

EFFECTIVENESS OF OZONATION IN DECOMPOSITION OF CLOFIBRIC ACID AND BISPHENOL A IN MODEL WATER SOLUTIONS

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Summary: The article contains a brief characteristic of the compounds counted among PPCPs (Pharmaceuticals and Personal Care Products) and EDCs (Endocrine Disrupting Compounds) along with the presentation of their removal methods used in typical WWTPs (Wastewater Treatment Plants), WTPs (Water Treatment Plants) as well as different methods examined in laboratory conditions. The article also shows the results of the tests on decomposition of the selected compounds (clofibric acid, bisphenol A) in model water solutions with the use of advanced oxidation technique – ozonation. The compounds were selected because of their commonness and large volume of production. The main purpose of the research is to design an appropriate equipment generating ozone that could be used in a technical scale. The mechanisms of the compounds migration as well as their sources in the environment are described in the article. Further studies concerning identification of the by-products of these compounds decomposition as well as recognition of the precise mechanisms occurring during different methods application need to be examined in the future.

Key words: PPCPs, EDCs, clofibric acid, bisphenol A, ozonation

1. INTRODUCTION

Occurrence and the fate of EDCs identified in water are the main scientific issues taking environmental chemistry into account. The presence of at least 80 different pharmaceuticals counted among PPCPs and EDCs is proved in the effluents and in the surface water all over the world [Kolpin et al., 2002, Ternes et al., 1998]. It is worth noting that many of PPCPs and EDCs still remain unidentified, and the knowledge concerning their properties, transformation course as well as their concentration is still insufficient. The scientific research that is carried out can be divided into three categories as following: 1) EDCs identification and detection methods of the results caused by their appearance in the environment; 2) development and improvement of the analytical procedures leading

to the determination of these compounds; 3) modification and application of the methods and devices allowing high level of these harmful substances or their metabolites removal or degradation. One of the first reports concerning EDCs were connected with the incomplete removal of steroids during wastewater treatment processes [Strumm-Zolinger & Fair, 1965]. Starting from the 70's and 80's, the presence of the pharmaceuticals as a large group among the EDCs and human hormones was confirmed in the effluents from WWTPs [Tabak & Bunch, 1970, Aherne & Briggs, 1989]. However at that time, despite many new reports, no direct attention was given to the group of EDCs, mainly due to the lack of information concerning their toxicity and their insignificant concentrations. Nevertheless, even then some of the researchers considered pharmaceuticals and their metabolites as contamination of the environment [Hignite & Azarnoff, 1977].

Endocrine disrupters started to draw more attention when a relation between production of synthetic pharmaceuticals and their toxic influence on water organisms was observed [Purdom et al., 1994, Snyder et al., 2001]. Simultaneously the research results showed that synthetic hormones and other compounds counted as EDCs can be responsible for sexual disorders in animals and human. The reports informed about sperm decrease [Shaw & McCully, 2002, Richthoff et al., 2003, Dalinga et al., 2002], they suggested other harmful effects or influence like cancer, reproductive organs dysfunctions, motor condition decrease [Snyder et al., 2002]. The influence of PPCPs was described in the work of Kavanagh and coworkers. The research group documented the case of discovering spawn in the male fish living in the upper side of the river reaching Saint Clair Lake in Canada, North America [Kavanagh et al., 2004].

It is very important to underline that the compounds included as EDCs are xenobiotic and exogenous and they are responsible for the disruption of natural work of endocrine system in animals and human. The major dysfunctions consist in imitation and/or inhibition of synthesis, secretion, transport and binding of natural hormones. The proper work of endocrine system controls the homeostasis processes, reproduction, metabolism, growth, and other main, vital functions of the organisms [US EPA Report, 1997]. The natural hormones that can be given as examples are estrogen, testosterone, or thyroid hormones: thyroxine, triiodothyronine [Orton et al., 2009, Campbell et al., 2006]. Many of human tissues and organs can be influenced by different estrogen compounds eg. brain, immune system, blood-vascular system, lungs, mammary glands, liver, kidneys, bones, reproductive glands, prostate gland, fat tissues and many others [Muller, 2004]. Endocrine disrupting compounds can be accumulated in the organisms and transferred to the offspring, what was documented on the basis of the research conducted on rats tissues [Kuriyama et al., 2007].

There are several ways of introduction pathways of PPCPs and EDCs to the water environment. The effluents from traditional WWTPs are considered to be

the most important source of these compounds in the surface water, as people use many different products including pharmaceuticals, personal care products, detergents etc. Pharmaceuticals and their metabolites constitute a significant group in wastewater as their way is predictable (urine, feces) [Khan & Ongerth, 2002], but we should also remember about the fate of outdated pharmaceuticals which often end in the toilets as well. Pharmaceuticals removal from the organisms is also realized by liver with bile, by intestines, by lungs and by skin with sweat.

