

Electrochemical treatment of cefalexin with Sb-doped SnO₂ anode: Anode characterization and parameter effects

Ayşe Kurt^{*1}, Hande Helvacioğlu² and Taner Yonar^{**2}

¹Central Research Laboratory for the Scientific and Technological Supports, Bursa Uludag University, Gorukle Campus, 16059, Bursa, Turkey

²Environmental Engineering department, Bursa Uludag University, Faculty of Engineering, Gorukle Campus, Bursa 16059, Turkey

(Received February 22, 2021, Revised September 24, 2022, Accepted September 27, 2022)

Abstract. In this study, it was aimed to evaluate direct oxidation of aqueous solution containing cefalexin antibiotic with new generation Sn/Sb/Ni: 500/8/1 anode. The fact that there is no such a study on treatment of cefalexin with these new anode made this study unique. According to the operating parameters evaluation COD graphs showed clearer results compared to TOC and CLX and thus, it was chosen as major parameter. Furthermore, pseudo-first degree kd values were calculated from CLX results to show more accurate and specific results. Experimental results showed that after 60 min of electrochemical oxidation, complete removal of COD and TOC was accomplished with 750 mg L⁻¹ KCl, at pH 7, 50 mA cm⁻² current density and 1 cm anode-cathode distance. Also, the stability of the Sn/Sb/Ni anode was evaluated by taking SEM and AFM images and XRD analysis before and after of electrochemical oxidation processes. According to the results, it was not occurred too much change on the anode surface even after 300 h of electrolysis. Thus, it was thought that the anode material was not corroded to a large extent. Furthermore, the removal efficiencies were very high for almost all the time and conditions. According to the results of the study, electrochemical oxidation with new generation Sn/Sb/Ni anodes for the removal of cefalexin antibiotic was found very successful and applicable due to require less reaction time complete mineralization and doesn't require pH adjustment step compared to other studies in literature. In future studies, different antibiotic types should be studied with this anode and maybe with real wastewaters to test applicability of the process in treatment of pharmaceutical wastewaters containing antibiotics, in a better way.

Keywords: anode stability; cefalexin; current density; electrochemical oxidation; Sn/Sb/Ni anode

1. Introduction

In worldwide, pharmaceuticals (antidepressants, analgesic, antidiabetics, antibiotics, contraceptives, painkillers, growth regulators, drugs, tranquilizers and impotence) are one of the most important and dangerous problems causing to the environmental contamination and toxicology (Aydin *et al.* 2018, Souza *et al.* 2017). Drug and antibiotic residues have endocrine disrupting properties having serious effects on reproductive system and thyroid function of human and animals. These organic pollutants are toxic, carcinogenic and may cause teratogenic effects in infants as well as impair the reproductive function (Kurt and Yonar 2016). Antibiotics are the most important pollutant compounds among the other pollutants for causing to the microorganism resistance in the environment with having stability and endocrine disruptor properties (Tran *et al.* 2016, Vergili *et al.* 2005). Antibiotics can not be metabolized in the living organisms, or they are excreted as an intermediate product depending on their chemical

structures (Mompelat *et al.* 2009). They enter to the receiving environment by treated or untreated wastewater streams, generally. Continuous antibiotic intakes into the environment cause unexpected adverse effects on aquatic and land-based organisms. High concentration levels may persist for long periods of time (Petrović *et al.* 2005).

In Europe, cephalosporin group is accepted as the second most prescribed antibiotic class and among them, cefalexin (CLX) is the most prescribed (Weist and Högberg 2016). According to the EHI (Weist and Högberg 2016), cefalexin is one of the most prescribed antibiotic and is produced in huge quantities for human and animal treatment in pharmaceutical industries. They are used widely in Turkey and throughout Northern European countries for the protection and treatment of human and environmental health. The rate of usage of CLX in Turkey is relatively higher than in other countries (Kurt and Yonar 2016). Therefore, in this study it was studied with cefalexin antibiotic.

