ELECTROCHEMICAL OXIDATION OF WASTEWATERS CONTAINING ANTIBIOTICS

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Abstract - Synthetic chemicals polluting water resources are increasing day by day in terms of variety and component. Such as hospital and drug factory discharges with high endocrine disrupting pharmaceuticals are very dangerous and need further consideration. Antibiotic compounds are the most dangeroustypes of endocrine disruptor pharmaceuticals, for the microorganism resistance and they have widespread use in our country and around the world.However, conventional treatment methods are inefficient for their removal from wastewaters. Various advanced treatment methods such as carbon adsorption, advanced oxidation processes (AOP), membrane processes are proposed for the removal of antibiotics instead of conventional methods.Electrochemical advanced oxidation processes (EAOPs) show both the conversion performance of pollutants to harmless products by oxidation and the lower energy consumption requirement due to the use of direct current compared to other AOPs.Another advantage of the EAOPs is the less need for additional chemicals and pH arrangement.Because of these reasons, in this study, for the removal of antibiotics,the role of electrochemical advanced oxidation processes and combinations of them with other AOPswere considered. In most of the studies, it was seen that, full mineralizations were achieved at shorter reaction times and this increased the biodegradabilities.Also, in researchs it was seen that the application of Sn/Sb/Ni-Ti anodes are very limited. These anodes were highly tested in electrochemical ozone production and are known to be more successful than older generation PbO_2 and Pt anodes.

Keywords - Antibiotic, β-lactam, macrolids, fluoroquinolones, endocrine disruptors, electrochemical oxidation, ozone, anodic oxidation

I. INTRODUCTION

Water pollution sources are mainly considered under two general headings, industrial and domestic. Synthetic chemicals that pollute water resources are increasing day by day in terms of variety and component. Wastewaters that are discharged into the environment uncontrolled or not well treated by conventional treatment methods causes significant damages to the aquatic ecosystem. Wastewater types such as hospital and drug factory discharges with high endocrine disrupting pharmaceuticals are also very dangerous and need further consideration (Walsh, 2003; Sanderson et al., 2004; Kim et al., 2007; de Souza et al., 2009; Yu et al.,2009).

Endocrine Disruptorsare exogenous substances or substances mixture that changes the development and function of the endocrine system. These substances affect the production, release, binding, transport, activity and destruction of hormones and excretion of them from the body(Bigsby et al., 1999). Antibiotics that having endocrine disruptor properties, can not be metabolized in body of living organismsdepending on their chemical structure, or they are released to the environment as an intermediate product from (Mompelat et al., 2009). Continuous intake of antibiotics causes unexpected adverse effects on aquatic and terrestrial organisms, high concentration levels persist for long periods of time. According to the majority of researchers, antibiotics constitute a potential risk for antibiotic resistance, which is the biggest problem among pollutants in the environment (Petrovic, 2005; Blackwell, 2004). Turkey is one of the most prominent countries in the use of antibiotics and the most commonly prescribed and used antibiotic types are shown in Table 1 (IMS, 2014).

ATC* codes	Antibiotic Group	Sales from stores to pharmacies (units)
J01CR	Beta lactamazinh-Penicillin comb.	64.947.073
J01DB	1. generation cephalosporins	39.025.015
J01DC	2. generation cephalosporins	35.300.611
J01FA	Macrolides	22.036.078
J01MA	Fluoroquinolones	11.157.950
J01CE	Beta lactamase sensitive penicillins	7.182.484
J01GB	Other aminoglycosides	6.051.868
J01 E	Sulfonamide and trimethoprim combinations	1.848.681
J01XC	Steroid antibacterials	921.541
J01XA	Glycopeptide Antibacterials	208.345
J01DH	Carbapenems	153.823
J01XB	Polymyxins	46.643
J01BA	Amphenicols	6.910
Total		188.887.022

