Membrane Hybrid System for Sustainable Removal of Organic Micropollutants and Biofoulants from Reverse-Osmosis Concentrate

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This forum paper explores the performance and potential applications of the submerged membrane hybrid system (SMHS) integrated with adsorption and ion exchange resins in the removal of organic micropollutants (OMPs) from reverse-osmosis concentrate (ROC).

ROC and Its Implications on the Environment

Reverse-osmosis (RO) plants, operating with water recoveries ranging from 35% to 85%, generate significant volumes of reverse-osmosis concentrate as a by-product. This ROC comprises all the rejected compounds, including salts, dissolved organics, and various types of organic micropollutants (OMPs), such as pharmaceuticals, personal care products, herbicides, pesticides, etc. The discharge of OMPs into inland and marine water bodies poses a potential risk of adverse eco-toxicological effects, threatening aquatic ecosystems (Fig. 1).

In ROC from municipal sewage treatment systems, OMPs like carbamazepine (2,240 ng/L), caffeine (1,410 ng/L), trimethoprim (974 ng/L), atenolol (466 ng/L), and naproxen (443 ng/L) are detected at elevated concentrations (Devaisy et al. 2023; Shanmuganathan et al. 2017), although they remain below the critical environmental concentrations (CEC). On the contrary, certain OMPs such as verapamil (cardiovascular agent), amitriptyline (neurotransmitter), and simvastatin (lipid regulator) are found at lower concentrations (83, 45, and <5 ng/L, respectively), yet they surpass or approach their respective CECs. The aforementioned values are mean values of the selected OMPs from several samples. The range (with the deviation) is given in the Table 1.

Regardless of their actual concentrations, exposure to multiple OMPs simultaneously for extended periods can adversely impact organisms through processes like bioaccumulation, biomagnification, and other toxic effects (Artifon et al. 2019). Therefore, to mitigate these risks, OMPs in the ROC need to be removed effectively prior to discharge into the aquatic environment. Numerous treatment methods have been employed, including coagulation-flocculation, advanced oxidation (ozonation, Fenton process, photo-oxidation, photocatalysis, and electrochemical oxidation). Among these, adsorption of OMPs using either powdered or granular activated carbon (PAC or GAC, respectively) and ion exchange resins emerge as highly efficient approaches compared to coagulation-flocculation and oxidation methods (Bourgin et al. 2018; Jamil et al. 2021). Apart from OMPs, activated carbon (AC) also removes effluent organic matter (EfOM) which is hydrophobic, small sized, low molecular weight (LMW) neutrals and building blocks, while ion exchange resins (IEX) removes humics fraction from EfOM (Jamil et al. 2020). The removal of OMPs is significant when the EfOM concentration is low due to competitive adsorption. Gidstedt et al. (2022) observed that the OMP removal was higher for tertiary treated wastewater where dissolved organic carbon or EfOM concentration is low.

SMHS in Water Reuse

Previous studies have demonstrated that integrating a submerged membrane hybrid system with either GAC or ion exchange resin in a single-stage treatment effectively eliminates OMPs (Fig. 2) (Shanmuganathan et al. 2017; Jamil et al. 2021; Piombini et al. 2021; Khan et al. 2023). Beyond its adsorption/ion exchange capabilities, this configuration excels in reducing membrane fouling through a scouring effect. Particles of carbon/resins and air bubbles in circulation gently interact with the membrane surface, causing physical abrasion and removing foulants, thereby preventing their accumulation on the membrane surface. This process reduces the buildup of transmembrane pressure (TMP), thereby minimizing

