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Treatment of nanofiltration membrane concentrates: Organic micropollutant and NOM removal

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ABSTRACT

In the Nanofiltration (NF) membrane systems utilised for river water treatment for drinking water production purposes, 15–25 % of the feed is rejected by the membrane as the concentrate. It contains natural and synthetic organic matter (COD ca. 30 mg/L) and its composition may vary with raw water quality, membrane pre-treatment and NF membrane cut-off. This study aims to achieve complete elimination of pesticides and the elimination of 60% of the natural organic matter (NOM) retained during nanofiltration step. The investigation included testing conventional water treatment techniques—adsorption, coagulation, ozonation—and the combination of ozonation and adsorption processes. Eight pesticides detected most commonly in French surface waters were selected as model micropollutants: atrazine, sulcotrione, bentazone, isoproturon, diuron, glyphosate, amitrole and acetochlore. Simultaneous combination of ozonation and powdered activated carbon (PAC) adsorption proved to be an efficient method for the elimination of the polar and ozone resistant pesticides at low carbon and ozone concentrations. This combination also achieved faster NOM removal than PAC adsorption only. It was observed that even with the use of high PAC concentrations, addition of low ozone dosages were necessary to degrade highly polar pesticides together with the NOM. No significant modification of the carbon activity and surface properties was observed at low ozone concentration levels, ca. 3 mg/L.

Keywords: Concentrate; Pesticide; Organic matter; Nanofiltration; Adsorption; Ozonation

1. Introduction

NF systems are commonly used for drinking water production purposes, mainly to remove micropollutants, such as pesticides, and natural organic matter and for water softening. NF systems utilized for river water treatment usually operate with feed recovery rate typically ranging from 75–85% and produce a concentrate with no suspended solids but relatively high levels of dissolved components. Their composition significantly varies with the raw/membrane feed water quality that depends on the industrial and agricultural activities of the region, weather conditions, etc. Concentrate also contains acidifying, e.g. H_2SO_4 and HCl and/or anti-scaling agents e.g. phosphonates added during the pre-treatment stages. The pH is generally higher than its feed due to high rejection of carbonate species. The available options for disposing of or re-using membrane concentrates can be listed as follows: discharge into the source or to a waste water treatment plant, deep well injection, evaporation ponds or used as gray water [1].

Currently, the concentrate is discharged back to its source where high dilution levels avoid any negative impacts on the environment. However, in order to protect existing water resources, before discharging the concentrate in the nature, it is necessary to eliminate pollutants and NOM retained by the membrane. Pesticides are widely used mainly for agricultural purposes for crop protection

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purposes or for the elimination of weed on motorways or railways. They are however, also toxic, carcinogenic and mutagenic to living organisms and they also pollute surface and ground water resources [8]. European legislation (10) limits the total concentration of pesticides in surface waters used for drinking water production to 5 μg/L. Although not toxic, natural organic matter particularly creates problems for the water supply industry. It colours the water, increases the disinfection demand, introduces the problem of bio-film formation in the distribution system and potential formation of harmful chemical disinfection by-products as a result of chlorination. The efficiency of the organic treatment process strongly depends on the character of the organics present and the required final treated water quality. A range of treatment options, e.g. chemical coagulation, adsorption, advanced oxidation and membrane filtration, have been evaluated to remove NOM in order to produce potable water to overcome the problems listed above [11]. Although, treatment of organic and synthetic pollutants in surface/ground waters and wastewaters was extensively studied, number of works published on concentrate treatment is limited. Some patents have demonstrated the feasibility of implementing a treatment scheme to selectively remove the phosphonate-based anti-scalants [2] and improve the recovery factor [3] in the concentrate.

Removal of NOM and pesticides by adsorption onto activated carbon is a common method [12]. However pesticides with high polarities require some sort of destruction method, such as degradation by ozone. In addition, it is known that basic activated carbon can initiate a radical-type chain reaction in the aqueous phase that accelerates the transformation of ozone into OH° radicals. This system was named “carbozone” [4]. So the combination of adsorption onto a basic carbon and oxidation by ozone may allow better separation and degradation performances.

