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Comparison of AOP, GAC, and Novel Organosilane-Based Process for the Removal of Microplastics at a Municipal Wastewater Treatment Plant

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Abstract: Wastewater treatment plants (WWTPs) have been identified as important point sources of micropollutants and microplastics into the environment. Existing fourth cleaning steps are designed to remove dissolved micropollutants, however do not target dispersed solids such as microplastics. Therefore, the ability of an Advanced Oxidation Process (AOP) and Granular Activated Carbon (GAC) in parallel and serial connection to remove microplastics was investigated and determined. The pilot plants were operated at the municipal WWTP Landau, Germany, a three-step biological waste treatment plant with a capacity of 80,000 population equivalents. A Nile red-based detection method was applied to quantify microplastics. Neither method showed a significant removal of microplastics. To achieve a simultaneous removal of microplastics and dissolved micropollutants, a pilot plant using organosilanes for microplastics' removal was connected in series with the GAC. When added to the water, the organosilanes attach to the microplastics and collect them in agglomerates by chemically binding them in a water-induced sol–gel process. The pilot plant for microplastics' removal was operated with a flow rate of 12 m^3/h and a retention time of 10 min; the GAC with 2 m^3/h and a retention time of 1 h. An average reduction in micropollutants by 86.2 ± 2.0% and a reduction in microplastics by 60.9 ± 27.5% was reached. Thus, there is an effective reduction in micropollutants and a significant reduction in microplastics. Further optimizations of the pilot plant are expected to result in a more stable and higher removal performance.

Keywords: microplastics; micropollutants; wastewater treatment plant; microplastics removal; Nile red; advanced oxidation process; granular activated carbon; organosilanes; sol–gel process

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1. Introduction

One of the biggest challenges of modern wastewater treatment is the removal of micropollutants and microplastics from wastewater to reduce their entry into the environment [1–5]. For years, the wastewater industry has been confronted with a continuous change in micropollutants' concentrations in water (Figure 1). The final goal of water quality management under the Water Framework Directive (WFD) is to ensure good water quality of European surface and groundwater bodies (EU Directive 2000/60/EC). The EU Urban Wastewater Treatment Directive (UWWTD) works in synergy with the WFD; the recent proposal for a revised UWWTD includes a requirement for certain wastewater treatment plants to be equipped with an additional treatment that targets micropollutants' removal [6].

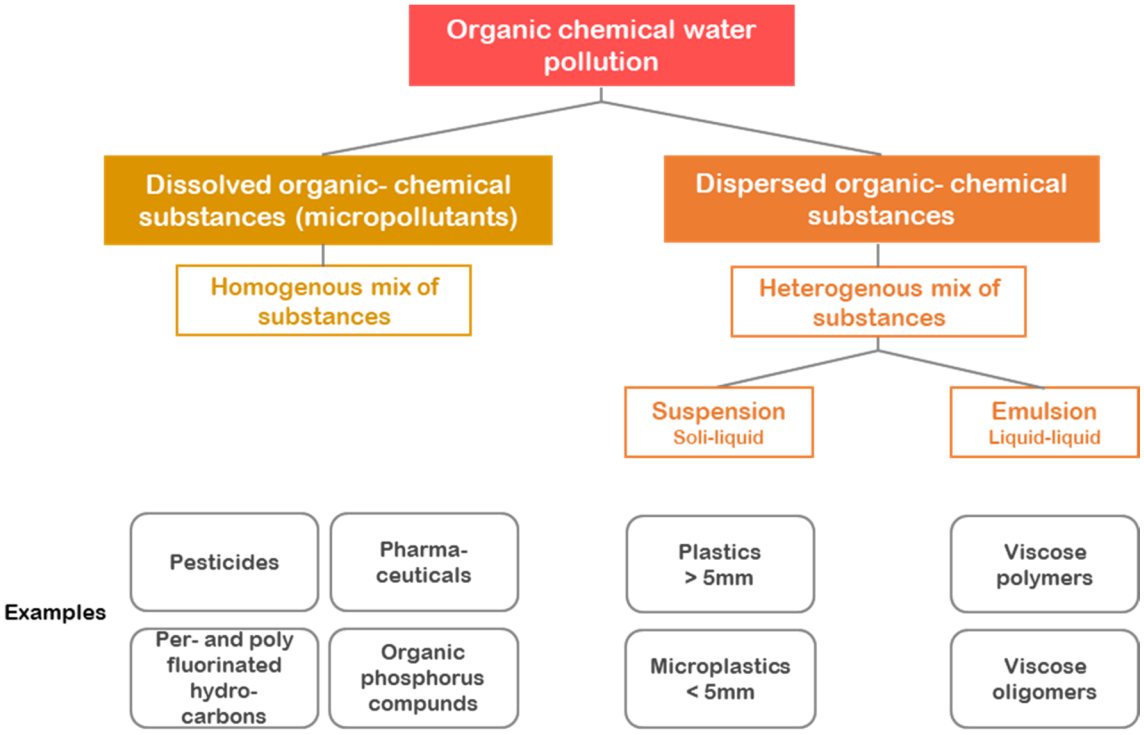

Figure 1. Overview of micropollutants that are discharged into the environment or receiving waters via wastewater treatment plants (Source: Wasser 3.0).