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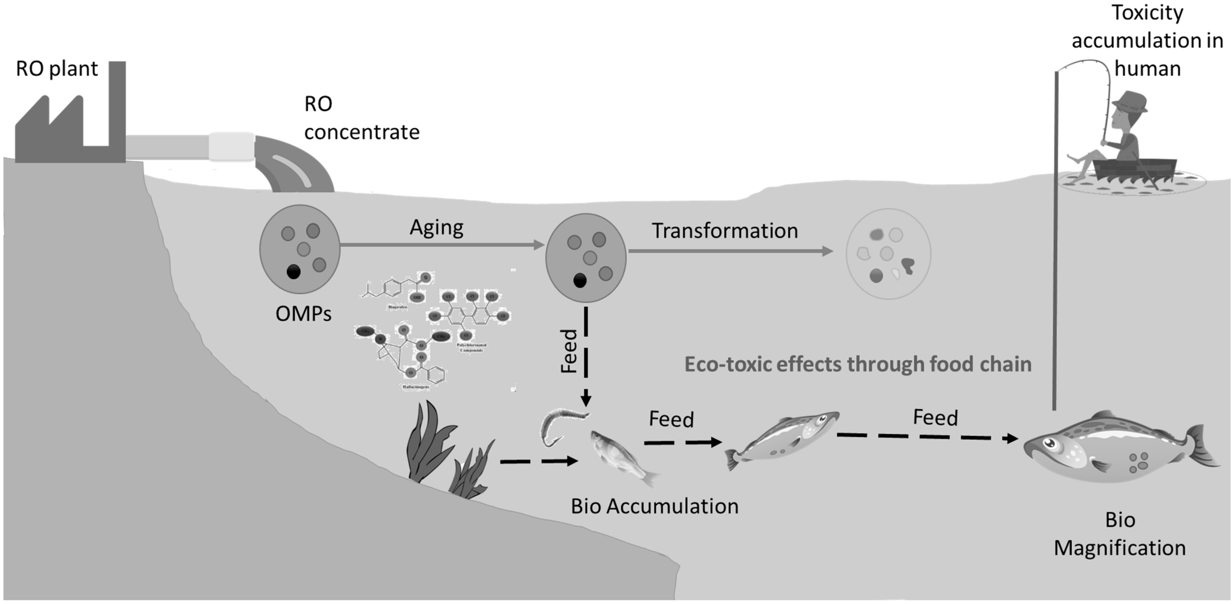

Fig. 1. Fate of OMPs in the aquatic environment upon discharge of ROC.

Table 1. Removal of OMPs using SMHS-GAC and SMHS-IEX system

Micropollutants	LOQ	Log Kow	Charge	MW (g/mol)	Raw ROC	Removal (%) by GAC	Removal (%) by Purolite A502PS
Atenolol	5	0.16	+	266	466 ± 12	>99	93 ± 0.2
Sulfamethoxazole	5	0.89	–	253	144 ± 18	76	**84 ± 1**
Primidone	5	0.91	–	218	26 ± 5	81	**>81**
Caffeine	10	−0.07	0	194	1,410 ± 116	>98	95 ± 0.5
Trimethoprim	5	0.91	+/0	290	974 ± 50	99	98 ± 0.2
Simazine	5	2.18	0	201	80 ± 8	84	>93
Carbamazepine	5	2.45	0	236	2,240 ± 145	96	**98 ± 0.5**
Fluoxetine	5	4.10	+	309	47 ± 2	89	88 ± 1
Clozapine	5	3.53	—	326	68 ± 4	93	>92
Amtriptyline	5	4.92	+	277	45 ± 8	>89	>86
Verapamil	5	3.79	+	454	83 ± 4	94	>92
Ketoprofen	5	3.12	–	254	377 ± 12	>99	>96
Naproxen	5	3.18	–	230	443 ± 24	98	98 ± 0.5
Gemfibrozil	5	4.77	–	250	344 ± 10	97	97 ± 1
Triclosan	5	5.34	0	290	211 ± 9	98	87 ± 2
Diclofenac	5	4.51	–	296	337 ± 14	99	96 ± 0.5
Triclocarban	10	4.90	0	316	162 ± 6	94	89 ± 2

Source: Adapted from Devaisy et al. (2023).
Note: The OMPs (sulfamethoxazole, caffeine, and primidone) that exhibit superior removal by SMHS-IEX compared to SMHS-GAC are shown in bold.

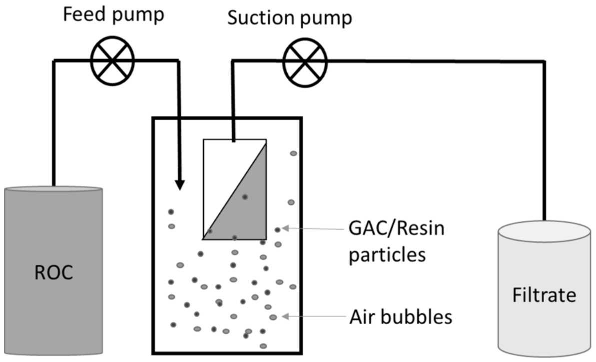

Fig. 2. Submerged membrane hybrid system (SMHS).

the need for frequent membrane cleanings (Johir et al. 2011; Johir and Vigneswaran 2021). This significantly extends the operational lifespan of the SMHS.