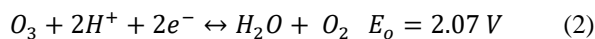
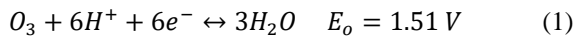
Due to these facts, antibiotics are a major risk especially in the aquatic environment. However, conventional treatment methods (physical, chemical and biological) are inefficient in terms of removal of these endocrine disrupting compounds. Also conventional disinfection processes, such as chlorination and UV applications, are also not effective in controlling of resistance developing through bacteria. In this respect, advanced treatment methods (active carbon

*Corresponding author, Ph.D.,
E-mail: kurtayse1987@gmail.com

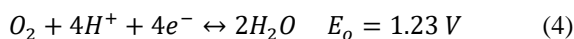
**Co-corresponding author, Professor,
E-mail: taneryonar@yahoo.com

adsorption, advanced oxidation, membrane processes) are more advantageous than the other conventional methods, due to complete mineralization capacity. However, these advanced processes need usually high energy consumptions and operational cost (Christensen *et al.* 2009). In this way, Electrochemical oxidation processes are promising methods because of their easy applicability and low energy requirements (Isarain-Chávez *et al.* 2017, Souza *et al.* 2017). However, there is a lack of studies in the literature about electrochemical oxidation of wastewaters especially with new generation Sn/Sb/Ni-Ti anodes. Also, there is no any investigation about electrochemical degradation of cefalexin antibiotic with new generation Sn/Sb/Ni-Ti anodes.

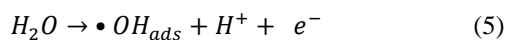
Indeed Sn/Sb/Ni-Ti anodes were first used for electrochemical ozone generation and it was found very successful results (Christensen *et al.* 2013). However, there is no precise and quantitative analytical evidence on the composition of Ni/Sb-SnO₂ anodes to establish the relation between structure/activity correlations, thus, efforts to understand the mechanism of ozone formation in these materials would remain speculative for a while. However, Parsa and Abbasi (2012) assumed the presence of Ni(III) in Ni/Sb-SnO₂ anodes without experimental evidence and a mechanism by which Ni(III) facilitates the adsorption of molecular oxygen; water is then oxidized to the •OH radicals in adjacent Sb(V) regions, which react with adjacent adsorbed O₂ to give •HO₃ radicals rapidly oxidized to O₃ (Parsa and Abbasi 2012). The occurring of these reactions are possible in two way: as direct electrochemical oxidation (anodic oxidation) and indirect oxidation. Also, the ozone formation reactions occur at anode (Eq. 1 and 2) with cathodic reactions (Eq. 3).



Anodic oxidation (direct electrochemical oxidation): direct electrochemical oxidation of aqueous solution of organic compounds is recommended at low potential values before water oxidation to oxygen molecule stated in Eq. 4.



•OH radicals occur at anode by oxidation of water as stated in Eq. (5).



Eqs. (1), (2) and (3) show that ozone could be produced electrochemically with water electrolysis. O₃ occurs on the anode surface and in water by preventing the O₂ formation. According to the Eq. (2) oxygen occurs at lower voltages than ozone need (Parsa and Abbasi 2012). Occurrence of all these electrochemical reactions are affected directly from electrode material, configuration of the reactor, current efficiency, pH, salt content etc. (Cui *et al.* 2009). Anode material is one of the most important parameter among these and it should be strong enough for ensuring

polarization. Several anodic materials were used by researchers for anodic oxidations, such as; PbO₂, platinum (Pt), gold (Au), lead (Pb), SnO₂, boron doped diamond (BDD) and carbon type anodes. Although BDD anodes showed satisfying results for antibiotic removal, they have high capital cost and not are practical as the Sn/Sb/Ni-Ti anodes (Wirzal *et al.* 2013). In contrast to BDD anodes, Sn/Sb/Ni-Ti anodes are cost-effective. With using Sn/Sb/Ni-Ti anodes, 37% current efficiency can be reached at room temperature (Abbasi *et al.* 2014). At this respect, Sb-doped SnO₂ anodes are advantageous with their cost efficiencies and practical application. For all these reasons mentioned, the aim of this study is to investigate the treatability of cefalexin in wastewaters with using new generation Sn/Sb/Ni-Ti anode. Thus, it was planned to study on synthetic wastewater containing cefalexin antibiotic with direct and indirect anodic oxidation by using Sn/Sb/Ni-Ti anode.

