Micropollutant, Micropollutant Metabolites and Toxin Removals in a Drinking Water Treatment Plant Using Some Novel and Economical Removal Processes

Delia Teresa Sponza*, Yudam Blylk Aras

Environmental Engineering Department, Dokuz Eylül University, Buca-Izmir, Turkey

ABSTRACT

The aim of this study was to detect the levels of heptachlor (1, 4, 5, 6, 7, 8, 8-Heptachloro-3a, 4, 7, 7a-tetrahydro-4, 7-methano-1H-indene) and acetochlor (2-Chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)-acetamide) Micropollutants (MK), their Metabolites (M) (heptachlor epoxide and fenthion and fenthion sulfoxide and some Toxins (T) (mycrocystin and aplysiatoxin from cyanotoxin) in the raw water of a drinking water treatment plant. Measurement procedures for the MK, M, and Ts have been developed. A sequential treatment process consisting of a Granulated Activated Carbon (GAC)/contact aerobic Membrane Bioreactor (MBR), Electro Fenton (EF) and Nano Filtration (NF) were found to be efficient in the treatment of MK, M and T. The maximum heptachlor and acetachlor removals in GAC by adsorption was 64% and 14%, respectively, while the Dissolved Organic Carbon (DOC) yields were recorded as 68% after 24 h. In the GAC/MBR contact aerobic reactor system, acetachlor and heptachlor yields were recorded as 89% and 27%, respectively. The heptachlor metabolite heptachlor epoxide was produced in this stage (30 ng/l) while the fenthion and fenthion sulfoxide metabolites of acetochlor were recorded as (120 ng/l) and (280 ng/l), respectively. These metabolites were removed with yields of 94.4%, 98%, and 94%, respectively, in the MBR. In NF the total yields of both pesticides and their metabolites varied between 96% and 98%. The toxin concentrations were reduced to (0.01 ng/l) and (0.02 ng/l) in the effluent of NF. The total cost of treating 1 m³ of raw drinking water was calculated as €1.98.

Keywords: Acetochlor; Drinking water; Electro fenton; GAC/MBR Contact reactor; Heptachlor; Micropollutant; Nano-filtration

INTRODUCTION

The conventional treatment processes used in the treatment of drinking water do not provide sufficient removals of MK, M, and T released by algae and cyanobacteria. The waste and toxicity thus produced threaten human health and microorganisms present in the ecosystems [1]. Water containing some pesticides is derived from farms and from fertilizers leaching into lakes and into drinking water [2]. Dichloromethane in drinking water was treated by the aerated GAC/C-packet reactor system (78%) [3]. A micropollutant, namely, perfluoroalkyl was removed by anion change and GAC [4]. Some resistant microorganisms (Cryptosporidium oocysts and Giardia) were removed with low yields (35%-45%) by coagulation, flocculation, sedimentation, flocculation, and filtration, while they were removed with high efficiencies by the GAC contact bioreactor and NF (97%-99%) [4]. Some pesticides, namely, acetochlor and alachlor are removed in the MBR reactor with co-metabolic biological treatment [3]. With NF high MK, M, and T removals were obtained [4]. Heptachlor is a hydrophobic pesticide and is dissolved in biological treatment processes. It can be removed with high yields in the electro fenton process and GAC with an aerobic contact rector system [5]. Acetochlor is a hydrophilic herbicide and can be removed with high yields (93%-97%) with GAC adsorption/aerobic contact reaktor and NF membrane [3]. The microcystin and aplysiatoxins generated by *Synechococcus sp.*, Cyanobacteria, piko/nanoplankton, were not removed in conventional treatment plants [2]. Ye et al. identified hydroxyl acetochlor and 2 methyl 6 ethylaniline (MEA) as acetochlor biodegradation products and speculated that dechlorination-hydroxylation was the first step in the biodegradation of acetochlor [6]. Considerable research into acetochlor biodegradation has been carried out, and many acetochlor degrading bacteria have been isolated, for example, *Shinella sp.* [7]

and *Achromobacter sp.* D-12 [8]. The MBR technology might be more efficient than conventional activated sludge in the removal of persistent compounds and micropollutants. The membrane retains the whole biomass inside the reactor, furthermore, it is possible to work at high Sludge Retention Time (SRT) and, hence, to promote the growth of a slow bacteria community [9]. Iglesias et al. found 87% pesticide removals in groundwater [10]. According to Oturan et al. 89% tetracycline yield was detected using the electro-fenton process after 80 min [11] while Plakas et al. investigated the removal of toxic organics [12]. They found 89% removal of the toxic compounds. Sirles et al. showed that the electrochemical oxidation process eliminates both hydrophobic and lipophilic organics with high yields [13].

In this study, it was aimed to detect the presence and the levels of heptachlor and acetochlor micropollutants in a drinking water treatment plant. The metabolites of both micropollutants were analyzed. The toxins produced by some cyanobacteria and algae (microcystin and cyanotoxin aplysiatoxin) were isolated and measured. The removals of these micropollutants, metabolites, and toxins were researched in the GAC/aerobic MBR contact reactor; the electro fenton and NF treatment processes by their sequential utilization of the prototypes as mentioned above.

MATERIALS AND METHODS

Reactor configurations

Diagrams showing the GAC/aerobic MBR contact reactor, Electro-Fenton (EF), and Nano Filtration (NF) processes are given in Figure 1. The resin in GAC (A-600/Purolite) contained quaternary ammonium and consisted of a polystyrene-divinylbenzene copolymer jell matrix. The diameter and the surface area were 610 ± 5 μm and 8 m^2/g, respectively, while the mean size of the macropore was 6 Å. The MBR was aerobic and was aerated with a sparger that supplied coarse bubbles in a separated unit. This reduced fouling of the membrane. Specific air demand was based on the membrane area (SADm=QA/Am) and specific air demand was based on permeate volume (SADp=QA/J. Am) were 0,075 Nm^3/hm^3 and 3,68 m^3air/m^3 permeate, respectively. QA was the membrane aeration rate (m^3/h) and Am was the total membrane surface area (m^2) while J was the design flux (0,5 l/m^2.h). The Electro-Fenton reactor was designed using one pair of cathodic and anodic steel-graphite electrodes that were positioned 1,4 cm away from each other and were placed directly in the drinking water samples. All electrodes were in contact with thin metal perforated disks made of stainless steel which acted as current carriers to the electrodes. The voltage applied between each pair of anode/cathode electrodes was regulated to 0,5, 1,2, 2,2, 2,8, and 3,0 V. The effective surface area of the electrode was 0.3 dm^2. The power supply was used to produce 7 A current input and increasing electricity potential mentioned above to the electrodes. In each run, 500 ml of drinking water was placed in the electrolytic cell contained in an ice bath to control the temperature and prevent evaporation. 10 ml 10% ferrous sulfate was added as an iron source to the samples before the current was applied. NF experiments were carried out in a DSS Lab-unit M20 with a membrane surface area of 0.216 m^2. The volumetric flow rates varied between (2 l/h, 4 l/h, 10l/h,15 l/h, 20 l/h and 30 l/h) with a pore size of 0.2 nm while the pressure varied between 0.8, 1.2 and 2.1 bar.

