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# Technological Approaches for the Reduction of Microplastic Pollution in Seawater Desalination Plants and for Sea Salt Extraction

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and Adrian Frank Herbort*

## Abstract

An increasingly serious and widespread problem is the introduction of plastics into the water cycle. The poor degradability leads to the plastic waste remaining in water for a long time and over time it fragments into smaller and smaller plastic particles. Both the visible plastic parts and in particular their decomposition products and functionalized plastic particles are an enormous burden. Seawater desalination and sea salt extraction are highly dependent on the quality of the seawater in terms of process utilization and cost structures, i.e., on the level of pollution. Especially microparticles represent a significant potential for blocking the microfiltration membranes (pore size > 100 nm) in the pretreatment and the very costly reverse osmosis (RO) membranes (pore size > 5 nm). An innovative approach for the removal of microplastics from industrially used seawater combines a chemically induced agglomeration and a new technological implementation step. The particular challenge in removing the synthetic impurities is not only their small size but also their inert properties against most of the physical and chemical additives for flocculation. With an easy implementation to existing systems, an economic aspect and a strong impact on the maritime ecological balance will be expected.

**Keywords:** microplastics, desalination, sea salt extraction, reverse osmosis, filtration, agglomeration, add-on technology

## 1. Introduction

The oceans perform a vital function as a regulator of the climate and absorb 25% of the CO<sub>2</sub> generated [1]. Through the production and consumption of foodstuffs, industrial and consumer goods, humankind produces large quantities of waste, whereof a considerable proportion ends up in the ocean sooner or later. Three-quarters of the waste in the ocean consists of plastic. This plastic is a steadily growing problem, costs the lives of ten thousands of animals every year and can also endanger humans.

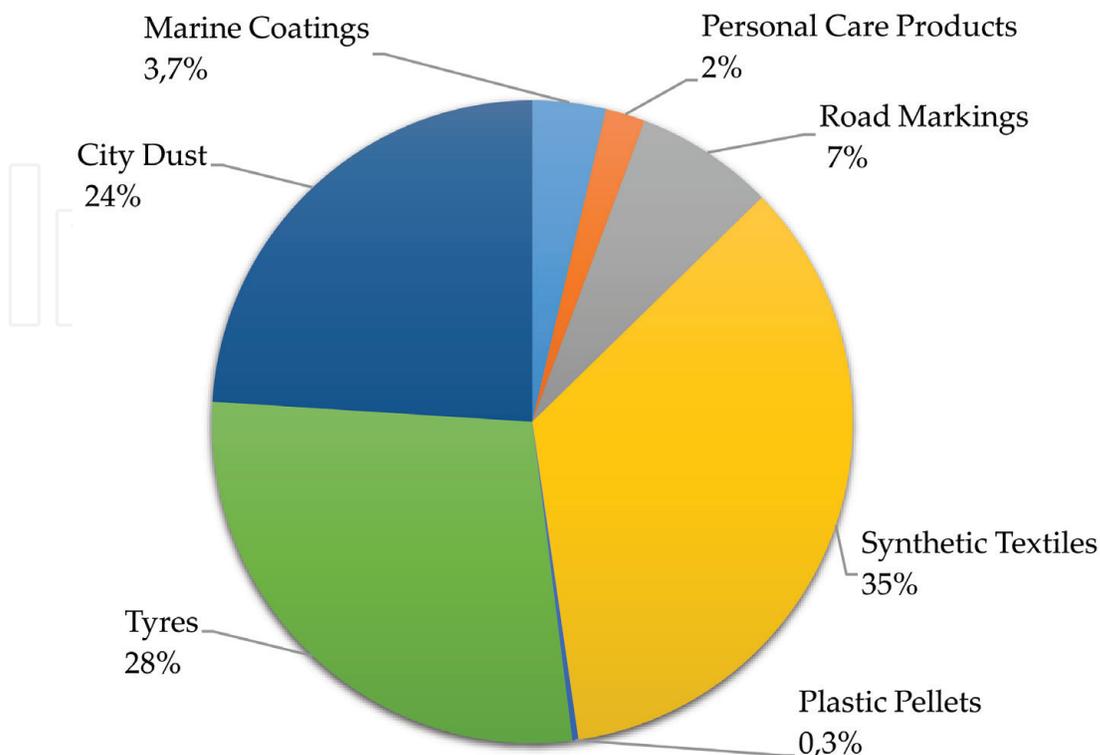
Over 80% of the plastic material entering the ocean annually originates from land-based sources, which correlates with the fact that half of the world population lives in coastal regions [2, 3]. Large plastic waste represents the main contribution, including everyday objects like drink bottles and other types of plastic packaging. An estimated 4.8–12.7 million tons enter here annually [2]. The remaining input comes from plastic, which is released at sea, mainly from fishing—for example, due to lost and discarded fishing gear, which is estimated at 0.6 tons a year [4]. About 94% of the large plastic parts, which end up in the sea, sink with time to the ocean floor. Today, an average of 70 kg of plastic can be found on every square kilometer of the ocean floor.

Approximately, 350–400 years can pass before the plastic is completely degraded. As it moves through the seas, the plastic changes. Through weather conditions and waves, for example, it disintegrates into smaller and smaller fragments and from the macroplastic, the so-called secondary microplastics are formed [5]. If it directly enters the environment, it is designated as primary microplastics.