Other migration pathways of EDCs include: drain overflows and illegal connections to the sewerage network, pharmaceutical industry, pesticides used in the agriculture, illegal distribution of the compounds showing narcotic effects [Weyer & Riley, 2001]. Moreover some specific pollutants like veterinary antibiotics used in birth surgeries in pigs were determined on the water reservoirs in close neighborhood of pigs breeding farms [Weyer & Riley, 2001]. There are also data confirming EDCs presence in shallow subsoil water and in ground water [Heberer, 2002].

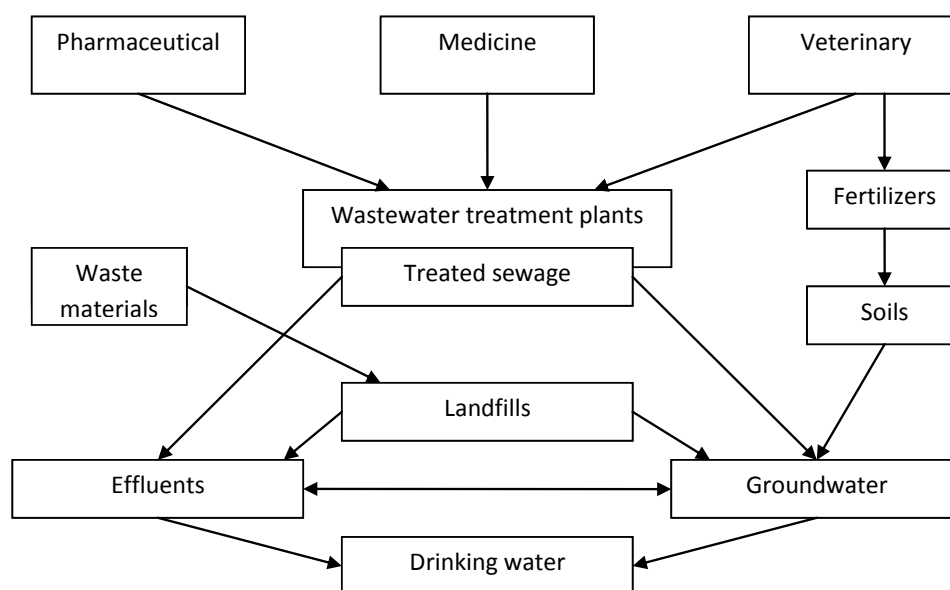


Fig 1. The ways of EDCs migration to the environment [Jorgensen et al., 2000]

Most of the pharmaceuticals (mainly antibiotics and painkillers) that are present in surface water reach the concentration exceeding the level of ppb [Ashton et al., 2004]. The research show that most of the registered pharmaceuticals (50 – 90 %) are excreted in the same or biologically similar, active forms [Braghetta et al., 2002], what indicates a great influence on water organisms.

The possibility of water pollution by different PPCPs and EDCs is high but depends on many factors: the compounds physico-chemical properties; type of technology used in WWTP; climate conditions, where temperature, precipitation frequency, insolation, and also the level of effluent dilution in the receiver is taken into account.

Each of the pharmaceuticals or compounds counted as EDCs separately present in the environment in the trace levels can be neutral and harmless for the organisms, but the mixture of these substances even in these insignificant concentrations may induce undesired changes, mainly on the cell level. Pomati et al. in their in vitro experiments showed that the mixture of 13 pharmaceuticals at the concentrations comparable with the environmental ones causes the growth reduction of the embryonic cells of human kidney reaching 10-30%. The experiment was also run for each pharmaceutical separately. Despite the same 48 hours exposition, no similar changes were observed [Pomati et al., 2006].

Endocrine disruptors show their potential toxic activity towards living organisms at the concentration levels oscillating from ppb to ppt. The above fact proves that EDCs presence in different environmental elements, mainly water, became a serious problem in the global scale [Petrovic et al., 2004]. Trace EDCs amounts induce a specific challenge for different scientists e.g. chemical analysts working on new methods of different compounds detection, technologists and designers trying to find effective methods for their removal and many others. EDCs constitute a ubiquitous and heterogeneous group of compounds, with different molecular structure, presence of various functional groups and specific activity. Due to the significant variety of these compounds the classification covers different categories Table 1.

Table 1. EDC's classification [Barcelo, 2003]

Compounds class		Examples
Pharmaceuticals	Veterinary and human antibiotics	Trimethoprim, Erythromycin, Sulfamethoxazole, Chloramphenicol, Metronidazole
	Analgesics and anti-inflammatory drugs	Codein, Ibuprofen, Paracetamol, Acetaminophen, Acetylsalicylic acid, Diclofenac, Ketoprofen, Naproxen, Tramadol, Mefenamic acid, Fenoprofen, Tramadol
	Psychiatric drugs	Diazepam,
	Antiepileptic drugs	Carbamazepine, Gabapentin,
	Beta-andrenoceptor blocking drugs	Propranolol, Metoprolol, Atenolol, Timolol, Betaxolol, Sotalol,
	Lipid regulatory agents	Clofibric acid, Bezafibrate, Pravastatin, Simvastatin, Fenofibric acid,
	β_2 – Sympathomimetics	Terbutalin, Salbutamol
	X-ray contrast media	Iopromide, Iopamidol, Diatrizoate

