Treatment of Two Recalcitrant Neonicotinoid Insecticided (Imidacloprid and Thiamethoxam) from the Surface Water Near Agricultural Lands using Forward Osmosis (FO) and Pressure Retarded Osmosis (PRO)

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ABSTRACT

Two neonicotinoid insecticides namely Imidacloprid 1-[(6-chloro-3-pyridmyl)methyl]-N-mtro-2-imidazolidinimine) (IMD) and Thiamethoxam (3-(2-Chloro-5-thiazolylmethyl) tetrahydro-5-methyl-N-nitro-4H-1,3,5-oxadiazin-4-imine) (THM) were identified from a surface water near two agricultural lands in the Agean Region İn İzmir Turkey. A forward osmosis (FO) containing a flat sheet aquaporin membrane, was used as a membrane treatment process to treat the neonicotinoid insecticides (imidacloprid and Thiamethoxam) while the effluents of FO was compared by using a PRO process having a hollow fiber aquaporin membrane. THM exhibited higher yields in FO and PRO membranes than that IMD since TMH HAS has high water solubility and low octanol/water partitions compared to IMD. This neonicotinoid insecticide exhibited high rejection and removal efficiency in PRO due to it's low fouling property and low ICP effect. This CAN BE ATTRİBUTED the smaller pore size of the PRO membrane compared to the FO membrane the identified IMD metabolites were olefinic acid, 4-OH imidacloprid, 5-OH imidacloprid and 2-OH imidacloprid while the identified THM metabolites were Desmethyl-Thiamethoxam, thiamethoxam; TMX-dm, desmethyl-thiamethoxam and tri-methyltriazinone.

Keywords: FO; PRO; Neonicotinoid Insecticides; Imidacloprid; Thiamethoxam; Surface water; Metabolites

INTRODUCTION

Neonicotinoids are the most widely used insecticides in the world, which have been extensively applied in agroforestry, aquaculture and our daily life for crop protection, pest management or parasite control. They can be applied flexibly in a variety of ways, such as sprays, trunk injections, seed dressings and root drenches [1]. Along with the properties of relatively long half-life in soil and high solubility in water, neonicotinoids have the potential to accumulate in soil and leach into surface water and groundwater, which could pose a direct threat to non-target organisms, especially honeybees [2]. The residues of neonicotinoids in agricultural environment can also enter food chains and pose a threat to human health through trophic transfers [3,4]. Therefore, suitable methods are desperately needed to alleviate the contamination which results from neonicotinoids persistence and accumulation. Previous studies have exhibited different approach to remedy the agricultural pollution, which is based on chemical, physical, biological processes or a combination [5]. All neonicotinoids exhibit high water solubility that makes them amenable for use as systemic insecticides. In addition, they also have long half-lives in soil and in water, where they are resistant to hydrolysis at neutral or acidic pH and under anaerobic conditions; although some of them are subject to rapid photodegradation under favorable conditions. Their chemical properties, particularly their high water solubility and partitioning properties (low log KOW) and low soil adsorption (log KOC), promote movement of these insecticides through surface and subsurface runoff [6,7] and result in extended persistence under simulated environmental conditions [8]. Local environmental conditions can modify the persistence of neonicotinoids in water (e.g., increasing pH and turbidity enhances persistence) [9,10]. The major transport routes to aquatic ecosystems include surface runoff after rain events [10], soluble or insoluble fractions transported via snowmelt [10,11], leaching into groundwater [11,12] with associated subsurface discharge into wetlands and other surface waters [13], talc and graphite dust associated with seeding drills at the time of planting [14,15], decay of systemically treated plants in water bodies [16], and deposition of treated seeds, soil or spray drift into water bodies or depressions. The majority of surface water contamination is expected to be through runoff after major precipitation events [17].