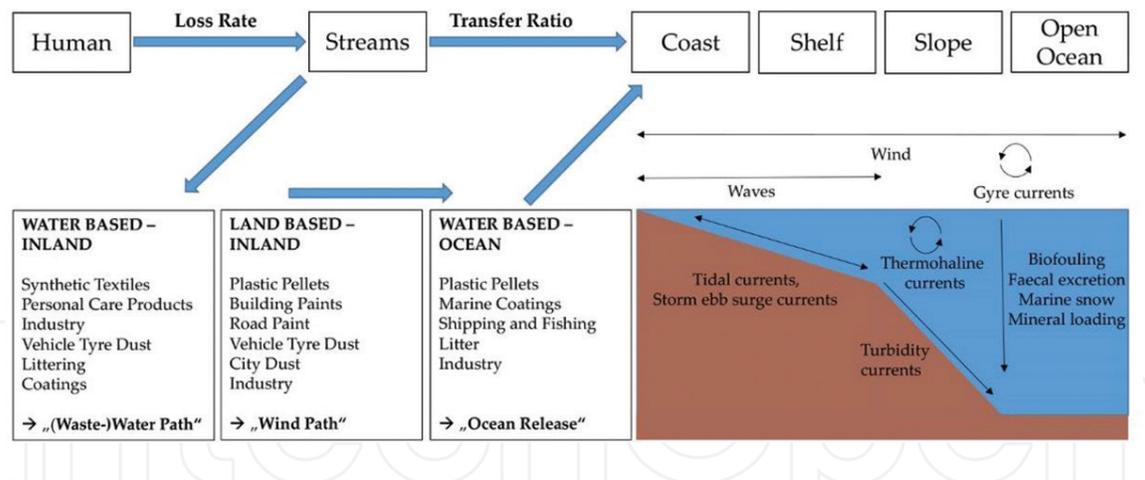
By definition, microplastics are small, solid, and water-insoluble plastic particles under 5 mm in size. In the meantime, these particles can be found in all bodies of water. They could even be detected in the Arctic [6].

The input of primary microplastics is estimated at 0.8–2.5 tons a year [7]. This enters mainly through tire abrasion and textile fibers, which enter the wastewater through washing clothes and thus end up in the environment. But also the dust from the wear on road paint, microplastics used in personal care products, marine coatings, and lost plastic pellets are important entry routes (**Figure 1**).

In general, a strong correlation can be observed between the population density and the microplastics concentration [8, 9]. The proximity to densely populated regions and poor waste management lead to particularly high levels of contamination [10, 11]. Sewage treatment plants or plastics manufacturing respectively processing companies are also important point sources and can release high volumes of plastic and microplastics locally (**Figure 2**) [12, 13].



**Figure 1.** Global release of primary microplastics to the world oceans [7].



**Figure 2.**  
 Microplastic inputs and transport paths into the ocean [7, 15].

Ports and industrial areas are especially contaminated with microplastic particles [14]. The majority of the microplastics remain near the shore [10]. In the Arabian Gulf along the coast,  $4.38 \times 10^4$ – $1.46 \times 10^6$  microplastic particles/km<sup>2</sup> could be detected in the surface water [15].

Off the coast of South Africa, there were  $257.9 \pm 53.36$  to  $1215 \pm 276.7$  microplastic particles/m<sup>3</sup> of water [12]. At the mouth of the Yangtze in the East China Sea,  $4137.3 \pm 2461.5$  microplastic particles/m<sup>3</sup> could be detected, whereby the concentration in the open sea was only  $0.167 \pm 0.138$  microplastic particles/m<sup>3</sup> [13].

The most common polymer types occurring in seawater are, in addition to polyethylene, polypropylene, and polystyrene, also polyamide, polyester, polymethylmethacrylate, polyvinyl chloride, polyoxymethylene, polyvinyl alcohol, polymethylacrylate, polyethylene terephthalate, alkyd resins, and polyurethane [16]. They are found in descending prevalence in the seawater.

The quantification of the inputs into the environment is, as a rule, based on a loss rate, which is calculated against the produced quantity of preproduced plastic [17]. The categorization of the industries, which manufacture preproduced plastic, is organized in producers (manufacture plastic material from raw materials), intermediaries, converters (convert preproduced plastic into products, or individual components), external waste disposers, and shipping companies (transport the material). By means of the difference between the respectively processed plastic quantities and the loss rate, the plastic quantities, which are released into the environment by the plastics industry alone, are revealed.

Forecasts assume an increasing plastic production volume in the future, which will lead to an increasing entry quantity of plastic and microplastics in the environment and seas [2]. In addition, microplastics arise continuously through the constant fragmentation of plastic already in the environment [5]. This leads to an ever higher contamination of the marine environment with microplastics.

Since the current analytical methods to detect microplastic in the aquatic environment have numerous shortcomings [18], the contamination of the marine environment can only be estimated. Particularly problematic here is that small plastic particles cannot be captured in most monitoring cases. The lower detection limit in the marine environment is usually 300 µm. With increased efforts, the lower detection limit can be reduced to 20–10 µm [16]. However, this is seldom practiced. Particles below the detection limit are not captured. Additionally, studies are not readily comparable, since there is no standardized monitoring procedure [18].