Conventional treatment methods (physical, chemical, biological) are inefficient for the removal of these endocrine disrupting antibiotics. (Ternes, 1998; Kümmerer, et al., 2000 and Heberer, 2002). Conventionaldisinfection processes, such as chlorination and UV applications, are also not effective in the controlling of bacteria developing resistance to the antibiotics. For these reasons, various advanced treatment methods such as carbon adsorption, advanced oxidation processes (AOP), membrane processes are proposed as an alternative and innovative technological solution for the removal of antibiotics (Kosutic et al., 2007). However, the main problem of these methods; either the pollutants are concentrated in atmosphere or concentrated streams are discharged into the environment in a more dangerous way. It is a fact that advanced oxidation processes are known to be effective in the conversion of pollutants to final products. However, the most serious problem in this regard is the need for high energy. However, electrochemical advanced oxidation processes show both the conversion performance of pollutants to harmless products by oxidation and the lower energy consumption needdue to the use of direct current. A further advantage of electrochemical oxidation is the less need for additional chemicals and pH adjustment(Yonar et al., 2018).

In recent years electrochemical oxidation has become one of the most important processes. Because, anodic oxidation is notable for both energy consumption and organic compounds due to the high potential for complete mineralization in a short time. In particular, it is possible to use various anode materials for anodic oxidation. Another advantage is that it is largely independent of an extra chemical input such as many processes. However, it is important that anodic oxidation consists of a durable material. The most important disadvantages of such processes,materials are depleted in a short time and need to be continuously substituted constitute. For thesereasons, the treatability of wastewater samples containing antibiotics of β-lactam group (cephalexin, cefazolin, cefoperazon, cefazolin, cefuroxime and ampicillin), macrolide (erythromycin, roxithromycin, azithromycin) and fluoroquinolone group (ofloxacin, ciprofloxacin, norfloxacin)which have common use in Turkey among the antibiotic compounds having endocrine disrupting properties were considered in this study with electrochemical oxidation and othe advanced treatment porcesses.

II. ENVIRONMENTAL EFFECTS OF ANTIBIOTICS

Drinking and potable water resources, which is extremely important for human health, is rapidly polluted in the current ecological balance. Therefore, these resources need protection under constant check and control. Since the water pollutants have changed day by dayin terms of variety and component, the current analysis technologies used for their control are unfortunately limited and are insufficientin some areas. In recent years, the environmental effects of endocrine-disrupting compounds are being investigated by scientists rather than the effects of classical pollutants and studies on the removal of endocrine disruptors (drug residues, antibiotics, etc.) from water and wastewater are highly appreciated (Vergili et al., 2005). Studies were intensified on advanced oxidation processes and ozone applications, that one of these processes (Baig et al., 2008; Gao et al., 2008).

Researchs on endocrine disrupting chemicals gained speed in 1990s. Although endocrine disruptors affect the reproductive system and thyroid function, it was determined that there are many other effects (Kelce and Wilson, 2001; Metzler and Pfeiffer, 2001). These organic pollutants are toxic, carcinogenic and can cause teratogenic effects in infants besides impairing the reproductive function (Büyükgebiz, 2014). Endocrine disruptors; exogenous substance or substance mixtures that alter the development and function of the endocrine system. These compounds are found naturally in the environment as well as in various synthetic and industrial products (Bigsby et al., 1999; Lee, 2007). Major species include organohalogens, pesticides, phthalates, antibiotics, contraceptives, diethylstilbestrol and cimetidine. In this study, antibiotic compounds were chosen due to they are considered as the most dangerous pollutant species for the microorganism resistance which have widespread use in our country and around the world.
Natural or chemical substances created by fungus or similar microorganisms, which stop the development of microorganisms and other organisms, and even kill them, are called "antibiotics". Antibiotics are compounds that have high potential to affect negatively both human health and environment in case they are consumed intensively and unconsciously. The most important negative effect for human health is that it contributes to the development of antibiotic resistant microorganisms at high level and triggers the emergence of new antibiotic resistant speciesat higher amounts. They are thrown by the urinary system and are easily accessible to the aquatic environments and all living organisms such as aquatic organisms are affected negatively by them. On the other hand, the use of antibiotics in other animals, especially in livestock, is also very high. In literature, only human use of antibiotics is approximately 200 million per year. Although there is no exact information about its other use and dosage, it is expected that this amount won't decrease. All of antibiotic species can be expected to have a unique environmental impact.
Antibiotics are among the most widely used drugs worldwide. 35% of health budgets of developing