Pressure Retarded Osmosis (PRO) is one of the technologies to harvest osmotic energy through an osmotically-driven membrane process [12]. During the PRO process, water spontaneously flows through a semi-permeable membrane from a low salinity feed solution to a high salinity draw solution against an applied hydraulic pressure. The osmotic energy is then generated via a turbine or energy recovery device due to the increased volume of the pressurized draw solution. Compared with the conventional energy generation processes, negligible CO_2 is emitted from the PRO process. Thus, PRO can be regarded as a cleaner and more environmentally friendly technology [18]. Many PRO researches were focused on the mixing of river water and seawater due to the easy accessibility and large energy potential [12]. In a recent PRO pilot study, PRO membranes could produce a stable power density of 6.7 W/m² using SWBr and tap water as the feed pair [19]. Once the tap water feed was replaced by WWRe, the PRO power density quickly dropped to 0 W/m² within 2 h because of membrane fouling by WWRe. With such a quick fouling, conventional backwash strategies are no longer practical because of the high frequency of cleaning and long process downtime. Neonicotinoids, broad-spectrum systemic insecticides, are the fastest growing class of insecticides worldwide and are now registered for use on hundreds of field crops in over 120 different countries. The environmental profile of this class of pesticides indicate that they are persistent, have high leaching and runoff potential, and are highly toxic to a wide range of invertebrates. Therefore, neonicotinoids represent a significant risk to surface waters and the diverse aquatic and terrestrial fauna that these ecosystems support.

Wanga et al., [20] investigated the degradation of imidacloprid (IMP) treatment using UV-activated persulfate (UV/PS) and peroxymonosulfate (UV/PMS) processes. The reaction rate constants between IMP and the sulfate or hydroxyl radical were calculated as 2.33 × 109 or 2.42 × 1010 M 1 s 1, respectively. The pH range affecting the degradation in the UV/PS ana UV/PMS systems. The removal yields of IMP was detected as 68%. Sablas et al., [21] 91% IMD removals was found with Catalytic percarbonate oxidation in aqueous phase. It was found that Humic acid and bicarbonate can inhibit the oxidation process. Rates of reaction were expressed in terms of the apparent rate constants (k_{app}) and were observed to satisfactorily follow pseudo-first-order kinetics. Inhibitory effects of humic acid and various coexisting ions on IMD degradation were examined and the trend was observed as follows: $NO_2^- > PO_4^{3-} > NH_4^+ > Cl^- > NO_3^-$. Wu et al., [22] found 76% imidacloprid (IMD) removal using from wastewater, a terbium ped Ti/PbO_2 (denoted as Ti/PbO_2-Tb) dimensionally stable Ti/PbO_2-Tb anode with one-step electrodeposition path via electrocatalytic degradation.70.05% of chemical oxygen demand and 76.07% of IMD are removed after 2.5 h of degradation under current density of 8 mA cm⁻², pH 9, temperature 30°C and 7.0 gL⁻¹ NaCl electrolyte. The imidacloprid remediation efficiency was found as 68% with Fe alginate gel beads in a study performed by Iglesias et al., [23] Fe alginate gel beads act as catalysts when maintained at a pH near the natural solution. The photodegradation of the neonicotinoid insecticide Nitenpyram (NPY) under UV and solar irradiation has been investigated in RİVER water [24]. NPY was rapidly photodegraded (yield was %67) following a first-order model and with half-lives varying from seconds to<10 min. Nitro-ethylene was dertected as moiety of the parent insecticide. Conversely to the lability of NPY, its TPs were more photo-stable in both ultrapure and river water. In a study perpared by Liua et al., [25], series S–O co-doped carbon nitride (SOCNx) materials were

prepared fort he he photocatalytic degradation of neonicotinoids under visible light. The optimal SOCN material (SOCN8) ensured an efficient degradation rate in seven neonicotinoids removal in aqueous solutions. The effective factors including catalyst dosages, concentration of neonicotinoids, and active species were discussed entirely. The possible mechanism of the degradation process was also proposed. Removal of Neonicotinoids via Sorption onto Granular Activated Carbon was studied Mengling et al., [26]. IMD and THM neonicotinoids studied exhibited relatively rapid removal via sorption onto GAC, with >80% removal in suspensions after 1 h of contact time [27]. The rejection of the TrOCs by a commercial cellulose acetate asymmetric forward osmosis membrane, as well as a "tight" commercial thin-film composite Nanofiltration (NF) membrane, was systematically investigated and compared under three different operating modes: Forward Osmosis (FO), Pressure Retarded Osmosis (PRO). Results revealed that the cellulose acetate membrane had considerably smaller water and salt permeabilities as well as less negative surface charge in FO and PRO modes. Nevertheless, the NF membrane displayed consistently better TrOC rejection than the HTI membrane. In RO mode, electrostatic interactions played a dominant role in governing the rejection of charged TrOCs. In FO and PRO modes, the rejection of charged TrOCs was governed by both electrostatic interaction and size exclusion, while rejection of neutral compounds was dominated by size exclusion, with rejection increasing with TrOC molecular weight. Operating in PRO mode resulted in a higher water flux but a notably lower TrOC rejection as compared with FO mode, because of more severe Internal Concentration Polarization (ICP) phenomenon.