	Steroids and hormones	Estradiol, Estrone, Estriol, Diethylstilbestrol, Testosterone, Androstenedione
	H ₂ – receptor antagonists	Ranitidine, Cimetidine, Sulfasalazine, Sulfapyridine, 5 – Aminosalicylic acid
	Diuretics	Furosemide
	Triazides	Bendroflumethiazide
	Cardiac glicozides	Digoxin, digoxigenin
	Angiotensin II antagonists	Valsartan
	Calcium channels blockers	Diltiazem
	Bronchodilators	Salbutamol
	Antidepressants	Amitriptyline
Personal care products	Fragrances	Nitro, polycyclic and macrocyclic musks
	Sunscreen agents	Benzophenone, Methylbenzylidene camphor, Oxybenzone
	Insect repellents	N, N – Dimethyltoluamide (DEET)
	Antiseptics	Triclosan, Chlorophene
	Flame retardants	Polybrominated diphenyl ethers (PBDE's), Tetrabromobisphenol A, Tris(2-chloroethyl)phosphate (TCEP)
	Stimulants	Caffeine, Theine, Taurine
Miscellaneous products	Surfactants and surfactant metabolites	Alkylphenol ethoxylates (APEO), Alkylphenols, Alkylphenol carboxylates, Pentafluorooctane sulfonate (PFOS).
	Industrial additives and agents	Chelating agents (EDTA), aromatic sulfonates
	Gasoline additives	Dialkyl ethers, Methyl 4-butyl ether (MTBE)
	Algal and cyanobacterial toxins	Saxitoxin, Anatoxin-a, Mycrocystin, Nodularin, Cyclindrospermopsin
	Disinfection by-products	Iodo-THM's, Bromoacids, Bromoacetonitriles, Cyanoformaldehyde, Bromate, NDMA
	Combustion by-products	Dioxin
	Industrial chemicals	Bisphenol A, Phthalates, 4-n-tert-Octylophenol
Pesticides		Atrazine, DDT
Illicit drugs		Amphetamine, Cocaine, Benzyloecgonine (cocaine metabolite)

With regard to such diversity of EDCs many programs came into being. U.S. EPA made an attempt to stabilize this situation by creating Endocrine Disruptor Screening Program (EDSP), which main goal was to develop official methods of

monitoring and support toxicological research on over 87000 compounds suspected of causing endocrine disruption. European Organization for Economic Co-operation and Development (OECD) tried to create and develop reliable methods of confirming EDCs presence in the environment [Hecker et al., 2007]. Nevertheless, some of the proposed solutions were not fully accepted by the scientific institutions [Snyder et al., 2003]. Despite many efforts with the object of preparing official instructions and directives concerning EDCs, many of the issues concerning these substances still remains unclear. Many synthetic and natural chemicals are considered as EDCs, but still an unknown number of them remains unidentified in the environmental resources and may be regarded as potential endocrine disruptors. Moreover there are still new chemicals synthesized in the laboratories and industry because of the growing demand of the users in the manufacturing sector. Routine procedures of EDCs monitoring are not able to answer all the questions concerning the influence and changes in human body or other living organisms because of the fact that some of the disruptions may be revealed after a very long time of exposure. As an example, the metamorphosis of frogspawn was inhibited with the use of insignificant amount of perchlorate after 70 days of exposition, while the permissible time of exposure defined by the Endocrine Disrupter Screening and Testing Advisory Committee's (EDSTAC) should not exceed two weeks [McGovern, McDonald, 2003]. Nevertheless, it is important to remember that water organisms are exposed to EDCs through their whole live as their main environment is subjected to many anthropogenic changes.

There were also some efforts taken by the U.S. EPA to establish the guidelines concerning the concentrations of EDCs in case of short time and chronic exposition. On the basis of the regulations of Ambient Water Quality Criteria the assumed values for nonylphenol in fresh water are the following: 28 ppb for the short time exposition (1 hour exposition time) and 6.6 ppb for the chronic (4day exposure period, occurring more than once over 3 years) [U.S EPA, 2006]. In case of saline water the short time exposure criterion is 7.0 ppb, while chronic is 1.7 ppb. It is worth to mention that these guidelines are not law regulations, these are just some proposed arrangements which may allow controlling the quality of surface water and protection of water organisms.

Water reaching the environment should be free from contaminants which are dangerous for organisms including EDCs and PPCPs. One of the biggest problems is the lack of unequivocal law regulations and rules referring to the limits of specific contaminants (e.g. pharmaceuticals residues) release to the environment. Furthermore, conventional methods used in WWTPs designed to remove typical contaminants present in wastewater, may not give satisfying results towards EDCs because of their specific properties. Some of the pharmaceuticals and their metabolites can undergo mineralization (to CO₂ and H₂O) by microorganisms eg. aspirin. Most compounds among PPCPs are more polar than tradi-

tional contaminants, their functional groups are acidic or alkaline [Snyder et al., 2003], sometimes ionic bonds can be found in their structure and they are often hydrophobic and characterized by quite low molecular mass [Weyer & Riley, 2001], what affects their concentrations in wastewater. Biodegradability for each of these compounds can differ significantly depending on their nature [Kagle et al., 2009]. Most of the persistent EDCs characterized by a high polarity are not degraded in wastewater treatment stations and they migrate to the natural water environment easily.