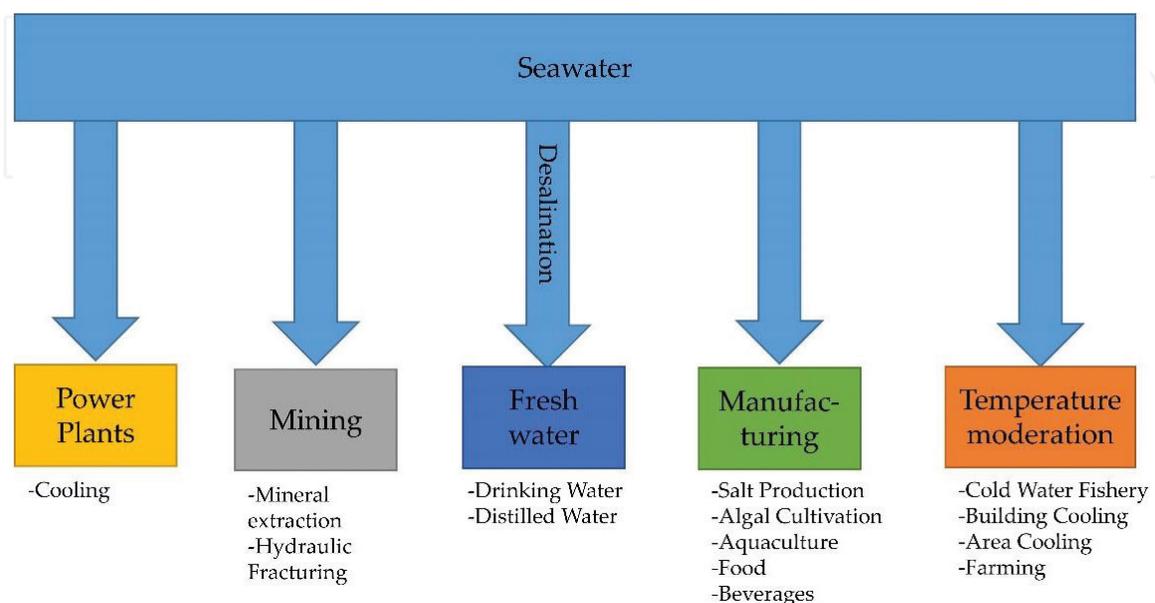
## 2. Seawater utilization

Seawater utilization can be divided in three primary use areas: the use for agriculture, for the home, and for industry [19]. While the principal portion is used for agriculture in developing countries, a significantly increased proportion for use in households and industry can be seen in industrialized countries. Advancing industrialization also causes increased water consumption. Over the last century, the world population has quadrupled, while the water demand has increased sevenfold.

In general, usable water comes from surface water, groundwater, or fossil aquifers. In order to increase the supply of usable water, processes such as the desalination of seawater have been moving into focus for some time [20]. Seawater has most commonly been used as a coolant in energy generation and in industrial processes so far. It is also used in mining to extract minerals as well as for the hydraulic fracturing of gas and oil. It is additionally applied in production processes, such as sea salt extraction, aquaculture, algal cultivation as well as food manufacturing [21]. It is also used for temperature moderation in buildings and areas as well as for cold water fishery (Figure 3).

Two characteristic economic seawater application sectors are seawater desalination and sea salt extraction. For sea salt extraction, seawater is diverted into large basins. Over time, the water evaporates by the heat of the sun and wind and the previously dissolved salt remains [22]. The media currently reports again and again about the contamination of sea salt with high quantities of microplastics. Thus, 50–280 microplastic particles/kg of salt were detected in Spanish sea salt and in Chinese sea salt 550–681 microplastic particles/kg of salt [23, 24].

Seawater desalination is the production of drinking water and process water for industrial facilities or power plants from seawater through the reduction of the salt content. The desalination can be based on various processes, which remove the salts and minerals from the water. To some extent, usable ancillary products like table salt accrue. In addition to the already present burden from anthropogenic stressors, the chemicals added to the seawater against fouling and scaling as well as the metals dissolved by corrosion threaten marine ecosystems, e.g., in the Red Sea. An



**Figure 3.** Overview of the different seawater applications [21].

investigation of 21 plants, which together produce 1.5 million m<sup>3</sup>/day, accounted for 2.7 kg of chlorides, 3.6 kg of copper, and 9.5 kg antiscaling agents piped into the sea per day of seawater desalination [25].

Seawater desalination is practiced in numerous coastal semiarid regions [20]. In addition to small plants in areas with insufficient infrastructure with only a few hundred cubic meters of water a day, there are also large desalination plants, e.g., in southern Europe (Barcelona Seawater, 200,000 m<sup>3</sup>/day), the USA (Claude Bud Lewis Carlsbad, 204,000 m<sup>3</sup>/day), Israel (Sorek, 624,000 m<sup>3</sup>/day), Australia (Kurnell, 250,000 m<sup>3</sup>/day), and the United Arab Emirates (Dschabal Ali Block M, >2,000,000 m<sup>3</sup>/day). Significant expansion of production capacities for seawater desalination is, for example, planned in the Persian Gulf. Due to the development of the steel, petrochemical, cement, aluminum, and energy industry, there will be a demand of roughly 940,000 m<sup>3</sup>/day only for use in these sectors until 2030 in Iran alone [26].

### 3. Impact of increasing microplastic burden on seawater utilization and the water use cycle

An increasing microplastic burden not only has implications for the costs and efficiency of the sea water utilization process, but also for the marine ecosystem and, as a consequence, also for humankind (Figure 4).

