REMOVAL OF PESTICIDES FROM WASTEWATER BY MEMBRANE PROCESS

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Abstract

Purpose: The aim of this study was to investigate the removal performances of four pesticides (tributyl phosphate, flutriafol, dicofol and irgarol) by RO membranes.

Methods: Three different RO membranes (BW30-LE, SW30-XLE and GE-AD) were used to reject pesticides in two transmembrane pressures of 10 and 20 bar in bench-scale membrane filtration cell. Tributyl phosphate and flutriafol were detected by GC/MS and dicofol and irgarol were monitored by HLPC instruments.

Results: While the highest removal of tributyl phosphate was obtained by the BW30-LE and GE-AD membranes with 98-99%, all membranes (BW30-LE, SW30-XLE and GE-AD) rejected irgarol with around 98% performance at 10 and 20 bar pressures. Irgarol and dicofol removal performances of all the RO membranes tested were higher than 95%.

Conclusion: Among the membranes tested, the BW30-LE membrane showed superior performance in the removal of all four pesticides, with removal efficiencies of 98-99%. Increasing TMP from 10 bar to 20 bar did not significantly affect pesticide removal efficiencies.

Keywords: Dicofol, irgarol, tributyl phosphate, flutriafol, wastewater, reverse osmosis.

Introduction

Environmental pollution has become a very important issue all over the world, especially in the last 20 years, since the presence of a large number of pollutants in ng/L and µg/L levels in aquatic environments. Pesticides is one class of these micropollutants and most of them banned for its toxicity and persistency in many countries (Silva *et al.*, 2017; Khanzada *et al.*, 2019). Since they are very difficult to treat with conventional processes, they pose a serious danger to human health if micro-pollutants reach the receiving environments used as a source of drinking water in various ways (Lui *et al.*, 2009). Among the treatment processes, membrane filtration has great impact due to its the inherent characteristics, low cost energy consumption, and simple operation and high removal efficiency (Silva *et al.*, 2017; Taghizade Firozjaee *et al.*, 2018). The objective of this study is to investigate the removal of tributyl phosphate, flutriafol, irgarol and dicofol by reverse osmosis (RO) process.

Materials and Methods

Membrane filtration experiments were designed to evaluate removal of pesticides at 10 and 20 bar operating pressures by the different RO (SW30-XLE, BW30-LE and AD) membranes. For the preparation of feed samples, pesticides were injected to treated municipal wastewater at 100 µg/L concentration for tributyl phosphate and flutriafol and at 1000 µg/L concentration for irgarol and dicofol. In order to keep the concentration constant in feed, the experiments were conducted in total recycle mode in which both concentrate and permeate were channelized to the feed tank. Feed and permeate samples were collected during operation at different time intervals to monitor flux developing and rejection of pesticides. All experiments were performed at feed water temperatures of 25 ± 5 °C. Tributyl phosphate and flutriafol were analysed by GC/MS instrument (Shimadzu QP-2010 Ultra) equipped with MS column (Restek 5-MS: 30 m, 0.25 mm (i.d.), 25 µm) according to dispersive liquid-liquid micro extraction method (Rezaee *et al.*, 2006; Berijani *et al.*, 2006). Dicofol and irgarol analysis were performed via Shimadzu Prominence-i HPLC with a reverse phase C18 column (Shim-pack Velox SP-C18) and a UV wavelength detector.

Results and Discussion

The results obtained through the RO experiments performed for the treatment of tributyl phosphate, flutriafol, irgarol and dicofol are summarized in Table 1. The effect of transmembrane pressure on the removal performances and flux of three RO membranes (GE-AD, BW30-LE, SW30-XLE) tested were concerned. Flux decline for each membrane type was determined based on the differences between clean water and raw water fluxes at steady state. By increasing the pressure, clean, raw water and clean water after treatment fluxes were increased especially in all membranes for all pesticides.