Operational conditions of all reactors used in this study

The effects of contact times (6, 24, 30, and 40) h and increasing pHs (4, 7, and 10) on the adsorption yields of heptachlor and acetochlor were researched in the GAC. In order to investigate the kinetics of MK, M, and T adsorption on the GAC beads, pseudo-first-order, pseudo-second-order, and intra-particle diffusion model
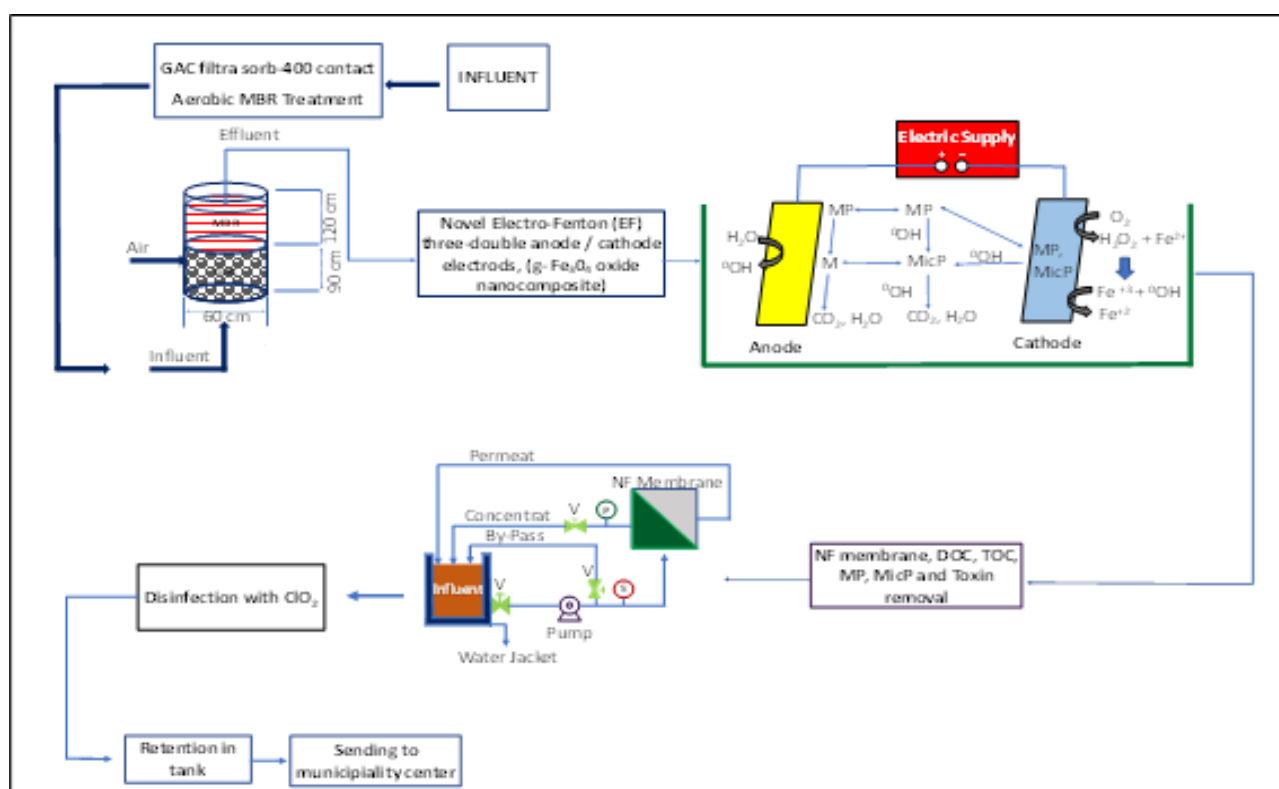

Figure 1: Sequential treatment process proposed to treat drinking water for removal of the 2 micropollutants, their metabolite, and toxins.

was used to fit the kinetics data. The effects of Hydraulic Retention Times (HRTs) (60, 70, 120, 280, and 600) min on the yield of MBR were researched. The effects of retention times (20, 30, 40-50 and 60) min and of the volumetric flow rates (2 l/h, 4 l/h, 10 l/h, 15 l/h, 20 l/h and 30 l/h) on the production of H_2O_2 levels and removals of heptachlor and acetochlor, their metabolites and toxins by adsorption in the electro fenton reactor were investigated. The effects of recirculation flow rates (20%, 50%, and 80%), increasing electricity potential (0.5, 1.2, 2.2, 2.8 and 3 V) and the increase of Trans-Membrane Pressures (TMP) (0, 8, 1, 2, 2, 1 and 6 bar) on the removals of the studied parameters were researched in the NF reactor. All the reactors were operated at a room temperature of 21˚C.

Characterization of raw drinking water

Table 1 summarizes the pollutant parameters present in the raw drinking water. The raw wastewater contained 650 ng/l heptachlor and 780 ng/l acetochlor while no metabolites of these micropollutants were detected. The toxins, namely microcystin and cyanotoxin levels were measured as 0.9 ng/l and 0.4 ng/l respectively.

Table 1: Micropollutant, metabolites, and toxins present in the raw drinking water.