Certain studies have highlighted the versatility of the SMHS as a pretreatment for various wastewater streams applications (Devaisy et al. 2022, 2023, 2017; Jeong et al. 2013). Many small water reclamation plants are currently treating biologically treated sewage effluents, producing ROC that constitutes only 8%–10% of the influent volume. Shanmuganathan et al. (2017) investigated the performance of the SMHS-GAC concerning the removal of OMPs from ROC sourced from a water reclamation scheme in Sydney, generating 300 m^3 of ROC per day (equivalent to 8% of the treated biologically treated sewage effluent). In an experimental system spanning 10 days with an initial GAC dosage of 10 g/L (replaced daily at 10%), the SMHS achieved OMP removals ranging from 60% to >99% on Day 1 and >81% to 99% on Day 7. A shorter-term study (6 h) by the same authors, using GAC doses of 5 g/L (Shanmuganathan et al. 2015b) and 2 g/L (Shanmuganathan et al. 2015a), exhibited OMP removals of 65% to >89% and 27.7% to >79.2%, respectively. These findings highlight the necessity to identify an optimal GAC dosage to achieve higher OMP removals in the SMHS.

The efficacy of AC in OMP removal depends on factors such as surface charge, hydrophobicity, and surface functional groups promoting hydrogen bonding, π-π electron donor-accepter interaction, and van der Waals' forces (Jamil et al. 2019, 2021). Molecular size, surface area, and porosity of the adsorbent also play crucial roles in adsorption (Zhang et al. 2022). The SMHS-GAC system displayed effective removal of OMPs characterized by higher hydrophobicity and negative charges.

Despite the widespread use of AC for organic removal, it may not always be efficient, especially for hydrophilic and negatively charged OMPs. In addressing this challenge, the SMHS-ion exchange resin (IEX) system proved effective in removing OMPs not captured by GAC in the ROC. Studies have demonstrated that the SMHS-IEX system, utilizing commercially available Purolite A502PS resin, selectively removes hydrophilic and negatively charged OMPs from ROC (Table 1). For instance, OMPs like sulfamethoxazole, caffeine, and primidone (hydrophilic and negatively/neutral charged) exhibit superior removals compared to the SMHS integrated with AC (Devaisy et al. 2023; Jamil et al. 2021). These values are highlighted in bold in Table 1.

Potential Applications of SMHS in Water Reclamation

To safeguard the environment, the SMHS, with either AC or IEX, can potentially be used as a treatment system to remove OMPs from ROC prior to discharge into receiving waters.

Membrane Adsorption Hybrid System as a Pretreatment to Wastewater Reclamation

In dual membrane hybrid systems, commonly employed in small water reclamation schemes, microfiltration (MF) can be replaced with the SMHS-GAC system. A portion of the effluent from the SMHS-GAC system can be blended with RO permeate to produce OMP-free water suitable for reuse purposes. As GAC does not remove essential nutrients (N, P, S, Ca, Mg, and K), treated ROC holds potential for irrigation due to the retention of vital nutrients crucial for plant growth. However, it is crucial to monitor the sodium (Na) level in the treated water to maintain an appropriate sodium absorption ratio (SAR) suitable for the specific crop variety. The concentrations of heavy metals were negligible after the passage of ROC through the SMHS-GAC system. Previous researches indicate the RO concentrate bears a significant level of salinity, but traces of heavy metals (Panagopoulos et al. 2019; Omerspahic et al. 2022).

Beyond the effective removal of OMPs from ROC, the positioning of the SMHS-GAC configuration has been observed to mitigate RO fouling by reducing the organic load and foulants before reaching the membrane surface. The cost of GAC required to treat 1 m^3 of ROC is remarkably low, as low as \$0.25, especially when considering the environmental damage that can occur upon the discharge of untreated ROC. Hence, this approach can be regarded by the scientific community as a cost-effective, simple, and efficient method for OMP removal before discharge into the environment.

