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Review

ADVANCED OXIDATION PROCESSES (AOPs) APPLIED FOR WASTEWATER AND DRINKING WATER TREATMENT. ELIMINATION OF PHARMACEUTICALS

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Due to their insufficient removal in conventional wastewater treatments, advanced drinking and wastewater treatment options should be considered for the removal of pharmaceutically active compounds (PhACs) from urban, hospital and industrial wastewaters. This paper summarizes the current state-of-the-art in two often applied advanced oxidation processes (AOPs), namely TiO_2 assisted photocatalysis and photo-Fenton process. Their possibilities in removing PhACs are discussed, giving examples for several most studied compounds.

Key words: advanced oxidation processes, solar photocatalysis, pharmaceuticals, wastewater, transformation products.

Primjena naprednih oksidacijskih procesa (AOPs) u obradi otpadne i pitke vode. Uklanjane farmaceutika. Razmatrane su mogućnosti primjene naprednih oksidacijskih procesa za uklanjanje farmaceutskih aktivnih tvari prisutnih u gradskim vodama, vodama iz bolnica i industrijskim otpadnim vodama uslijed neadekvatnog uklanjanja istih konvencionalnim postupcima obrade voda. U ovom radu prikazana su trenutno najnovija dostignuća u dva područja često korištenih naprednih oksidacijskih procesa, fotokataliza potpomognuta s TiO_2 i foto-Fenton procesa. Diskutirane su mogućnosti uklanjanja farmaceutskih aktivnih tvari (PhACs) navedenim procesima uz primjere najčešće proučavanih spojeva.

Ključne riječi: napredni oksidacijski procesi, solarna fotokataliza, farmaceutici, otpadne vode, produkti transformacije.

INTRODUCTION

Pharmaceutically active compounds (PhACs) and other products that are used in large quantities in every-day life (e.g., personal care products (PPCPs), surfactants and their residues, plasticizers and various industrial additives) are termed as “emerging contaminants”, since they are unregulated or in the process of regularisation [1]. PhACs are designed to have specific pharmacologic and physiologic effects at low doses and thus are inherently potent, often with unintended outcomes in wildlife. After their usage for the intended purpose, a large fraction of these substances will be discharged into the wastewater unchanged or in the form of degradation products that are often hardly eliminable in conventional wastewater treatment plants (WWTPs). Depending on the efficiency of the treatment and chemical nature of a compound, they can reach surface and ground waters. In the worst-case scenario they are encountered in the drinking water, in spite of the expensive treatment steps [2].

Besides direct WWTP discharges that are usually a consequence of the incomplete removal of PhACs, other environmental exposure pathways are manufacturing and hospital effluents, land applications (e.g., biosolids and water reuse), concentrated animal feeding operations (CAFOs), and direct disposal/introduction to environment. Due to their continuous input into the aquatic media through wastewater as a main point-source, PhACs are considered to be “pseudo-persistent”. Therefore, considering the ubiquity and pseudo-persistence of PhACs, end-of-pipe treatment of wastewater might increase the ecotoxicological risk for the environment and eventually humans. In light of these facts, advanced drinking and wastewater treatment options should be considered for removal of PhACs from urban, hospital and industrial wastewaters. One of the possible strategies for up-grading treatment in DWTPs and WWTPs is application of advanced oxidation processes (AOPs).

The versatility of AOPs reflects in different options for production of $^{\bullet}OH$ radicals, depending on the requirements of the specific treatment. The AOPs are characterized by a variety of radical reactions that involve combinations of chemical agents (e.g., O_3, hydrogen peroxide H_2O_2, transition metals, and metal oxides) and auxiliary energy sources (e.g., UV-VIS radiation, electronic current, γ-radiation and ultrasound). Other examples of AOP include H_2O_2/UV, Fenton (Fe^{2+}/H_2O_2), photo- and electro-Fenton, chelating agent assisted Fenton/photo-Fenton, heterogeneous photooxidation using titanium dioxide (TiO_2), γ-radiolysis, and sonolysis [3]. The $^{\bullet}OH$ radicals are extraordinarily reactive species with the rate constants of reactions with the majority of organic molecules in the order of 10^6-10^9 $M^{-1}s^{-1}$. Also, their lack of selectivity is an advantage when dealing with highly contaminated waters. The major advantage of the photolytic oxidation based processes are operation at room temperature and the possibility to effectively use sunlight or near UV for irradiation, which could result in considerable economic savings especially for large-scale operations.

Due to the usage of expensive reactants such as H_2O_2 and O_3, AOPs should not replace the more economic, biological treatment [4]. Moreover, AOPs can be installed either as tertiary treatment after the biological (secondary) treatment of wastewater, or as pre-treatment stage in order to enhance the biodegradability of trace organic contaminants (see Fig. 1). In the latter case, the usage of AOPs for partial oxidation of trace organic contaminants might not be an appropriate approach in the cases where other organic matter is predominantly present, since the oxidant requirement can be exceedingly high in order to achieve effective degradation of trace organics.