Micropollutants are synthetically produced contaminants typically found at concentrations of nano- to microgram per liter [7,8]. They include substances such as pharmaceuticals, pesticides, PFAS (PFC), industrial compounds (e.g., solvents, benzene, and benzidine), and microplastics. A distinction is made between the total organic chemical loadings in dissolved and insoluble organic chemical compounds (Figure 1). Each compound has a specific behavior in WWTPs, and therefore is either completely or partially degraded or transformed; sorbed to sludge; volatilized; or unchanged, during the three purification steps of the WWTP, prior to entering the environment, the ecosystem, or both [8].

As many micropollutants can pass unhindered through the three treatment steps of a municipal wastewater treatment plant (WWTP), there is a need for a fourth cleaning step for central wastewater treatment, which should remove substances that are classified as potentially hazardous. The revised EU Urban Wastewater Treatment Directive (2022/0345 (COD)) has identified 13 micropollutants in two categories that can pollute waters even at low concentrations [6]. All WWTP for >100,000 p.e., and facilities with >10,000 p.e. discharging into risk areas, must upgrade their facilities to target micropollutants' removal. Limit values will be identified and an 80% removal of at least 6 of the 13 substances must be achieved.

The most commonly applied fourth cleaning steps are powdered or granular activated carbon (PAC or GAC), ozonation, or advanced oxidation processes (AOP) [9–11]. While PAC and GAC remove the micropollutants from water by adsorption, ozonation and AOP degrade the substances through oxidation. Those technologies are designed to remove dissolved organic micropollutants, but not to remove microplastics.

Various methods, such as rapid sand filtration, membrane filtration or drum and disc filters, are currently discussed for microplastics' removal from waters and wastewaters [12–14]. Microplastic characteristics, such as their shape and size, impact on their potential removal rates and necessary operational parameters. The smaller the microplastics that should be removed, the higher the technical complexity of the filtration process, resulting in increased costs, maintenance requirements, and energy consumption [15–17]. For example, membrane-based filtration techniques can remove microplastics efficiently, but suffer from high

energy consumption and membrane fouling that results in high maintenance needs [16–18]. Sedimentation and flotation are not suited to remove microplastics efficiently, due to the small particle size resulting in low sinking or settling speeds and the various densities of the different plastic types, which are often close to the density of water [19]. Techniques such as dissolved air flotation are also inefficient for microplastics' removal and have a high energy consumption [20]. Commonly used flocculants and coagulants are hardly applicable, due to the highly varying surface properties of different microplastics which makes finding appropriate flocculants challenging [21].

Therefore, there is a need for new and innovative approaches for microplastics' removal from water. Examples for novel methods are the application of metal–organic frameworks (MOF) or heteroaggregation with magnetic iron-based nanoparticles followed by magnetic sedimentation [22–24].

A promising approach to remove microplastics from water is to use organosilanes for agglomeration and their subsequent removal [25–28]. It has been tested and validated at laboratory scale for various polymer types (polyethylene, polypropylene, polyamide, polyester, and polyvinyl chloride) in both wastewater and seawater [29]. The used organosilanes consist of a silica atom as the core atom together with reactive groups, which gives it its specific reactivity and organic groups, which can interact and attach to microplastics dispersed in water [25–28]. Thus, the water initiates a hydrolysis of reactive groups of the organosilane, followed by a condensation, whereby they form chemical siloxane bonds and a three-dimensional hybrid silica network (sol–gel process) [30]. This hybrid silica formation fixes and collects the microplastics in solid agglomerates, which float on the water surface and can be easily removed by skimming processes.

Fourth treatment steps such as AOP and GAC are designed to remove dissolved organic micropollutants, but not to remove microplastics. However, their potential to remove microplastics from wastewater is often discussed [31–33]. This study evaluates the ability of GAC and AOP pilot plants to remove microplastics from wastewater using a microplastics' detection method based on Nile red. The pilot plants are operated in parallel and in series at the effluent of a tertiary municipal WWTP in Landau, Germany.

In order to create a holistic process that removes both dissolved organic micropollutants and microplastics, the GAC is combined with a novel method for microplastics removal based on organosilane-induced agglomeration, creating a fourth cleaning step and microplastics' removal [25–28]. The pilot plant for microplastics' removal can be applied as an add-on before or after existing cleaning processes.

2. Materials and Methods

2.1. Study Area

The pilot plants were operated at the tertiary WWTP Landau-Moerlheim. The WWTP has a capacity of 80,000 population equivalents. Primary treatment consists of rakes, a sand trap, and a fat separator. The secondary biological treatment is followed by a tertiary phosphate elimination. The catchment area contains households, industry, and agriculture, mainly viticulture.

The flow rate ranges from 9000 to 13,000 m^3/d during dry weather periods and up to 40,000 m^3/d during rain events. The average hydraulic retention time (HRT) is 24 h and the average sludge retention time is 12–14 d. The treated wastewater in the effluent has an average chemical oxygen demand (COD) of 20 mg/L, 6.5 mg/L nitrate, <1 mg/L ammonia, and a total phosphorus concentration of 0.3 mg/L.

2.2. GAC and AOP Pilot Plants

The AOP (Advanox™; Van Remmen UV Technology, Wijhe, The Netherlands) used H_2O_2 (Nouryon, Amsterdam, The Netherlands) as an oxidant in combination with photolytic degradation by UV light. It was equipped with four UV reactors (Focus 200) with individual 600 W low-pressure UV-C lamps. During testing, the flow rate was set to

6 m^3/h, the UVC dose to 7.5 kJ/m^2, and the H_2O_2 dose at 30 ppm for a transmission range of 60–72% T10.

