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## ENDOCRINE DISRUPTING COMPOUNDS (EDCs) - ENVIRONMENTAL HAZARDS AND THEIR PHOTOCHEMICAL DEGRADATION

### KSENOESTROGENY - ŚRODOWISKOWE ZAGROŻENIA I ICH FOTOCHEMICZNA DEGRADACJA

**Abstract:** Some of xenoestrogens presented in aqueous environment can mimic or/and block natural hormones (Endocrine disrupting compounds - EDCs). Those hazardous contaminants consist of many natural and synthetic organic compounds, but are mostly man-made substances such as pharmaceuticals and additives for personal care products. The presence of EDCs in the aquatic environment at low concentrations, coupled with their toxicity to microbe cause that the classical method of water purification, including biodegradation are ineffective. Removal of EDCs from the aquatic environment can be effectively carried out by oxidation using advanced oxidation processes and photosensitized oxidation. Applications of photochemical processes permit to obtain a high degree of reduction of EDCs in relatively short time. Photosensitized oxidation, that has shown satisfactory results, has an unquestionable advantage in being able to use oxygen from the air and the energy of sunlight. The paper presents the application of several photochemical methods for degradation of phenolic compounds belonging to the EDCs - parabens, chlorophenols, phenylphenol.

**Keywords:** endocrine disrupting chemicals - EDCs, advanced oxidation processes, photosensitized oxidation

The scientific studies provide data that some chemical compounds *endocrine disrupting compounds* (EDCs) found in the surface waters can influence on animal and human endocrine systems. It is well-established that aquatic wildlife in marine and freshwater is exposed to natural and synthetic EDCs which are able to interfere with the hormonal system, thus possibly causing adverse effects on the intact physiology of organisms [1]. EDCs are highly diverse and include synthetic chemicals used as plasticizers, detergents, pesticides, and pharmaceuticals, natural and synthetic hormones. Widespread use of these compounds can cause their accumulation and the occurrence of irreversible changes in nature. Generally EDCs are present in water at low levels concentration ( $1 \text{ ng/dm}^3$  -  $1 \text{ } \mu\text{g/dm}^3$ ) which makes their removal in conventional sewage treatment plant inefficient. Many pharmaceuticals, pesticides and other compounds that demonstrate estrogenic effects are not removed by physical methods. Research conducted over the degradation of EDCs using biological methods are relatively slow and indicate low efficiency [2]. The degradation of EDCs in aerobic and anaerobic sludge permitted on the above 90% concentration reduction of contaminant, but this process took over 30 days [3]. For this reasons EDCs are emerging as a major concern for water quality.

The use of UV light for disinfection of water has been known for several decades. The absorption of light energy may result in photodegradation, but some of molecules are recalcitrant to photolysis. Chemical methods like advanced oxidation processes (AOP) are very effective in removing pollutants present in wastewater at low concentrations. Mainly AOP rely on the formation of reactive and short-lived oxygen intermediates such as

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*hydroxyl radicals* ( $\cdot\text{OH}$ ). The hydroxyl radicals are a powerful, non-selective chemical oxidant (the redox potential is 2.80 V [2]). In literature several AOPs have been described: UV combined with  $\text{H}_2\text{O}_2$ , UV combined with ozone ( $\text{O}_3$ ),  $\text{O}_3$  in combination with  $\text{H}_2\text{O}_2$ , UV combined with  $\text{O}_3$  and  $\text{H}_2\text{O}_2$ . Apart from a direct reaction of ozone with the organic pollutants, aqueous solutions of ozone especially at high pH lead to ozone transformation to hydroxyl radicals give reactions. Other methods, like heterogeneous photocatalysis (eg  $\text{TiO}_2/\text{h}\nu$  or  $\text{ZnO}/\text{h}\nu$ ) are based on the use of wide-band gap semiconductors (3.2 eV for  $\text{TiO}_2$ ) [4]. Homogeneous photo-Fenton produces  $\cdot\text{OH}$  in the reaction of  $\text{H}_2\text{O}_2$  with dissolved iron salts [5]. Both processes can occur under UV-Vis radiation and after some modification can be indicated by the solar light. Although AOPs have been shown to be effective, removal of pollutant from wastewater is a process with high energy consumption, where cost and efficiency are the key limit for their potential application. Introduction of AOPs before a biological treatment process may be likely because of the chemical/photochemical oxidation renders recalcitrant EDCs more biodegradable and less toxic, and improves their degradation in the following treatment process. To reduce the cost of energy consumed in the AOP, generally available solar energy should be applied for the degradation of compounds. However, among the advanced oxidation methods, many of them are unsuitable for degradation of pollutants in the environment with the use of solar energy. Only photocatalysis and photo-Fenton reaction under modification can use the solar radiation.