Names of micropollutants and metabolites	Unit	Level
Heptachlor	(ng/l)	650
M: Heptachlor epoxide	(ng/l)	-
Acetochlor	(ng/l)	780
M: Fenthion	(ng/l)	-
M: Fenthion sulfoxide	(ng/l)	-
DOC	(mg/l)	270
T: Microcystin	(ng/l)	0.9
T: Aplysiatoxin (cyanotoxin)	(ng/l)	0.4

Analytical procedures

The analysis of the micropollutants, their metabolites, and toxins were performed with the solid-phase microextraction (HS-SPME or DI/SPME) method using HPLC and GC-MS. After the extraction procedure, the extract was connected with GC-MS using a microchannel at an injection temperature of 250˚C-280˚C with a desorption time of 3-5 min. According to the polarity and volatilization properties of analytics, the GC capillary column was used. The Dissolved Organic Carbon (DOC) and H_2O_2 were measured according to standard methods. The batch adsorption studies of acetochlor and heptachlor on GAC were performed under dark conditions for (60 hs) at a room temperature of 21 ˚C in sealed stainless steel reactors. Increasing concentrations of acetochlor

and heptachlor with a purity of 99.99 (Merck) was added to the closed reactors. The micropollutant containing reactors were filled with 2, 5, and 10 g GAC. The samples taken during different time intervals were analyzed for acetochlor and heptachlor levels. The control reactor was operated without GAC to detect the adsorption levels. Three different reaction kinetics were researched to detect the adsorptions on GAC. The pseudo-first-order reaction kinetic was defined with Eq. (1) [14].

$$\ln\left[q_e - q(t)\right] = \ln q_e - k_1 t \qquad (1)$$

Where q is the amount of adsorbed solute, q_e its value at equilibrium, k_1 the pseudo-first-order rate constant and t the time.

The second kinetic was the pseudo-second-order reaction kinetic and it can be defined with Eq. (2)

$$\frac{t}{q(t)} = \frac{1}{q_e} + \frac{1}{k_2 q_e^2} \qquad (2)$$

Where k_2 is the pseudo-second-order kinetic rate constant.

The Weber Morris kinetic model is given in Eq. (3) [15].
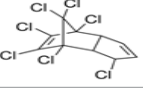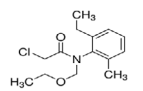
$$\ln q_t = a \log(t) \qquad (3)$$

q_t is the adsorption mass (mg/g) t is the adsorption time and k is the Weber-Morris adsorption kinetic constant (time $^{-1}$).

RESULTS

Effect of contact time and pH on the adsorption of micropollutants on GAC

Although some environmental conditions such as temperature, initial concentration, and ionic strength affect the adsorption yield, in this study, only the effects of contact time and pH on the adsorption of acetochlor and heptachlor on GAC were studied. Table 2 exhibits the physicochemical properties of heptachlor and acetochlor. Heptachlor is a hydrophobic micropollutant with high Log K_{OW} (6.10 unitless) and low solubility (<0.1 mg/ml) properties compared to acetochlor. As shown in Table 2 acetochlor Log K_{OW} is low (4.14 unitless) and its solubility is high (233 mg/ml) with low volatility properties (1,67 × 10^{-7} mm Hg at 26 ˚C). The maximum adsorption yield for hydrophobic heptachlor was obtained within 24 h as 64% while the hydrophilic acetochlor removal was recorded as 14% at a neutral pH at a room temperature of 21˚C (Table 3). As the adsorption time was increased from 6 h to 24 h the heptachlor and acetochlor adsorption yields increased from 23% to 64% and from 5% to 14%, respectively. Further increase of the adsorption time did not affect the adsorption yields in both parameters. The extent of adsorption in drinking water with contact time is an important factor affecting the adsorbed mass. In this study, the pollutants diffuse onto the porous structure of the GAC quickly

Table 2: Physicochemical properties of two micropollutants in drinking water.

Pollutants	Chemical structure	Molecular formula	Molecular weight (g/mol)	Vapor pressure (mm Hg at 26°C)	Solubility (mg/ml)	Log $_{Kow}$ (unitless)
Heptachlor		$C_{10}H_5Cl_7$	373.3	0,0003	<0.1	6.10
Acetochlor		$C_{14}H_{20}ClNO_2$	269.76	1.67 × 10^{-7}	233	4.14

with a short contact time (24 h) and attained an equilibrium. The active points of the GAC were fully occupied with acetochlor and heptachlor within 24 h. Therefore, at longer contact times no further adsorption was detected. As mentioned in Table 3, no metabolite production and toxin removal were recorded at this stage. The maximum DOC yield was 67% after 24 h. We found that the adsorption process depends on the pH of the wastewater. Hydrophobic interaction is mainly responsible for this adsorption process. GAC is the more common adsorbent, which is frequently used in the removal of hydrophobics. Due to its high surface area and porosity, it is very effcient in the removal of different varieties of pesticides, as reported by Plakas et al. [12]. Areerachakul et al. also observed high adsorption yields (73%) in the adsorption of chlorinated herbicides [16]. pH is one of the most important parameters affecting the adsorption process. In this study, the adsorption of heptachlor and acetochlor on the GAC was researched at pH 7.0. The heptachlor and acetochlor removals via adsorption were low at basic and acidic pHs. The maximum removals of both micropollutants and DOC were obtained at neutral pH. The rate of adsorption of both micropollutants decreased at higher pH levels at the surface of the GAC with the formation of species containing oxygen. The formation of these metabolites on the GAC surface led to a lower accessibility of the adsorption sites to heptachlor and acetochlor and, as a result, reduced the adsorption efficiency by 64%. On the other hand, at higher pH values, the heptachlor and acetochlor were converted rapidly to the negatively charged anion. This negatively affected the adsorption on the GAC. At higher pH values the electrostatic repulsion force or diffusion of the heptachlor and acetochlor ions on the surface of GAC was increased, therefore the equilibrium adsorption decreased as pH rose above 7.0 by 67%. Therefore, in this study, pH 7.0 was found to be the optimal pH in order to achieve a high adsorption yield. A significant decrease was observed in the adsorption yields at pH levels lower than 7.0 and more than 7.3.

Table 3: Effect of contact time and pH on the adsorption of heptachlor and acetochlor on GAC.