Our aim was to treat the concentrate prior to its rejection by focusing mainly on the removal of micropollutants and NOM in order to obtain a composition similar to nanofiltration feed water quality to protect existing drinking water resources. Eight most commonly detected pesticides in French surface waters, i.e. atrazine, sulcotrione, bentazone, isoproturon, diuron, glyphosate, acetochlore, some of their main metabolites were selected as the model micropollutants. Total elimination of the pesticides and a partial elimination of the natural organic matter, i.e. 60% was targeted. For this purpose, conventional water treatment techniques, i.e. adsorption, oxidation by ozone and carbozone were tested and the impact of operational parameters, e.g. temperature, pH was investigated. Due to high oxidation capacity of ozone, the changes in the morphology and adsorption capacity of the carbon were also investigated in order to estimate its lifetime and re-use in the presence of ozone.

Concentration of the concentrate was also carried out to obtain concentrates with different NOM concentration levels in order to study the impact of the NOM concentration on the elimination of the pesticides. Daines et al. patented the idea of further concentrating the concentrate using nanofiltration technique to improve the efficiency of potable water production system by increasing the conversion of the membrane feed into drinking water from 85–97% [3]. This system creates small volumes of concentrate rich in natural organic matter. Elimination of pesticides and the NOM was also studied in concentrated concentrate (CC) samples using combined adsorption and ozonation processes.

2. Experimental details

2.1. Membrane concentrates

Real membrane concentrates were regularly collected from a river water treatment site in France. Pre-treatment is composed of clarification, ozonation, filtration antracite+sand, anti-scaling agent addition and pre-filtration (5 μm). Concentrate samples are spiked with 10 μg/L of each of the studied pesticides, i.e. atrazine, sulcotrione, bentazone, diuron, glyphosate, acetochlore (Cluzeau Info Labo, France) and isoproturon (Sigma Aldrich, France), to enable the quantitative analysis and obtain various pesticide concentration levels detected in the surface waters at different times of the year.

Concentrate has a complex composition and it is very difficult to precisely identify each of its components. Therefore, in order to have an idea on NOM and mineral concentrations some of its properties were analysed quantitatively and tabulated in Table 1. Concentrate samples are stored in a 500 L polyethylene water tank under atmospheric conditions and their possible evolution is observed via regular analysis of COD, TOC and UV. No change in the COD, TOC or UV values were observed.

2.2. Concentration of the nanofiltration membrane concentrates

Concentration of the concentrate was carried out using a system equipped with a single NF200 (Dow Filmtec, USA) spiral wounded nanofiltration module, a

Table 1
Properties of concentrates tested.

Parameter	Value
pH (at 22°C)	7.5–8.08
Conductivity (μS/cm)	1590–2000
[Ca] (mg/L)	100–400
[Mg] (mg/L)	30–70
TOC (mg/L)	8.95–17.74
COD (mg/L)	19.32–40.6

Table 2
NOM concentration of the permeate (P), Concentrate (C) and Concentrated Concentrate (CC) produced following the reconcentration process.

Origin	COD (mg/L)			TOC(mg/L)			UV(cm^{-1})		
	P	C	CC	P	C	CC	P	C	CC
26/09/2007(I)	1,9	19,93	60,6	1,58	10,01	27,4	0,018	0,602	1,323
26/09/2007(II)	5,99	35,33	74,1	1,25	14,33	35,67	0,03	0,79	1,2
14/12/2007	6,18	27,37	72,83	1,66	12,03	36,07	0,01	0,77	1,16

high pressure pump and a 5 µm pre-filter. Permeate and concentrate-feed flowrates were set according to selected concentration levels. COD, TOC and UV absorbance levels of the produced CCs and perm eates are tabulated in Table 2.

2.3. Adsorption

Adsorption of the NOM onto powdered activated carbons was tested. Previously Picasorb 16 (PICA, France) was used for pesticide elimination [5]. In this study, it is also used for the removal of the natural organic matter. Powdered activate carbons were kindly supplied by PICA and CECA Carbons, France. They are wood based carbons activated either thermally or chemically or both methods. Some of their physical properties are as follows: density: 0.22–0.45 kg/m^3, Iode indice: 700–1500 mg/g. All experiments were carried out under atmospheric conditions. A mechanical agitator (AGITELEC, France) was employed for adsorption experiments. In order to separate the solution and the carbon, vacuum filter with a 0.45 µm filter paper (WATMAN) is utilised.