This paper summarizes current state-of-the-art in two often applied AOPs, namely TiO_2 assisted photocatalysis and photo-Fenton process and discus their possibilities in removing PhACs.

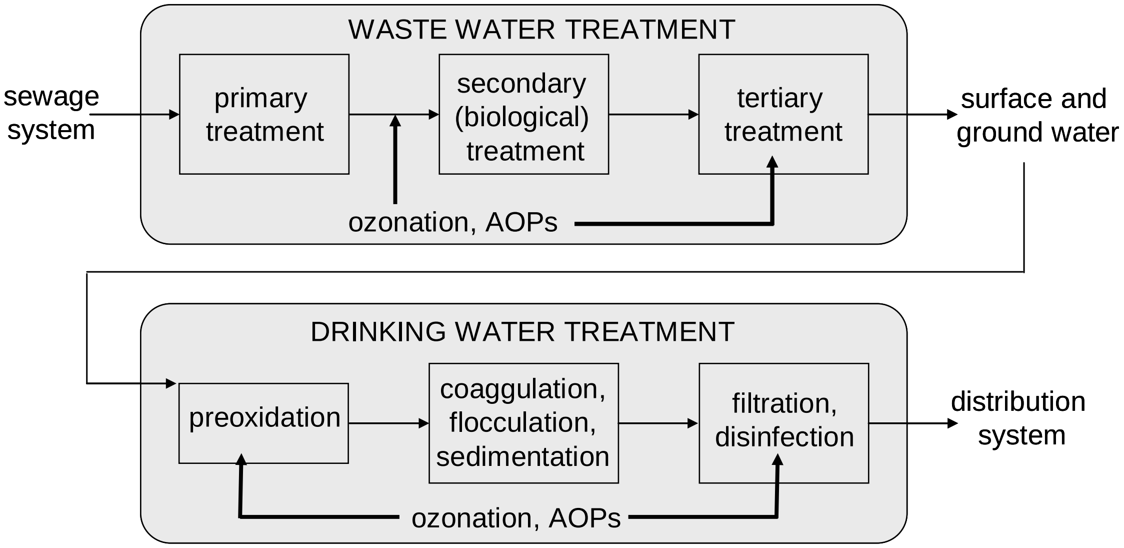

Figure 1. Possible applications of ozonation and AOPs in wastewater and drinking water treatment.

Slika 1. Mogućnosti primjene ozoniranja i naprednih oksidacijskih procesa (AOPs) u obadi otpadne i pitke vode.

Advanced oxidation processes for the removal of pharmaceuticals

TiO_2 assisted photocatalysis

The photocatalyzed degradation of organic environmental pollutants in the presence of a semiconductor catalyst has become a subject of increasing interest over the last 10 years. The literature reports a variety of photocatalytic reactions involving several metal oxides such as TiO_2, ZnO, Fe_2O_3, WO_3 as well as other semiconductors (i.e., CdS) [5]. However, considering the toxicity, availability, photocorrosion resistance, catalytic efficiency and cost, TiO_2 is the preferred choice. Semiconductor photocatalysis with a primary focus on TiO_2 as photocatalyst has been applied in the past as additional treatment in water and air purification; it was efficient in destroying bacteria, viruses, inactivating cancer cells, photosplitting water to produce the hydrogen gas, fixating nitrogen, cleaning up of oils and it was also used for odour control [6].

Besides some drawbacks of solar heterogeneous photocatalysis (e.g., necessity of real waters to be transparent in the UV-VIS spectral region, slow complete mineralization of compounds having heteroatoms at low oxidation degree), it offers interesting advantages such as low cost and TiO_2 catalyst, stable of in a wide range of pH, system applicable at low concentrations, possibility of coupling with other types of water treatment (e.g., biological), and total mineralization can be achieved for most of the organic pollutants [7].

Factors influencing the removal of PhACs in semiconductor photocatalysis

The rate of photocatalytic degradation is governed by the initial concentration of the contaminant, temperature, mass of catalyst, light intensity, wavelength of irradiation, radiant flux, quantum yield, O_2 pressure, and presence or absence of electron acceptors (e.g., H_2O_2) or radical scavengers (e.g., bicarbonate species) [8].

The properties of pharmaceutical to be treated such as *pKa* and structure will determine not only the efficiency of it photocatalytic degradation but also the mechanism of product formation (i.e., contribution of $^{\bullet}OH$ radical and valence band holes oxidation pathway). Palominos et al [8] evaluated the effects of $^{\bullet}OH$ radical (addition of isopropranolol, and use of acetonitrile as a solvent instead of water) and h^+ scavengers (addition of iodide anion) in order to elucidate their contribution to the TiO_2 photocatalytic degradation of quinolone antibiotic flumequine. They employed addition of isopropranolol and used of acetonitrile as a solvent instead of water for scavenging the $^{\bullet}OH$ radicals, whereas addition of iodide anion served for scavenging the valence band holes. Moreover, benzoquinone was added in a separate experiment in order to evaluate the participation of $O_2^{\bullet-}$ ion. In the presence of $^{\bullet}OH$ radical scavengers flumequine was degraded after approximately 60 min, thus indicating that radicals were not the only degradation route. With the addition of iodine ion the reaction was completely inhibited, thus indicating a preponderant participation of holes in the oxidation mechanism of flumequine. On the other side, the addition of benzoquinone provoked only a partial inhibition of the degradation process.