Bonded in microplastics, pollutants like, for example, dichlorodiphenyltrichloroethane (DDT), dioxins, or heavy metals can be transported and accumulated in organisms via ingested food [28]. Due to the manufacturing process, most polymer blends also contain harmful substances like softening agents or monomers, which in return can be released upon ingestion of the particles via food and exert a direct influence on the organism, since these substances are mostly classified as potentially harmful and/or carcinogenic [29]. It has already been shown in laboratory experiments that microplastics smaller than 150 µm can, after ingestion via food, enter the surrounding tissues, the bloodstream and, through these, the internal organs and also the brain [30]. There is then the risk of the formation of lesions and inflammations. Furthermore, oxidative stress, necrosis, and damage to DNA can be triggered, which again increases the risk of cancer. Neurological behavioral disorders are also possible [31]. Thus, there is a potential risk to human health from microplastics.

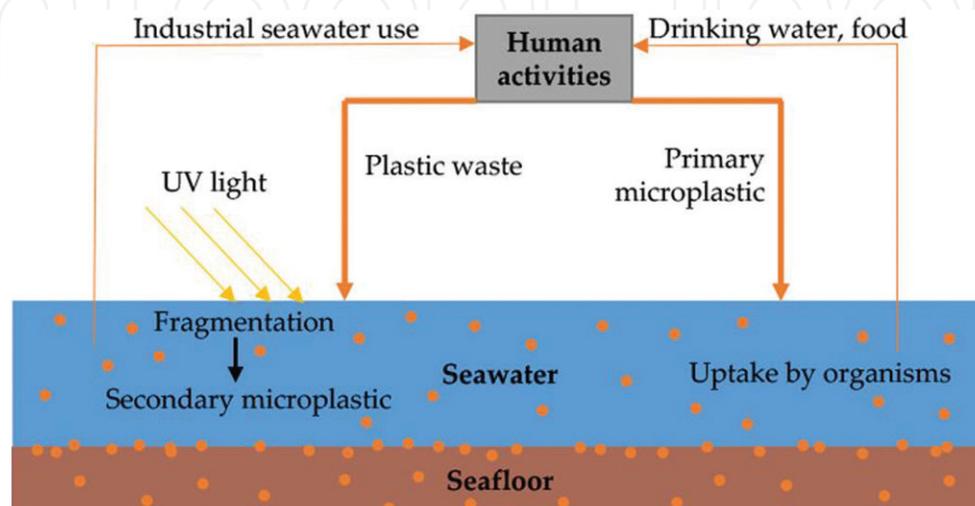


Figure 4.  
Microplastics in the marine water cycle [27].

In addition to the decrease in improper disposal, the search for replacement substances and the prohibition of microplastics as a product addition for everyday products, ensuring that the aquiferous processes are free of microplastics also represents a chance to reduce the degree of contamination due to microplastics in the water cycle. Besides the implementation of new technologies for the purification of wastewater in sewage treatment plants, this also includes the conceptual and technical development of new add-on technologies in seawater utilization processes in order to filter microplastics out of the inflowing seawater and eliminate it prior to the seawater utilization processes.

#### **4. Ecological-chemical approach to the reduction of the microplastic burden in seawater-based processes**

At this time, there is no economical possibility yet to remove microplastics simply and cost-effectively from seawater. A promising research approach based on the adaptation of a concept by Herbort and Schuhen for freshwater systems and the simultaneous development of add-on technology for static (e.g., waterside plants) and mobile (e.g., ships) seawater utilization processes [32].

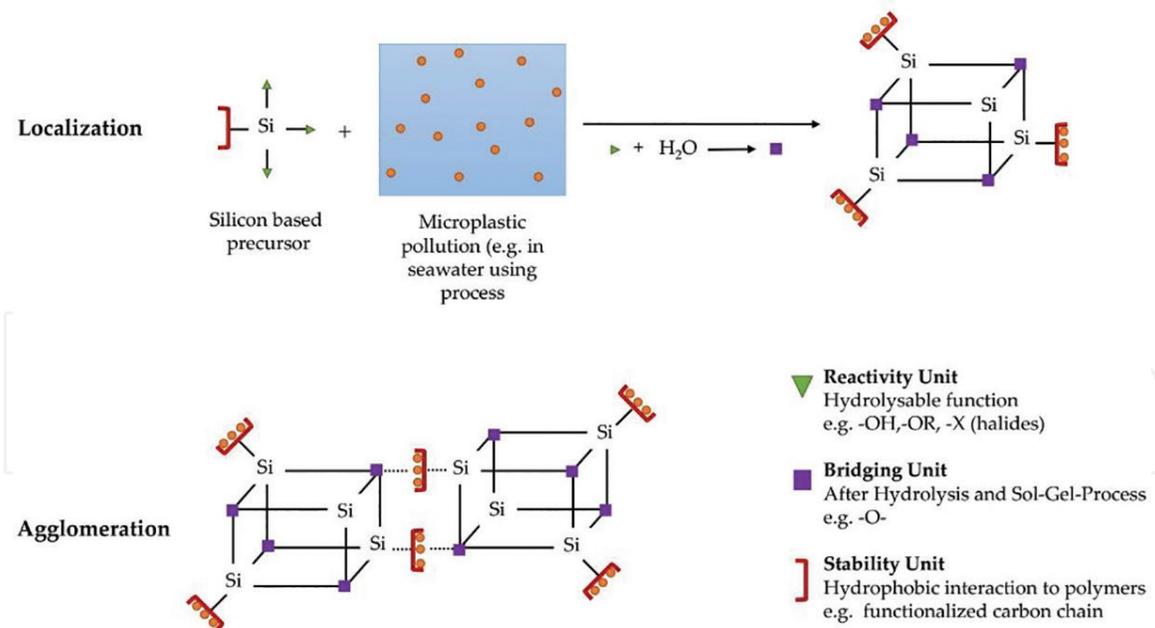
In the process developed by Herbort and Schuhen, silane-based microplastic agglomerates are formed according to the cloud point principle through the application of special organosilane-based precursors, which, via Van der Waals forces, have a high affinity to unreactive microplastics (IOCS, inert organic-chemical macromolecules) and, at the same time, a high reactivity in water. [32–35]. A Video shows the fixation process in a batch reactor for use in wastewater treatment [36].