Pollutant	Removal percentage (%)						
	Time				pH		
	6 h	24 h	30 h	40 h	4	7	10
Heptachlor	23	64	64	64	34	64	30
M: Heptachlorepoxide	0	0	0	0	0	0	0
Acetochlor	5	14	14	14	2	14	2
M_1: Fenthion	0	0	0	0	0	0	0
M_2: Fention sulfoxide	0	0	0	0	0	0	0
DOC	12	68	68	69	27	69	20
T: Microcystin	0	0	0	0	0	0	0
T: Aplysiatoxin (cyanotoxin)	0	0	0	0	0	0	0

Table 4: GAC adsorption kinetics of heptachlor and acetochlor.

		First-order kinetic	Second-order Kinetic	Weber-Morris Kinetic	C0
		k_1 (min^{-1})	k_2 (min^{-1})	k_{int} (min^{-1})	(ng/L)
Acetochlor	Rate Contstants	0.045	0.059	0.69	789
	R^2	0.98	0.96	0.99	
Heptachlor	Rate Contstants	0.019	0.022	0.12	650
	R^2	0.97	0.96	0.99	

Table 5: The influent and effluent concentrations and removal yields of all pollutant parameters produced metabolites and toxin levels versus HRTs.

Concentration of micropollutants (ng/l) and DOC (mg/l)			Concentrations (ng/l) and removal efficiencies (%) in the effluent of MBR versus increasing SRTs									
Pollutants	Concentration in raw drinking water (ng/l)	Concentration removed in GAC (ng/l)	Concentration in the influent of MBR (ng/l)	HRT 60 min (% removal efficiency	Effluent of MBR (ng/l) after 60 min	HRT 70 min (% removal efficiency)	Effluent of MBR (ng/l) after 70 min	HRT 120 min (% removal efficiency)	Effluent of MBR (ng/l) after 120 min	HRT 280 min (% removal efficiency)	Effluent of MBR (ng/l) after 280 min	HRT 600 min (% removal efficiency)	The effluent of MBR (ng/l) after 600 min
Heptachlor	650	416	234	15	198.9	17	165.09	27	120.57	27	120.57	27	120.57
M: Heptachlor epoxide	-	-	-	50	30 and 15	60	50 and 20	94.4	90 and 5	94.4	90 and 5	94.4	90 and 5
Acetochlor	780	109.2	670.80	34	443	67	146.19	89	16.09	89	16.09	89	16.09
M1: Fenthion	-	-	-	91	120 and 10	95	150 and 6	98	180 and 0.22	98	120 and 0.22	98	0.22
M2: Fention sulfoxide	-	-	-	72	280 and 80	86	300 and 23.6	94	320 and 2.78	94	16.8 and 2.78	94	16.8 and 2.78
DOC (mg/L)	270	186.30	83.7	67	27.62	70	8.26	82	1.48	82	1.48	82	1.48
T: Microcystin	0.9	-	0.9	23	0.69	48	0.56	84	0.144	84	0.144	84	0.144
T: Aplysiatoxin (Cyanotoxin)	0.4	-	0.4	34	0.264	50	0.20	81	0.076	81	0.076	81	0.076
M: metabolit ; T: toxin												

Kinetic studies may provide important information about the fate of the pollutants in the aqueous phase. In order to detect the acetochlor and heptachlor adsorption kinetics; first order, second order, and Weber-Morris kinetic were applied to the data observed from the adsorption process (Figure 1). Based on the aqueous solubility and octanol-water partition coefficient acetochlor was expected to be adsorbed to a greater extent than heptachlor. Among these kinetics, it was found that both micropollutants were adsorbed according to the first-order reaction kinetic with meaningful adsorption rate constants (k1) of 0.045 min^{-1} and 0.019 min^{-1} for acetochlor and heptachlor, respectively, with high regression coefficients of 0.97 and 0.98 exhibiting the linearity (Table 4).

Effect of HRT on the removals of micropollutants and toxins in MBR

Since the effluent of the GAC was supplied to the MBR, the effluent concentrations of the acetochlor and heptachlor coming into the MBR were tabulated in Table 5. The degree of removal of the micropollutants studied was related, among other factors, to the hydrophobicity coefficients (defined as log K_{ow} and solubility) of both acetochlor and heptachlor. Their removal percentages increased with respect to HRT. As the HRT was increased from 60 min and 70 min to 120 min the biodegradation yields of the pollutants increased (Table 5).

The acetochlor and heptachlor concentrations in the influent in the MBR were (109.2 ng/l) and (670.80 ng/l), respectively. The optimum HRT for maximum removals of micropollutants and toxins was found as 120 min (Table 5). The maximum biodegradation yields for acetochlor (89%) were found to be high compared to heptachlor (27%) after 120 min HRT due to its