Although $^{\bullet}OH$ radicals react at diffusion-controled rates, they were found to posses certain selectivity. For example, Maldonado et al noticed that the photoreactivity of pesticides with TiO_2 was directly related to whether the substituents at the aromatic ring are e^- donors or acceptors, i.e. activating or deactivating groups for the electrophilic attack of $^{\bullet}OH$ radical. However, in the photocatalytic degradation of aromatic compounds, rapid dearomatization was observed even in the case when deactivating substituents were attached to the aromatic ring (e.g., Cl, NO_2, $CONH_2$, COOH) [8]. For chlorinated molecules, Cl^- ions are easily released in photocatalytic reaction, which could be of interest when coupling AOP with the biological treatment that is generally inefficient with chlorinated compounds (e.g., diclofenac, clofibric acid).

Besides the potential by-products of higher MW (i.e., close to the MW of the parent compound), final oxidation products such as nitrate and ammonia ions, and carboxylic acids are also generated. Nitrogen-containing molecules are mineralized into ammonia ions (NH_4^+) and mostly nitrate ions (NO_3^-). The NH_4^+ ions are relatively stable, whereas the proportion depends mainly on the initial oxidation degree of nitrogen and on the irradiation time [10]. The pollutants containing sulfur atoms are mineralized into sulphate ions [8,11]. From the oxidation of aromatic ring, rather stable formate (HCO_2^-) and acetate (CH_3COO^-) ions are formed, which slows down total mineralization. As it was suggested by Perez-Estrada et al [11], light-weight carboxylic acids (e.g., acetate, formate, pyruvate, and oxalate) cannot be accumulated at significant concentrations in TiO_2 photocatalysis since they are continuously forming and degrading.

The suppression of by-products, especially when they are toxic, is one of the criterions for a good photocatalyst. The formation of by-products can be influenced by the type of catalyst used, as demonstrated in several studies where degradates were formed in markedly higher concentrations when using TiO_2 Degussa P25 than other commercially available TiO_2 powders (e.g., TiO_2 Sachtleben Hombikat UV 100) [12,13]. In some cases, intermediates of photocatalytic reactions can be persistent to further degradation and/or act as "inner filters". For example, Theurich et al [13] noticed that the intermediates benzoquinone and hydroquinone formed during the photocatalytic treatment of 4-chlorophenol were inhibiting the degradation of the compound. This was explained by the existence of photocatalytic balance between benzoquinone and hydroquinone through fast electron shuttle mechanism, whereas only when oxidizing benzoquinone to hydroxybenzoquinone the 4-chlorophenol can be further degraded. Also, low total organic carbon (TOC) removal during heterogeneous photocatalysis of tetracycline was assigned to the formation of recalcitrant intermediates [14]. Moreover, when dealing with real wastewater containing many organic and inorganic compounds, condensation products can be formed between reactants due to the radical-mediated mechanism of AOP [8].

Photo-Fenton photocatalysis

During the past 15 years a growing interest has been observed in the practical utilization of Fenton and photo-assisted Fenton reactions in water and soil treatment. The solar homogeneous photocatalytic treatment (photo-Fenton) is based on the production of $^{\bullet}OH$ radicals by Fenton reagent (H_2O_2/Fe^{2+}). This reaction is strongly accelerated by irradiation with UV-VIS light, since the photolysis of Fe^{3+} complexes allows Fe^{2+} regeneration and occurrence of Fenton reactions due to the present H_2O_2.

The main advantage of photo-Fenton process is the possibility of using solar irradiation (i.e., sensitivity to $\lambda \leq 600$ nm) which considerably reduces the costs of the process, especially when applying photo-Fenton for the treatment of high volumes of water. Other benefits of photo-Fenton are low-cost equipment, simplicity of operation, and use of reagents that are safe to handle and non-threatening to the environment (i.e., H_2O_2 used does not load in the system and is decomposed to harmless substances, whereas only analytical amount of Fe-ion ca be used). However, a major disadvantage of the process is a strong dependence on the pH of the aqueous solution and the concentrations of H_2O_2 and Fe^{2+}/Fe^{3+}. The requirement for the pH 2-4 is a major drawback in natural waters, especially in the case of highly buffered wastewater. Zhao et al tried to overcome the pH limitation of photo-Fenton process by using a novel catalyst α-FeOOHR, also offering a possibility of recycling the catalyst. Also, iron salts may be considered as pollution source, thus the pH of the effluent needs to be neutralized in order to precipitate the dissolved iron as $Fe(OH)_3$, which raises the problem of iron sludge disposal.