In tributyl phosphate removal tests (Table 1), the highest flux declines were observed for BW30-LE membranes by 38% and 42% at 10 and 20 bar pressures, respectively. The lowest flux declines were observed for GE-AD membrane with 15% and for SW30-XLE membranes with 5% at 20 bar pressure. All membranes provided high removal of tributyl phosphate over 98% efficiency. Increasing in transmembrane pressure did not significantly affect conductivity removal that the removal performances for all membranes at two pressures were 98-99%.

The highest flux declines in flutriafol removal tests were obtained for BW30-LE membranes by 10% and 9% at 10 and 20 bar pressures, respectively (Table 1). The lowest flux declines were observed for SW30-XLE membrane with 4% at 20 bar pressure. On the other hand, no flux decline was occurred during filtration test by GE-AD membrane. GE-AD membrane was the membrane that provides the highest flutriafol removal among other membranes. The removal performances of GE-AD membrane were 97.9% and 99% at pressure 10 and 20 bar, respectively. The lowest removal of flutriafol was obtained by BW30-LE membrane with 92.1% at 20 bar pressure. Generally, increasing transmembrane pressure enhanced flutriafol for GE-AD and SW30-XLE membranes but not for BW30-LE membrane. Similarly, GE-AD and SW30-XLE membranes provided more than 98% conductivity removal.

As it is seen in both Table 3 and 4, irgarol and dicofol removal performances of all RO membranes were over than 95%. In addition, the increase in pressure improves the removal performance of pesticides for all RO membranes tested. The highest irgarol removal efficiency with 98% and the highest flux recovery with 98.45% were obtained for BW30-LE membrane at 10 bar pressure. The highest dicofol removal efficiency as 99% and the highest flux recovery as 94% were obtained for BW30-LE membrane at 20 bar pressure. All of the results mentioned above suggest that the irgarol and dicofol micropollutants considered are nearly completely removed by the RO membranes tested.

Table 1. The pesticides removal and flux performance of GE-AD, BW30-LE, SW30-XLE membranes at two different transmembrane pressures.

Membranes	**Pressure (bar)**	**JW* (L/m²/h)**	**JWW** (L/m²/h)**	**JCW*** (L/m²/h)**	**Flux Recovery (%)**	**Flux Decline (%)**	**Removal (%)**
			Tributyl Phosphate				
GE-AD	10	6.37	4.91	5.65	89	23	99
	20	18.31	15.53	18.51	101	15	99
BW30-LE	10	32.47	20.21	24.68	76	38	99
	20	72.18	41.65	52.25	72	42	99
SW30-XLE	10	3.9	3.25	4.15	106	17	98
	20	13.48	12.82	12.39	92	5	98
			Flutriafol				
GE-AD	10	11.58	10.37	14.12	106	0	97.9
	20	37.27	33.83	31.36	130	0	99.0
BW30-LE	10	46.75	48.51	49.45	122	10	97.6
	20	98.9	107.14	128.57	84	9	92.1
SW30-XLE	10	15.49	16.69	16.07	104	0	98.5
	20	36.7	35.22	40.81	111	4	98.9
			Irgarol				
GE-AD	10	7.04	6.93	6.52	93	7	97.85
	20	15.05	14.43	13.71	91	9	95.26
BW30-LE	10	16.88	16.31	16.55	98	2	98.45
	20	43.20	40.89	37.35	86	14	98.33
SW30-XLE	10	2.20	2.11	2.02	92	8	97.98
	20	7.19	7.04	6.19	86	14	98.14
			Dicofol				
GE-AD	10	6.66	6.11	5.94	89	11	98.83
	20	16.03	12.84	13.16	82	18	99.07
BW30-LE	10	23.89	22.13	17.97	75	25	98.43
	20	53.35	52.22	50.24	94	6	99.00
SW30-XLE	10	2.00	1.82	1.42	71	29	95.16
	20	7.95	6.48	6.85	86	14	97.66

* clean water flux (L/m²/h), ** wastewater flux (L/m²/h), ***cleaned water flux (L/m²/h)

Acknowledgements

The authors gratefully acknowledge The Scientific and Technological Research Council of Turkey (TUBITAK) for the financial support with the project number 115Y013.

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