The GAC procedure was performed with a DynaSand® carbon filter (Nordic Water, Neuss, Germany) filled with 1.1 m^3 AquaSorb™ 2000 (Jacobi Carbons, Premnitz, Germany). The activated carbon had a size range from 2.36 to 0.60 mm with an average of 1.4 mm, an iodine value of min. 1000 mg/g, and a surface area of 950 m^2/g. An airlift pump circulates the activated carbon in the filter, which prevents clogging. With a flow rate of 2 m^3/h, the contact time was 33 min.

In the series connection, the AOP effluent was used as the inflow for the GAC. The flow rate was set to 6 m^3/h, resulting in a GAC contact time of 11 min.

2.3. Wasser 3.0 PE-X® Pilot Plant

The Wasser 3.0 PE-X® pilot plant is made of stainless steel and has a capacity of 2 m^3. It was operated via pumps with a flow rate of 12 m^3/h or 288 m^3/d. The dosing of the organosilane used for the agglomeration and fixation of the microplastics (abcr eco Wasser 3.0 PE X®, AB 930003; abcr GmbH, Karlsruhe, Germany) was conducted manually. At the beginning of the pilot plant commissioning, 15 mL of abcr eco Wasser 3.0 PE X® and 15 g of a microplastics' mixture of polyethylene and polypropylene was added, to create the first agglomerates to which the microplastics within the wastewater could bind. Further, 5 mL/d was added during the duration of the tests. After completion of the test series, the agglomerates were removed using a stainless-steel sieve with a mesh size of 5 mm.

2.4. Micropollutant Measurements

To evaluate the performance of the fourth treatment step pilot plants, representative composite samples were taken from the effluent of the third treatment step (which represented the influent of the fourth treatment step), and from the effluent of the fourth treatment step. For a qualified sample, 6 subsamples were taken at 10-min intervals over a 1 h period and transferred to a collection vessel for mixing. The offset time (20 min for AOP and 1 h for GAC), which resulted from the retention time of the water in the pilot plants, must be considered during sampling. Samples were placed in sample vials and frozen until transport to the external analytical laboratory. To remove residual hydrogen peroxide from the AOP sample, 300 µL of catalase (AB139273; abcr GmbH, Karlsruhe, Germany) was added to a 600 mL sample before freezing.

The following 10 micropollutants (Table 1) were analyzed according to DIN standards by Limbach Analytics GmbH, Mannheim Laboratory, Germany [34].

Table 1. Analytical methods used to analyze the water samples for micropollutants.

Parameter	Test Procedure
Candesartan *	LAM-MLC.M.0051: 2015-08 **
Carbamazepine *	LAM-MLC.M.0051: 2015-08 **
Diclofenac *	LAM-MLC.M.0051: 2015-08 **
Hydrochlorothiazide *	LAM-MLC.M.0051: 2015-08 **
Ibuprofen	LAM-MLC.M.0051: 2015-08 **
Irbesartan *	LAM-MLC.M.0051: 2015-08 **
Metoprolol *	LAM-MLC.M.0051: 2015-08 **
Sulfamethoxazole	LAM-MLC.M.0051: 2015-08 **
Benzotriazole *	LAM-MLC.M.0051: 2015-08 **
Sum of 4- and 5-methylbenzotriazole *	LAM-MLC.M.0051: 2015-08 **

Notes: * Micropollutants identified for targeted removal and monitoring in the revised EU Urban Wastewater Treatment Directive (2022/0345 (COD)); ** In-house standard by Limbach Analytics GmbH, oriented on DIN 38407-47:2017-07.

2.5. Microplastics Detection

The microplastics' detection was performed by the following the procedure [35]. Sampling was performed using a stainless-steel filter cartridge with a mesh size of 10 µm

(01WTGD; Wolftechnik Filtersysteme GmbH & Co.KG, Weil, Germany) and a 0.9 kW centrifugal pump (MG80B C-B-CMS1B; Grundfos, Erkrath, Germany). The inlet tubing was made of black polyvinyl chloride (PVC), which does not show a fluorescent signal when dyed with Nile red and therefore does not contaminate the sample. A total of 100 l samples from the influent and effluent of the fourth treatment steps were taken. The samples were transferred to 2.5 L glass bottles for transport and storage.

In the laboratory, samples were then processed and stained with Nile red for microplastics detection. Then, 500 mL of each sample was filtered through a 10 µm stainless-steel sieve (custom made, Ø 47 mm; Wolftechnik Filtersysteme GmbH & Co.KG, Weil, Germany; DURAN® filtration apparatus, Cat. No. 257106304; DWK Life Sciences GmbH, Mainz, Germany).

To chemically digest natural particles in the sample, each sieve was placed in a 250 mL beaker and covered with 20 mL H_2O_2. Then, 3–5 grains of ferrous sulfate were added, and the beaker heated. Once it was brought to a boil, it was reduced to 80 °C for 4 h and left at room temperature for another 20 h.

The stainless-steel sieves were removed and rinsed into the beaker containing the remaining H_2O_2. To remove the digested organics, the mixture in the beaker was then filtered through a 10 µm stainless-steel sieve and rinsed with 100 mL of water. The particles from the sieve were washed from the surface of the sieve into the beaker and filled up to 100 mL with distilled water.

For staining with the fluorescent marker, 100 µL of a 1 g/L Nile Red stock solution in acetone was added to each beaker (c = 0.1 mg/L) and left for 24 h. Each sample was then filtered through a black circular filter (Metricel® Black PES Membrane Disc Filters; Pall Cooperation, Dreieich, Germany) and stored in a glass Petri dish.