Membrane Adsorption Hybrid System as a Pretreatment to Seawater Desalination

The membrane adsorption bioreactor hybrid system (submerged membrane adsorption bioreactor; SMABR) emerges as a valuable pretreatment option for seawater desalination in small desalination plants. In Australia alone, there are 600 small-scale desalination plants and 10 large desalination systems. A study conducted by Jeong et al. (2013) focused on a SMABR, essentially a membrane bioreactor (MBR) equipped with PAC as an adsorbent. The daily PAC replacement of 1.5% into the system achieved 72% of organics removals during 50 days of operation. This system served as a pretreatment step before RO in the desalination process.

In the SMABR (Fig. 3), PAC is introduced and circulated within the MBR, where it adsorbs organic compounds. Over time, a microbial layer forms on the PAC, aiding in the degradation of the adsorbed organics. Remarkably, a mere 2.14 g of PAC proved sufficient for treating 1 m^3 of seawater. The SMABR pretreatment effectively removed a significant portion of organics, achieving up to 72% removal, while only a minimal increase in TMP was detected. Moreover, it maintained stable biological activity. Notably, this pretreatment increased the initial permeate flux of RO by 20%, equivalent to 6.2 $L/m^2 \cdot h$ (LMH), compared to RO operation without pretreatment (Jeong et al. 2012).

During a 45-h run, the permeate flux decline in RO operation was limited to 34%, and the RO membrane displayed reduced fouling, characterized by a decreased presence of biopolymers. These promising initial findings underscore the necessity for a comprehensive, long-term investigation employing a semi-pilot scale MBR as a sustainable pretreatment to minimize biofouling. Importantly, up to this point, this technology had not been utilized as a pretreatment in seawater reverse-osmosis (SWRO) desalination. The presently-used coagulation and deep bed filter can only reduce biofouling on RO membranes by 10%–15%. Even ultrafiltration used as pretreatment cannot significantly reduce RO biofouling.

Extensive on-site testing of SMABR was conducted, varying the doses of PAC over an extended period. The extent of biofouling on the membrane was assessed based on DNA (cell) and polysaccharide distribution. In the absence of PAC in the MBR, severe fouling occurred on the membrane. However, the introduction of PAC into the MBR effectively reduced organic fouling and mitigated the formation of biofilm on the membrane surface without damaging the membrane. Biofouling of RO membranes is primarily caused by LMW organic substances, and PAC plays a critical role in their removal. It was observed that assimilable organic carbon (AOC) is directly linked to LMW organics. Importantly, even small amounts of PAC, ranging from 2.4 to 8.0 g per m^3 of seawater, proved effective in mitigating biofouling. These results underscore the

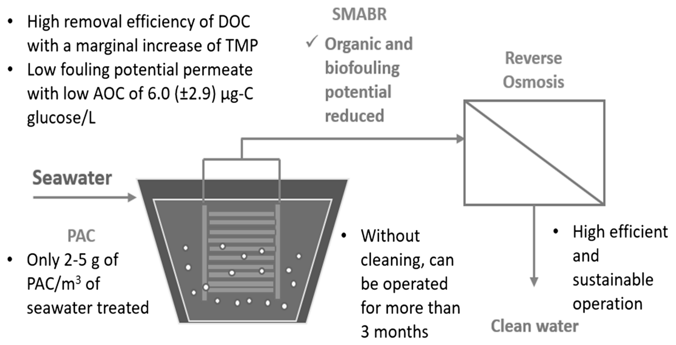

Fig. 3. Summary of long-term operation of SMABR.

environmental-friendliness of SMABR as a biological pretreatment for reducing biofouling in SWRO (Jeong et al. 2014).

The brine produced during the regeneration of resin may cause several environmental impacts. Elevated levels of Na+, OH- ions, and the eluted OMPs may result in soil/water salinity, and toxicity upon the discharge of brine into land/aquatic environment. Future research should focus on exploring environmentally safe and cost-effective methods of regeneration or disposal of GAC and IEX to make the SMHS treatment system sustainable.

Data Availability Statement

No data, models, or code were generated or used during the study.

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