hydrophilic character and high solubility properties, as reported in (Table 2). As the HRT was increased from 60 min to 70 min and 120 min the biodegradation yields of acetochlor increased from 34% to 60% and 89% while the biological heptachlor removals increased from 15% to 19% and 27% (Table 3). The persistence of heptachlor in the MBR can be attributed to its hydrophobic structure with a high log K_{ow} of 6.10 unitless, the low solubility of <0.1 ng/ml and high molecular weight of 373.3 g/mol suggesting that the microorganisms have not adapted to degrade the acetochlor (Table 2). This result in this study is in agreement with previously reported values by Hai et al. [17] Radjenovic et al. [18] and Melin et al. [19]. As the HRT was increased from 60 min to 120 min the removal yields increased. However, further increase of the HRT did not affect either of the micropollutant yields. During the biodegradation process, the degradation of both heptachlor and acetochlor was accompanied by the production of metabolites. From 234 ng/l heptachlor 30 ng/l heptachlor epoxide was produced at the start of 60 min HRT (Table 5). The MBR reactor was operated for 45 days in each HRT. At the end of this period, heptachlor epoxide was also biodegraded by the aerobic microorganisms and its concentration decreased to 15 ng/l with a yield of 50%. At 70 min HRT from 234 ng/l heptachlor; 50 ng/l heptachlor epoxide was released at the start of this HRT period. The concentration of this metabolite decreased to 20 ng/l with a yield of 60% at the end of this HRT. At 120 days HRT; 90 ng/l heptachlor epoxide was generated and its concentration decreased to 5 ng/l at the end of 120 min HRT period The removal yield of this metabolite was recorded as 94.4% (Table 5). The heptachlor was ultimately biodegraded to heptachlor epoxide besides CO_2 and H_2O since the concentration of this metabolite was recorded as 5 ng/l after 120 min HRT in the MBR effluent. At low HRTs (60-70
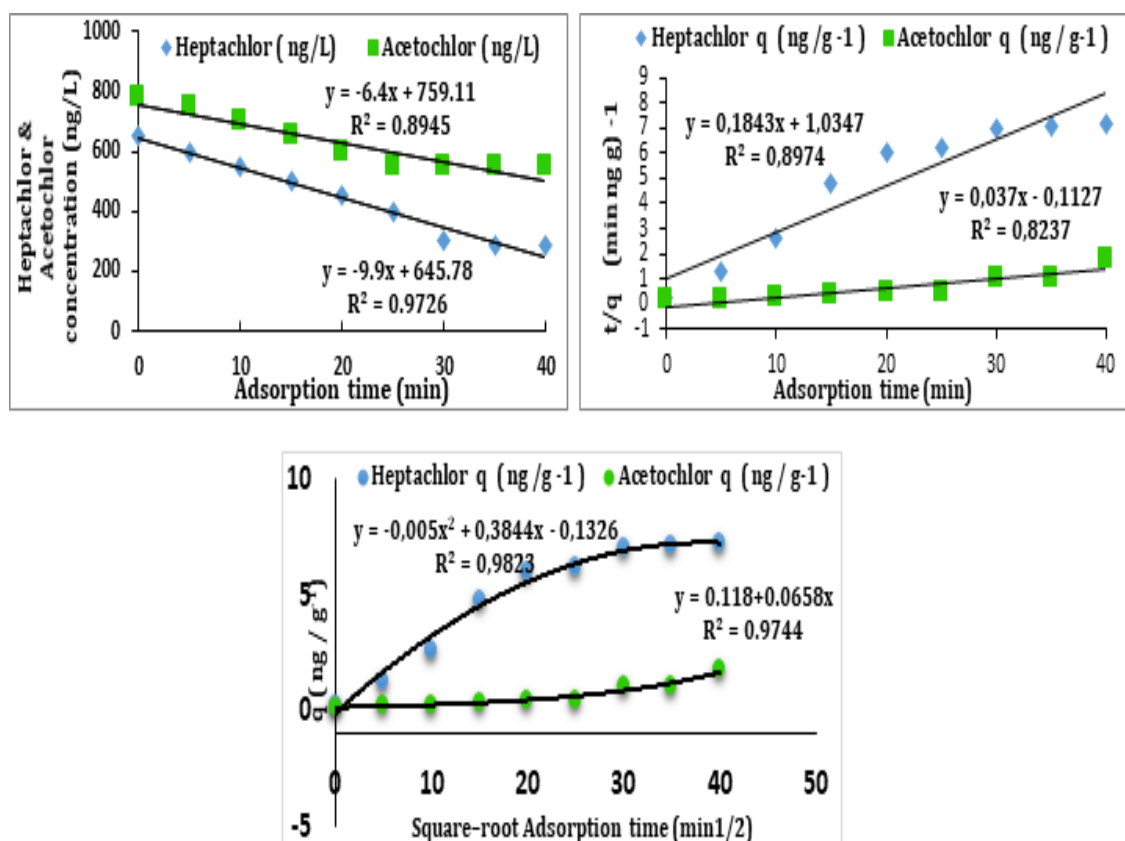

Figure 2: (a): First order kinetic model; **(b):** Second order kinetic model; **(c):** Weber-Morris kinetic models for acetochlor and heptachlor.

min) the heptachlor epoxide removal was low, while after 120 min HRT this metabolite was removed with a yield of 94.4% and resulted in a low concentration in the effluent of the MBR (Table 5). Although heptachlor epoxide has similar toxicity to heptachlor, this low concentration (5 ng/l) was found to have no toxicity as reported by Purnomo, McManus et al. [21] and Abdo et al. [22]. Hydrophobic heptachlor can be easily degraded to more biodegradable heptachlor epoxide metabolite. Since this micropollutant is hydrophobic it is expected that it should strongly interact with the bacteria and hydrophobic partial adsorption of this compound to the membranes of the bacteria is expected in the MBR. However, in this study, it was found that both biodegradation and hydrophobic adsorption (data not shown) was detected for the removal of heptaclor.

In accordance with the high water solubility, acetochlor was dissolved in water and it could easily be removed via biodegradation in the MBR. The acetochlor was removed during MBR operation and its yield increased significantly as the HRT was increased from 60 min to 70 min and 120 min. The maximum acetochlor yield was recorded as 89% at 120 min HRT. The metabolites of acetochlor were fenthion and fenthion sulfoxide. From 670.80 ng/l acetochlor 120 ng/l fenthion and 280 ng/l fenthion sulfoxide were produced at an HRT of 60 min while these metabolites concentrations decreased to 10 ng/l and 80 ng/l at 60 mn HRT after 45 days of operation with removal efficiencies of 91% and 72%, respectively. As the HRT increased to 70 min and 120 min the fenthion and fenthion sulfoxide concentrations increased to 150 ng/l and 180 ng/l and to 300 ng/l and 320 ng/l, respectively. As the HRT was increased the long contact times of the micropollutants in the drinking water with the membrane bacteria caused a rise in the levels of these metabolite concentrations (Table 3). At 70 min and 120 min HRTs after 45 days of operation the effluent fenthion and fenthion sulfoxide concentrations were recorded as 23.6 ng/l and 2.78 ng/l. These results agree with the studies performed by Bernhard et al. [23]. They mentioned that chlorinated micropollutants are poorly eliminated in the MBR because they have low hydrophobicity and limited biodegradability. However, with the increase in SRT-HRT,

