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Submerged membrane filtration adsorption hybrid system for the removal of organic micropollutants from a water reclamation plant reverse osmosis concentrate

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HIGHLIGHTS

- A water treatment plant RO concentrate had 19 organic micropollutants (OMP).
- Submerged membrane filtration GAC adsorption removed all OMP to <detection limits.
- This hybrid system helps to produce additional amounts of nutrient-rich water.

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ABSTRACT

Reverse osmosis (RO) is a widespread water treatment process utilised in water reuse applications. However, the improper discharge of RO concentrate (ROC) containing organic micropollutants such as pharmaceuticals into the environment may cause potential health risks to non-target species and particularly those in aquatic environments. A study was conducted using a submerged membrane-filtration/granular activated carbon (GAC) adsorption hybrid system to remove organic micropollutants from a water treatment plant ROC by initially adding 10 g GAC /L of membrane reactor volume with 10% daily GAC replacement. The percentage of dissolved organic carbon removal varied from 60% to 80% over an operation lasting 10 days. Removal of organic micropollutants was almost complete for virtually all compounds. Of the 19 micropollutants tested, only two remained (the less hydrophobic DEET 27 ng/L and the hydrophilic sulfamethoxazole 35 ng/L) below 80% removal on day 1, while five of the most hydrophobic micropollutants were detectable in very small concentrations (<5–10 ng/L) with >89%–>99% being removed. High percentages of micropollutants were removed probably because of their high hydrophobicity or they had positive or neutral charges and therefore they were electrostatically adsorbed to the negatively charged GAC.

1. Introduction

Inadequate clean water for potable and non-potable use has become a major problem worldwide due to the increasing demand and shortage of water resources. Water recycling by treating wastewater is a useful approach to alleviate this problem. However, wastewater contains many contaminants, which need to be removed before it can be beneficially utilised. In this context, membrane technology is currently growing at a great rate due to its excellent ability to remove contaminants and smaller footprint requiring less space compared to conventional treatment technologies. Of the different types of membrane filtration, reverse osmosis (RO) is widely used in water reuse applications due to its greater efficiency in removing contaminants including organic micropollutants, for example, pharmaceuticals and personal care products (PPCPs), insecticides, surfactants, endocrine disruptors, and hormones [1]. However, the rejected micropollutants are discharged normally into surface water bodies with the RO concentrate (ROC). The improper discharge of organic micropollutants with the ROC into the environment may cause potential health risks to non-target species particularly in aquatic environments [2]. Subsequently, the application of proper treatment techniques is essential to ensure safe disposal of ROC free of organic micropollutants into the natural environment.

The concentration of various organic micropollutants in Australian waters is summarised in Table 1. These contaminants are commonly found at trace levels in the environment ranging from nanogram to microgram per litre (ng/L–μg/L) and as such are also known as trace organics. Wastewater treatment plants (WWTPs) constitute the major

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Table 1
Concentrations of organic micropollutants in Australian waters [11].

Compounds	WWTP effluent (ng/L)	Freshwater, rivers, canals (ng/L)
Trimethoprim	58–321	4–150
Ciprofloxacin	42–720	23–1300
Sulfamethoxazole	3.8–1400	1.7–2000
Naproxen	128–548	11–181
Ibuprofen	65–1758	28–360
Ketoprofen	–	<0.4–79.6
Diclofenac	8.8–127	1.1–6.8
Carbamazepine	152–226	25–34.7
Propranolol	50	–
Gemfibrozil	3.9–17	1.8–9.1

sources that continuously release organic micropollutants into water bodies [3–5], and it is now well known that organic micropollutants are ubiquitous contaminants in WWTP effluents [4]. Generally, during primary treatment, many of these pollutants are mainly removed by adsorption onto the sludge produced [6], but the amounts of some of them that are removed, such as naproxen, and sulfamethoxazole, are insignificant [7]. Secondary treatment can remove the organic micropollutants via biodegradation, biotransformation, and adsorption [8]. However, concentrations of some of them such as sulfamethoxazole and sulfapyridine might increase in the effluent compared to those in the influent due to their transformation back into the parent compounds [9]. Thus, the possibility of detecting organic micropollutants in the effluent of WWTP is inevitable because, first, most of the WWTPs in operation are not specially designed to remove these pollutants completely and, second, no monitoring actions/precautions for micropollutants have been defined [10].

Several treatment technologies have been applied to remove organics from ROC such as coagulation-flocculation processes and advanced oxidation processes, namely, ozonation, Fenton process, photocatalysis and photo-oxidation, sonolysis, and electro-chemical oxidation. Many studies have found that adsorption of organic micropollutants onto activated carbon either in the form of powdered activated carbon (PAC) or granular activated carbon (GAC) is a simple and very efficient technique [1,12]. This is particularly so when comparing it to coagulation–flocculation processes [13] and ozone oxidation [14].