In this study, it was aimed to treat a surface water containing high concentrations of contaminated with to insecticides namely IMD and THM from the farms and from the agricultural lands. The removals, the rejections of both insections in FO and PRO membrane reactors. The metabolites of IMD and THM were identified and their removal efficiencies were correlated in both two reactor.

MATERIALS AND METHODS

Properties of FO and PRO membranes

To prepare FO and PRO membranes, two types of polyamide selective layer were formed on the inner surface (i.e., the lumen side) of PES hollow fiber substrates by means of interfacial polymerization. The FO and PRO membranes have a dense polyamide selective layer formed via interfacial polymerization between an MPD aqueous solution and a TMC hexane solution. The resultant TFCPES membrane modules were used for LP-RO and PRO operations. The FO membrane has a loose polyamide selective layer formed through interfacial polymerization between a PIP aqueous solution and a TMC hexane solution. The Average pore diameter in FO and PRO membranes were 0.07 and 0.03 nm, respectively. The properties of FO ana PRO membranes were tabulated in Table 1.

Analytical procedures

Analytical method Aqueous samples were analyzed using a Waters HPLC system equipped with a Phenomenex-Kinetex 2.6 mm, C-18 column, 717þ auto sampler, binary pump, and 2487 absorbance detector set at 254 nm. Neonicotinoid separation was carried out in isocratic mode at a flow rate of 1 mL/min with a mobile phase of acetonitrile-water (15:85%, v/v). For analytical separation, we used the injection volume of 50 mL and noted that all 3 neonicotinoids were eluted within a 10-min run. The retention times for

thiamethoxam, and imidacloprid were found to be, 2.7 min, and 4.2 min, respectively. This retention time is consistent with the solubility of the neonicotinoids, with highly soluble dinotefuran eluting first and the least soluble imidacloprid eluting last. A standard curve of known concentration versus absorbance was plotted and used for quantifying the unknown concentrations in the samples exposed to natural sunlight and controls. The COD, TOC, DOC, electrical conductivity were measured use in Standard Methods [28].

The physicochemical properties of IMD and THM were tabulated in Table 2.

RESULTS AND DISCUSSION

Comparison of the rejection of MgSO$_4$ in FO and PRO processes

In the RO process, the rejection of MgSO$_4$ is Lower than that Pro due to a lower irreversible fouling propensity of PRO compared TO RO (Table 3). The flat-sheet membranes in PRO can withstand hydraulic pressures up to 22 bar with corresponding power density of 18 W/m^2, and hollow fiber membranes can withstand hydraulic pressures up to 20 bar with corresponding power density of 27 W/m^2 using 1 M MgSO$_4$, and deionized water as feeds. These PRO performances are superior to others reported in the literature. Moreover, outer-selective PRO hollow fiber membranes, which may have a less pressure drop along the fiber, have been demonstrated. Fouling in PRO membranes is more complicated than that in FO because the feed stream faces the porous substrates in PRO operations. In addition, the reverse salt flux may facilitate fouling

and complicate fouling mechanisms. In PRO mode, transport of trace organics (TOC, DOC, micro insecticides) across the membrane is concurrent with the flow of all other solutes. In FO mode, transport of water through the membrane is coupled with reverse salt flux. The reverse salt flux can be hinder the diffusion of the TrOCs, leading to higher rejection in PRO mode than in FO mode.

In aqueous and soil environments when exposed to natural sunlight, The IMD and THM insecticides exhibit strong firstorder degradation rate kinetics in the aqueous phase, with rate constants k$_{IMD}$, and k$_{THM}$ of 0.18 h^{-1}, and 0.30 h^{-1}, respectively [29]. Both insecticides exhibit strong first-order degradation rate kinetics in the aqueous phase.