Organosilanes are hybrid compounds of inorganic silanes and organic hydrocarbons [37]. Through the selection of the functional groups in the organic unit (functional design), it is possible to exploit an adaptable system for the respective application (e.g., removal of reactive and/or inert organic-chemical compounds). By means of the substituent pattern within the organic unit and also directly on the silicon atom, the affinity of the organosilanes can be adapted to various polymer types and, simultaneously, the reactivity respectively the stability can be controlled.

Organosilanes with corresponding reactivity can react to organic-inorganic hybrid silica gels in the sol-gel process [38, 39]. In the first step, disposal groups are split off and reactive silanol groups generated through hydrolysis. The silanol groups subsequently form silanone bonds in a condensation reaction and link the organosilanes via a bridging unit (**Figure 5**).

A three-dimensional networked hybrid silica gel forms, which is stabilized via the respective bridging unit. Through the selection of the disposal groups and the organic groups, the properties and reactivity of the organosilanes can be specifically controlled. The selection of the disposal groups is decisive for the hydrolyzability of the organosilanes [40, 41].

The organic groups influence the water solubility, the stability of the resulting silanols, and the affinity of the organosilanes respectively the ability of the resulting silanols to fix microplastic particles. By choosing specific organic groups, the affinity to different polymer types can be controlled. Groups with low polarity can be used to attach to polymers with lower polarity like polyethylene or polypropylene. More polar polymers containing, e.g., heteroatoms, like polyester or polyamide, can be fixed by using organic groups with a similar chemical structure and polarity.



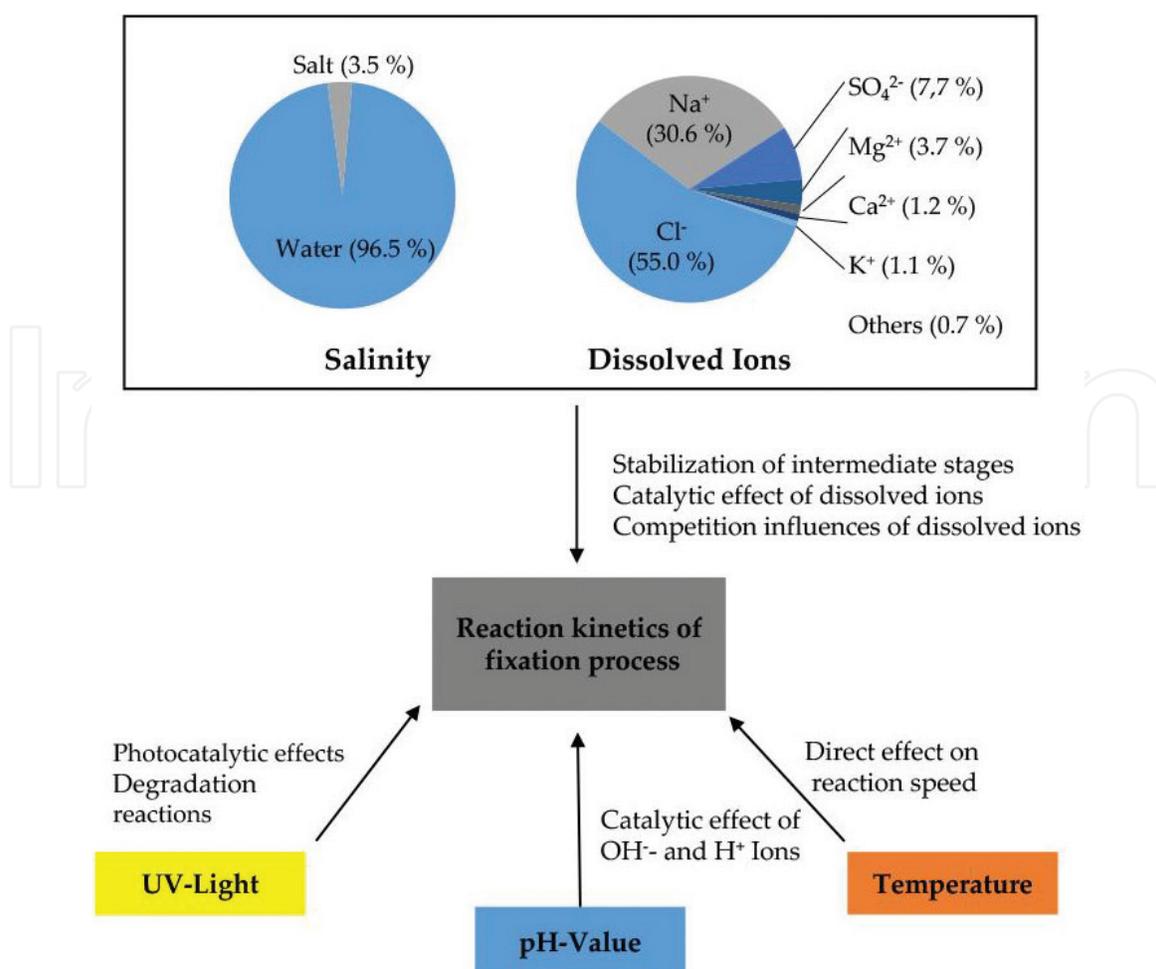
**Figure 5.**  
 Localization and agglomeration of microplastic particles [42].