Microplastic detection was performed using a Leica DMS300 light microscope (Leica Mikrosysteme Vertrieb GmbH, Wetzlar, Germany) and LAS-X 3.0.1423224 software. For fluorescence imaging, the microscope was modified with a UV flashlight (TATTU U3S; Taitu (Shenzhen) Outdoor Supplies Co., Ltd., Shenzhen, China) with a peak wavelength of 365 nm as the light source for fluorescence excitation and a yellow-colored color film (Shenzhen Neewer Technology Co., Ltd., Shenzhen, China) for the detection filter. Images and corresponding fluorescence images of 5 squares with a size of 3 × 3 mm were acquired for each sample. The particles were classified as microplastics based on their fluorescence signal.

For contamination control, only glass and metal equipment were used in the laboratory. Beakers and vessels were always covered with aluminum foil. The laboratory was cleaned with lint-free cotton cloths and a HEPA filter was operated to remove particulates from the air. A lint-free protective suit (4510M; 3M Deutschland GmbH, Ness, Germany) was worn and cleaned with a lint brush prior to entering the laboratory, to prevent the entry of clothing fibers. To control for sample contamination, blank samples were measured. An average blank value of 5.17 microplastics/L was subtracted from all results.

3. Results and Discussion

3.1. Removal Performance of GAC and AOP for Microplastics

A previous study investigated the dissolved micropollutants removal from wastewater for the AOP and GAC systems presented within this study. Average micropollutants' removals of 76.4 ± 6.2% for AOP and 90.0 ± 4.6% for GAC showed that dissolved micropollutants can be removed efficiently by these pilot plants [36]. The capability of these pilot plants to remove microplastics is shown in Figure 2.

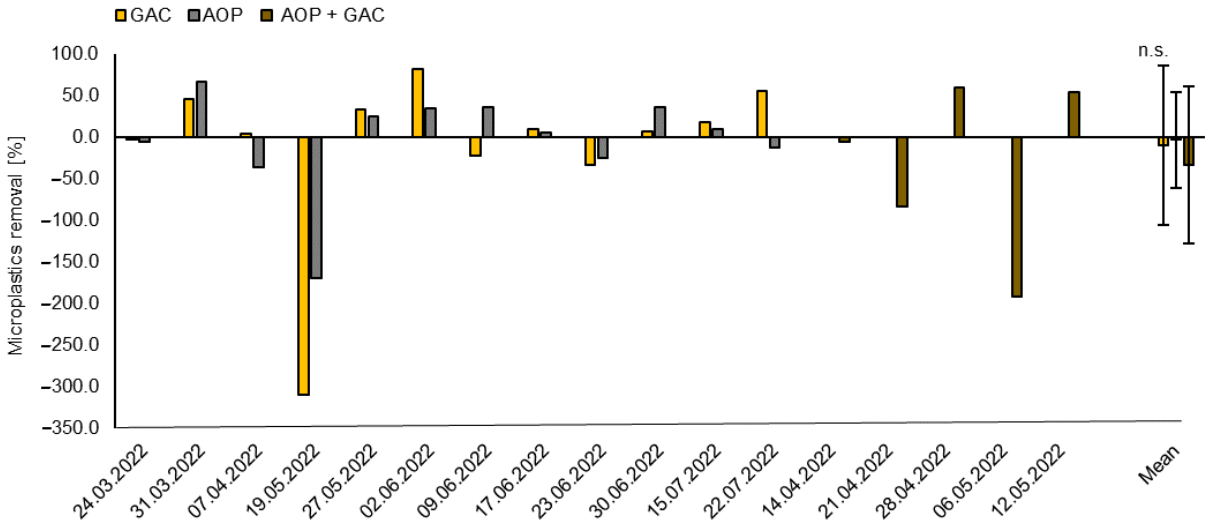

Figure 2. Measured microplastics' removal using GAC and AOP in parallel and series connection (AOP before GAC). The reduction is measured as the difference in microplastics' concentrations between the influent and effluent of the fourth cleaning step. Every sample was performed as a duplicate. n.s.—not statistically significant, *t*-test, paired, 1-sided, $p < 0.05$.

The microplastics' contamination of the effluent of the third cleaning step, with respect to the influent of the fourth cleaning step, ranged from 6.4 microplastics/L to 62.1 microplastics/L with an average of 29.1 ± 15.1 microplastics/L, which is a typical contamination for wastewater treatment plants [37]. For all tested setups, the measured microplastics' removal shows high fluctuations between the test runs. For GAC, the measured removal ranges from −310% (3.1 times increase) to 82.5% with an average reduction of −9.1 ± 95.5% over all 12 test runs. For the AOP, there is an average reduction of −2.8 ± 57.7% ranging from −170% (1.7 times increase) to 66.7%. The serial connection of AOP and GAC showed removals from −192% (1.9 times increase) to 59.8%. On average, a 33.4 ± 94.5% increase in microplastics was measured. Overall, due to the high fluctuations between the test runs, no significant microplastics' removal is detected with any of these combinations (*t*-test, paired, two sided). This shows that the AOP and GAC have no measurable effect on the microplastics' concentrations.