Factors influencing the removal of PhACs in photo-Fenton photocatalysis

The photo-Fenton treatment is more suitable for the removal of low MW organic compounds between 0.5 and 4 kDa, which is an advantage relative to the conventional treatment where such compounds are usually poorly removed. Moreover, several studies indicated that most of the TOC removed by photocatalytic process corresponds to hydrophobic components, which predominate in natural organic matter (NOM) from raw water [17,18]. This can be explained by greater aromaticity of the hydrophobic fraction and thus higher reactivity with oxidation species. Buchanan et al [276] identified the refractory hydrophilic fraction as short-chain aliphatic amines, alcohols, aldehydes, esters, ketones, $<C_5$ aliphatic amides, polyfunctional alcohols, carbohydrates, cyclic amides and polysaccharides. Nevertheless, as stated previously, NOM can be both a source and a sink of hydroxyl radicals, the concentration of which in natural waters is influenced by both the nature and the concentration of dissolved organic compounds.

It has been demonstrated that the degradation of organic compounds is improved when the concentration of iron is increased [19]. The iron source employed will also influence the efficiency of photo-Fenton degradation of certain compounds [20,21]. Trovó et al [22] observed better removal of bezafibrate and paracetamol when FeOx was used instead of $Fe(NO_3)_3$ (98 % removal *vs.* 89 and 53 %, respectively), whereas for amoxicillin the choice of iron source had no influence on the efficiency of the process. However, in all cases the elimination of TOC was higher when using FeOx. Also, Bautitz et al [21] observed improved degradation of tetracycline when using $Fe(NO_3)_3$ compared to the ferrioxalate, independently of H_2O_2 concentration.

Humic acids, also present in natural water, can contribute to the transformation of organic compounds through the formation of complexes with Fe(III) [22]. These Fe(III)- humate complexes are more easily reduced to Fe(II) by $H_2O_2/HO_2^{\bullet}/O_2^{\bullet -}$ when compared with Fe(III)-H_2O complexes, thus whereas Fe(II) thus formed reacts with H_2O_2 to yield $^{\bullet}OH$ radical. In addition, humic acids themselves can photo-degrade through formation of complexes with Fe(III) [23]. Addition of oxalate has been also reported to enhance the photo-Fenton reaction.

Transformation products of pharmaceuticals formed during TiO_2-assisted and photo-Fenton photocatalysis

There are several studies concerning the photocatalytic intermediates of nonsteroid anti-inflammatory drugs (NSAIDs). Zhang et al identified [24] the reaction intermediates of TiO_2 photocatalytic degradation of acetaminophen by GC-MS analysis. Direct h^+ oxidation and *ipso*-substitution were found to be the initial step of acetaminophen degradation, leading to the formation of hydroquinone and 1,4-benzoquinone as the main intermediates. During TiO_2 photocatalytic degradation of ibuprofen under simulated solar radiation, the initial reaction pathway was assumed to proceed by hydroxylation, i.e. inclusion of $^{\bullet}OH$ radical in the methylpropyl phenyl positions and in the arylcarboxylic moiety [243]. Pérez-Estrada et al [25] elucidated the degradation pathway of diclofenac during the photo-Fenton treatment. The main degradation pathway went through the hydroxylation at C-5 atom, in the *para*-position to the NH substituent at the activated aromatic ring (see Fig. 2). This afforded a product 5-hydroxydiclofenac that after exposure to sunlight and initiation of the photo-Fenton reaction converted into diclofenac-2,5-imonoquinone. Besides this main degradation route via quinine-imine derivatives, alternative pathway resulted in direct reactions on the aliphatic chain of diclofenac, oxidation-hydroxylation, decarboxylation and opening of the non-chlorinated ring.