The interaction of the disposal groups and organic basis units must be so coordinated that the highest possible affinity to microplastics and optimal reaction kinetics are achieved [33]. The reaction kinetics takes on a decisive function within the research approach. It is influenced, among other things, by the water matrix and the temperature. Knowing that an increase in the water temperature accelerates the speed of the sol-gel process and that the temperature of seawater is subject to seasonal fluctuations and spatial variations, challenges are presented for the implementation of the concept in the seawater environment [39]. In addition, the factors of salinity, temperature, UV radiation, and pH value play a determining role and are also to be considered (**Figure 6**) [43].

Dissolved salts influence reaction speed and the reaction mechanism, for example, through the electrolyte effect [44, 45]. It results in the stabilization of the intermediate stages with higher ionic strength as well as catalytic effects or competitive influences of dissolved ions. The pH value influences reaction kinetics through the catalytic effect of hydroxide and oxonium ions [39]. Temperature differences directly influence the reaction speed [46, 47]. Thus, a temperature increase of 10°C is accompanied, as a rule, by approximately double the reaction speed. UV light can also facilitate the formation of reactive intermediate stages via a photocatalytic effect and thus accelerate the reaction [46]. However, it can also break down the precursors used or already linked molecules.

Initial experiments at a laboratory scale show that the salinity has a slowing influence on the fixation process and the entire process of agglomeration formation also works in an artificial salt water matrix. To produce the salt water (3.5% salt by mass), 27.5 g NaCl, 5 g MgCl<sub>2</sub>, 2 g MgSO<sub>4</sub>, 1 g KCl, and 0.5 g CaCl<sub>2</sub> were dissolved in distilled water. This results in a mass concentration of 58.8% chloride (Cl<sup>-</sup>), 29.6% sodium (Na<sup>+</sup>), 4.7% sulfate (SO<sub>4</sub><sup>2-</sup>), 4.9% magnesium (Mg<sup>2+</sup>), 1.5% calcium (Ca<sup>2+</sup>), and 0.5% potassium (K<sup>+</sup>).

Subsequently, 0.1 g polyethylene powder (PE) (average particle size 350 μm), 0.1 g polypropylene powder (PP) (average particle size 350 μm), and 0.1 g of a 50:50 mixture of PE and PP were stirred in a beaker with 1 l of salt water respectively distilled water at room temperature. After 24 h, 0.15 ml agglomeration reagent was added and the mixture was stirred for an additional 24 h. The formed