The high fluctuations between the test runs, with both increases and decreases in microplastics' concentrations depending on the sampling day, are caused by the temporal variations in the microplastics in the wastewater, which have been discussed in a previous long-term study that investigated the microplastics' contamination in the effluent of the wastewater treatment plant in Landau over a period of one year [37]. This previous study showed an average microplastics' concentration of 41 microplastics/L with a high variation between the sampling days ranging from 1 to 145 microplastics/L. In addition, it was observed that in a time span of 15 min the microplastics' concentration can vary by a factor of 10. These variations make it difficult to quantify the removal performance and it needs an effective and robust removal process to achieve reproducible results. GAC and AOP do not meet these criteria.

As AOPs have been shown to successfully remove micropollutants from wastewater, their potential use for microplastics' removal has also been tested in various laboratory experiments [32,33]. However, these experiments involved exposure times of several hours up to several days. Typically, the chemical transformation of the surfaces, cracking, or fragmentation are observed. Some polymers are partially degraded, but at slow degradation rates, which depend on the used AOP and polymer [33]. Further, incomplete oxidation may result in the formation of toxic intermediate products [38,39]. Therefore, currently tested AOP processes are unsuitable for the removal of microplastics from wastewater.

The application of activated carbon for microplastics' removal is less discussed, as GAC targets dissolved pollutants rather than suspended solids. A recent study could show a partial removal of nano plastics using activated carbon, depending on the flow rate, contact time, aging of the activated carbon, and aging of the nano plastics [40]. Long contact times, slow flow rates, and fresh activated carbon are all beneficial for the removal process. Removal performances between 35 and 79% were reached. In addition, the study performed a combination of ozonation and GAC treatment on lab scale. Surface transformation of the microplastics by ozonation showed only a slight increase of 2% in the nano plastics removal. This is in line with the findings of this study, where the combination of AOP and GAC had no significant effect on the microplastics' removal efficiency. Moreover, Kim and Park (2021) found a significant removal of 92.8% by applying a granular-activated carbon with thermal regeneration [31]. The study worked with a lower flow rate (0.42 m^3/h) and a comparable amount of carbon (800 kg). Thus, the removal may have been induced by the thermal regeneration, the longer contact time, or the type of GAC used.

There is currently a large emphasis on the use of advanced treatment methods to remove micropollutants from wastewaters. However, due to the current lack of policies on microplastics' production and regulations surrounding the input of microplastics into the environment, microplastics are not yet targeted by such advanced treatment processes. The ability of such methods to remove microplastics is currently ineffective and often not considered when determining their feasibility for use at WWTPs.

3.2. Organosilane-Induced Microplastics' Removal Combined with GAC

To achieve the simultaneous removal of dissolved microscopic substances and microplastics, the effluent of the Wasser 3.0 PE-X process for removing microplastics was connected in series with the influent of the GAC. This resulted in an average micropollutants' reduction of (Figure 3) 86.2 ± 2.0% and average microplastics' reduction of 60.9 ± 27.5%. Thus, there is an effective reduction in micropollutants and a significant reduction in microplastics.

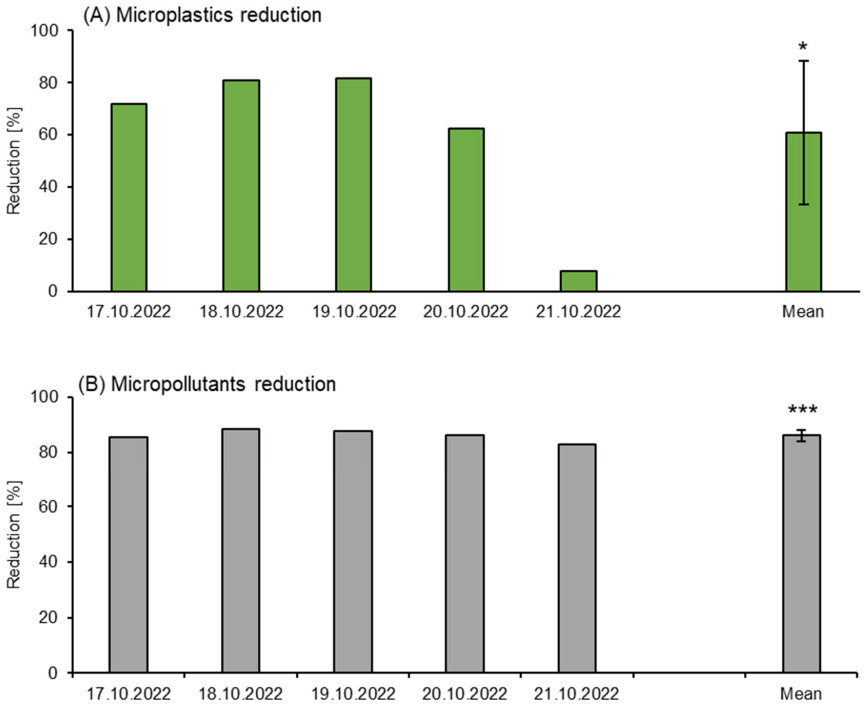

Figure 3. Removal of (**A**) microplastics and (**B**) micropollutants within the pilot plant trails for organosilane-induced microplastics removal combined with GAC. The reduction is measured as the difference in concentrations between the influent and effluent of the fourth cleaning step. * = $p < 0.05$; *** = $p < 0.001$, *t* test, paired, 1-sided.

The removal performance of the micropollutants ranges from 82.7 to 88.6% and is in the range observed in the previous long-term study [36]. Since the removal performance of GAC shows fluctuations over time and decreases with the treated wastewater volume, a direct comparison of these data of GAC without Wasser 3.0 PE-X is not possible, and it cannot be determined whether the Wasser 3.0 PE-X reactor has a positive influence on the micropollutants' reduction.