countries are spent on antibiotics (Topal et al., 2015). In many developing countries, antibiotics are used incorrectly and excessively (Hart, 1998). In some countries, antibiotics can be sold even in markets (Saltoğlu, 2005). Release of antibiotics into the environment; depends on the dose used, the frequency of excretion from the body, the tendency to retain the solid matters and the metabolic ability of microorganisms in wastewater treatment plant for transformation(Daughton and Ternes, 1999). High antibiotic concentration disrupts the ecological balance by causing toxicity for the organisms in the ecosystem. After being used by humans, while some of them are used by the metabolism, the unused portion is excreted by the urine (Kümmerer, 2001, Kolpin et al.,2002).

In this way, they reach to the sewagesystem and from there to the treatment plants. If they are not biodegradable or cannot be removed in treatment plants, they can reach to the drinking water resources. In addition to the antibiotic drugs used in hospitals and houses, the sewage system and disposed drugs are the main sources of pollution (Holm et al., 1995). Thus, detection and treatment of antibiotics is very important environmental concern. Conventional treatment plants are inadequate in terms of efficiency for antibiotic removal which are used very often today, in Turkey and Northern European countries (Ternes, 1998; Kummer, et al., 2000, and Heber, 2002). In this case, various advanced treatment methods such as carbon adsorption, advanced oxidation processes (IOP), modern pressure-driven membrane processes, reverse osmosis and nanofiltration (NF/RO) are proposed as an alternative and innovative technological solution (Kosutic et al., 2007). Nowadays, antibiotics have an important role in increasing the strength efficiency of animals and in treatment processes and prevention of diseases. However, in order to accelerate the development of animals after 1950s, the widespread use of antibiotics as feed additives has led to the emergence of resistant species in susceptible bacteria (Akkan and Karaca, 2003).Turkey is one of the most prominent countries in use of antibiotics.

III. ELECTROCHEMICAL OXIDATION PROCESSES

For the electrochemical oxidation processes, anodes are used which are constitute of platinium (Pt), titanium dioxide (TiO_2), iridium oxide (IrO_2), lead dioxide (PbO_2), Ti-based alloy,graphite and boron doped diamond (BDD) with suitable electrolytes (NaCl, KCl et al.). Boron doped diamond anodes were started to use for treatment of pharmaceutical wastewaters in recent years highly, due to they produce weak sorbed hydroxyl, highly, that improves the oxidation of organic compounds (Eq. 1) (Zhu et al., 2016). Type of electrode, current density, pH value of the solution and electrolyte type and dose effect the electrochemical advanced oxidation processes (EAOPs) (Giusy et al., 2017).

$$BDD + H_2O \rightarrow BDD(^{\bullet}OH^{-})_{ads} + H^{+} + e^{-} \quad (1)$$

Electrochemical oxidation reactions occur in two ways as stated below;
i)direct oxidation:electrochemical reactions occur without any oxidants that means direct anodic electron transfer reaction.
ii)indirect oxidation: the reactions occur with oxidants (O_3, H_2O_2, chlorine, hypochlorite, $^{\bullet}OH$).

The testing studies of new materials on this subject are increasing in recent years. In particular, electrochemical ozone production is an area where remarkable developments are experienced. Electrochemical oxidation and ozone production are processes that could be carried out with stable and durable anodic materials. The electrolysis production of ozone was first obtained by Schönbein in 1840 by electrolysis of water in anode, similar to that in the electric arc. Equation (2) and (3) gives the formation of O_3 and $O_2$from the electrolysis of water.

$$O_3 + 6H^{+} + 6e^{-} \Leftrightarrow 3H_2O \qquad E_0: 1{,}51\ V \quad (2)$$

$$O_2 + 4H^{+} + 4e^{-} \Leftrightarrow 2H_2O \qquad E_0: 1{,}23\ V \quad (3)$$

However, the application of Sn/Sb/Ni-Ti anodes out of this area are very limited. These anodes are highly tested in electrochemical ozone production and are known to be more successful than older generation PbO_2 and Pt anodes. Namely; since 1840, the literature on this subject has been very limited and has been largely related to the use of PbO_2 and Pt & carbon based anodes.