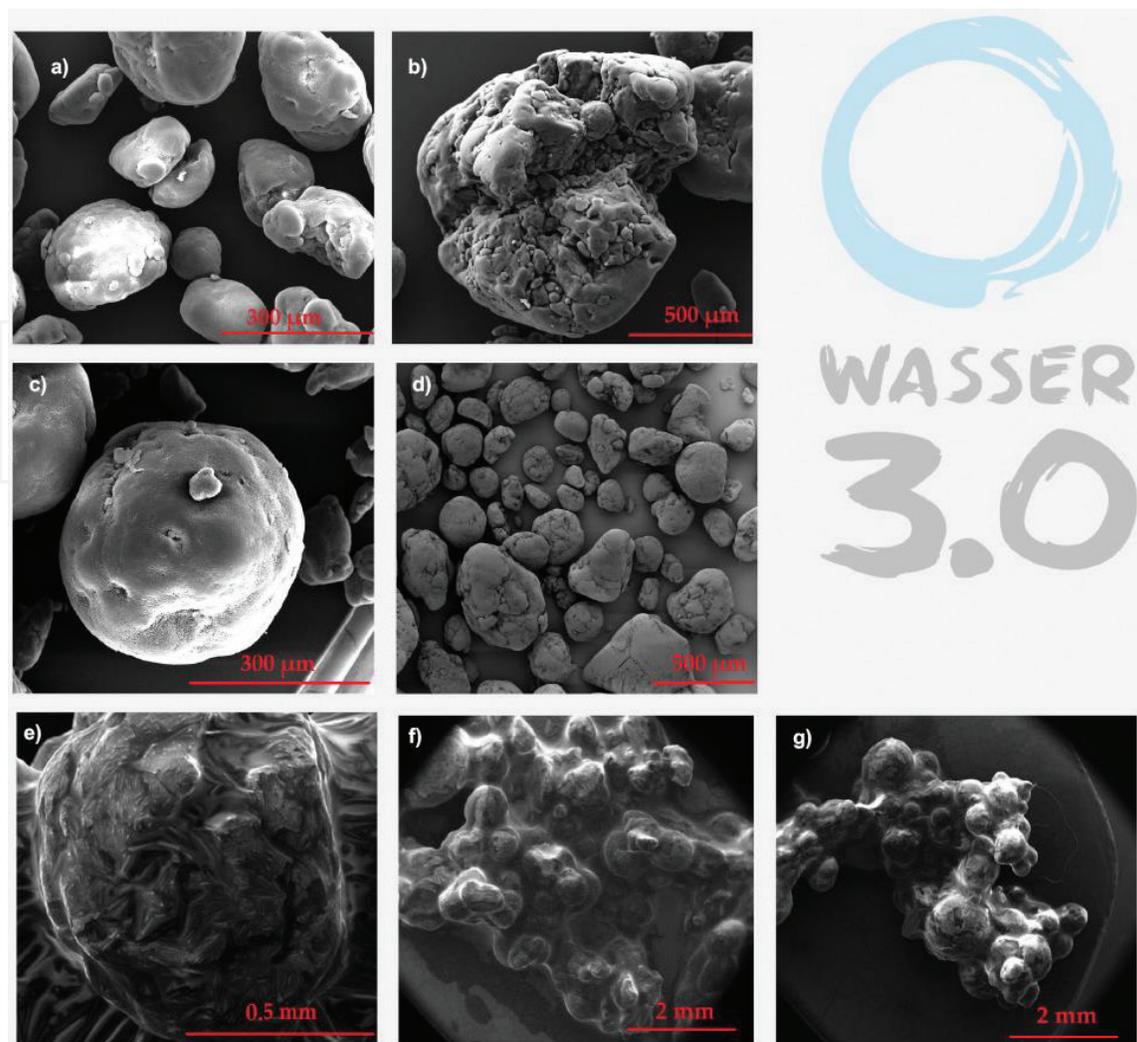


**Figure 6.**

*Influence on the reaction kinetics of the fixation process in the marine environment (percentage by mass) [39, 43–47].*

aggregates were removed and dried at 60°C for 24 h. ESEM images were taken using a FEI Quanta 250 ESEM (FEI Company, Hillsboro, USA) equipped with a large field detector (LFD). The chamber pressures were between 60 and 80 Pa and the acceleration voltage between 7 and 20 kV. The remaining water was filtered using a paper filter (Rotilabo 111A, 12–15 µm pore size). The tare weight of the filter was noted before filtration using a AX105DR (Mettler Toledo, Switzerland). Afterward, the filter was dried at 105° C for 24 h and weighted again, to check if there is remaining microplastic in the water (accuracy ±0.2 mg).

In distilled water, an aggregation of the microplastic particles begins 15 s after the addition of the agglomeration reagent. After 2–3 min, the agglomeration is completed and an aggregate is present, which contains all of the microplastics. In the artificially produced salt water samples, the agglomeration process begins after 10 min and is concluded after 15 min. It is, therefore, significantly slower, but nevertheless fixes all the microplastics. This shows that salt water has a stabilizing effect on the reactive intermediate stages and thus slows down the sol-gel process, whereby the agglomeration starts later and also takes longer. **Figure 7** shows ESEM images of the microplastic particles used and their aggregates formed during the fixation process respectively fragments of the aggregate prepared for the images. How the microplastic particles are linked and embedded by the agglomeration reagent can be observed, where a considerable increase in size results. As the agglomeration reagent reacts to a solid hybrid silica, which will be removed within the aggregates from the water, residues in the water will be avoided. To ensure a complete removal of the agglomeration reagent even in the trace substance range, further TOC analysis and particle analysis will be proceeded [48, 49].



**Figure 7.**  
*SEM images of the microplastic blanks (a, b = PE; c, d = PP) and of the agglomerates formed during the fixation process (e = PE; f = PP; g = PE/PP (50:50)).*

## 5. Procedural implementation of microplastic elimination in seawater utilization processes

The procedural implementation pursues the goal of increasing the service life of the existing desalination plants by already holding back the microplastic particles (0.1–5  $\mu\text{m}$ ) initially in pretreatment, which cause blockages of the membranes (pore size 0.002–0.1  $\mu\text{m}$ ). On the one hand, the service life of the microporous membranes can be thus extended and the operational expenses reduced (without the addition of suspect additives, such as, e.g., antiscalants) as well as, on the other hand, sustainably eliminating the much-criticized microplastic particles from the water cycle. As the removal is based on a physicochemical agglomeration process, it is not limited by particles size or shape like a filtration process. The agglomeration reagent can bind to fibers, films, and fragments in all size classes and fix them in big agglomerates. As a consequence, the quality of the water on the removal side near the coast/surface as well as on the output side will be improved through the reduction of the microplastic particle load.

In the application in sea salt extraction, contamination of the resulting sea salt and thus the transmission to people will be effectively avoided through the removal of microplastics from the seawater flowing into the evaporation basins.