Adsorption of pesticides from the concentrate is carried out using adsorption from solution method. Selected amount of concentrate sample and the adsorbent are placed in a funnel and agitated for contact times between 2 and 30 min. Once the selected contact time is elapsed sample is filtered and analysed as described in the following section.

Table 3
Properties of Picasorb-16 and BB105.

Carbons	Picasorb16	BB105
Precursor	Wood	Wood
Activation	Thermal	Physical
Apparent Density (kg/m^3)	0.41	0.45
Median pore diameter (µm)	15–35	10–40
BET	ca. 1000 m^2	ca. 1000 m^2
Micropore Area	757 m^2/g	–
Micropore Volume	0.364 cm^3/g	–
Median Pore Diameter	8.56 Å	–
Iode indice	980 mg/g	1000 mg/g

2.4. Oxidation by ozone and combination of PAC and O_3

Oxidation by ozone has been carried out to observe the participation of oxidation in NOM and pesticide degradation during the combined PAC+O_3 tests. OZOTEST [5] method was employed for the ozonation tests in this study. Concentrate sample is placed into a 1 L glass funnel and ozone is introduced in the system via a 100 ml gas tide syringe (Thermofina, France). BMT 802 × ozone generator (Messtechnik, Berlin) was used to produce ozone (0–120 g/Nm^3) from pure oxygen. Ozone dosage was varied between 3 and 30 mg/L of concentrate. Funnel is then agitated by a mechanical agitator (AGITELEC, France) and once the selected contact time is elapsed, concentrate is collected and analyzed. Ozone residual in liquid and gas phases was measured via indigo colorimetric [9] and iodometry methods, repectively. Oxidation by ozone is combined with adsorption process by adding PAC in the system prior to injection of ozone. The amount of PAC varied between 30 and 3000 mg/L. PAC was separated by vacuum filtration.

2.5. Quantitative analysis of pesticides and NOM

Quantitative analysis of pesticides was carried out by a laboratory specialised in environmental analyses based in Paris, "Centre d'Analyses Environnementales (CAE). The techniques utilised for each pesticide is listed in Table 4. NOM concentration was determined by TOC (BIORITECH O.I. Analytical 1010), DOC (LCK414, HACH-Dr Lange) and UV absorbance at 254 nm (DR 4000, HACH-Dr Lange) analyses.

3. Results and discussion

3.1. Pesticide elimination

Elimination of the pesticides in the concentrate was previously studied in detail [5]. It was concluded that in order to completely eliminate selected pesticides it was necessary to couple adsorption and ozonation processes. Operational parameters were further optimised. Fig. 1 shows the pesticide elimination yields

Table 4
Pesticide characterisation.

Pesticide	Quantification Limit µg/L	Method
Desethydesisopropyl atrazine (DEDIA), Sulcotrione	0.2	Solid/liquid extraction followed by UPLC analysis and MS-MS detection
Bentazone	0.2	Solid/liquid extraction followed by HPLC analysis and DAD detection
Acetochlore	0.2	Liquid/liquid extraction followed by CPG analysis and ECD detection
Triazines and urea substitutes	0.05	Solid/liquid extraction followed by HPLC analysis and UV detection
Glyphosate, AMPA, Amitrole	0.01	Solid/liquid extraction followed by HPLC analysis and fluoresence detection

of adsorption and ozonation and carbozone with optimised carbon and ozone dosages, i.e. 30 and 3 mg/L. Elimination of pesticides was also tested in CC samples with increased carbon dosages and results are shown in Fig. 2. High elimination levels, i.e. >80% were obtained in both C and CC with the combined system with relatively low contact times, i.e. 2 min. It was observed that it was necessary to add ozone in the system to degrade amitrole and glyphosate even with high PAC dosages, i.e. 300 mg/L.