Conventional processes like coagulation, flocculation and precipitation used for contaminants removal do not show satisfying effectiveness in case of EDCs, which molecular weight is between 100 to 500 Da [Ternes et al., 2002]. More advanced separation methods like adsorption, filtration with the use of membranes and ion exchange gave much better results exceeding 95% of effectiveness, depending on the properties of examined compounds [Barcelo, 2003]. The separation with the use of reversed osmosis and nanofiltration is described by many authors as an effective method in these micropollutants removal (Kim et al., 2005, Yoon et al., 2006)

Because of the low concentration of EDCs the properties of the membrane like hydrophobicity and surface charges are significant [Comerton et al., 2007]. The presence of natural organic matter in water can also influence on the effectiveness of used membranes [Comerton et al., 2008]. Modified nanofiltration membrane, which surface was completely neutral, with the pH of 6.5 gave better results for BPA separation reaching above 95%, in comparison to original membrane. The decrease of surface tension can have an effect on the efficiency of separation of the selected compounds, what was observed in case of ibuprofen and salicylic acid [Kim et al., 2008]. The separation methods including the group of low-pressure processes with the use of microfiltration, ultrafiltration and loose nanofiltration combined with reversed osmosis have limited application because of the size of the pores [Shon et al., 2006], but coupled with adsorption phenomenon [Chang et al., 2009], biodegradation processes [Chang et al., 2006] or catalysis [Kim et al., 2008] can result in better selectivity of EDCs in wastewater technologies. The knowledge concerning separation processes can affect significantly the modifications of existing technologies in WWTPs, where standard two-stage or three stage treatment is typical.

1.1. EDCs removal with the use of adsorption

Adsorption with the use of granular activated carbon often gives satisfying results in most organic pollutants removal, including EDCs [Kik et al., 2007]. Stability of the adsorption process strongly depends on many parameters and factors eg. contact time, adsorbats solubility, type of activated carbon, kinetics and equilibrium constant and others, which should be precisely monitored [Ternes et al., 2002, Yoon et al., 2003]. There were also research run focusing

on adsorption selectivity of selected EDCs depending on the used adsorbents and their modifications [Inumaru et al., 2006].

Le Noir and coworkers presented their technique using moving-bed reactors combined with microporous adsorbing medium as an effective method in EDCs removal. Polyvinyl alcohol with the fragments of molecularly imprinted polymer was used as an adsorbing medium [Le Noir et al., 2009]. In another research modified macroporous silica obtained by grafting of alkylosilanes groups to medium length chain was used to remove nonylphenol effectively from water samples with the presence of phenol [Inumaru et al., 2006]. Different types of macroporous silicas with modified surfaces were synthesized and compared to activated carbon in efficient, selective BPA removal [Yamaguchi et al., 2006]. Research results showed that BPA was removed in a lesser degree in comparison to the trial where activated carbon was used, but the efficiency during next runs was better when modified silica was used. Also other combinations of different methods with adsorption gave satisfying results in selected EDCs removal eg. combining oxidation with H_2O_2 with specially modified adsorbent (iron-tetrasulfophthalocyanine – (FeTsPc) removed BPA, diclofenac and ibuprofen efficiently [Kim et al., 2009]; using zeolites as sorbents and photolysis with the use of UV was tested to selectively remove estrogen [Wen et al., 2009].

1.2. Biological and chemical degradation

EDCs removal during the treatment in WWTPs strongly depends on the implemented technology. Conventional biological processes like biofiltration, activated sludge or soil aquifer treatment are insufficient in EDCs removal, mainly because of the compounds persistence, low biodegradability and the presence of other molecules attached to them [Joss et al., 2005]. Nevertheless there are some reports concerning the activity of nitrification bacteria in EDCs removal [Forrez et al., 2009]. Kasprzyk-Hordern and coworkers monitored the fate of a large group of contaminants belonging to the group of EDCs treated in two WWTPs using different treatment technologies. The observation results showed that EDCs removal efficiency in the WWTP using trickling filter beds was below 70%, while for the other plant using activated sludge it exceeded 85% [Kasprzyk-Hordern et al., 2009]. The results clearly indicate that conventional treatment processes degrade EDCs to some extent, but because of high toxicity of even very low doses reaching environment it is needed to work out more efficient methods. Development of other effective methods like advanced oxidation techniques eg. chlorination, ozonation and others gives the opportunity to lower the concentrations of the undesired compounds in the effluents. The degree of the compounds removal is proportional to the force of oxidation and is a function of the compound structure to the used oxidation dosage [Snyder et al., 2003, Westerhoff et al., 2005]. The structure of the compound is thought to be significant in oxidation processes so compounds with aromatic ring should be easily