IV. ELECTROCHEMICAL ADVANCED OXIDATIONCOMPARED TO OTHER ADVANCED TREATMENT METHODS FOR THE ANTIBIOTIC REMOVAL

For the removal of antibiotic compounds from wastewaters and control of bacteria developing resistance to the antibiotics,conventional treatment methods (physical, chemical, biological) and conventional disinfection processes (chlorination and UV) are inadaquate (Ternes, 1998; Kümmerer, et al., 2000 and Heberer, 2002). Due to this reason, advanced treatment methods such as carbon adsorption, advanced oxidation processes (AOP), membrane processes are proposed (Kosutic et al., 2007). However, unfortunately either the pollutants can be discharged into the environment in a more dangerous way as toxic intermediate products. In this way, advanced oxidation processes are known to be more effective in conversion of pollutants to final products than the other advanced treatment methods.

But, the need for high energy is the most serious problem with thesemethods. However, electrochemical advanced oxidation processes show both the conversion performance of pollutants to harmless products, the lower energy consumption need due to the use of direct current, the less need for additional chemicals and pH arrangement(Yonar et al., 2018). The studies made on this subject are stated below.

In particular, studies on cephalexin have been carried out with conventional processes. The removal of cephalexin by active carbon adsorption method was investigated by Kong et al. (2016) and it was observed that low concentration of activated carbon adsorbed approximately 95% of cephalexin. Guo and Chen (2015), evaluated the removal of cephalosporins from the green algae Chlorella pyrenoidosa by applying an activated sludge-algae combination system for the removal of cephalosporins in their study and obtained 94,9% cephalexin removal efficiency. The activated sludge process is another method for the removal of cephalexin and ampicillin antibiotic groups. With this method, the target antibiotics cephalexin and two sulfonamides were mainly removed by biodegradation in fresh water and salt water treatment systems. Ampicillin, norfloxacin, ciprofloxacin, ofloxacin, tetracycline, roxithromycin and trimethoprim were mainly removed by adsorption. However, the input concentrations used in this study were very low concentrations, such as 100 μg L^{-1}, and their removal efficiency (30-90%) was reported(Li and Zhang, 2010).In another study, the removal of 28 antibiotics in Brisbane, Australia was evaluated in two wastewater treatment plants (AAT) using conventional (activated sludge) and advanced (microfiltration/reverse osmosis) treatment methods, and inputs in wastewater;cephalexin (med 4,6 μg L^{-1}, frequency 100%, ciprofloxacin (med 3,38 μg L^{-1}, frequency 100%), cefaclor (med 0,5 μg L^{-1}, 100% frequency), sulfamethoxazole (med. 0,36 μg L^{-1}, frequency 100%) and trimethoprim (med 0,34 μg L^{-1}, frequency 100%) antibiotics were found to be dominant in wastewater inputs. The results showed that both treatment plants significantly reduced antibiotic concentrations with an average removal rate of 92% from the liquid phase (A.J., E.J., S.D., 2007).In Hong Kong's two wastewater treatment plants (AATs), 20 antibiotics were selected from seven antibiotic classes, and 1 year of composite samples (24 hours) were studied in different seasons. The antibiotics