an increase in the efficiency of elimination of these pesticides can be observed. In our study, an optimum HRT (120 min) for maximum biodegradation of both micropollutants and metabolites was observed. A further increase of the HRTs to 280 min and 600 min did not affect the biodegradation yields of either micropollutant and their metabolites. The probable degradative pathways of acetochlor can involve dechlorination, hydroxylation, deethoxymethylation, cyclization, carboxylation, and decarboxylation [24]. The biodegradation pathway of heptachlor is not hydroxylation and dechlorination, as reported by Wang et al. [25] and Li et al. [26]. The heptachlor biodegradation pathway was epoxidation of heptachlor to heptachlor epoxide. This metabolite was not further transformed to chlordene epoxide by dechlorination reaction, or degraded to heptachlor diol by hydrolysis reaction as reported by Dictor et al. [27] and Li et al. [26] since these metabolites were not detected in the GC-MS analysis. In the molecular structure of acetochlor, electron acceptor functional groups (chlorides) were detected. Based on these groups exhibited low biodegradability [28]. Although in its molecular structure acetochlor has electron-winning functional groups (chlorides), it also has a moderate hydrophobic character, and adsorption in sludge can be the main elimination mechanism. Li et al. [29] found that acetochlor was transformed by *S. quisquiliarum* to an intermediate 2-chloro-n-(2-methyl-6-ethylphenyl) acetamide which was further transformed to 2-methyl-6-ethylaniline. The probable biodegradation of acetochlor was the generation of 2-chloro-n-(2-methyl-6-ethylphenyl) acetamide by n-dealkylation. This metabolite was transformed into 2-methyl-6-ethylaniline by cleavage of the amide bond. These metabolites were also detected by Li et al. [29] and Yao et al. [30]. On the other hand, acetochlor has ethoxymethyl and methylphenyl groups, and they could be degraded by the cleavage of these functional groups [31]. In this study, it can be speculated that dechlorination-hydroxylation was the biodegradation pathway of acetochlor. During hydroxylation, the phenyl aromatic ring was cleaved [30]. On the other hand, the amide nitrogen in the alkyl side chain also was cleaved. By the deethoxymethylation of ethoxymethyl group and cyclization of n-substitute with one of

Table 6: Effects of time and electricity potential on the production of H_2O_2 in electro fenton process.

Applied electricity potential (V)	H_2O_2 production (µg/l)				
Time (min)	20	30	40	50	60
0.5	50	70	150	150	150
1.2	180	260	340	340	340
2.2	400	590	870	870	870
2.8	600	750	960	960	960
3	600	750	960	960	960

Table 7: Effects of time on the adsorption efficiencies of all parameters studied in the electro-fenton process.

Pollutant names and removal percentage (%)	20 min	40 min	300 min	400 min
Heptachlor	67	99	70	70
M: Heptachlor epoxide	70	96	70	60
Acetochlor	75	86	67	56
M: Fenthion	80	86	67	60
M: Fhention sulfoxide	76	88	70	56
DOC	70	93	65	60
T:Microcystin	75	92	60	54
T: Aplysiatoxin (Cyanotoxin)	80	90	79	60

Table 8: Effect of TMP and recycle ratio on the removals of pollutants in NF.

Pollutant names	TMP and R						
	TMP (bar)				Recycled ratio (%)		
	Removal efficiencies (%)						
	0.8 bar	1.2 bar	2.1 bar	6 bar	R:20%	R: 50%	R: 80%
Heptachlor	89	99	78	76	89	99	80
M: Heptachlor epoxide	87	98	78	76	89	99	79
Acetochlor	80	99	78	78	80	98	80
M: Fenthion	90	98	70	70	80	99	80
M: Fenthion sulfoxide	88	97	70	70	86	98	79
DOC	87	99	70	70	87	97	80
T: Microcystin	88	97	70	70	88	99	80
T: Aplysiatoxin (cyanotoxin)	86	96	70	70	89	97	80

Table 9: Cost analysis treatment of drinking water in the pre-filter, GAC and MBR, electro fenton and NF reactors.

Reactors	Cost analysis (€)
Pre-filtration device	0.03
GAC reactor	0.04
MBR reactor	0.12
Electro-fenton reactor	0.11
Nanofiltration reactor	0.18
Electricity consumption in all reactors	0.7
Electrodes in electro-fenton reactor	0.4
Membranes in gac and mbr	0.4

the ethyl groups, the acetochlor was ultimately biodegraded to fenthion and fenthion sulfoxide. The adsorption of acetochlor was determined extensively by some researchers. High adsorption yields were detected for acetochlor (56%, 63% and 78%) [32,33]. Bioaccumulation of acetochlor on soils and in sediment and sludge was detected [29,33]. Lower chronic toxicity of acetochlor to the tested algae and observed recovery of soil microbial activity together demonstrate that facilitated dechlorination in modified soils resulted in enhanced detoxification of acetochlor [29].

Dissolved Organic Carbon (DOC) in drinking water may contain, hydrophobic bases, hydrophobic neutrals, hydrophilic acids, hydrophilic bases, and hydrophilic neutrals. The quality of the DOC is expected to affect its fate in a treatment plant, since a considerable proportion of DOC is not biodegradable, and it may remain in the drinking water. DOC yields increased from 60% to 70% and 82% as the HRT was raised from 60 min to 70 min and 120 min. The effluent DOC was measured as 1.68 ng/l after 120 min HRT in the MBR effluent. The toxins, namely microcystin (0.9 ng/l) and aplysiatoxin (0.4 ng/l) were degraded in the MBR. As the HRT increased from 60 min to 120 min the microcystin and aplysiatoxin toxins were biodegraded by yields of 84% and 81% with effluent concentrations of 0.144 ng/l and 0.076 ng/l, respectively.

Effect of time and applied electricity potential on H_2O_2 production in the electro phenton process

In this step of this study, among the volumetric flow rates applied (2 l/h, 4 l/h, 10 l/h, 15 l/h, 20 l/h and 30 l/h) it was found that at 30 l/h volumetric flow rate the maximum H_2O_2 concentration was obtained. Therefore the studies were performed with a 30

l/h volumetric flow rate. The H_2O_2 production yields increased as the applied electric potential was increased up to an electric potential of 2.8 V. The optimum time for the maximum H_2O_2 production was detected as 40 min. For the production of H_2O_2 necessary time is required for the conditioning of the electron pairs (Table 6). The results showed that for the electricity potential >2.8 V; the H_2O_2 concentration remained stable. At high retention times also the H_2O_2 productions remained stable. This could be attributed to the contact of H_2O_2 with the surface of anodes and cathodes of the electro filter was not performed effectively, as reported by Sklari et al. [34] and Thiamet et al. [35]. This hindered the oxidation of H_2O_2 to O_2 in the anode or a possible reduction of H_2O_2 occurs at the cathode surface. As a result, the produced H_2O_2 was not increased.