Some studies investigated a combined PAC–ultrafiltration (UF) system in the tertiary treatment phase to remove organic micropollutants along with a coagulation treatment phase [14,15]. This combination emerged as the most suitable one because the effective removal of contaminants occurred without forming problematic by-products [14]. Löwenberg et al. [15] studied the PAC/UF system to remove five organic micropollutants, specifically sulfamethoxazole, carbamazepine, mecoprop, diclofenac, and benzotriazole from a wastewater effluent (DOC 8.8 $\pm$ 1.2 mg/L). They reported that a PAC dose of 20 mg/L was enough to remove 60–95% of the micropollutants. Margot et al. [14] studied the removal of 70 organic micropollutants from wastewater effluent (DOC 7.3 $\pm$ 1.9 mg/L) in which on average >70% of them were removed at an average dose of 13 mg/L of PAC. In addition to the removal of micropollutants, the PAC can reduce membrane fouling by adsorbing dissolved bulk organics which are the major fouling agents. In these treatment systems, the PAC adsorption and membrane filtration (MF) were carried out separately one after the other.

Vigneswaran et al. [16] studied the combined/hybridised form of carbon adsorption and MF together in a single stage of treatment for the removal of dissolved organics. In addition to carbon adsorption of the organics, this configuration was observed to be effective in terms of fouling reduction due to the membrane scouring effect. The direct contact of carbon particles with membrane surface can produce mechanical scouring effect by means of physical abrasion. This may mitigate the accumulation of foulants on top of the membrane surface and subsequently reduce build-up of transmembrane pressure (TMP). These two advantages of the submerged MF adsorption hybrid system are believed to reduce the membrane fouling further, and as such the operation can be extended for the long term. Furthermore, the frequency of membrane cleanings can be minimised.

In some membrane adsorption hybrid system studies, PAC was used as the suspended adsorbent to remove organics [17–20]. In these studies, the removal of organics was observed to increase when the PAC dosage rose. However, the high concentration of PAC dose formed a PAC cake on the membrane surface and consequently the flux declined. Guo et al. [21] reported that the initial PAC dose of 1 g/L was effective in a membrane-adsorption hybrid system in terms of organics removal and stable filtration flux, while the increase of initial PAC dose to 5 g/L dropped the filtration flux rapidly due to cake development. It should be noted that in the above study, only the initial dose was 5 g/L of reactor, and only 5 mg PAC/L of the reactor was added (or replaced) on a daily basis, which corresponded to <25 mg PAC/L dose.

Using larger particle size of activated carbon would be better than smaller ones due to the greater membrane scouring effect and higher fouling reduction [22]. Kim et al. [18] reported that the use of GAC along with MF reduced the TMP development and frequency of chemical cleaning by half. Pradhan et al. [23] concluded that adding GAC to MF not only provided mechanical scouring but also helped to reduce air scour. Another analysis noted that an increase in the particle size of Purolite A502PS significantly reduced TMP while maintaining low membrane fouling [24].

Only a few studies have been conducted on the use of PAC or GAC/MF hybrid system for the removal of organic micropollutants. Löwenberg et al. [15] investigated the efficiency of removing only five organic micropollutants from municipal wastewater treatment plant effluent using a pressurised PAC/UF system and a submerged PAC/UF system. They found that the latter system removed slightly larger amounts of organic pollutants compared to the former system. Shanmuganathan et al. [25,26] reported that a GAC/MF system was very effective in removing most of the 9 and 17 organic micropollutants tested in a biologically treated sewage effluent [25] and ROC [26], respectively. However, the previous study on ROC was only of a short-term duration lasting 6 h [26].

The aim of this study was to examine the feasibility of using the GAC/MF hybrid system as a long-term (10 days) continuous treatment option with daily replacement of GAC to achieve superior removal of organic micropollutants from ROC. The mechanisms for removing 19 micropollutants were evaluated by considering electric charges and hydrophobicity values obtained from chemical software that are more accurate than the previously used values obtained from equations. In addition to the removal of organic micropollutants and DOC, the GAC can also provide scouring to the membrane surface, and consequently reduce membrane fouling.

2. Materials and methods

2.1. Materials

2.1.1. Reverse osmosis concentrate

Reverse osmosis concentrate (ROC) collected from an advanced water treatment plant in Sydney, Australia, treating secondary effluent was used as feed water. The plant process consists of both continuous flow microfiltration (CMF) and reverse osmosis to treat the biologically treated effluent. The RO units produced an ROC, which contained all the contaminants rejected by RO. The water quality characteristics of the ROC are presented in Table 2.

2.1.2. Granular activated carbon

A coal-based premium grade (MDW4050CB) GAC obtained from James Cumming and Sons Pty. Ltd. served in this study as an adsorbent. Three different sizes of GAC (150–300 μm, 300–600 μm, and 600–1200 μm) were tested, and the GAC size of 300–600 μm was found to