentini, P. Colombo, Removal of ammonium from wastewater with geopolymer sorbents fabricated via additive manufacturing, Mater. Des. 195 (2020) 109006, https://doi.org/10.1016/j.matdes.2020.109006.

[43] A. Maleki, Z. Hajizadeh, V. Sharifi, Z. Emdadi, A green, porous and eco-friendly magnetic geopolymer adsorbent for heavy metals removal from aqueous solutions, J. Clean. Prod. 215 (2019) 1233–1245, https://doi.org/10.1016/j.jclepro.2019.01.084.

[44] S. Sanguanpak, A. Wannagon, C. Saengam, W. Chiemchaisri, C. Chiemchaisri, Porous metakaolin-based geopolymer granules for removal of ammonium in aqueous solution and anaerobically pretreated piggery wastewater, J. Clean. Prod. 297 (2021) 126643, https://doi.org/10.1016/j.jclepro.2021.126643.

[45] M.A.H. Bhuyan, T. Luukkonen, Adsorption of methylene blue by composite foams containing alkali-activated blast furnace slag and lignin, Int. J. Environ. Sci. Technol. 21 (2024) 3789–3802, https://doi.org/10.1007/s13762-023-05245-5.

[46] X. Xue, Y.-L. Liu, J.-G. Dai, C.-S. Poon, W.-D. Zhang, P. Zhang, Inhibiting efflorescence formation on fly ash–based geopolymer via silane surface modification, Cem. Concr. Compos. 94 (2018) 43–52, https://doi.org/10.1016/j.cemconcomp.2018.08.013.

[47] G. Ouyang, L. Wu, C. Ye, J. Wang, T. Dong, Effect of silane coupling agent on the rheological and mechanical properties of alkali-activated ultrafine metakaolin based geopolymers, Constr. Build. Mater. 290 (2021) 123223, https://doi.org/10.1016/j.conbuildmat.2021.123223.

[48] C. Zhang, Z. Hu, H. Zhu, X. Wang, J. Gao, Effects of silane on reaction process and microstructure of metakaolin-based geopolymer composites, J. Building Eng. 32 (2020) 101695, https://doi.org/10.1016/j.jobe.2020.101695.

[49] C. Zhang, X. Wang, Z. Hu, Q. Wu, H. Zhu, J. Lu, Long-term performance of silane coupling agent/metakaolin based geopolymer, J. Building Eng. 36 (2021) 102091, https://doi.org/10.1016/j.jobe.2020.102091.

[50] M.A.H. Bhuyan, C. Kurtulus, A. Heponiemi, T. Luukkonen, Peracetic acid as a novel blowing agent in the direct foaming of alkali-activated materials, Appl. Clay Sci. 231 (2023) 106727, https://doi.org/10.1016/j.clay.2022.106727.

[51] R. Zhang, H. Zhao, Small-angle particle counting coupled photometry for real-time detection of respirable particle size segmentation mass concentration, Sensors. 21 (2021) 5977, https://doi.org/10.3390/s21175977.

[52] K. Pasupathy, M. Berndt, A. Castel, J. Sanjayan, R. Pathmanathan, Carbonation of a blended slag-fly ash geopolymer concrete in field conditions after 8years, Constr. Build. Mater. 125 (2016) 661–669, https://doi.org/10.1016/j.conbuildmat.2016.08.078.

[53] Y. Xiang, Y. He, W. Zhang, B. Li, H. Li, Y. Wang, X. Yin, W. Tang, Z. Li, Z. He, Superhydrophobic LDH/TTOS composite surface based on microstructure for the anti-corrosion, anti-fouling and oil-water separation application, Colloids Surf A Physicochem Eng Asp. 622 (2021) 126558, https://doi.org/10.1016/j.colsurfa.2021.126558.

[54] M. Ma, Y. Zhang, W. Yu, H. Shen, H. Zhang, N. Gu, Preparation and characterization of magnetite nanoparticles coated by amino silane, Colloids Surf A Physicochem Eng Asp. 212 (2003) 219–226, https://doi.org/10.1016/S0927-7757(02)00305-9.

[55] E. McCafferty, J.P. Wightman, Determination of the concentration of surface hydroxyl groups on metal oxide films by a quantitative XPS method, Surf. Interface Anal. 26 (1998) 549–564, https://doi.org/10.1002/(SICI)1096-9918(199807)26:8<549::AID-SIA396>3.0.CO;2-Q.