The rejection of two herbicides (Imidacloprid and Thiamethoxam)

The rejection percentages of IMD and THM was tabulated in Table 4. There results showed that the PRO exhibiter higher rejection percentages than that IMD. The PRO reactor exhibited higher rejection persentages compared to FO. First-order degradation rate kinetics in the aqueous phase, with rate constants kDNT, kIMD, and kTHM of 0.30 h^{-1}, and 0.18 h^{-1}, respectively. The recent studies showed that the persistence of imidacloprid (IMD) and thiamethoxam (THM) are difficult. The imidacloprid is not readily degradable due to low water solubility (0,61 g/l) compared to THX (4,1 g/L) WİTH low molecular weigth of IMD (255, 7 g/mol) compared to THM (291,7 g/l). Photolysis studies of imidacloprid using a mixed solvent system (acetonitrile and water) with simulated sunlight (250 W, sun lamp) reported a half-life of 3.0 h [9]. Enhanced photolysis of imidacloprid has been observed with the addition of photosensitizers such as TiO$_2$, whereas the addition of acetone appears to inhibit photolysis [30]. Stability of imidacloprid in most compounds is higher than 99%, which have a MW lower or equal than the MWCO of the RO membrane, which can be estimated as 150 Da. First-order degradation rate kinetics in the aqueous phase, with high rate constants of kIMD

Table 1: Properties of membranes used in FO ana PRO.

	FO	PRO
Pure water permeability, A, (L m^{-2} h^{-1} bar^{-1})	3.52	
Salt permeability, (L m^{-2} h^{-1})	1.26	1,99
B/A (bar)	0.28	0,39
Salt rejection at 10 bar, Rs, (%)	92	97
Structural parameter, S, (μm)	540	569
Pure water flux in FO mode (L m^{-2} h^{-1})	12	12.6
Pure water flux in PRO mode (L m^{-2} h^{-1})	29	13.8
Reverse salt flux in FO mode (g m^{-2} h^{-1})	4	9
Reverse salt flux in PRO mode (g m^{-2} h^{-1})	8.60	9,99
Specific salt flux in FO mode (g/L)	0.37	0,56
Specific salt flux in PRO mode (g/L)	0.54 ± 0.05	0,78
Contact angle °	37	99
Zeta potential at pH=5.3 mV	⁻64	⁻89
Hollow fiber aquaporin membrane		
Pure water flux in FO mode (L m^{-2} h^{-1})	17	34
Reverse salt flux in FO mode (g m^{-2} h^{-1})	2,67	5,67
Specific salt flux in FO mode (g/L)	0,22	0,69

Table 2: Physicochemical properties of IMD and THM.

Physicochemical properties/name of neonicotinoid insecticides	IMD	THM
Molecular weithgh (g/mol)/	255,7	291,7
Water solubility (g/L)	0,61	4,1
Water pressure (Pa)	4 × 10^{-10}	6,6 × 10^{-9}
Henry low constant (Pa.m^3/ mol)	4,7 × 10^{-7}	1,7 × 10^{-10}
Log octanol/ water partitions (g/m^3)	0,57	0,13

Table 3: The rejection percentages of FO and PRO for MgSO$_4$.

Time (min)	Mg SO$_4$ concentration	Rejection percentage (%) for FO	Rejection percentage (%) for PRO
5	0,1 M	58	42
10	0,1 M	67	56
15	0,1 M	87	66
20	0,1 M	93	70
25	0,1 M	97	76
30	0,1 M	98	80
35	0,1 M	99	82

Table 4: The rejection percentages of IMD ana THM in FO and PRO.

Time (min)	IMD concentration	THM concentration	Rejection percentages (%)			
	(μg/L)	(μg/L)	FO		PRO	
			IMD	THM	IMD	THM
5	2,3	4,6	60	64	73	86
15	2,3	4,6	68	74	78	90
20	2,3	4,6	78	80	86	93
25	2,3	4,6	80	84	88	96
30	2,3	4,6	83	87	92	98
35	2,3	4,6	85	90	93	99,90

(0,18 h⁻¹) compared to kTHM (0.30 h⁻¹,) due to high solubility of THM, respectively [29].

As shown in Table 4, in the more hydrophilic pollutant; THM, the rejection increases over time due to not formation of the fouling layer, which increases the hydrophilicity of the surface and promotes partitioning of these contaminants into the DS side. For IMP, rejection of hydrophobic neutrals decreases over time, which can have the same decreasing tendency. The cake layer formed in the surface of the membrane increases the effect of External Concentration Polarization (ECP), and even though the rejection of the IMP of the clean membrane (SS as feed water), ECP plays an important role in the reduction of rejection over time for the hydrophobic neutral compounds. For the PRO membrane used, no fouling can be seen on the surface of the membrane; however, when the membrane is used with SWWE as feed, foulants accumulate on the surface.