ampicillin, cephalexin, sulfamethoxazole, sulfadiazine, sulfamethazine, chlortetracycline and vancomycin were effectively eliminated in this study (52-100%). Ampicillin and cephalexin were effectively eliminated in 91-99% of the active sludge process (Bing andTong, 2011). However, there are some publications that report negative opinions about the removal of antibiotics biologically (Kim and Aga, 2007; Sukul and Spiteller, 2007). Because the concentrations studied in the publications mentioned above are relatively low. However, it is not clear in these studies whether an antibiotic of this value is also biodegradable or nonbiodegradable. Both increased high concentrations and bioaccumulation are highly likely to make the treatment of antibiotics difficult with conventional processes. According to Antoine et al. (2009), the elimination of antibiotics was attributed to three different mechanisms: (i) rapid detachment of the b-lactam ring (reduction), (ii) adsorption of AMX and AMP to iron corrosion products, and (iii) AMX and AMP, retention with iron hydroxides (precipitation with iron corrosion products). NaCl supplements accelerated the consumption of Fe^0 and shortened the life of Fe^0 treatment systems.In one study, fenton and photo-fenton reactions of antibiotic ampicillin (AMP) were discussed. The most favorable conditions for the fenton and the photo-fenton reactions were pH 3,5, about 400 mol L^{-1} H_2O_2 and 87 mol L^{-1} Fe (II). The ampicillin was completely removed after 10 minutes and 3 minutes for fenton and photo-fenton reactions under the optimized conditions.For both systems having a high degree of degradation (close to 90%), a very similar removal profile was observed in the first 2 minutes of reaction. This observation was confirmed by COD and TOC removal during reactions (Oscaret al., 2010). In another treatment, ampicillin antibiotic was used to treat with H_2O_2 and modified granular activated carbon. When H_2O_2 and activated carbon were used together, COD and TOC removal efficiency was found to be 91,2% and active carbon used alone was 79,5%. The use of activated carbon in combination with H_2O_2 gave a more effective result than using it alone.Macrolide antibiotics are also widely used in our country (1 g per capita per year). It is reported in the literature that the degradation of them in wastewater treatment plants is difficult. It is possible that the removal by ozone is still possible. However, it is clear that the cost of operating this method is higher than the cost of operation (Lange et al., 2006). Lange et al. (2006), performed ozonationof clarithromycin from macrolide antibiotics. The optimum pH was determined as 7. Clarithromycin antibiotic contains dimethylamino group, making it easier to bind to ozone. Ozonation products were characterized by HPLC/MS-MS. In another study, deterioration of macrolide antibiotics with ozonation under various conditions such as concentration, contact time, pH, and H_2O_2/O_3 molar ratio was investigated. O_3 is dominant oxidant and consistent with aqueous concentration, higher at low pH. The degradation of erythromycin having a completely saturated structure is slower and more effective at higher pH or additional H_2O_2 under conditions contributing to the removal of the saturated compound. The optimum pH thus, depends on the target compounds to be treated and buffered pH 7