3.2. NOM elimination

In addition to pesticide elimination, NOM removal/degradation was also achieved with the combined system with low PAC and ozone dosages, i.e. 30 and 3 mg/L. However elimination yield was low and insufficient for this application, as seen in Fig. 3. The major fraction of the NOM is removed by adsorption, so the PAC dosage had the greatest impact on the process efficiency. A series of experiments were carried out to observe any possible catalytic activity of PAC in the combined process.

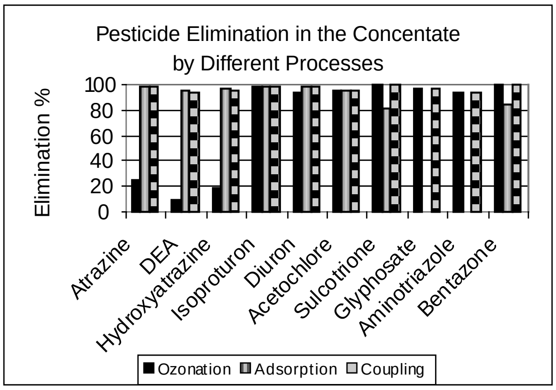

Fig. 1. Pesticide Elimination by ozonation, adsorption and carbozone. 30 mg/L PAC, 3 mg/L ozone, tc = 10 min.

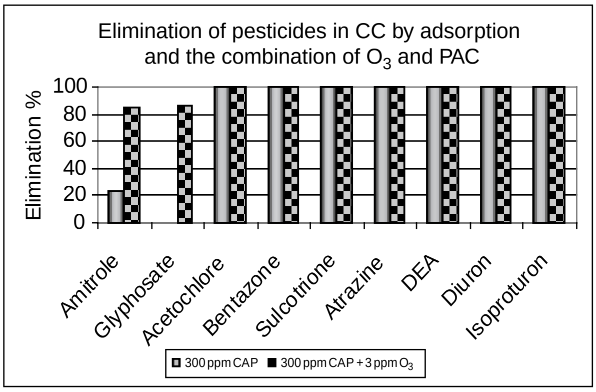

Fig. 2. Pesticide elimination in CC by adsorption and carbozone. 300 mg/L PAC, 3 mg/L ozone, tc = 5 min.

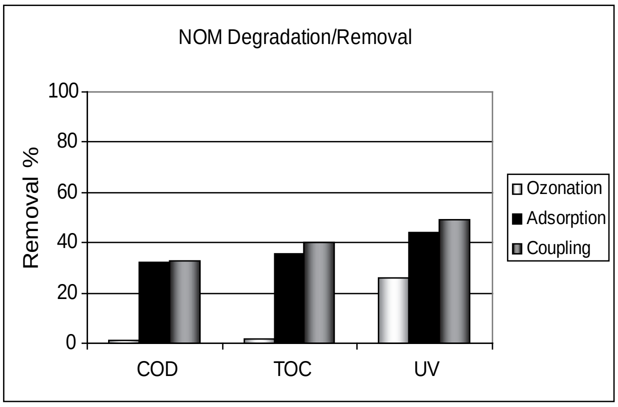

Fig. 3. NOM elimination with 30 mg/L PAC and 3 mg/L ozone, tc = 10 min.

Relatively high ozone concentration, i.e. 30 mg/L was selected for NOM removal to make sure that ozone concentration will be in excess in the system and PAC concentration was varied between 5 and 1500 mg/L. As can be seen from the results in Fig. 4, up to 300 mg PAC

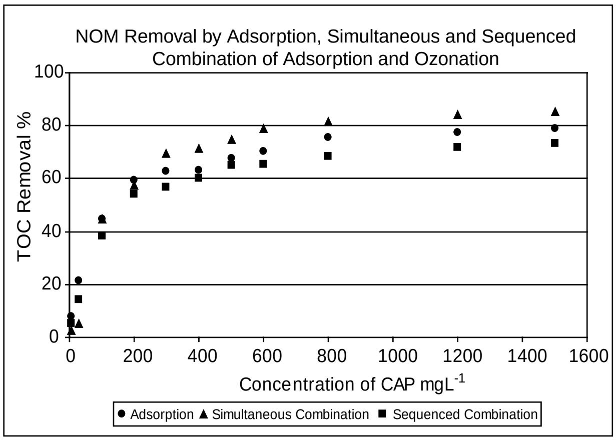

Fig. 4. Impact of PAC concentration on NOM elimination in carbozone system. CO_3 = 30 mg/L, tc = 10 min.