The removal efficiencies of two herbicides (Imidacloprid and Thiamethoxam) in FO and PRO membrane processes

The effluent of PRO characteristics are significantly better in PRO than that FO while the HTM yields were comparably higher that IMD in both reactor systems (Table 5). In the FO, A hydraulic pressure WAS not applied resulting in a lower irreversible fouling propensity compared to PRO. However, conventional Thin Film Composite (TFC) and Cellulose Triacetate (CTA) membranes suffer from low permeability or selectivity in FO applications that could be a constraint in the viability of FO process for drinking water treatment. A considerable amount of endeavors has been devoted to modify the support layer of FO membrane and this leading to a decreased membrane structural parameter (S) and consequently a minimized internal concentration polarization in FO [10,19]. In the PRO process an aquaporin membrane was used [18]. These are natural membrane and living organisms

have been harnessed to develop so-called biomimetic membranes with a similar structure and functionality providing a selective passageway for water molecules. An example of such membranes is aquaporin membrane. Aquaporins are embedded proteins in the polymer matrix membranes inducing water conduction across the membrane and at the same time rejecting solutes and ions.

To date, only few research groups have investigated the potential of aquaporin membranes to removal of trace organic contaminants. The performance of the aquaporin flat sheet membrane in the removal of a wide range of trace organics with a variation in hydrophilicity and charge of the species [12]. It was also tested the first generation of hollow fiber aquaporin prototype to reject some micropollutants. They reported rejection of >99% for all the tested compounds [18]. However, these few studies on the use of aquaporin membranes for the rejection neonicotinoid insecticides for PRO membranes using a flat aquaporin membrane containing a hollow fiber structure.

The effluent concentrations of IMD ana THM herbicides and some conventional parameters in FO and PRO reactors were given in Table 5.

The best effluent concentrations for BOD, TOC, COD and some other conventional parameters was obtained in HTM at PRO membrane system.

The identified imidacloprid (IMD) metabolites were olefinic acid, 4-OH imidacloprid, 5-OH imidacloprid and 2-OH imidacloprid. Thiamethoxam (THM) metabolites were Desmethyl-Thiamethoxam, thiamethoxam; TMX-dm, desmethyl-thiamethoxam and tri- methyltriazinone. From 2,5 μg/l IMD; 0,8 μg/l olefinic acid, 0,6 μg/l 4-OH imidacloprid, 0,4 μg/l 5-OH imidacloprid and 0,35 μg/l 2-OH imidacloprid were produced as metabolites in PRO (Table 6). From 4,8 μg/l THM; 2,4 μg/l

Table 5: Removal efficiencies of IMD and THM in FO and PRO membranes.

Time (min)	Variation of IMD concentration in FO	Variation of IMD concentration in PRO	Variation of THM concentration in FO	Variation of THM concentration in PRO	Removal efficiencies (%)			
	(μg/L)		(μg/L)		FO		PRO	
					IMD	THM	IMD	THM
5	2,3	2,3	4,6	4,6	60	64	73	86
15	2,0	1,9	4	3,6	68	74	78	90
20	1,8	1,6	3,2	2,5	78	80	86	93
25	1,6	1,4	2,8	2,0	80	84	88	96
30	1,3	1,1	2,0	1,0	83	87	92	98
35	0,9	0,7	1,3	0,01	85	90	93	99,90

Table 6: Effluent concentrations of IMD ana THM herbicides and some conventional parameters in FO ana PRO membrane reactors.

Name of process	FO		PRO	
Name of neonicotinoid insecticides	IMD	HTM	IMD	HTM
Parameters in effluent, concentration	(μg/L)	(μg/L)	(μg/L)	(μg/L)
TOC	0,1	0,02	0,001	0
Conductivity (μS/cm)	0,01	0,01	0,001	0
BOD (mg/L)	0,02	0,01	0,010	0
COD (mg/L)	0,02	0,01	0,002	0
UV254 (cm⁻¹)	0,01	0,02	0,001	0
Turbidity (NTU)	0,02	0,01	0	0
DOC (mg/L)	0,03	0,01	0	0
IMD	0,2	0,03	0,001	0
HTM	0,1	0,01	0,001	0

Table 7: Removal efficiencies in metabolites of IMD and THM in PRO processes.