This is possible through the combined development of a pretreatment stage of a series of stirred tanks and the inorganic-organic functional material. In addition, a high-performance cascade process is developed as add-on technology in order to

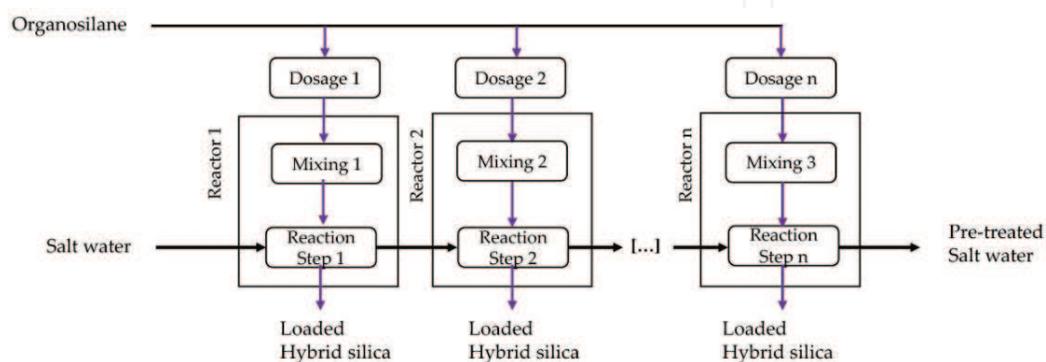
facilitate the material reaction and to make a throughput of  $>600 \text{ m}^3$  a day possible. Continuous operation is sought by connecting several cascades. The adapted concept as well as the related technological implementation strategy provides for the first time the opportunity to remove plastic particles with a particle size of  $<5 \mu\text{m}$  effectively and sustainably from salt water in an upstream, modular pretreatment step. The diagram of the process is presented in **Figure 8**.

The process is divided in the following stages:

- Inlet duct salt water/feed stream
- Dosing devices
- Mixing concept (in the reactor)
- Reactor
- Material discharge
- Outlet stream

The feed stream, that is the extracted seawater with unwanted microplastic load, is piped to the first partial reactor via an existing suction pipe. This should take place by means of upstream, abrasion, and corrosion-resistant pumps and use the suction pipes present in the existing seawater desalination plants. Depending on the load of the feed stream, a defined amount of the organosilanes is simultaneously added by means of the dosing device and blended with the salt water already in the first partial reactor through a mechanical mixing concept.

In accordance with the concept, the addition of the material takes place in several steps within the process. In this way, the required initialization period of the material and the reaction time can be responded to through the variable design, dimensioning, and number of dosing stages, mixing installations as well as partial reactors. For this purpose, können reactors of different sizes respectively different volumes can be used so that, for example, the reaction starts in the first partial reactor and continues to react optimally in the subsequent reactors. The organosilane is mixed with the salt water according to the required concentration in the respective partial reactors, at which time it is successively bonded to the microplastics to be removed. Through injection or chemical interaction, the concentration of free,



**Figure 8.**  
*Process flow chart.*

Removal of microplastics from seawater (based on particle count)	≥85%
Removal of organics	Very high, >99%
Minimum size of removed particles (μm)	0.1
Use of additives	Low, product is an ecotoxicologically harmless agglomeration material
Reaction product (properties)	Particle load < 0.1 μm
Expected by-product (properties)	Loaded, inactive agglomeration material
Process and plant technology	
Process safety	High; in case of overdosing no ecotoxicologically negative effects
Plant availability	>95%
Plant requirements	Low, installation surface for container solution
Number of process steps	1 (agglomeration-flotation step)
Scalability	High, modularizable, and adaptable to degree of pollution

**Table 1.**  
 Technical target criteria.

nonbonded microplastic particles should continuously decrease along the length of the reactor respectively the residence time. A consistent residence time of the material in the reactor is needed so that a complete conversion can be surmised. This is essential for the process, since an incomplete conversion would mean additional burdens through further foreign substances/particles.

In order to prevent the disintegration of the agglomerates, the reactor has a strict and clearly defined residence time distribution (RTD) so that ideally all particles can pass through the reactor in the same ideal time frame and grow and that the disintegration of the agglomerates can be avoided. The implementation of microplastic elimination in seawater utilization plants pursues the technical target criteria presented in **Table 1**.

## 6. Conclusions

The innovative add-on technology for the removal of microplastics from industrial seawater utilization plants pursues the first problem solution regarding the risk of blocking from the immense microplastic particle load in the sea, among other things, in industrial, membrane-based seawater desalination plants (especially RO plants). Due to the significant reduction of the microplastic load in the pretreatment stage, alleviation results for the downstream RO membranes. The service life of the RO membranes will be significantly increased and the membranes can, thanks to the improved performance, be operated on a smaller scale and more cost-effectively.

Through the application of new add-on technology in sea salt extraction, the entry of potentially harmful microplastics in sea salt is reduced and thus, at the same time, also the contamination of everyday food. Based on the future increasing contamination of the oceans with microplastics, this technology helps to ensure the sustainable use of seawater.

## Acknowledgements

The research projects of Wasser 3.0 ([www.wasserdreinull.de](http://www.wasserdreinull.de)) are conducted by means of the financial support by the German Federal Ministry for Economic Affairs and Energy through the provision of ZIM (Central Innovation Program for SME) project funds. The enterprise abcr GmbH ([www.abcr.de](http://www.abcr.de)) from Karlsruhe (Germany) and Zahnen Technik GmbH ([www.zahnen-technik.de](http://www.zahnen-technik.de)) from Arzfeld (Germany) are directly involved in the project as industrial partners for the material science scale-up as well as for plant construction and engineering. Michael Sturm thanks the German Federal Environmental Foundation (DBU) for the support with a PhD scholarships (Aktenzeichen: 80018/174). The authors thank Carolin Hiller, Lukas Pohl, and Laura O'Connell for their contributions.

## Conflict of interest

We have no conflict of interest to declare. This research has not been submitted for publication nor has it been published in whole or in part elsewhere. We attest to the fact that all authors listed on the title page have contributed significantly to the work, have read the manuscript, attest to the validity and legitimacy of the data and its interpretation, and agree to its submission to the book.

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