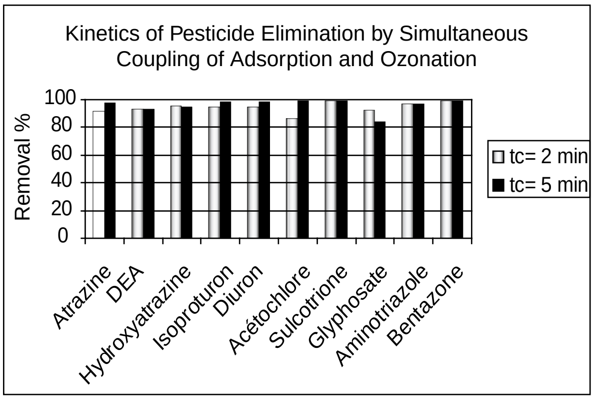

Fig. 5. Kinetics of pesticide elimination, 100 mg/L PAC and 6 mg/L ozone.

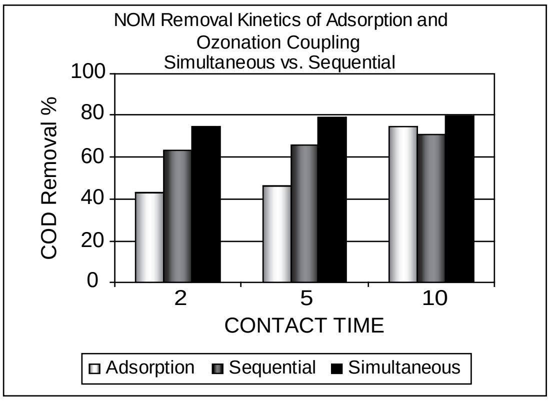

Fig. 6. NOM Removal Kinetics.

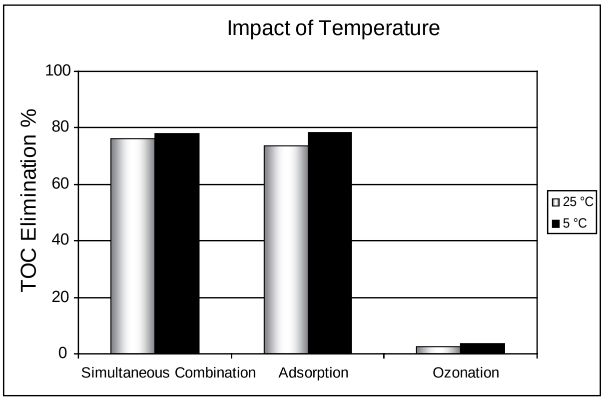

Fig. 7. Impact of temperature on NOM elimination. 600 mg/L PAC, 6 mg/L Ozone, tc = 10 min.

dosages adsorption performance is greater than simultaneous application of PAC and O_3, with 10 min contact time. However, simultaneously combined adsorption and ozonation systems achieves a better NOM elimination performance starting from 300 mg/L. This could either be due to an increase in the number of available hydroxyl sites on the carbon to catalyse ozone decomposition or decreased negative impact of ozone on the carbon adsorption capacity. On the other hand at elevated ozone concentrations, ozone is likely to be adsorbed by PAC. Although from the simultaneous system with one would expect a decreased adsorption performance increased polarity of the ozonation products, adsorption is faster. Pore blockage is reduced due to the smaller molecules formed by the reaction between OH° radicals and NOM in the combined system. NOM elimination kinetics by adsorption and combined systems is shown in Fig. 6.

Pesticide elimination kinetics was also determined for the combined system of 100 mg/L of Picasorb 16 and 6 mg/L ozone with 2 and 5 min of contact times. It was observed that 2 min achieved sufficient removal of the studied pesticides as seen in Fig. 5.

Influence of the concentrate temperature was also studied to observe any possible impact of the seasonal temperature changes on the combined system's performance. Similar NOM removal yields obtained from experiments carried out at 5 and 25°C, as seen in Fig. 7. TOC elimination was slightly greater at 5°C in all systems due to increased solubility of ozone and adsorption performance.