Adsorption of micropollutants, their metabolites, and toxins to electro filter

Adsorption studies were performed in continuous mode when the electrodes were at the saturation point with 2.8 V electricity. Among the volumetric flow rates applied (2 l/h, 4 l/h, 10 l/h, 15 l/h, 20 l/h and 30 l/h) it was found that at 30 l/h volumetric flow rate the maximum adsorption efficiency was detected (data not shown). The maximum adsorption yields for all micropollutants, metabolites, and toxins were detected as 40 min. The maximum adsorption yields were 99% and 96% for hydrophobic heptachlor and its metabolite heptachlor epoxide, respectively. For hydrophilic acetochlor and its metabolites, namely fenthion and fenthion sulfoxide slightly lower adsorption yields were detected (86%, 86%, and 88%) compared to heptachlor (Table 7). The DOC was effectively adsorbed to the electro filter and removed with high yields such as 93% while the toxins, namely microcystin and aplysiatoxin were also removed with high yields (92% and 90%). The saturation times for heptachlor-effluent/heptachlor-effluent and heptachlor epoxide-effluent/heptachlor epoxide-effluent were found as 800 min and 850 min, respectively (data not shown). The saturation times for acetochlor-effluent/acetochlor-effluent, and fenthion-effluent/fenthion-effluent and fenthion sulfoxide-effluent fenthion sulfoxide-effluent were found to be as 480 min and 502 min, respectively (data not shown). The differences observed in breakthrough times and adsorption yields between fenthion and heptachlor micropollutants are related to the hydrophilic character of acetochlor and its metabolites. The aforementioned

organic chemicals can compete with the adsorption sites of the electrodes with the carbonaceous substrate. Their diffusion rates decreased since the adsorption sides of the electrodes were occupied by the DOC since the DOC adsorption yield was recorded as 93%. Therefore, the adsorption efficiencies of the hydrophilic micropollutants and their metabolites were low.

Effects of TMP and recycle ratio on the removals of all studied parameters in NF

In this step of the study; the effects of trans membrane pressure and recycling ratio on the removal of micropollutants, metabolites, DOC, and toxins removals were studied in a nanofiltration reactor system. García-Vaqueroa et al. [36] reported that the nanofiltration membranes effciently removed hydrophobic materials from drinking water, making it even more hydrophilic. A high hydrophilic composition can cause biofouling problems in membrane systems. However, in this study both hydrophobic and hydrophilic micropollutants, their metabolites, and DOC were effectively removed in NF (Table 8). For maximum removals of heptachlor (99%), and acetochlor (99%) the optimum transmembrane pressure was detected as 1.2 bar with a recycle ratio of 50% (Table 8). The metabolites of micropollutants were also removed with high yields (between 97% and 99%), while the toxins (96%-97%) in drinking water were effectively removed.

Cost analysis

Cost analysis was investigated for $1 m^3$ drinking water. The total cost for the pre-filter, GAC and MBR, electro fenton, and NF reactors was € 0.41 to treat 1 m^3 raw drinking water (Table 9). The electricity cost for all reactors was calculated as € 0.7. All the consumption was tabulated in Table 9. The cost of membranes used in this study and the total electrode cost was calculated as € 0.8. The total cost for treating 1 m^3 of raw drinking water was calculated as € 1.98.

CONCLUSION

The results of this study showed that a sequential GAC/aerobic MBR contact reactor, electro fenton, and NF system is very effective in the treatment of the heptachlor (99%) and acetochlor (98%) micropollutants and DOC (99%) with high yields in a drinking water treatment plant. The metabolites of heptachlor (heptachlor epoxide-99%) and acetachlor (fenthion-99% and fenthion sulfoxide-98%) and the toxins, namely microcystin (99%) and aplysiatoxin (97%) were removed effectively.

REFERENCES

1. Bowman MC, Beroza M. Determination of fenthion and five of its metabolites in corn, grass, and milk. J Agric Food Chem. 1968;16:399-402.

2. Das S, Ray NM, Wan J, Khan A, Chakraborty T, Ray MB. Micropollutants in wastewater: fate and removal processes. Physico Chemical Treatment. 2017;75-117.

3. Huo F, Tang H, Wu X, Chen D, Zhao T, Liu P, et al. Utilizing a novel sorbent in the solid phase extraction for simultaneous determination of 15 pesticide residues in green tea by GC/MS. J Chromatogr A. 2016;1023:44-54.

4. Pokethitiyook P, Poolpak T. Heptachlor and its metabolite: accumulation and degradation in sediment. Rec Tren Pes Resi Ass. 2012; 217-252.

5. Banuelos JA, El-Ghenymy A, Rodríguez FJ, Manríquez J, Bustos E, Rodríguez A, et al. Study of an air diffusion activated carbon packed electrode for electro-Fenton wastewater treatment. Electrochimica Acta. 2014;140:412-418.

6. Ye CM, Wang XJ, Zheng HH. Biodegradation of acetanilide herbicides acetochlor and butachlor in soil. J Environ Sci. 2002;14:524-529.

7. Ni J, Shen W, Yan X, Li S. Isolation and characterization of an acetochlor-degrading strain Y-4 and its degrading characteristics. J Agric Environ Sci. 2011;30:946-951.

8. Xu C, Ding J, Qiu J, Ma Y. Biodegradation of acetochlor by a newly isolated *Achromobacter sp.* strain D-12. J Environ Sci Heal A. 2013;48:960-966.

9. Nguyen LN, Hai FI, Kang J, Price WE, Nghiem LD. Removal of trace organic contaminants by a membrane bioreactor-granular activated carbon (MBR–GAC) system. Bioresour Technol. 2012;113:169-173.

10. Iglesias O, de Dios MF, Tavares T, Sanromán MA, Pazos M. Heterogeneous electro-Fenton treatment: preparation, characterization, and performance in groundwater pesticide removal. J Ind Eng Chem. 2015;27:276-282.