The microplastics' removal ranges from 7.9 to 81.5%. In previous lab scale studies, the organosilanes used in this study showed an effective agglomeration (removal < 90%) of microplastics in different waters, including wastewater [26–29]. When added to water containing microplastics, the organosilanes attach to the microplastics and collect it in large agglomerates. Due to a water-induced sol–gel process the organosilanes form siloxane bonds creating a three-dimensional network, which chemically fixes the agglomerates, making them solid and easy to remove from the water. The agglomerates flow on the water surface and can be skimmed from the water. For the agglomeration process, the interaction of the organosilanes with the microplastics' surface are essential. Due to their better interaction with the organosilanes used in this study, non-polar polymer types as polyethylene and polypropylene are easier to remove than polar polymer types as polyamide or polyvinyl chloride [29]. In addition, the attachment of natural organic matter and biofilm growth can alter the microplastics' surface and influence the removal process [28].

A particular challenge of the upscaling and transfer of the process is the much lower microplastics' concentration of the treated wastewater compared to the laboratory experiments. For an effective agglomeration process, ideal flow conditions are needed that enable the microplastics to have contact with both existing agglomerates and the organosilanes, so that they can be fixed. The Wasser 3.0 PE-X pilot plant is the first prototype. Thus, it is expected to achieve a more stable and better removal performance by optimizing the water flow conditions and contact time. In comparison to the GAC and AOP process, the removal performance of the Wasser 3.0 PE-X pilot plant is effective and robust enough to compensate for the fluctuations in microplastics' concentrations in the wastewater and reach a statistically significant removal of microplastics. To further improve the quantification of the removal performance, future studies should obtain samples simultaneously from the influent and effluent over a longer period.

Compared to alternative methods that are often discussed for microplastics' removal at WWTPs, such as filtration or flotation techniques, the primary advantage of Wasser 3.0 PE-X is the low energy consumption, which can be further reduced if it is integrated into the hydraulic gradients of the WWTP [14]. Due to the simple setup of the reactor, low maintenance requirements and investment costs are also expected.

Summarized (Table 2) AOP and GAC can effectively remove dissolved micropollutants, but not microplastics. Wasser 3.0 PE-X can remove microplastics, however a possible reduction in micropollutants by sorption into the organosilanes is not yet investigated. The combination of Wasser 3.0 PE-X can effectively remove micropollutants and microplastics.

Table 2. Comparison of the investigated methods for the removal of microplastics and micropollutants from water.

Method	Microplastics Removal	Micropollutants Removal
AOP	No	Yes
GAC	No	Yes
Wasser 3.0 PE-X	Yes	Not investigated
Wasser 3.0 PE-X + GAK	Yes	Yes

4. Conclusions

Current wastewater treatment processes, along with advanced treatment steps, are not designed to target microplastics' removal. This study showed no significant removal of microplastics by the GAC or AOP pilot plants when used as fourth cleaning step in

parallel or serial connection. The measured microplastics' removal shows high fluctuations between the test runs. For GAC, the measured removals range from −310% to 82.5%; for the AOP from −170% to 66.7%; and for the serial connection of AOP and GAC, removals of −192% to 59.8% were found. Therefore, there is a need for an adaptation of the fourth cleaning steps to not only remove dissolved micropollutants, but additionally to target microplastics.

The combination of organosilane-induced microplastics' removal and GAC as a fourth cleaning step showed a good removal performance for dissolved micropollutants (86.2 ± 2%) and a significant removal of microplastics (60.9 ± 27.5%). In the pilot plant for microplastics' removal, organosilanes attached to the microplastics suspended in the water and collected them in large agglomerates, which were then easy to remove by skimming.

This shows the potential of organosilane-induced microplastics' removal as an effective add-on for microplastics' removal in advanced wastewater treatment. It can be combined with various existing fourth treatment steps. The advantages of this method are the low energy consumption compared to methods based on filtration or flotation, as well as the low technical effort and low maintenance requirements. Further optimizations of the pilot plant are expected to result in a more stable and higher removal performance.

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References

1. Luo, Y.; Guo, W.; Ngo, H.H.; Nghiem, L.D.; Hai, F.I.; Zhang, J.; Liang, S.; Wang, X.C. A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. *Sci. Total Environ.* **2014**, *473–474*, 619–641. [CrossRef] [PubMed]
2. Eggen, R.I.L.; Hollender, J.; Joss, A.; Schärer, M.; Stamm, C. Reducing the discharge of micropollutants in the aquatic environment: The benefits of upgrading wastewater treatment plants. *Environ. Sci. Technol.* **2014**, *48*, 7683–7689. [CrossRef] [PubMed]
3. Gautam, K.; Anbumani, S. Ecotoxicological effects of organic micro-pollutants on the environment. In *Current Developments in Biotechnology and Bioengineering*; Elsevier: Amsterdam, The Netherlands, 2020; pp. 481–501. ISBN 9780128195949.
4. Bayo, J.; Olmos, S.; López-Castellanos, J. Removal of Microplastics from Wastewater. In *Handbook of Microplastics in the Environment*; Rocha-Santos, T., Costa, M., Mouneyrac, C., Eds.; Springer International Publishing: Cham, Switzerland, 2020; pp. 1–20. ISBN 978-3-030-10618-8.