degraded with the use of ozone, while research show 60% reduction for atrazine and only 5% for tri(2-chloroethyl)phosphate (TCEP) [Westerhoff et al., 2005]. Ozone enhances the biodegradability and can be effective for the removal of EDCs that contains phenol or amino functional groups or unsaturated bonds (mainly double) [Weyer & Riley, 2001]. Ozone oxidation force can cause a break of the phenol ring, attack double bonds (creating carbonyls), and create hydroxylamines and amines oxides [Huber et al., 2003]. Although sometimes the compounds may not react directly with the ozone, their degradation may occur as a result of their reaction with hydroxylic radicals. Therefore advanced oxidation techniques coupled with other methods eg. ozonation combined with UV radiation, ultrasonic cavitation, Fenton reaction or hydrogen peroxide addition seem to be promising in EDCs degradation in water samples. The effectiveness of these methods in BPA removal from water was examined and the results were satisfying for most of the mentioned, combined methods [Westerhoff et al., 2005]. The mechanisms of BPA removal in these cases was similar and consisted in the destruction of the aromatic rings as a result of the attack of hydroxylic radicals.

It was proved that a hybrid method combining ozone and UV radiation results in degradation of phenols and PAHs reaching 90% [Vollmuth & Niessner, 1995]. Another research in which different method effectiveness was confirmed was combination of ozone and hydrogen peroxide in the following doses: 3.7 ppm and 1.4 ppm, respectively. The effectiveness results exceeded 90% in clofibric acid and ibuprofen reduction [Zweiner & Frimmel, 2000]. Andreozzi and co-workers also confirmed that the technique O_3/H_2O_2 is effective towards clofibric acid [Andreozzi et al., 2003] and Olmez-Hanci and his group in their research gained high mineralization degree of dimethyl phthalate using the same method [Olmez-Haci et al., 2009]. Some of the compounds under the influence of ozone may undergo partial mineralization (30-40%) like paracetamol and transformations like carbamazepine, which byproducts were found in water solutions [Carlson, 2000]. It is expected that partial mineralization and transformation of the selected endocrine disruptor diminishes its toxicological activity, and that its byproducts are less harmful. 17α -ethinylestradiol byproducts were proven to show considerably less estrogenic properties than the parent compound [Von Gunten et al., 2003]. The conclusion was derived from the tests run on yeasts. Nevertheless it is important to remember that various compounds under different conditions may give completely different byproducts. The presence of additional compounds in water solutions can improve or deteriorate the expected result. Andreozzi and his research group reports that the presence of natural organic matter (eg. humic acids) can act like filters towards some of the examined compounds and as photosensitizers towards others [Andreozzi et al., 2003]. Moreover, while estimating the total influence of ozone activity one should not omit the byproducts originating as a consequence of different reactions with natural

organic matter. Different, new methods are examined constantly by the researchers all over the world, as the problem of EDCs presence seems to be emerging.

2. MATERIALS AND METHODS

The tests of the degradation method effectiveness towards two selected endocrine disruptors were carried out in the Environmental Analysis Laboratory of the Environmental Engineering Faculty of Lublin University of Technology. Two compounds included as EDCs: clofibric acid and bisphenol A were selected to the study. Some of the characteristic physico-chemical parameters of both compounds are depicted in Table 2 and Table 3.

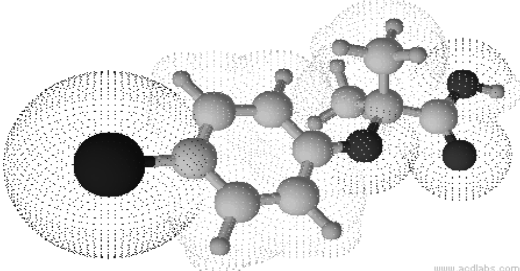
Table 2. Properties of target compounds

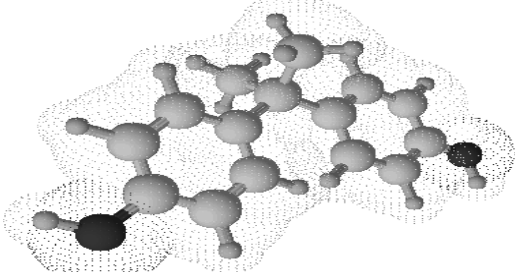
Compounds	Formula	LogP ⁽¹⁾	logS ⁽²⁾	CAS-RN	Function/Application
Clofibric acid	C ₁₀ H ₉ O ₃	2,728	-2,63	882-09-7	Lipid regulatory agent
Bisphenol A	C ₁₅ H ₁₆ O ₂	3,366	-2,30	80-05-7	Additive in epoxy resins and polycarbonate plastics

⁽¹⁾ partition coefficient calculated as miLogP structural descriptor obtain from Molinspiration Cheminformatics platform.