2. Materials and methods

2.1 Chemicals and other solutions

In this study, it was prepared synthetic wastewater containing cefalexin antibiotic and the electrolytes (NaCl and KCl) for the electrochemical oxidation processes. Cefalexin antibiotics were provided from a local pharmacy (Duzce, Turkey). Tin (IV) Chloride Pentahydrate (SnCl₄.5H₂O) and Nickel (II) oxide (NiO) were purchased from Alfa Aeser Company (Massachusetts, USA). Sodium chloride (NaCl), potassium chloride (KCl), antimony (III) oxide (Sb₂O₃), hydrochloric acid (HCl), formic acid (CH₂O₂), sulphuric acid (H₂SO₄), oxalic acid (C₂H₂O₄) and ethanol (C₂H₅OH) were supplied from Merck (Darmstadt, Germany). All of the chemicals were at the purity of ≥99%. Millipore Milli-Q (18MΩ cm) ultrapure water was used for the preparation of aqueous solution of CLX and all of the other solutions. The concentration of the CLX in the aqueous solution was 50 mg L⁻¹. Trovo *et al.* (2011) used 50 mg L⁻¹ amoxicillin active substance concentration in synthetic wastewater for the advanced oxidation with Photo-Fenton (Trovo *et al.* 2011). Additionally, Goncalves *et al.* (2012) studied the catalytic ozonation of 50 mg L⁻¹ sulfamethoxazole in synthetic wastewater (Goncalves *et al.* 2012).

2.2 Preparation of the anodes

At this study, Sb-doped SnO₂ anodes were prepared by pyrolysis with pyrolysis solution containing Sn/Sb/Ni in molar ratios of 500/8/1 according to the prescription of the University of Hong Kong (Wang 2006). They stated that, Sb-doped SnO₂ anodes are advantageous with their cost efficiencies and practical application. For this process titanium materials were coated by the pyrolysis solution (Wang 2006). First of all, titanium materials were cut into size of 2.5 cm × 2.5 cm (3Ti7-077FA material, Dexmet, USA). For the removal of impurities over the titanium materials, they were immersed into the boiling oxalic acid solution for a moment. At the next stage, titanium materials were sonicated in an ultrasonic bath for 3

times for 10 minutes (without rinse between the sonic periods). Then dried at room temperature for further dip coating process. Then, titanium materials were immersed into a pyrolysis solution, of which molar ratio; 500/8/1: Sn/Sb/Ni for 2 min and dried in an oven at 105 °C temperature (preheated) for 15 min. Then it was placed in a furnace at 520 °C for 15 min for annealing. The coating cycle was repeated for 19 times and final cycle, 20th was carried out for 75 min in the oven (Christensen *et al.* 2013). Cathode materials were supplied (5 × 5cm platinized titanium) from NRK Electrochem (Cornwall, UK).

2.3 Electrochemical oxidation

250 mL beakers were used for the electrochemical processes and the electrodes (anode and cathode) were placed inside the beakers mutually. The oxidation process was started by direct immersion of the anode and cathode into beaker filled with antibiotic aqueous solution. All these experiments were made at 25°C and atmospheric pressure. The current used in electrochemical processes was provided with DC power supply (Extech Instruments 382280). The samples were taken periodically every 5, 30, 60 and 90 min during anodic oxidation process to evaluate their COD, TOC and CLX removal efficiencies.