Time (min)	Variation of IMD METABOLİTES (Initial IMD conc: 2,5 µg/L) in PRO				Variation of THM Metabolites in PRO (initial THM conc: 4,8 µg/L)				
	(µg/L)				(µg/L)				
	olefinic acid	4-OH imidacloprid	5-OH imidacloprid	2-OH imidacloprid	Desmethyl-Thiamethoxam	Thiamethoxam	TMX-dm	Desmethyl-thiamethoxam	Tri-methyltriazinone
5	0,8	0,6	0,4	0,35	2,4	1,2	0,8	0,3	0,1
15	0,7	0,5	0,2	0,20	2,2	1	0,6	0,2	0,08
20	0,5	0,3	0,1	0,18	2	0,8	0,3	0,15	0,05
25	0,2	0,2	0,001	0,12	1,6	0,6	0,2	0,1	0,04
30	0,1	0,1	0	0,10	1,1	0,3	0	0	0,02
35	0,001	0	0	0,1	0	0,001	0	0	0

Table 8: Removal efficiencies in metabolites IMD and THM in FO process.

Time (min)	Variation of IMD Metabolites in FO (İnitial IMD conc: 2,5 µg/L)				Variation of THM Metabolites in FO (initial THM conc: 4,8 µg/L)			
	(µg/L)				(µg/L)			
	olefinic acid	4-OH imidacloprid	5-OH imidacloprid	2-OH imidacloprid	Desmethyl-Thiamethoxam	thiamethoxam	TMX-dm	tri- methyltriazinone
5	0,5	0,4	0,25	0,20	2,0	1,0	0,6	0,1
15	0,7	0,5	0,2	0,20	2,2	1	0,6	0,08
20	0,5	0,3	0,1	0,18	2	0,8	0,3	0,05
25	0,2	0,2	0,009	0,12	1,6	0,6	0,2	0,04
30	0,1	0,1	0,008	0,10	1,1	0,3	0,1	0,02
35	0,007	0	0,004	0,10	1,1	0,1	0,009	0,01

Desmethyl-Thiamethoxam, 1,2 µg/l thiamethoxam; 0,1 µg/l TMX-dm, 0,8 µg/l desmethyl-thiamethoxam and 0,3 µg/l tri-methyltriazinone were produces as metabolites in PRO (Table 7).

At the beginning of the operation in FO from 2,5 µg/l IMD; 0,5 µg/l olefinic acid, 0,4 µg/l 4-OH imidacloprid, 0,25 µg/l 5-OH imidacloprid and 0,20 µg/l 2-OH imidacloprid were produced as metabolites (Table 7). From 4,8 µg/l THM; 2,0 µg/l Desmethyl-Thiamethoxam, 1,0 µg/l thiamethoxam; TMX-dm, 0,6 µg/l desmethyl-thiamethoxam and 0,1 µg/l tri-methyltriazinone were produced as metabolites in FO (Table 7).

The metabolites of IMD and TMH were removed with high yields in PRO than that FO PROCESS. Althoug the molecular weitgh of THM is higher than IMD; the yields İN THM were higher than that IMD due to low solubilty of THM (4,1 g/l) is higher than that IMD (0,61 g/l) (Table 2). The metabolite yields in PRO reactor is higher than that of FO due to high pressure of PRO. Furthermore, the log octanol/water partitions of IMD is high then that of THM (Table 2).

The effluent of PRO characteristics are significantly better in PRO than that FO while the HTM yields were comparably higher than IMD in both reactor systems (Table 8). In the FO, A hydraulic pressure WAS not applied resulting in a lower irreversible fouling propensity compared to PRO. However, conventional Thin Film Composite (TFC) and Cellulose Triacetate (CTA) membranes suffer from low permeability or selectivity in FO applications that could be a constraint in the viability of FO process for drinking water treatment. A considerable amount of endeavors has been devoted to modify the support layer of FO membrane AND THİS leading to a decreased membrane structural parameter (S) and consequently a minimized internal concentration polarization in FO. In the PRO process an aquaporin membrane was used.

These are natural membranes and living organisms have been harnessed to develop so-called biomimetic membranes with a similar structure and functionality providing a selective passageway for water molecules. An example of such membranes is aquaporin membrane. Aquaporins are embedded proteins in the polymer matrix membranes inducing water conduction across the membrane and at the same time rejecting solutes and ions.

CONCLUSION

The removal efficiencies of imidacloprid metabolites namely olefinic acid, 4-OH imidacloprid, 5-OH imidacloprid and 2-OH imidacloprid were removed with yields of 87%, 89% and 87% in FO. These metabolites were removed with high efficiencies in PRO varying between 98% and 99%. Thiamethoxam metabolites namely Desmethyl-Thiamethoxam, thiamethoxam;TMX-dm, desmethyl-thiamethoxam and tri-methyltriazinone were detected.

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