⁽²⁾ solubility of compound calculated as AC_logS descriptor obtain from VCCLAB platform.

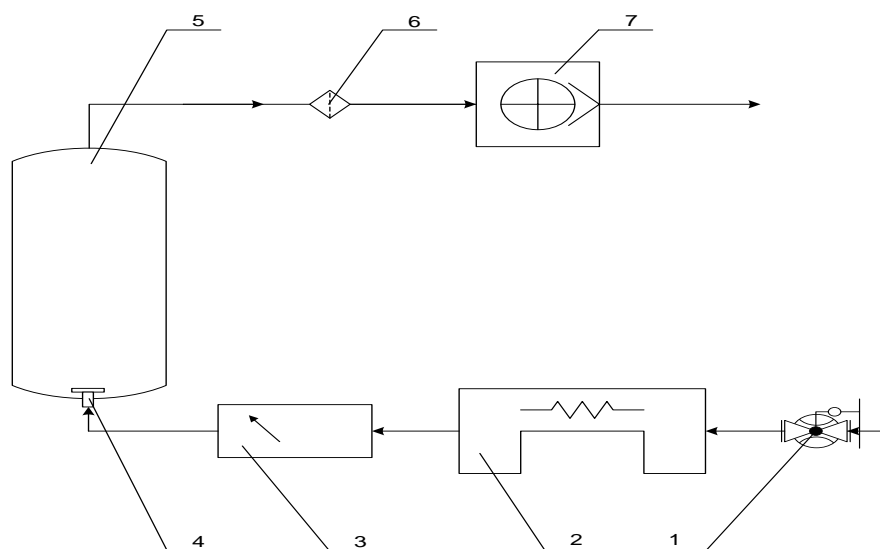
Table 3. Properties and structure of analyzed EDCs

Compounds	Structure 3D	NRTB ⁽³⁾	Molecular weight
Clofibric acid		3	214,648

Bisphenol A		2	228,291
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⁽³⁾ NRTB (number of rotatable bonds) – structural descriptor describes flexibility of the molecule – decide about ability to conformers formation.

Clofibric acid (CA) and bisphenol A (BPA) solutions were prepared by dissolving in methanol and afterwards the prepared solutions were diluted with water to the volume of 2 dm³ (HPLC-super gradient water in case of CA, and deionized water from the Milipore system for BPA). The initial concentration of CA in prepared solution was about 86 ppm, and BPA - 460 ppb. The solutions were each time introduced to the glass reactor with a special diffuser in the bottom, which allowed air and ozone flow (Figure 2). In the first stage of the experiment the prepared solution was mixed for 10-15 minutes with air, and a zero sample was taken. Then the ozonation part began.



1. Flow meter with adjustment, 2. Ozone generator, 3. Ozone concentration meter, 4. Diffuser, 5. Reactor chamber, 6. Ozone destroyer, 7. Suction pump.

Schemat stanowiska laboratoryjnego.

1. Miernik przepływu z regulacją, 2. Generator ozonu, 3. Miernik stężenia ozonu, 4. Dyfuzor, 5. Komora reakcyjna, 6. Destruktor ozonu, 7. Pompka ssąca.

Fig. 2. The scheme of laboratory test stand

Clofibric acid ozonation

The ozonation of CA solution lasted for 60 minutes. The first sample was taken after first 5 minutes of ozonation, and subsequent samples were taken at 10 minutes time intervals. The flow of ozone was $60 \text{ dm}^3/\text{h}$ and the concentration of ozone was $2.2 \text{ mg}/\text{dm}^3$. The volume of the sample was 10 ml. The samples were then prepared for the chromatographic analysis on a liquid chromatograph coupled with the MS/MS Q-Trap 4000 system.

Bisphenol A ozonation

The ozonation of BPA solution lasted for 30 minutes. The samples were taken at 5 minutes time intervals. The flow of ozone was $60 \text{ dm}^3/\text{h}$ and the concentration of ozone was $1.8 \text{ mg}/\text{dm}^3$. The volume of the sample was each time 100 ml. The samples were then extracted with the support of ultrasonic bath using n-hexane as a solvent. After collecting the organic phase the samples were analyzed on a gas chromatograph coupled with the mass spectrometer.

3. RESULTS AND DISCUSSION

The results obtained during CA ozonation, which lasted for 60 minutes, gave an average degradation efficiency of 10.7% (Figure 3).