2.4 Analytical measurements

TOC analysis were made by TOC analyser (TOC-L, Shimadzu, Kyoto, Japan). pH values were measured by pH-meter (Cyberscan, UK). Analytic analysis of CLX in the aqueous solutions were made by using UPLC (Ultra performance liquid chromatography) with photo diode array detector (PDA) (Thermo-scientific, Massachusetts, USA). 254 and 270 nm wavelengths were chosen for detector measurements. UPLC column properties are Hypersil GOLD, C-18 (50 × 2.1 mm; 1.9 μm) (Thermo-scientific, USA). The column temperature was arranged to be 35°C. Mobile phase solution was prepared with water including 0.1 % formic acid and methanol, [MeOH:H₂O]: 40:60 (v/v)]. 0.2 mL min⁻¹ flow rate was chosen for UPLC analysis. COD measurements were carried out according to the Standard Methods (Federation and Association 2005). All measurements were made in triplicate. EDS (Energy Dispersive Spectroscopy) (EDAX, USA), SEM (Scanning electron microscope) (Philips XL 30 SFEG, Netherlands), hpAFM (high performance atomic force microscopy) (NanoMagnetics, Turkey) and XRD (X-ray powder diffraction) (Rigaku Smartlab, ABD) were used for imaging and to perform qualitative and quantitative characterization of the anode. The energy consumption per unit COD removed (E_{COD}) was calculated according to the formulation, stated below (Eq. 6):

$$E_{COD} = (E_{cell} \times I \times t) / (V \times \Delta COD) \quad (6)$$

2.5 Kinetic evaluation

To obtain the pseudo-first degree kinetics during the application of electrochemical oxidation of CLX, kinetic coefficient was determined according to the formulation stated below (Eq. 7):

$$\ln(C/C_0) = k_d \times t \quad (7)$$

3. Results and discussion

3.1 SEM-EDS, AFM, and XRD analysis

The development of nanocomposites for the engineering applications such as mechanical, optical, electrical and magnetic processes is promising (Letti *et al.* 2017). In this regard, electrochemical oxidation processes with nanocomposites are promising because of their easy applicability and low energy requirements (Isarain-Chávez *et al.* 2017, Souza *et al.* 2017). In this study it was carried out electrochemical oxidation of antibiotics in aqueous solution with nanocomposite novel Sn/Sb/Ni-Ti anodes.

The weight and atomic percentages and the peak intensities in Fig. 2(a) and (b) were given in Table 1 for anode characterization; the peaks of Sn, Ni and Sb elements were identified by the analysis of anode materials coated by electrodeposition of ethanolic SnCl₄, NiO and Sb₂O₃. Coating on the materials (Ni/Sb-SnO₂) was thin to enough detection of Ti underlying. Typical SEM micrographs of the anode intersections (assuming thicker coating than strands) (Christensen *et al.* 2013) at various magnifications (×500, ×2000 and ×5000) prepared using the precursor solution were shown in Fig. 1 for used (unclean) and unused (clean) anodes, respectively. It was observed that the coating process of the materials caused a cracked morphology for clean anodes as stated in other studies (Kurt and Yonar 2016). It was thought that it was occurred by thermal shocking which is seen generally during cooling suddenly after taking of the anodes from the oven. Cracked morphology is seen in thicker anode types generally with large splits having three dimensional (3D) view (Christensen *et al.* 2012). However in unclean anodes, a smoother surface was observed that resulting from the coating of surface area with ions passing from the solution. At used material it was assumed that the surface of the electrode was filled with other ions (carbon) and salts (Fe₃(PO₄)₂(OH)₂) thought to be occurring in the solution.