A series of adsorption experiments were carried out with carbons obtained from CECA (France). PAC with highest NOM removal yield, i.e. BB105, was selected for carbozone tests and compared to Picasorb 16 as seen in Fig. 8. From the experiments carried out with 600 mg/L PAC in the presence of 6 mg/L ozone, it was seen that although both carbons had similar precursor, activation and surface properties, Picasorb 16 achieves slightly better elimination under these conditions.

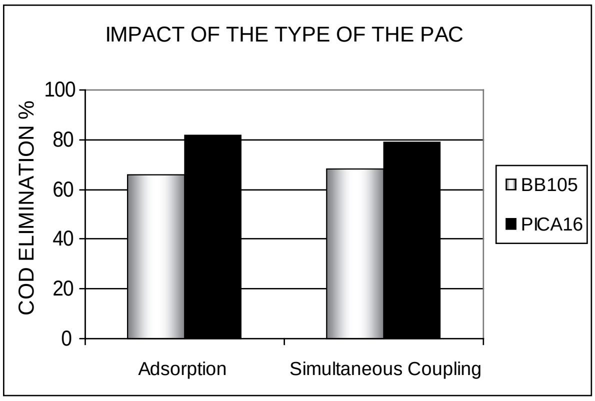

Fig. 8. Impact of the type of the PAC. 600 mg/L PAC, 6 mg/L ozone, tc = 10 min.

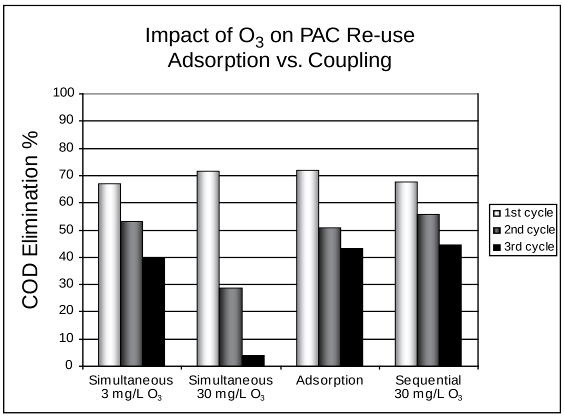

Fig. 9. Impact of Ozone Concentration on PAC and PAC re-use.

Impact of ozone on adsorption capacity, surface properties and the possibility of re-use of carbon were also studied in adsorption and carbozone systems. In the case of using high ozone concentrations, i.e. 30 mg/L in the combined system, significant decrease in the adsorption capacity of the PAC was observed compared to the PAC used in adsorption system. On the other hand, with the sequential application of carbon and ozone even with high ozone concentrations, i.e; 30 mg/L, it was possible to re-use the PAC. However, at real experimental conditions, i.e; 3 mg/L ozone, the impact of ozone on carbon was negligible as seen in Fig. 9.

This decrease observed with high ozone concentration can be due to modifications in the carbon morphology by gasification at high ozone concentrations and/or in the oxygen sites of the PAC. In order to observe any possible changes in the physical structure of the carbon, low temperature nitrogen adsorption analyses were carried out for the characterisation of the pore structure and the surface area of the following carbon samples; Picasorb-16, Picasorb-16 following sequential combination of ozonation and adsorption tests, Picasorb-16 following simultaneous combination of ozonation and adsorption tests. The results of low temperature nitrogen adsorption tests are tabulated on Table 5 and they confirm significant modification on the carbon morphology due to the presence of ozone in the simultaneous system.

3.3. Ozonation at basic conditions

Improved OH radical activity in NOM degradation was observed at basic conditions by several authors [6, 7]. In order to reduce scavenging effect of the HCO_3 ions concentrate solutions are basified with NaOH (30%) solution. Oxidation experiments with 6 mg/L of ozone were carried out at various pH levels, i.e. 8.35, 10 and 12. Highest NOM degradation yields were observed at pH 12, as shown in Fig. 10. In addition, it was observed that a part of NOM, i.e. 20% COD, was also removed during basification most probably due to encapsulation during $CaCO_3$ formation.