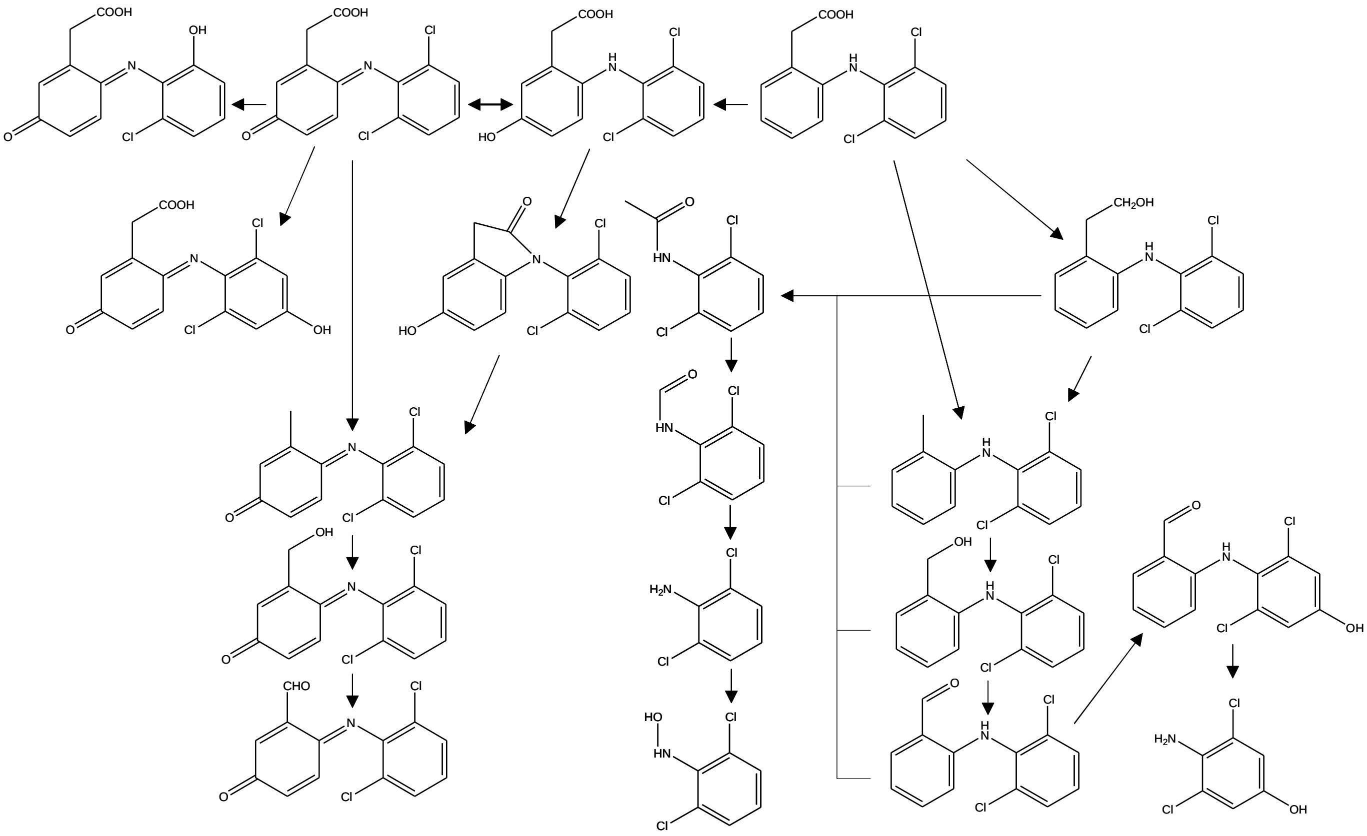

Figure 2. Proposed degradation pathway of pure diclofenac under photo-Fenton treatment. Adapted from Pérez-Estrada et al. **[**26**]**

Slika 2. Predloženi prijelazni spojevi degradacije čistog diklorfenaka uz foto-Fentonov proces. [26]

Combining the use of GC-MS and LC-ToF-MS, Perez-Estrada et al [26] elucidated structured of several degradation products of analgesic drug dipyrone, formed during TiO_2-assisted and photo-Fenton photocatalysis. Photo-Fenton turned out to be more efficient than TiO_2 photocatalysis, although following the same degradation pathway with aniline as the main degradation product, formed by the opening of the pyrazolinone ring.

Radjenovic et al. [27] studied the technical feasibility and performance of photocatalytic degradation of anti-inflammatory drug acetaminophen and *β*-blocker atenolol in a well-defined system of a pilot-plant scale Compound Parabolic Collectors (CPCs) under natural illumination. The main intermediate products of photocatalytic degradation of atenolol has been structurally elucidated by MS^2 experiments performed at quadrupole-time of flight (QqToF) mass analyzer coupled to ultra-performance liquid chromatograph (UPLC). Six transformation products were characterized, formed by consecutive attacks of hydroxyl ($^{\bullet}$OH) radical in concomitance with the disappearance of the primary compound (Fig. 3). The study revealed that the degradation of atenolol and acetaminophen in TiO_2 and photo-Fenton solar photocatalysis was complete and followed pseudofirst order reaction kinetics. The photo-Fenton treatment proves to be more efficient for degradation of two studied compounds than the TiO_2 photocatalytic treatment. Lower reaction rate for secondary effluent compared with distilled water were observed in all cases, mainly due to the detrimental effect of other organic compounds typically present in municipal wastewater effluents.