Christensen *et al.* (2013) investigated the effect of Ni and Sb oxide precursors and composition on ozone production in 1,0 M HClO₄ (Christensen *et al.* 2013). Typical SEM images of the anodes (93.3, 6.0 and 0.7% Sn, Sb and Ni respectively) were taken of the intersection (×5000 magnification) showed cracked morphology, while the coating on strands presented a smoother morphology assuming thinner coating than the intersection. With EDS spectra of the anode material, the peak with 4.52 eV may be sourced from underlying Ti, that could be derived from the thinner catalyst coating than the strands. Christensen *et al.* (2012) studied the effect of Ni/Sb-SnO₂ loading on electrocatalyst and they observed with the SEM images that the electrode was thicker and had very little pores (assuming thicker electrode at least is porous) having typical “cracked morphology” with deep crevices (Christensen *et al.* 2012). Moreover, it was observed that Ni/Sb-SnO₂ coating was thin sufficiently to able to detect Ti element underlying. Zhi *et al.* (2017) investigated the degradation of tetracycline antibiotics with Ti/SnO₂-Sb anode and used the sol-gel technique to coat the anode (Zhi *et al.* 2017). SEM images

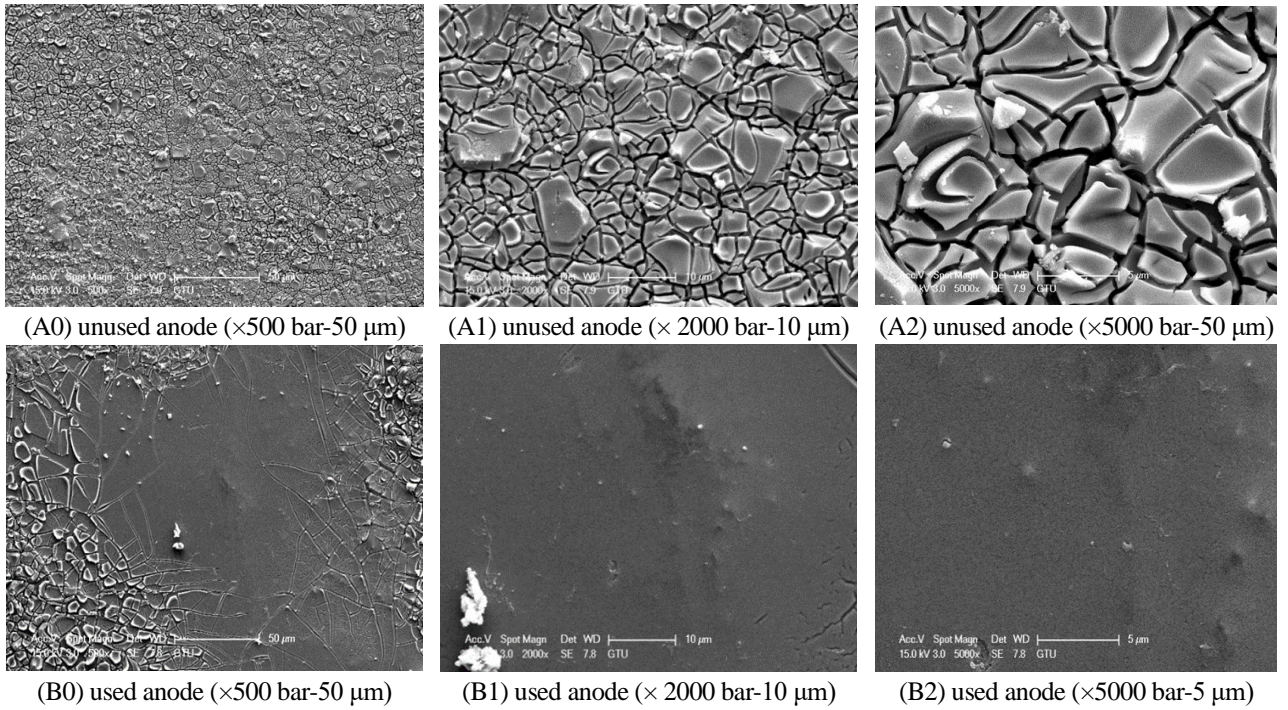
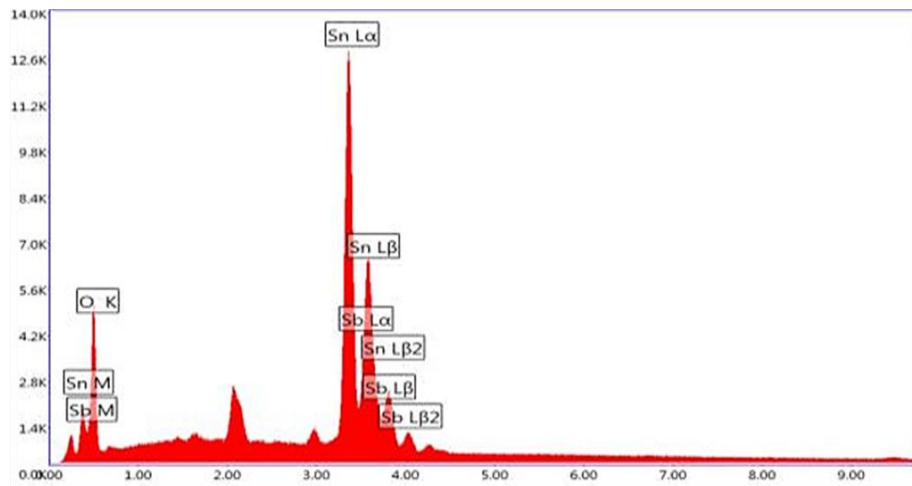
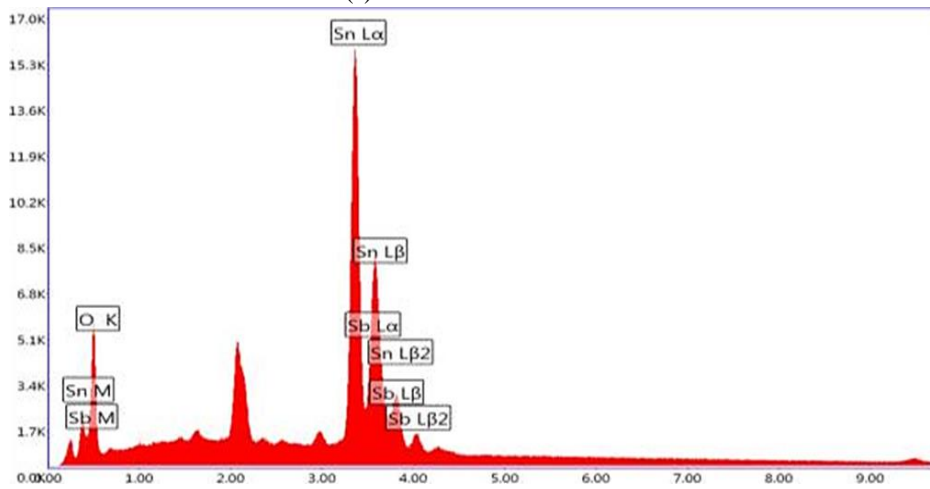