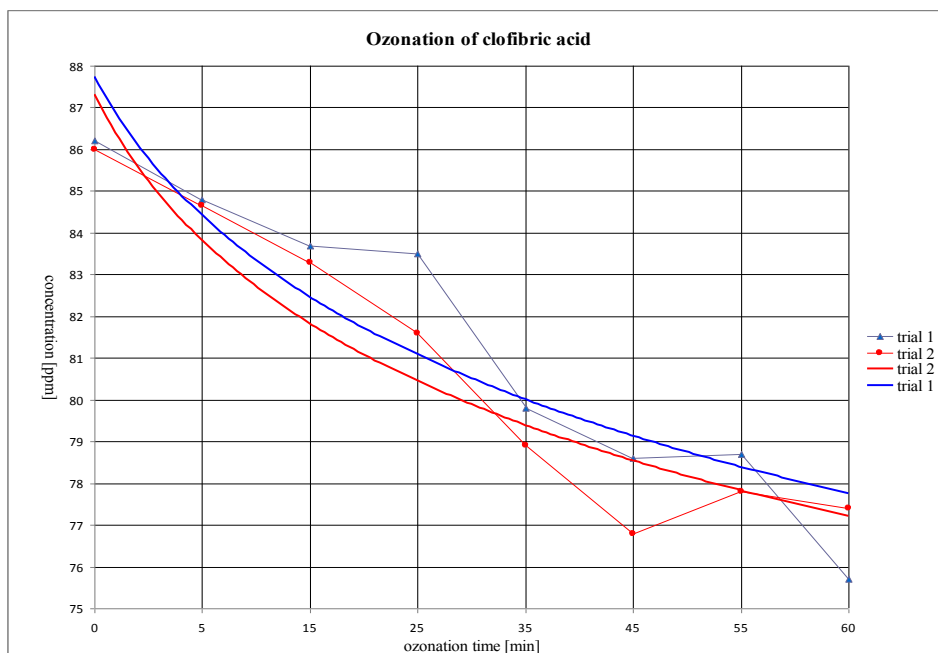


Fig. 3. Clofibric acid concentration changes during the ozonation process

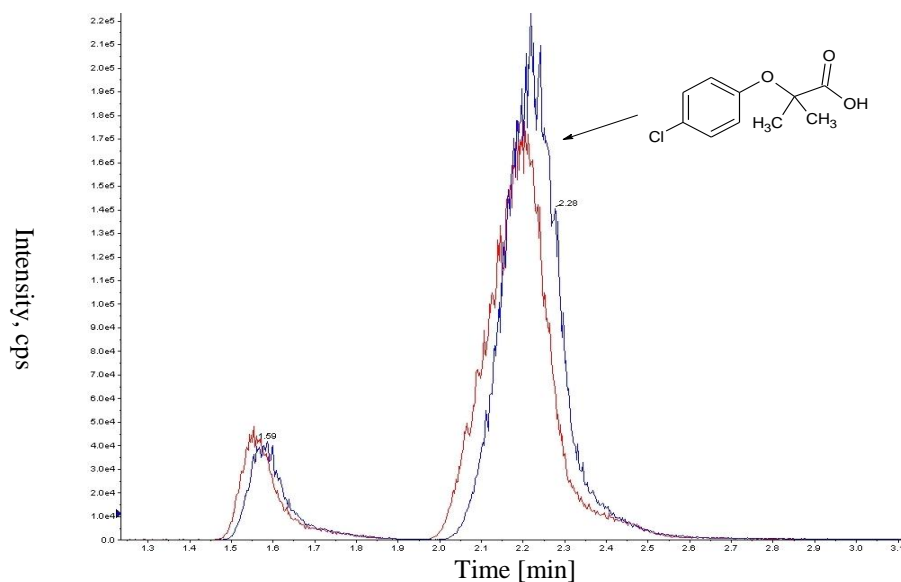


Fig. 4. The chromatogram of clofibric acid degradation (First trial results for zero sample and sample after 60 minutes of ozonation)

In case of BPA degradation the results were much more promising. Despite the trial lasted for 30 minutes the authors decided to show only the results obtained up to 15 minutes because they tripled the average effectiveness achieved for CA. The degradation degree after 15 minutes was about 34%.