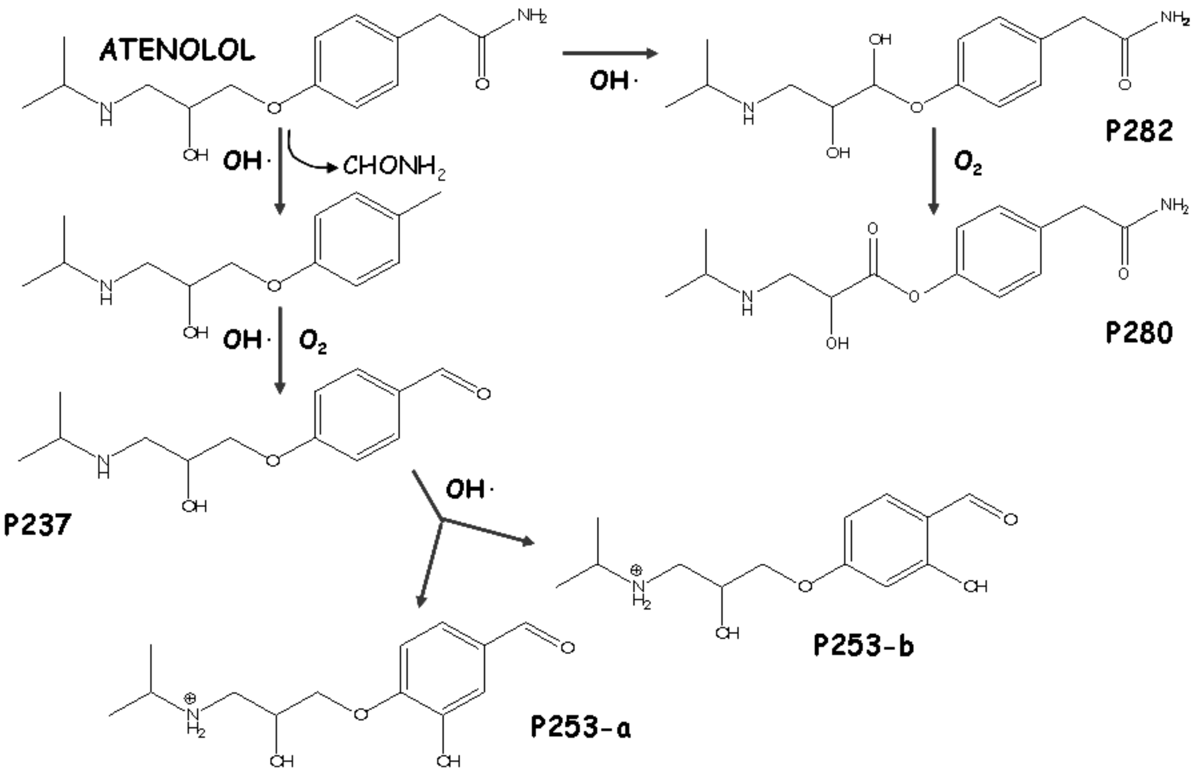

Figure 3. Proposed photocatalytic degradation pathway of atenolol in aqueous solution by solar TiO_2 and photo-Fenton treatment. Adapted from [27]

Slika 3. Predloženi prijelazni spojevi degradacije atenolola u vodenim otopinama uz solarni TiO_2 i foto-Fentonov proces. [27].

Among studies on photocatalytic degradation mechanisms of pharmaceuticals, significant attention has also been paid to lipid regulator and cholesterol lowering statin drugs. Using an HPLC-DAD and FLD, Doll et al [28] proposed a photocatalytic degradation pathway of compound frequently recalcitrant to biological degradation and ozonation, clofibric acid, in TiO_2 suspensions. After substitution of –Cl by –OH group in the *para*-position products such as 2-(4-hydroxyphenoxy)-isobutyric acid and hydroquinone were formed, whereas on the other side cleavage of isobutyric acid from the side chain afforded 4-chlorophenol and 4-chlorocatechol. Moreover, the generation of 2-(4-hydroxyphenoxy)-isobutyric was postulated to proceed either by reductive pathway of conduction band e^-, or oxidative pathway of valence band $^{\bullet}OH$ radicals, whereas 4-chlorophenol was formed by oxidative pathway of valence band h^+. Lambropoulou et al [29] used the GC-MS, LC-ToF-MS and HPLC-DAD technique to identify up to 17 degradation products of TiO_2 photocatalysis of a fibrate drug, bezafibrate, under simulated solar light. LC-ToF analysis was able to detect various hydroxylated products in the first stage of the treatment, whereas the $^{\bullet}OH$ radical attack preferentially occurred at the phenoxy ring, while the attack at the 4-chlorobenzoyl moiety was a minor route. This was explained by the lower reactivity of chlorine-containing ring with respect to the non-chlorinated one due to the electron-withdrawing effect of the –Cl group. Since $^{\bullet}OH$ has strong electrophilic character it will tend to attack the C-atoms with the highest e^- density, whereas the R-oxy substituent ($-O-C(CH_3)_2COOH$) has an additional activating effect on the non-chlorinated ring increasing its electron density. Also, derivative of the cleavage of the ethereal O-C (sp^3) bond of bezafibrate was observed, previously reported for another fibrate drug gemfibrozil [30]. The third pathway in the photodegradation of bezafibrate proceeded via breakage of the amide bond, although this degradation route was of minor importance. In the UV/TiO_2 photocatalytic degradation of gemfibrozil and non-steroidal anti-estrogen tamoxifen the main intermediates identified by GC-MS were formed by the breakage of the ethereal O-C (sp^3) bond [30**]**. In the case of tamoxifen this product was generated even without the catalyst, only by UV radiation, because of the decrease in ethereal bond stability due to strong electron delocalization effect of three aromatic rings near the bond.