Fig. 1 Typical SEM images of the anodes



(a) unused anode material

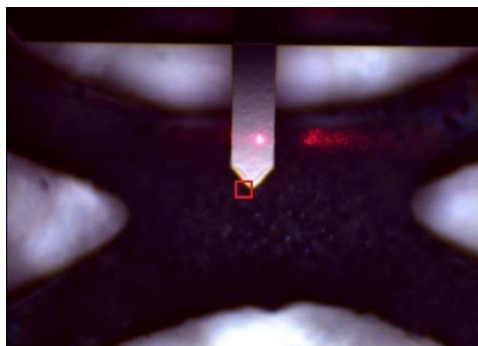


(b) used anode material

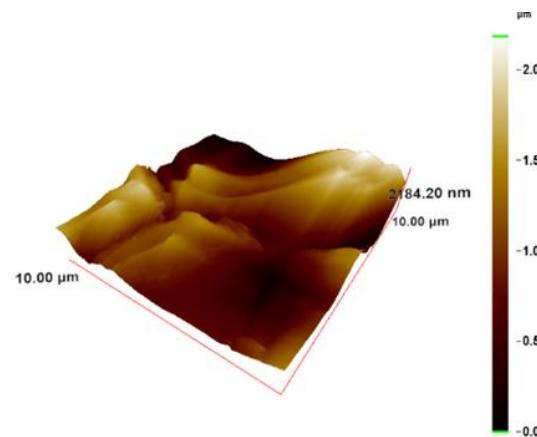
Fig. 2 EDS spectra of the anodes from the intersection