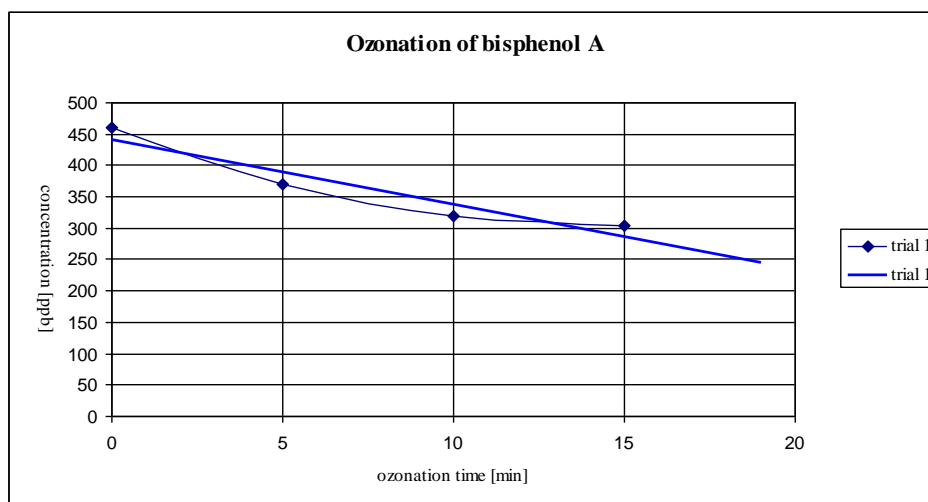


Fig. 5. Bisphenol A concentration changes during the ozonation process

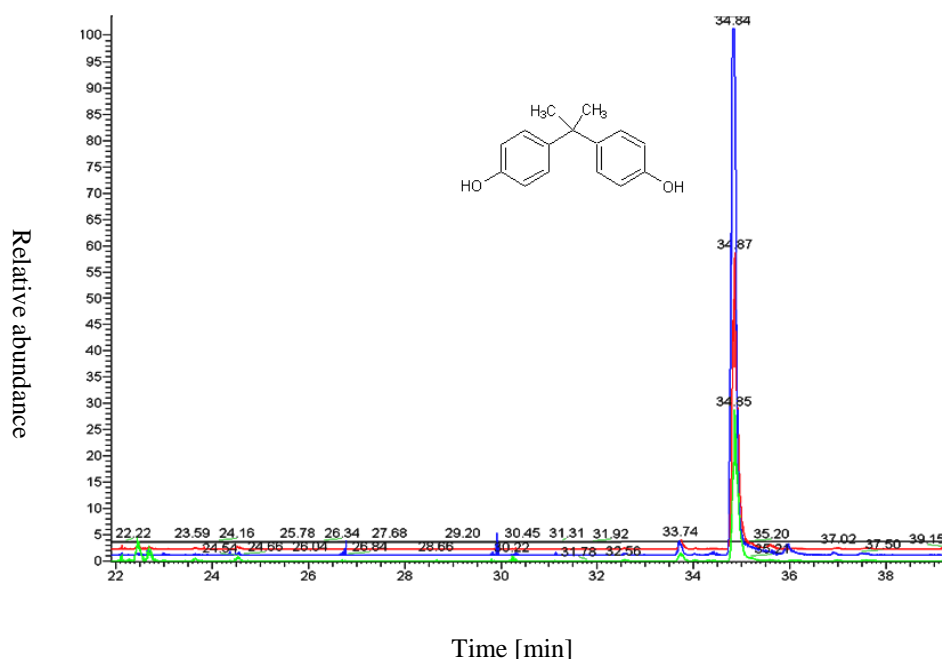


Fig. 6. The fragmentogram of bisphenol A degradation during ozonation process. (Results for zero sample and samples after 5 minutes and 15 minutes, respectively).

There were several trials run during the study, nevertheless the results show that BPA was degraded in a higher degree and in shorter time despite the fact that the used ozone concentration was lower in this case. There are still important things to verify for example the influence of longer period of ozonation on different EDCs, the optimal conditions for the process (ozone concentration and flow), byproducts formation and their toxicity and many others. The authors studies confirm that extension of the ozonation time improves the effectiveness of ozonation. Nevertheless there are still many questions asking for answers.

4. CONCLUSIONS

The article presents a brief review of knowledge concerning EDCs in the environment and also shows the results of the tests on decomposition of the selected compounds (clofibric acid, bisphenol A) in model water solutions with the use of advanced oxidation technique – ozonation. The results obtained during the tests suggest the usefulness of the ozonation in reduction of EDCs concentration. It is worth noticing that the tests were run with a relatively low concentration of ozone and different periods of time in shown trials indicate significant differences within the group of endocrine disruptors. At present the authors try to com-

pare ozonation with other methods allowing degradation of different compounds not only in water solutions but also some odorous, gas compounds (eg. dicyclopentadiene – DCPD).

5. ACKNOWLEDGEMENTS

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SKUTECZNOŚĆ OZONOWANIA W ROZKŁADZIE KWASU KLOFIBROWEGO
I BISFENOLU A W MODELOWYCH ROZTWORACH WODNYCH

Streszczenie

Artykuł zawiera krótką charakterystykę związków zaliczanych do grupy PPCP (Farmaceutyki i produkty pielęgnacyjne) i EDC (związki endokrynnie czynne) wraz z przedstawieniem metod ich usuwania stosowanych w typowych zakładach oczyszczalni ścieków, stacjach uzdatniania wody jak również opisem innych metod analizowanych w warunkach laboratoryjnych. Artykuł przedstawia także wyniki badań rozkładu wybranych związków (kwas klofibrowy, bisfenol A) w modelowych roztworach wodnych przy użyciu zaawansowanej techniki utleniania – ozonowania. O wyborze związków do badań zadecydowała głównie ich powszechność występowania oraz znaczna produkcja. Głównym celem badań jest zaprojektowanie odpowiedniej aparatury wytwarzającej ozon, która może być zastosowana na skalę techniczną. Dodatkowo w artykule opisano mechanizmy migracji tych związków wraz z określeniem ich źródeł w środowisku. Dalejsze etapy badań obejmują identyfikację produktów pośrednich rozkładu analizowanych związków, a także poznanie dokładnego mechanizmu zachodzącego podczas stosowania różnych metod degradacji.