As far as *ß*-blockers are concerned, Medana et al [31] used an LTQ Orbitrap-MS to structurally elucidate products of photocatalytic transformation of atenolol. They identified several mono-hydroxilated derivatives, due to the non-selective attacks of the $^{\bullet}OH$ radical to the activated aromatic ring and alkyl side-chain. Moreover, di- and tri-hydroxy intermediates, their keto-analogues and derivatives formed by demethylation of the isopropyl group and cleavage of lateral chain were also elucidated. The same research group investigated TiO_2 photocatalytic degradation of β_2-antagonist salbutamol [32]. Three degradation pathways were proposed: pathway A starting with the detachment of the $–CH_2OH$ group from the benzene ring and further breakdown of the molecule leading to hydroquinone and 2-(*tert*-butylamino)-acetic acid; pathway B that proceeds through the substitution of $–CH_2OH$ group by the –OH group, further oxidation of the –OH group at the side chain and demethylation of the *tert*-butylic group; pathway C that involved a reductive attack of CH_3 radical at the $–CH_2OH$ group.

Radjenovic et al. [33] studied degradation of H_2-receptor antagonist ranitidine dissolved in synthetic municipal wastewater in TiO_2 and photo-Fenton solar photocatalysis. Ranitidine was degraded at a similar rate by both processes, while its degradation was slower in the synthetic effluent compared to distilled water, mainly due to the detrimental effect of other organic compounds typically present in municipal wastewater effluents. The initial steps of photocatalytic degradation of ranitidine in both TiO_2 and photo-Fenton processes went through hydroxylation (i.e., OH radical attack), dealklylation, deamination, and oxidation by OH radicals and O_2. Carboxylic acids were detected at the end of TiO_2 and photo-Fenton experiments, which suggests that the initial large molecular weight intermediates were either mineralized or transformed to final, lower molecular weight products that can be expected to be less harmful for the environment.

For sulfonamide drugs (sulfamerazine, sulfadiazine, sulfadimethoxine and sulfathiazole) the degradation in aqueous TiO_2 suspensions irradiated with near-UV light was achieved through the cleavage of the S-N bond and $^{\bullet}OH$ attack at the aromatic ring [34]. The stability of $R\text{-}NH_2$ intermediates formed by the breakage of S-N bond was highly dependent on the nature of R, since in the case of sulfathiazole and sulfadimethoxine these products were further degraded through ring opening and release of nitrogen and sulphur, whereas for other two investigated sulfonamides the $R\text{-}NH_2$ derivatives turned out highly persistent. In the case of sulfadiazine and sulfamerazine, the $^{\bullet}OH$ attack could only occur at the anilic ring, whereas in the case of sulfathiazole and sulfadimethoxine the stability of the heteroatomic ring was compromised by the introduction of sulphur atom and methoxy groups, thus enabling $^{\bullet}OH$ attacks also at the thiazole and diazinic ring, respectively.

During TiO_2 photocatalysis of quinolone antibiotics ofloxacin and ciprofloxacin, the initial transformation pathways were confined to the piperazine moiety and to the methyl groups with unmodified fluoroquinolone core in the case of ofloxacin, whereas for ciprofloxacin the degradation involved both the piperazinic and quinolone moiety [35]. All of the identified intermediates were easily degraded, with the complete mineralization of nitrogen in the case of ofloxacin and interestingly only 1/6 of the nitrogen mineralized in the case of ciprofloxacin, suggesting that the fluoroquinolone core structure was preserved. Palominos et al [36] reported decarboxylation as the primary step in TiO_2 photocatalysis of antibiotic flumequine, followed by a photo-Kolbe mechanism. Also, Paul et al [37] used LC-MS^2 analysis performed at an IT-MS to identify six degradation products of UV and visible-light TiO_2 photocatalytic degradation of ciprofloxacin. All products were completely mineralized during UV photocatalysis, whereas in the visible-light assisted process the fluoroquinolone core structure was possibly preserved.

CONCLUSIONS

Photocatalytic degradation by photo-Fenton and TiO_2 catalysis has been established as effective treatments for water containing pesticides, endocrine disrupting compounds (EDCs), pharmaceuticals and other trace organic contaminants. However, radical-induced reactions occurring in photocatalytic treatments evolve through complex parallel consecutive pathways of intermediate products. Since hydroxyl-radicals are not selective, various by-products are formed at low concentration levels. The identification of these intermediates and determination of kinetics of their degradation is crucial due to their potential presence in the effluent of the treatment, and apprehension of their degradation pathways is necessary in order to determine the key steps of photodecomposition.

REFERENCES

[1] M. Petrovic, D. Barcelo, Anal. Bioanal. Chem. 385 (3), 2006, 422 – 424.

[2] R.L Oulton,. T Kohn, D.M Cwiertny, J. Environ. Monitor. 12 (11), 2010, 1956-1978.

[3] T. Oppenlander, Photochemical purification of water and air, Wiley-VCH Verlag, Weinheim, Germany, 2003.

[4] S. Malato, J. Blanco, A. Vidal, C. Richter, Applied Catalysis B: Environmental 37 (2002) 1-15.

[5] R.W. Matthews, Photocatalytic purification and treatment of water and air, Elsevier Science, Amsterdam/New York, 1993.