[56] A. Avila, I. Montero, L. Galán, J.M. Ripalda, R. Levy, Behavior of oxygen doped SiC thin films: an x-ray photoelectron spectroscopy study, J. Appl. Phys. 89 (2001) 212–216, https://doi.org/10.1063/1.1332796.

[57] Y.-Y. Wang, K. Kusumoto, C.-J. Li, XPS analysis of SiC films prepared by radio frequency plasma sputtering, Phys. Procedia. 32 (2012) 95–102, https://doi.org/10.1016/j.phpro.2012.03.524.

[58] M.E. Simonsen, C. Sønderby, Z. Li, E.G. Søgaard, XPS and FT-IR investigation of silicate polymers, J Mater Sci. 44 (2009) 2079–2088, https://doi.org/10.1007/s10853-009-3270-9.

[59] M. Van Do, T.X.T. Le, N.D. Vu, T.T. Dang, Distribution and occurrence of microplastics in wastewater treatment plants, Environ. Technol. Innov. 26 (2022) 102286, https://doi.org/10.1016/j.eti.2022.102286.

[60] M. Liu, X. Liu, S. Zheng, K. Jia, L. Yu, J. Xin, J. Ning, W. Wen, L. Huang, J. Xie, Environment-Friendly superhydrophobic sponge for highly efficient Oil/Water separation and microplastic removal, Sep. Purif. Technol. 319 (2023) 124060, https://doi.org/10.1016/j.seppur.2023.124060.

[61] O. Rius-Ayra, M. Carmona-Ruiz, N. Llorca-Isern, Superhydrophobic cotton fabrics for effective removal of high-density polyethylene and polypropylene microplastics: insights from surface and colloidal analysis, J. Colloid Interface Sci. 646 (2023) 763–774, https://doi.org/10.1016/j.jcis.2023.05.127.

[62] J. Talvitie, A. Mikola, A. Koistinen, O. Setälä, Solutions to microplastic pollution – removal of microplastics from wastewater effluent with advanced wastewater treatment technologies, Water Res. 123 (2017) 401–407, https://doi.org/10.1016/j.watres.2017.07.005.

[63] I.E. Napper, R.C. Thompson, Release of synthetic microplastic plastic fibres from domestic washing machines: effects of fabric type and washing conditions, Mar. Pollut. Bull. 112 (2016) 39–45, https://doi.org/10.1016/j.marpolbul.2016.09.025.

[64] F. De Falco, M.P. Gullo, G. Gentile, E. Di Pace, M. Cocca, L. Gelabert, M. Brouta-Agnésa, A. Rovira, R. Escudero, R. Villalba, R. Mossotti, A. Montarsolo, S. Gavignano, C. Tonin, M. Avella, Evaluation of microplastic release caused by textile washing processes of synthetic fabrics, Environ. Pollut. 236 (2018) 916–925, https://doi.org/10.1016/j.envpol.2017.10.057.

[65] J. Bayo, J. López-Castellanos, S. Olmos, Membrane bioreactor and rapid sand filtration for the removal of microplastics in an urban wastewater treatment plant, Mar. Pollut. Bull. 156 (2020) 111211, https://doi.org/10.1016/j.marpolbul.2020.111211.

[66] J. Wang, C. Sun, Q.-X. Huang, Y. Chi, J.-H. Yan, Adsorption and thermal degradation of microplastics from aqueous solutions by Mg/Zn modified magnetic biochars, J. Hazard. Mater. 419 (2021) 126486, https://doi.org/10.1016/j.jhazmat.2021.126486.

[67] N. Mohanan, Z. Montazer, P.K. Sharma, D.B. Levin, Microbial and enzymatic degradation of synthetic plastics, Front. microbiol. 11 (2020) 580709, https://doi.org/10.3389/fmicb.2020.580709.

[68] M.A.H. Bhuyan, A. Karkman, H. Prokkola, B. Chen, P. Perumal, T. Luukkonen, Alkali-activated foams coated with colloidal Ag for point-of-use water disinfection, ACS EST Water 4 (2024) 687–697, https://doi.org/10.1021/acsestwater.3c00711.