5. Ben-David, E.A.; Habibi, M.; Haddad, E.; Hasanin, M.; Angel, D.L.; Booth, A.M.; Sabbah, I. Microplastic distributions in a domestic wastewater treatment plant: Removal efficiency, seasonal variation and influence of sampling technique. *Sci. Total Environ.* **2021**, *752*, 141880. [CrossRef] [PubMed]
6. European Commission. Proposal for a DIRECTIVE OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL Concerning Urban Wastewater Treatment (Recast). Available online: https://environment.ec.europa.eu/system/files/2022-10/Proposal%20for%20a%20Directive%20concerning%20urban%20wastewater%20treatment%20%28recast%29.pdf (accessed on 19 January 2023).
7. Chavoshani, A.; Hashemi, M.; Mehdi Amin, M.; Ameta, S.C. *Introduction. Micropollutants and Challenges*; Elsevier: Amsterdam, The Netherlands, 2020; pp. 1–33. ISBN 9780128186121.
8. Margot, J.; Rossi, L.; Barry, D.A.; Holliger, C. A review of the fate of micropollutants in wastewater treatment plants. *WIREs Water* **2015**, *2*, 457–487. [CrossRef]
9. Ikehata, K.; Jodeiri Naghashkar, N.; Gamal El-Din, M. Degradation of Aqueous Pharmaceuticals by Ozonation and Advanced Oxidation Processes: A Review. *Ozone Sci. Eng.* **2006**, *28*, 353–414. [CrossRef]
10. Mansour, F.; Al-Hindi, M.; Yahfoufi, R.; Ayoub, G.M.; Ahmad, M.N. The use of activated carbon for the removal of pharmaceuticals from aqueous solutions: A review. *Rev. Env. Sci. Biotechnol.* **2018**, *17*, 109–145. [CrossRef]
11. Zepon Tarpani, R.R.; Azapagic, A. Life cycle environmental impacts of advanced wastewater treatment techniques for removal of pharmaceuticals and personal care products (PPCPs). *J. Environ. Manag.* **2018**, *215*, 258–272. [CrossRef]
12. Kurt, Z.; Özdemir, I.; James, R.A.M. Effectiveness of microplastics removal in wastewater treatment plants: A critical analysis of wastewater treatment processes. *J. Environ. Chem. Eng.* **2022**, *10*, 107831. [CrossRef]
13. Krishnan, R.Y.; Manikandan, S.; Subbaiya, R.; Karmegam, N.; Kim, W.; Govarthanan, M. Recent approaches and advanced wastewater treatment technologies for mitigating emerging microplastics contamination—A critical review. *Sci. Total Environ.* **2023**, *858*, 159681. [CrossRef]
14. Priya, A.; Anusha, G.; Thanigaivel, S.; Karthick, A.; Mohanavel, V.; Velmurugan, P.; Balasubramanian, B.; Ravichandran, M.; Kamyab, H.; Kirpichnikova, I.M.; et al. Removing microplastics from wastewater using leading-edge treatment technologies: A solution to microplastic pollution-a review. *Bioprocess Biosyst. Eng.* **2023**, *46*, 309–321. [CrossRef]
15. Bayo, J.; López-Castellanos, J.; Olmos, S. Membrane bioreactor and rapid sand filtration for the removal of microplastics in an urban wastewater treatment plant. *Mar. Pollut. Bull.* **2020**, *156*, 111211. [CrossRef]
16. Poerio, T.; Piacentini, E.; Mazzei, R. Membrane Processes for Microplastic Removal. *Molecules* **2019**, *24*, 4148. [CrossRef] [PubMed]
17. Golgoli, M.; Khiadani, M.; Shafieian, A.; Sen, T.K.; Hartanto, Y.; Johns, M.L.; Zargar, M. Microplastics fouling and interaction with polymeric membranes: A review. *Chemosphere* **2021**, *283*, 131185. [CrossRef]
18. Enfrin, M.; Wang, J.; Merenda, A.; Dumée, L.F.; Lee, J. Mitigation of membrane fouling by nano/microplastics via surface chemistry control. *J. Membr. Sci.* **2021**, *633*, 119379. [CrossRef]
19. Schuhen, K.; Sturm, M.T. Microplastic Pollution and Reduction Strategies. In *Handbook of Microplastics in the Environment*; Rocha-Santos, T., Costa, M., Mouneyrac, C., Eds.; Springer International Publishing: Cham, Switzerland, 2020; pp. 1–33. ISBN 978-3-030-10618-8.
20. Wang, Y.; Li, Y. 'n.; Tian, L.; Ju, L.; Liu, Y. The removal efficiency and mechanism of microplastic enhancement by positive modification dissolved air flotation. *Water Environ. Res.* **2020**, *93*, 693–702. [CrossRef] [PubMed]
21. Tang, W.; Li, H.; Fei, L.; Wei, B.; Zhou, T.; Zhang, H. The removal of microplastics from water by coagulation: A comprehensive review. *Sci. Total Environ.* **2022**, *851*, 158224. [CrossRef]
22. Shi, X.; Zhang, X.; Gao, W.; Zhang, Y.; He, D. Removal of microplastics from water by magnetic nano-Fe3O4. *Sci. Total Environ.* **2022**, *802*, 149838. [CrossRef]
23. Lee, J.; Wang, J.; Oh, Y.; Jeong, S. Highly efficient microplastics removal from water using in-situ ferrate coagulation: Performance evaluation by micro-Fourier-transformed infrared spectroscopy and coagulation mechanism. *Chem. Eng. J.* **2023**, *451*, 138556. [CrossRef]
24. Bakhteeva, I.A.; Medvedeva, I.V.; Filinkova, M.S.; Byzov, I.V.; Minin, A.S.; Zhakov, S.V.; Uimin, M.A.; Patrakov, E.I.; Novikov, S.I.; Suntsov, A.Y.; et al. Removal of microplastics from water by using magnetic sedimentation. *Int. J. Environ. Sci. Technol.* **2023**, *52*, 1704. [CrossRef]
25. Herbort, A.F.; Sturm, M.T.; Fiedler, S.; Abkai, G.; Schuhen, K. Alkoxy-silyl Induced Agglomeration: A New Approach for the Sustainable Removal of Microplastic from Aquatic Systems. *J. Polym. Environ.* **2018**, *62*, 4258–4270. [CrossRef]
26. Herbort, A.F.; Sturm, M.T.; Schuhen, K. A new approach for the agglomeration and subsequent removal of polyethylene, polypropylene, and mixtures of both from freshwater systems—A case study. *Environ. Sci. Pollut. Res. Int.* **2018**, *25*, 15226–15234. [CrossRef] [PubMed]
27. Sturm, M.T.; Herbort, A.F.; Horn, H.; Schuhen, K. Comparative study of the influence of linear and branched alkyltrichlorosilanes on the removal efficiency of polyethylene and polypropylene-based microplastic particles from water. *Environ. Sci. Pollut. Res.* **2020**, *27*, 10888–10898. [CrossRef]
28. Sturm, M.T.; Schuhen, K.; Horn, H. Method for rapid biofilm cultivation on microplastics and investigation of its effect on the agglomeration and removal of microplastics using organosilanes. *Sci. Total Environ.* **2021**, *806*, 151388. [CrossRef] [PubMed]
29. Sturm, M.T.; Horn, H.; Schuhen, K. Removal of Microplastics from Waters through Agglomeration-Fixation Using Organosilanes—Effects of Polymer Types, Water Composition and Temperature. *Water* **2021**, *13*, 675. [CrossRef]