Although promising, due to increased costs of basic reagent used to obtain pH 12, this method is not suitable for this application. The costs of the treatment of 1 m^3 of concentrate by adsorption and NaOH solutions for 30% TOC removal are 0.092 and 1.5 Euros, respectively. This technique however could find applications in industrial effluent treatment.

Table 5
Low temperature nitrogen adsorption characterisation of PAC samples.

Sample/Treatment	PAC (mg/L)	Ozone (mg/L)	Amount Adsorbed (mg/L)		BET (m^2/g)	Micropore Area (m^2/g)	External Surface Area (m^2/g)
			COD	TOC			
PAC/No Treatment	0	0	0	0	1359	1187	171
PAC/Sequential C.	100	30	10.5	4.3	984	878	105
PAC/Simultaneous C.	100	30	10	4.3	720	645	74

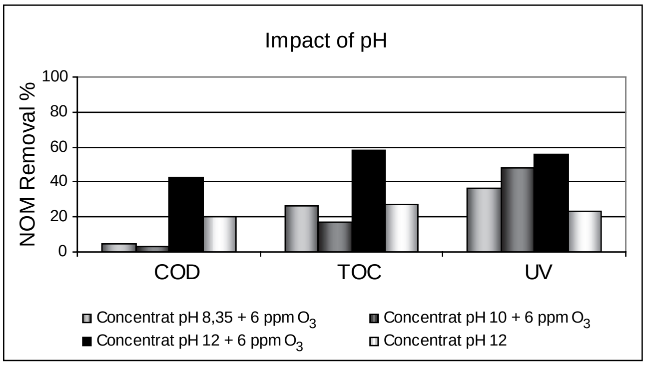

Fig. 10. Impact of pH on degradation of NOM.

4. Conclusion

Simultaneous elimination of pesticides and NOM was achieved by combining ozonation and adsorption processes both in concentrate and concentrated concentrate samples. It was observed that although the major part of NOM was removed by adsorption onto PAC it is necessary to introduce ozone into the system to completely eliminate studied pesticides. Carbozone system yields fast removal of pesticides and NOM compared to adsorption method. Seasonal temperature changes do not change the efficiencies of the techniques tested. Degradation of PAC by low ozone concentrations in carbozone system was negligible. It can be concluded that for the concentrate and concentrated concentrate samples treated in this study carbozone system with 300 mg/L PAC and 3 mg/L ozone proved to be the most suitable method to achieve targeted pesticide and NOM elimination level. Further investigation will include testing biological and combined H_2O_2/O_3 (peroxone) techniques for concentrate treatment and detailed characterisation by SEC-TOC technique.

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References

[1] E.N. Kenna, A.K. Zander (AWWA), Current Management of Membrane Plant Concentrate, USA, 2000.
[2] C. Daines, J.C. Schrotter, K. Drouet, K. Gaid. WO2008/055827.
[3] C. Daines, J.C. Schrotter, K. Drouet, P. Breant. Patent Pending.
[4] U. Jans, J. Hoigné. Ozone: Science and Engineering, 20 (1998) 67–90.
[5] B. Bozkaya, C. Daines, A.S. Lescourret, A. Bignon, P. Breant, J.C. Schrotter. Water Sci. & Tech.: Water Supply, 8 (2008) 223–230.
[6] M. Sanchez-Polo, E. Salhi, J. Rivera-Utrilla, U. von Gunten. Ozone: Science and Engineering, 28 (2006) 237–245.
[7] C.C Faria, J.J.M. Órfao, M.F.R Pereira. Ind. & Eng. Chem. Res. 45 (2006) 2715–2721.
[8] M.P. Ormad, N. Miguel, A. Claver, J.M. Matesanz, J.L. Ovelleiro, Chemosphere, 71 (2008) 97–106.
[9] H. Bader and J. Hoigné, Water Research 15 (1981) 449.
[10] European legislation 80/778/EEC.
[11] In J. Mellevialle and J. H Suffet (Eds.), Influence and removal of organics in drinking water Lewis Publishers, Boca Raton, Florida, 1992.
[12] Y. Matsui, T. Kamei, A. Yuasa, N. Tambo, Adsorption capacity of organic pesticides on granular activated carbon, Water supply, 14, 31–41.