Another possibility of removing the water pollutants using solar light is the photosensitized oxidation. The main reactant formed in this process is very reactive species - molecular singlet oxygen. Photochemical oxidation, particularly using molecular oxygen, is unquestionable one of the most important of photochemical methods, since it does not formed any additional pollutant. Important issue in this process is to find the proper photosensitizer characterized by high efficiency in initiating oxidation processes. Photosensitized oxidation may occur in homogeneous and heterogeneous systems. Disadvantage of the homogenous process is the necessity of removing photosensitizer from the solution as the reaction has been completed. This problem can be overcome by using immobilized photosensitizers which show the advantage of easy operation, but sometimes demonstrate a reduced rate of reaction due to mass transfer effects.

The best results for removing EDCs from wastewater gain method combining the characteristics of strong oxidants and UV or VIS radiation. The most effective methods employing photochemical reactions include: photocatalysis with titanium peroxide ( $\text{TiO}_2/\text{UV}$ ), ozonolysis or/and hydrogen peroxide with UV radiation ( $\text{O}_3/\text{UV}$ ,  $\text{H}_2\text{O}_2/\text{UV}$ ), photo-Fenton process ( $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$ ), photolysis and photosensitized oxidation or photocatalysis [6-9].

The paper presents the application of several photochemical methods for degradation of phenolic compounds belonging to the EDCs - parabens (Fig. 1), phenylphenols (Fig. 2), and chlorophenols (Fig. 3).

### **Parabens**

The literature about degradation of parabens is rather scarce. The degradation of *n*-butylparaben (BP) by direct irradiation using UV (254 nm) was inefficient [8]. In turn,

the application of  $H_2O_2/UV$  system for BP decomposition was proved to be extremely efficient [10]. Oxidation using chlorine resulted in a reduction of BP and *benzylparaben* (BeP) concentration after 15 min by 67 and 71%, respectively [11]. However in this process chlorinated byproducts appeared in the reaction solution [11, 12]. The use of solar radiation for BP and BeP degradation did not give satisfactory results [12]. Parabens were also degraded by photocatalysis and ozonation processes. Heterogeneous reaction in the system  $TiO_2/UV$  caused 90% (pH 6) and 100% (pH 9) reduction of methylparaben concentration in 120 min, and 180 min, respectively [2]. Degradation with ozone at pH 6.9 was the most effective method of removal parabens - 99% decomposition after 12 min [13]. Photosensitized oxidation was successfully applied for decomposition of BP and BeP with the successful effect as well in homogenous and heterogeneous systems. Both of pollutants were completely removed from the solution after 120 min [14, 15].

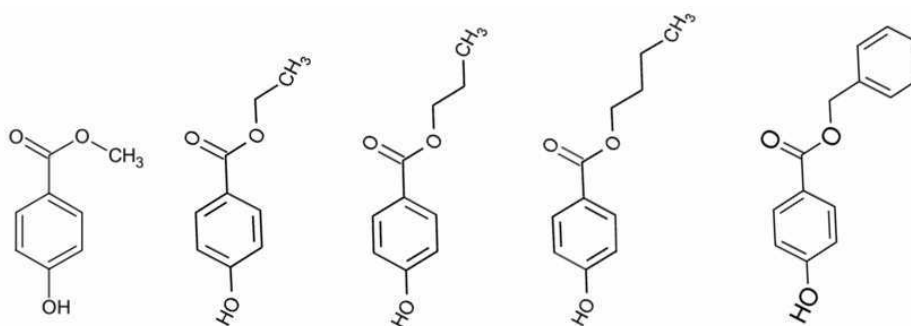


Fig. 1. General chemical structures of a parabens: methylparaben, ethylparaben, propylparaben, butylparaben, benzylparaben

### Phenylphenols

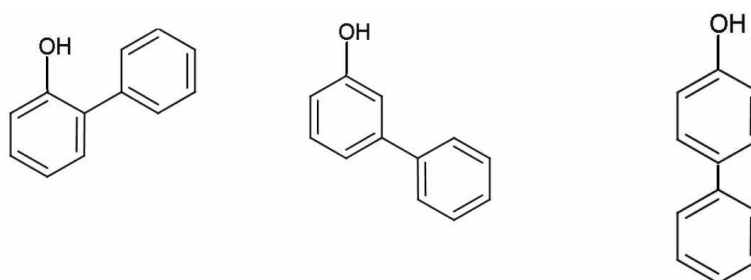


Fig. 2. General chemical structures of a phenylphenols: *ortho*-phenylphenol, *meta*-phenylphenol, *para*-phenylphenol