11. Oturan N, Wu J, Zhang H, Sharma VK, Oturan MA. Electrocatalytic destruction of the antibiotic tetracycline in aqueous medium by electrochemical advanced oxidation processes: effect of electrode materials. Appl Catal. 2013;140:92-97.

12. Plakas KV, Sklari SD, Yiankakis DA, Sideropoulos GT, Zaspalis VT, Karabelas AJ. Removal of organic micropollutants from drinking water by a novel electro-Fenton filter: pilot-scale studies. Water Res. 2016;91:183-194.

13. Sirés I, Brillas E, Oturan MA, Rodrigo, MA, Panizza M. Electrochemical advanced oxidation processes: today and tomorrow. Environ Sci. 2014;21:8336-8367.

14. Ho YS, McKay G. Pseudo-second order model for sorption processes. Process Biochem. 1999;34:451-465.

15. Dotto GL, Costa JAV, Pinto LADA. Kinetic studies on the biosorption of phenol by nanoparticles from *Spirulina sp.* LEB 18. J Environ Chem Eng. 2013;1:1137-1143.

16. Areerachakul N, Vigneswaran S, Ngo HH, Kandasamy J. Granular Activated Carbon (GAC) adsorption-photocatalysis hybrid system in the removal of herbicide from water. Sep Purif Technol. 2007;55:206-211.

17. Hai FI, Tessmer K, Nguyen LN, Kang J, Price WE, Nghiem LD. Removal of micropollutants by membrane bioreactor under temperature variation. J Membr Sci. 2011;383:144-151.

18. Radjenovic J, Petrovic M, Barceló D. Analysis of pharmaceuticals in wastewater and removal using a membrane bioreactor. Anal Bioanal Chem. 2007;387:1365-1377.

19. Melin T, Jefferson B, Bixio D, Thoeye C, De Wilde W, De Koning, et al. Membrane bioreactor technology for wastewater treatment and reuse. Desalination. 2006;187:271-282.

20. Purnomo AS, Mori T, Putra SR, Kondo R. Biotransformation of heptachlor and heptachlor epoxide by white-rot fungus Pleurotus ostreatus. Int Biodeterior. 2013;82:40-44.

21. McManus SL, Coxon CE, Richards KG, Danaher M. Quantitative solid-phase microextraction-Gas chromatography mass spectrometry analysis of the pesticides lindane, heptachlor and two heptachlor transformation products in groundwater. J Chromatogr A. 2013;1284:1-7.

22. Abdo W, Hirata A, Sakai H, El-Sawak A, Nikami H, Yanai T. Combined effects of organochlorine pesticides heptachlor and hexachlorobenzene on the promotion stage of hepatocarcinogenesis in rats. Food Chem Toxicol. 2013;55: 578-585.

23. Bernhard M, Müller J, Knepper TP. Biodegradation of persistent polar pollutants in wastewater: Comparison of an optimized lab-scale membrane bioreactor and activated sludge treatment. Water Res. 2006;40:3419-3428.

24. Xu J, Yang M, Dai J, Cao H, Pan C, Qiu X, et al.. Degradation of acetochlor by four microbial communities. Bioresour Technol. 2008;99:7797-7802.

25. Wang Y, Zhang X, Wang L, Wang C, Fan W, Wang M. Effective biodegradation of pentachloronitrobenzene by a novel strain Peudomonas putida QTH3 isolated from contaminated soil. Ecotoxicol Environ Saf. 2019;182:109463.

26. Li Y, Chen Q, Wang CH, Cai S, He J, Huang X, et al. Degradation of acetochlor by consortium of two bacterial strains and cloning of a novel amidase gene involved in acetochlor-degrading pathway. Bioresour Technol. 2013;148:628-631.

27. Dictor MC, Baran N, Gautier A, Mouvet C. Acetochlor mineralization and fate of its two major metabolites in two soils under laboratory conditions. Chemosphere. 2008;71:663-670.

28. Tadkaew N, Hai FI, McDonald JA, Khan SJ, Nghiem LD. Removal of trace organics by MBR treatment: the role of molecular properties. Water Res. 2011;45:2439-2451.

29. Li Y, Liu X, Wu X, Dong F, Xu J, Pan X, et al. Effects of biochars on the fate of acetochlor in soil and on its uptake in maize seedling. Environ Pollut. 2018;241:710-719.

30. Yao G, Jing X, Peng W, Liu X, Zhou Z, Liu D. Chiral insecticide α-cypermethrin and its metabolites: Stereoselective degradation behavior in soils and the toxicity to earthworm eisenia fetida. J Agric Food Chem. 2015;63:7714-7720.

31. Zhang J, Zheng JW, Liang B, Wang CH, Cai S, Ni YY, et al. Biodegradation of chloroacetamide herbicides by Paracoccus sp. FLY-8 in vitro. J Agric Food Chem. 2011;59:4614-4621.

32. Yi-Zhu P, Wan-Hong M, Man-Ke J, Xiao-Rong Z, Johnson DM, Ying-Ping H. Comparing the degradation of acetochlor to RhB using BiOBr under visible light: a significantly different rate-catalyst dose relationship. Appl Catal. 2016;181:517-523.

33. Tomic ZP, Ašanin D, Durovic R, Dordevic A, Makreski, P. Near-infrared spectroscopy study for determination of adsorbed acetochlor in the organic and inorganic bentonites. Spectrochlm Acta A. 2012;98:47-52.

34. Plakas KV, Karabelas AJ, Sklari SD, Zaspalis VT. Toward the development of a novel electro-Fenton system for eliminating toxic organic substances from water. Part 1. In situ generation of hydrogen peroxide. Ind Eng Chem Res. 2013;52:13948-13956.

35. Thiam A, Brillas E, Garrido JA, Rodríguez RM, Sirés I. Routes for the electrochemical degradation of the artificial food azo-colour Ponceau 4R by advanced oxidation processes. Appl Catal. 2016;180:227-236.

36. García-Vaquero N, Lee E, Castañeda RJ, Cho J, López-Ramírez, JA. Comparison of drinking water pollutant removal using a nanofiltration pilot plant powered by renewable energy and a conventional treatment facility. Desalination. 2014;347:94-102.