facilitates the removal of all tested compounds (Yu-Chen et al., 2009).Two pharmaceutical wastewater treatment plants were selected in China's Zhejiang Province to assess the removal mechanisms of fluoroquinolone antibiotics. In the wastewater treatment plant A, bioactive sludge was used in anoxic and aerobic units in the movable bed biofilm reactor and biological units were used under anaerobic, aerobic and anoxic conditions in pharmaceutical wastewater treatment plant B. Wastewater samples and solid samples (slurry and suspended solids) were analyzed using solid phase extraction and ultrasound performance liquid chromatography HPLC-MS spectrometry. Ofloxacin (OFX) was detected in each stage of the pharmaceutical wastewater treatment plant A and enrofloxacin and ciprofloxacin were detected in pharmaceutical wastewater treatment plant B. The concentrations of fluoroquinolone antibiotics ranged from 0,32 μg L^{-1} to 5,7 mg L^{-1}. Although fluoroquinolones were substantially removed in biological units (94,5% to 99,9%), the final effluent was discharged in large quantities (up to 88,0 ± 7,0 μg L^{-1}) and in dewatered sludge (up to 0,85 ± 0,24 mg kg^{-1}) (Guo et al., 2017).

Promisingfuture processesare advanced oxidation and electrochemical oxidation processes.In a study of antibiotics using fluoroquinolone group, the most commonly used antibiotic groups of three different classes (penicillins, cephalosporins and fluoroquinolones) (in 40 μmol L^{-1}) were treated by using, Ti/IrO_2 anode and an electrochemical system with a Zr cathode in the presence of NaCl (0,05 umol L^{-1}). Electrochemically produced chlorine has affected the breakdown of antibiotic rings. The procedure reduced more than 90% of the initial concentration of antibiotics following the decay sequence after only 20 minutes (fluoroquinolones>penicillins>cephalosporins). The application of the treatment to the synthetic hospital wastewater and antibiotic containing sea water showed that high amounts of chloride ions in sea water accelerated pollutant degradation. Whereas, the presence of urea and ammonium in the hospital wastewater delayed the removal of these antibiotics (Serna-Galvis Berrio-Perlaza and Torres-Palma, 2017). In a study by Yadav et al. (2018), the removal of certain fluoroquinolone group (ciprofloxacin, ofloxacin, norfloxacin) antibiotics from the aqueous solution was investigated using graphene oxide. Fourier transformed infrared spectroscopy, powder X-ray diffraction, thermogravimetric analysis and high-resolution transmission electron microscopy were characterized by graphene oxide. In studies performed, it was observed that the effect of pH on graphene oxide in adsorption of fluoroquinolones was significant. Optimum removals of ciprofloxacin and norfloxacin were determined at pH 7 and pH 4 for ofloxacin. However, it should not be forgotten that, the most important disadvantage of the processes studied is that the organic compounds with high persistence are further concentrated by phase change rather than by complete oxidation. This allows the danger to grow exponentially in the environment. However, completely oxidation ideal for these and similar pollutants. Tu et al. (2015), investigated the toxicity of pharmaceuticals ($C_{20}H_{18}NO_4$) in the synthetic wastewater, because of the acute toxicity of pharmaceutical and personal care products and are occuring resistant genes of bacteria to the antibiotics and could not be treated in the treatment plants. In their electrochemical oxidation, the Pt/Ti anode was compared with RuO_2/Ti, IrO_2/Ti and $RuIrO_2$/Ti anodes, and as a result, Pt/Ti under 2,5 V conditions and current density was much more successful than other anodes in terms of removal efficiency. Again in this study, NaCl and Na_2SO_4were used as electrolyte in for the of removal of berberin and NaCl gave much better results. 70% berberine removal was provided in Pt/Ti anodized Na_2SO_4 solution for 70 minutes, while 90% removal was provided in the NaCl solution for 90 minutes. It is possible to use many anodes or cathodes in electrochemical oxidation for treatment processes. Estrada et al. (2012), investigated the removal of cephalexin using the electro-Fenton process by Ru_2/Ti anodic oxidation as an advanced oxidation method. An effective COD removal could not be achieved, but in a different biological treatment process, COD removal was achieved sufficiently for obtaining biodegradability. Foller and Tobias (1982),studied electrochemical ozone oxidation process and they obtained high current efficiency (50%) using electrochemical cells, PbO_2 alloy anode, with 7,3M HPF6 solution and at 0 ºC temperature. However, it will be appreciated that the applicability of working conditions is not possible. Both the temperature is very low, and the electrolyte used for the electrochemical ozone production concentrated scientists away from this alloy. However, a current efficiency of 47% was reported by Fujishima et al. (2007), using polymer electrochemical membrane (PEM) cell (reactor) and boron-doped diamond anode at room temperature. Unfortunately, despite their high efficiency, high cell voltages were needed in these studies (20 - 25V) (Arihara et al., 2007). These high voltage values are also found in systems where electrochemical ozone production is performed using materials such as PbO_2, Ti/MOx/Pt, graphite, Pt, or alloys (da Silva et al., 2003; Stucki et al., 1985; Kaneda et al., 2005; Silva et al., 2006).The production of anodes wasdone by dip coating. The Ti substrate was prepared by immersion in the coating solution by preparing Sn, Sb and Ni chloride in a mixture of ethanol/HCl and pyrolysis at a temperature of 520 ºC and repeating this process 8 times. This really points to a remarkable activity of the classical electrode under ambient conditions. However, the anodes showed little stability. In a study,Chen et al. (2004), made by the use of Ni for the production of active surfaces for