[6] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Chemical reviews 95 (1995) 69-96.

[7] J.-M. Herrmann, Catalysis Today 53 (1999) 115-129.

[8] R. Palominos, J. Freer, M.A. Mondaca, H.D. Mansilla, Journal of Photochemistry and Photobiology A: Chemistry 193 (2008) 139-145.

[9] M.I. Maldonado, P.C. Passarinho, I. Oller, W. Gernjak, P. Fernandez, J. Blanco, S. Malato, Journal of Photochemistry and Photobiology A: Chemistry 185 (2007) 354-363.

[10] G.K.-C. Low, S.R. McEvoy, R.W. Matthews, Environ. Sci. Technol. 25 (1991) 460-467.

[11] L.A. Perez Estrada, S. Malato, A. Aguera, A.R. Fernandez-Alba, Catalysis Today 129 (2007) 207-214.

[12] J. Theurich, M. Lindner, D.W. Bahnemann, Langmuir 12 (1996) 6368- 6376.

[13] A. Mills, P. Sawunyama, Journal of Photochemistry and Photobiology, A: Chemistry 84 (1994) 305-309.

[14] M. Addamo, V. Augugliaro, A. Di Paola, E. Garcia-Lopez, V. Loddo, G. Marci, L. Palmisano, Journal of Applied Electrochemistry 35 (2005) 765-774.

[15] Y. Zhao, J. Hu, Applied Catalysis B: Environmental 78 (2008) 250-258.

[16] C. Murray, S. Parsons, Chemosphere 54 (2004) 1017-1023.

[17] W. Buchanan, F. Roddick, N. Porter, M. Drikas, Environ. Sci. Technol. 39 (2005) 4647- 4654.

[18] S. Liu, M. Lim, R. Fabris, C. Chow, K. Chiang, M. Drikas, R. Amal, Chemosphere 72 (2008) 263-271.

[19] P.R.F. Nogueira, J.R. Guimaraes, Water Research 34 (2000) 895-901.

[20] I.R. Bautitz, R.F.P. Nogueira, Journal of Photochemistry and Photobiology A: Chemistry 187 (2007) 33-39.

[21] A.G. Trovo, S.A.S. Melo, R.F.P. Nogueira, Journal of Photochemistry and Photobiology A: Chemistry 198 (2008) 215-220.

[22] D. Vione, F. Merlo, V. Maurino, Environmental Chemistry Letters 2 (2004) 129-134.

[23] M. Fukushima, K. Tatsumi, S. Nagao, Environ. Sci. Technol. 35 (2001) 3683-3690.

[24] X. Zhang, F. Wu, X. Wei Wu, P. Chen, N. Deng, Journal of Hazardous Materials 157 (2008) 300-307.

[25] L.A. Perez-Estrada, S. Malato, W. Gernjak, A. Aguera, E.M. Thurman, I. Ferrer, A.R. Fernandez-Alba, Environmental Science and Technology 39 (2005) 8300-8306.

[26] L.A. Perez Estrada, S. Malato, A. Aguera, A.R. Fernandez-Alba, Catalysis Today 129 (2007) 207-214.

[27] J. Radjenovic, C. Sirtori, M. Petrovic, D. Barcelo, S. Malato, Applied Catalysis B: Environmental 89 (2009) 255–264.

[28] T.E. Doll, F.H. Frimmel, Water Research 38 (2004) 955-964.

[29] D.A. Lambropoulou, M.D. Hernando, I.K. Konstantinou, E.M. Thurman, I. Ferrer, T.A. Albanis, A.R. Fernandez-Alba, Journal of Chromatography A 1183 (2008) 38-48.

[30] S. Yurdakal, V. Loddo, V. Augugliaro, H. Berber, G. Palmisano, L. Palmisano, Catalysis Today 129 (2007) 9-15.

[31] C. Medana, P. Calza, F. Carbone, E. Pelizzeti, H. Hidaka, C. Baiocchi, Rapid Communications in Mass Spectrometry 22 (2008) 301-313.

[32] V.A. Sakkas, P. Calza, C. Medana, A.E. Villioti, C. Baiocchi, E. Pelizzetti, T. Albanis, Applied Catalysis B: Environmental 77 (2007) 135-144.

[33] J. Radjenovic, C. Sirtori, M. Petrovic, D. Barceló, S. Malato, Chemosphere 79 (2010) 368–376.

[34] P. Calza, C. Medana, M. Pazzi, C. Baiocchi, E. Pelizzetti, Applied Catalysis B: Environmental 53 (2004) 63-69.

[35] P. Calza, C. Medana, F. Carbone, V. Giancotti, C. Baiocchi, Rapid Communications in Mass Spectrometry 22 (2008) 1533-1552.

[36] R. Palominos, J. Freer, M.A. Mondaca, H.D. Mansilla, Journal of Photochemistry and Photobiology A: Chemistry 193 (2008) 139-145.

[37] T. Paul, P.L. Miller, T.J. Strathmann, Environ. Sci. Technol. 41 (2007) 4720-4727.