30. Brinker, C.J.; Scherer, G.W. *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*; Academic Press: Boston, MA, USA, 1990; ISBN 978-0-12-134970-7.
31. Kim, K.T.; Park, S. Enhancing Microplastics Removal from Wastewater Using Electro-Coagulation and Granule-Activated Carbon with Thermal Regeneration. *Processes* **2021**, *9*, 617. [CrossRef]
32. Shen, M.; Song, B.; Zhou, C.; Hu, T.; Zeng, G.; Zhang, Y. Advanced oxidation processes for the elimination of microplastics from aqueous systems: Assessment of efficiency, perspectives and limitations. *Sci. Total Environ.* **2022**, *842*, 156723. [CrossRef] [PubMed]
33. Kim, S.; Sin, A.; Nam, H.; Park, Y.; Lee, H.; Han, C. Advanced oxidation processes for microplastics degradation: A recent trend. *Chem. Eng. J. Adv.* **2022**, *9*, 100213. [CrossRef]
34. Kompetenzzentrum Spurenstoffe. Handlungsempfehlung für die Vergleichskontrolle und den Betrieb von Verfahrenstechniken zur Gezielten Spurenstoffelimination. Available online: https://koms-bw.de/cms/content/media/KomS_Handlungsempfehlung_2018.pdf (accessed on 1 February 2023).
35. Sturm, M.T.; Myers, E.; Schober, D.; Korzin, A.; Schuhen, K. Development of an Inexpensive and Comparable Microplastic Detection Method Using Fluorescent Staining with Novel Nile Red Derivatives. *Analytica* **2023**, *4*, 27–44. [CrossRef]
36. Sturm, M.T.; Myers, E.; Schober, D.; Thege, C.; Korzin, A.; Schuhen, K. Adaptable Process Design as a Key for Sustainability Upgrades in Wastewater Treatment: Comparative Study on the Removal of Micropollutants by Advanced Oxidation and Granular Activated Carbon Processing at a German Municipal Wastewater Treatment Plant. *Sustainability* **2022**, *14*, 11605. [CrossRef]
37. Azizi, N.; Nasseri, S.; Nodehi, R.N.; Jaafarzadeh, N.; Pirsaheb, M. Evaluation of conventional wastewater treatment plants efficiency to remove microplastics in terms of abundance, size, shape, and type: A systematic review and Meta-analysis. *Mar. Pollut. Bull.* **2022**, *177*, 113462. [CrossRef]
38. Ricardo, I.A.; Alberto, E.A.; Silva Júnior, A.H.; Macuvele, D.L.P.; Padoin, N.; Soares, C.; Gracher Riella, H.; Starling, M.C.V.M.; Trovó, A.G. A critical review on microplastics, interaction with organic and inorganic pollutants, impacts and effectiveness of advanced oxidation processes applied for their removal from aqueous matrices. *Chem. Eng. J.* **2021**, *424*, 130282. [CrossRef]
39. Rout, P.R.; Mohanty, A.; Aastha; Sharma, A.; Miglani, M.; Liu, D.; Varjani, S. Micro- and nanoplastics removal mechanisms in wastewater treatment plants: A review. *J. Hazard. Mater. Adv.* **2022**, *6*, 100070. [CrossRef]
40. Pulido-Reyes, G.; Magherini, L.; Bianco, C.; Sethi, R.; von Gunten, U.; Kaegi, R.; Mitrano, D.M. Nanoplastics removal during drinking water treatment: Laboratory- and pilot-scale experiments and modeling. *J. Hazard. Mater.* **2022**, *436*, 129011. [CrossRef] [PubMed]