ozone production is very important. Wang et al., (2005) could not determine the Ni, Sn/Sb: 7:1 (molar ratio) while, Ni-doped SnO_2 indicated that the actual concentration of Ni may deviate from the expected concentration. Chen and Chan (2004) reported that Sb-doped SnO_2 anodes (molar ratios; 500:8:1-Sn/Sb/Ni) alloyed to a 1 cm x 1 cm titanium screen containing very little Ni produced ozone with a flow efficiency of 35%. Ozone production was performed at room temperature (25 °C) with 0,5 M sulfuric acid solution and <3V cell voltage. After this date, this alloy became the main material for the production of electrochemical ozone. Because, in the production of electrochemical ozone with these anodes, the electrode must be stable and remain stable at the ozone formation voltage of 1,51 V. The other anodes are either not stable or are inhibited by the formation of 1,23 V oxygen after a period of time, or the stability of 1,51 V is achieved by lowering the temperatures. This is why the Sn/Sb/Ni-Ti anodes are promising. Another advantage of these anodes is that they complete the endurance tests more successfully than other anode materials. (Christensen et al., 2013; Christensen et al., 2014). In order to make these anodes more resistant in the studies carried out, both the flow efficiencies (around 40%) and their strengths (1000 hours) were increased by using oxide forms of Sn, Sb and Ni elements. The results of the studies are presented in the literature. (Christensen et al., 2013, Christensen et al., 2014). However, it is interesting that, this anode (Sn/Sb/Ni-Ti), which exhibits serious performance in such a challenging area, there has been far little testing in both synthetic and real wastewaters. The majority of the studies are on textile dyestuffs and phenol compounds. One of the studies carried out on this subject and carried out by Zakaria and Christensen (2014) and 100% removal efficiency of 1000 mg L^{-1} reactive blue 50 dyestuff fed to membrane electrochemical electrode reactor system was provided in 5 minutes using Sn/Sb/Ni anode - platinum titanium cathode. It was also reported that a power of 8 kWh kg^{-1}. In the research made by Basiri and Abbasi (2012), ozone was produced by electrochemical oxidation method and the decomposition of anthraquinone dye was investigated using reactiv blue 19 (RB19) dye. Sn/Sb/Ni-Ti electrode was used as anode for ozone formation. The ozone concentration and the RB19 decay were increased as the applied voltage increased by 1 M $HClO_4$ at electrolysis time and room temperature. Color and COD removal was 48,2% after 3 minutes and 100% after 15 minutes reaction time. In the light of these knowledges, there is a serious expectation to investigate the removal of the most commonly used antibiotics both in human and animal health.Yonar and Sivrioglu (2017), tested the Sn/Sb/Ni-Ti anodes for electrochemical ozone oxidation of dairy plant wastewaters.Electrochemical oxidation results revealed that after 15 min the degradation efficiency of COD could reach up to 99% at pH 4 and temperature of 25°C which are the optimum conditions.Silvaet al. (2018), investigated the roles of the anode material, boron-doped diamond (BDD), with different boron (B) and substrate silicon (Si) or niobium (Nb), and dimensionally stable anode (DSA) for electrochemical oxidation of norfloxacin (NOR). The best current efficiency results were obtained for Si. However, Nb presented a similar current efficiency and 60% lower energy consumption. Perea et al. (2018) investigated cephalexin degradation using active chlorine produced on ruthenium and iridium oxide anodes and they found degradation rates of 22,5, 3,96, and 0,76 μmol L^{-1} min^{-1} were observed fordeionized water (DW), municipal wastewater (MWW) and urine respectively. Even if 16% of initial TOC was removed, BOD_5 tests proved the ability of electro- generated Cl_2-active to transform the antibiotic into biodegradable compounds.

CONCLUSIONS

Effects of endocrine disruptor pharmaceuticals have been investigated by the researchers rather than the effects of classical pollutants,in recent years.For the microorganism resistance and having widespread use in Turkey and around the world,antibiotics were considered as the most dangerous types of endocrine disruptor pharmaceuticals and removal of them with electrochemical advanced oxidation processes and combinations of them with AOPs were evaluated. EAOPs seem to be promising methods for degradation of antibiotics and other toxic pharmaceuticals due to having up to fully mineralizations at shorter reaction times and less need for additional chemicals and additional pH arrangement phases. Additionally, it was seen that the application of Sn/Sb/Ni-Ti anodes are very limited in literature which were highly tested in electrochemical ozone production and are known to be more successful, cheaper and more practical than older generation PbO_2, Pt and boron doped diamond anodes.

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