There are a limited number of literature data on the degradation of phenylphenol isomers in an aqueous solution. Among the tested biodegradation processes two methods can be distinguished by using enzymes [16, 17] and activated sludge [18]. Enzymatic degradation of phenylphenol proceeds relatively quick however the preparation

of enzymes to the process are very tedious and expensive. Photocatalytic degradation of *para*-phenylphenol in the presence of  $\text{TiO}_2$  leads to the formation of bicyclic aromatic compounds [19]. Sarakham et al studied the photosensitized oxidation of *meta*- and *para*-phenylphenol [20]. These compounds were total removed from the solution after 50 min, but the received final product was identified as oligomers of phenylphenols. Photocatalytic degradation of *2-phenylphenol* (2-PP) irradiated between  $\lambda = 300$  and 450 nm was examined. The use of  $\text{ZnO}$  caused the 80% reduction of 2-PP concentration during 7 h, while the use of  $\text{TiO}_2$  in the same time removed 50% of 2-PP. In both cases, the main identified photoproducts were hydroquinone, *p*-benzoquinone, phenylhydroquinone, phenylbenzoquinone, 2,2- and 2,3-dihydroxybiphenyls [21]. During ozonation process at neutral solution 2-PP was completely removed just after 250 s [22].

### Chlorophenols

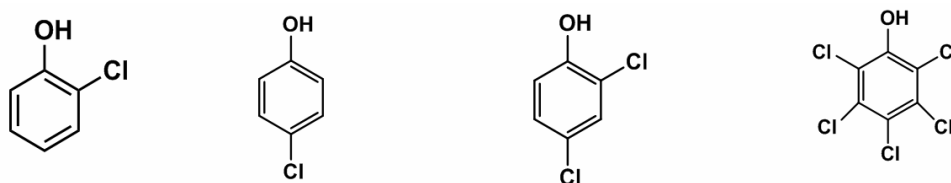


Fig. 3. The molecular structures of chlorophenols which are belonging to EDCs: 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol and pentachlorophenol

Chlorophenols are a group of contaminants whose degradation was most extensively studied. Several methods were successfully applied for chlorophenol degradation: UV radiation [23], photochemical methods (using hydrogen peroxide, Fenton reaction, ozone [24, 25]), electrochemical methods [26] and photocatalysis with  $\text{TiO}_2$  [27-29]. Photodegradation of chlorophenols using singlet oxygen in a homogeneous system has been also thoroughly studied [30-33]. The level of chlorination of phenol molecule influenced on the efficiency of all photodegradation methods and higher substituted phenols demonstrated lower reactivity. The efficiency depended also on the position of chlorine substituent in the aromatic ring.

### Summary

Applying AOPs for effective water pollutants degradation, they had several disadvantages. The application of photocatalytic technology with  $\text{TiO}_2$  to wastewater treatment is limited to the wavelength range of radiation. Modification of  $\text{TiO}_2$  leading to its activation under visible radiation can lead to the broad employment of this method [27]. The drawbacks of  $\text{H}_2\text{O}_2/\text{UV}$  process consist in the high energy requirements associated with the use of UV lamps and the need of the use of high  $\text{H}_2\text{O}_2$  concentrations [34]. Disadvantages of photo-Fenton reactions are connected with the necessity of acidic reaction condition and the difficulty in removing the sludge containing iron ions after the treatment [35].

AOPs are effective methods for removing EDCs from water solution, but the costs of the processes are high due to the use expensive reagents such as  $\text{H}_2\text{O}_2$  and  $\text{O}_3$  and electric

energy when UV radiation is applied. For this reason interesting option among the photochemical processes seems to be the use of photosensitized oxidation. The main advantage of this process is the use of visible light or solar energy and using oxygen from air.

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## KSENOESTROGENY - ŚRODOWISKOWE ZAGROŻENIA I ICH FOTOCHEMICZNA DEGRADACJA

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**Abstrakt:** Niektóre ksenoestrogeny występujące w środowisku wodnym mogą naśladować lub/i blokować naturalne hormony (EDCs). Do grupy tych groźnych substancji zaliczyć można wiele naturalnych i syntetycznych organicznych związków, ale głównie są to substancje stworzone przez człowieka, takie jak farmaceutyki czy środki higieny osobistej. Obecność EDCs w środowisku wodnym w niewielkich stężeniach i często toksycznych wobec mikroorganizmów powoduje, że klasyczne metody oczyszczania wód łącznie z biodegradacją są nieefektywne. Usuwanie EDCs ze środowiska wodnego może być skutecznie realizowane na drodze utleniania poprzez zastosowanie *zaawansowanych technik utleniania (AOP)* oraz fotosensybilizowanego utleniania. Zastosowanie procesów fotochemicznych pozwala na uzyskanie wysokiego stopnia redukcji EDCs w relatywnie krótkim czasie. Metoda fotosensybilizowanego utleniania posiada niekwestionowaną zaletę, jaką jest możliwość wykorzystania tlenu z powietrza i energii światła słonecznego. W pracy przedstawiono zastosowanie szeregu fotochemicznych metod do degradacji związków fenolowych zaliczanych do EDCs - parabenów, chlorofenoli, fenylofenoli.

**Słowa kluczowe:** ksenoestrogeny, zaawansowane metody utleniania, fotosensybilizowane utlenianie