Table 1 Weight and atomic percentages and the peak intensities of EDS spectra of the anodes

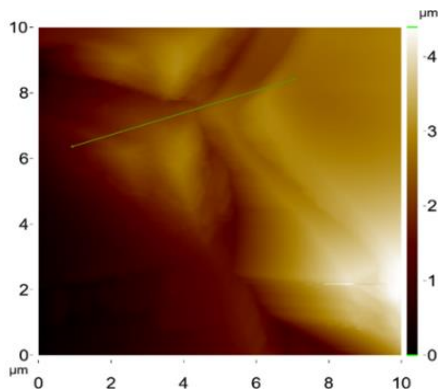
	Element	Weight %	Atomic %	Net peak int.	Net peak int. error
Unused anode material	Sn	81.82	49.83	2683.22	0
	Sb	8.15	4.84	239.81	0.06
	Ni	6.02	27.20	276.68	0.006
	Ti	25.075	7.52	345.855	0.008
Used anode material	Sn	82.65	52.1	3270.5	0
	Sb	8.18	5.03	290.4	0.06
	Ni	1.84	8.58	100.97	0.002
	Ti	22.925	107.2	1262.15	0.02



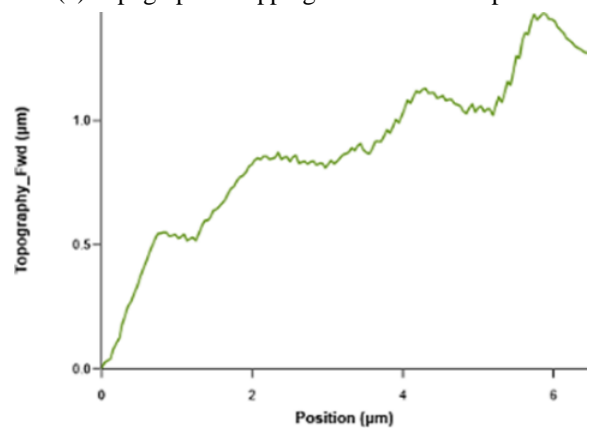
(a) AFM image of measurement point



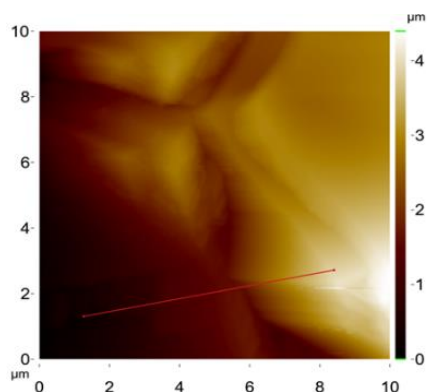
(b) Topographic mapping of measurement point



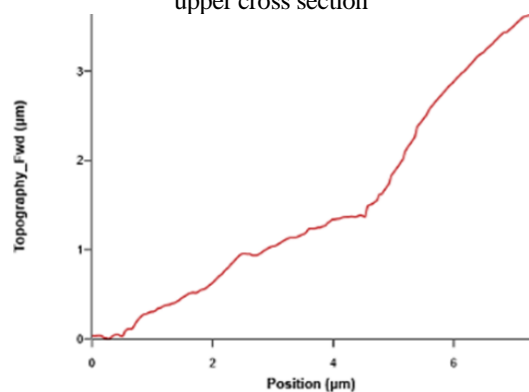
(c) AFM image of upper cross section



(d) Topographic height change (μm) related to position (μm) of upper cross section



(e) AFM image of bottom cross section



(f) Topographic height change (μm) related to position (μm) of bottom cross section

Fig. 3 AFM images and analyzes of intersection on surface of the unused anode

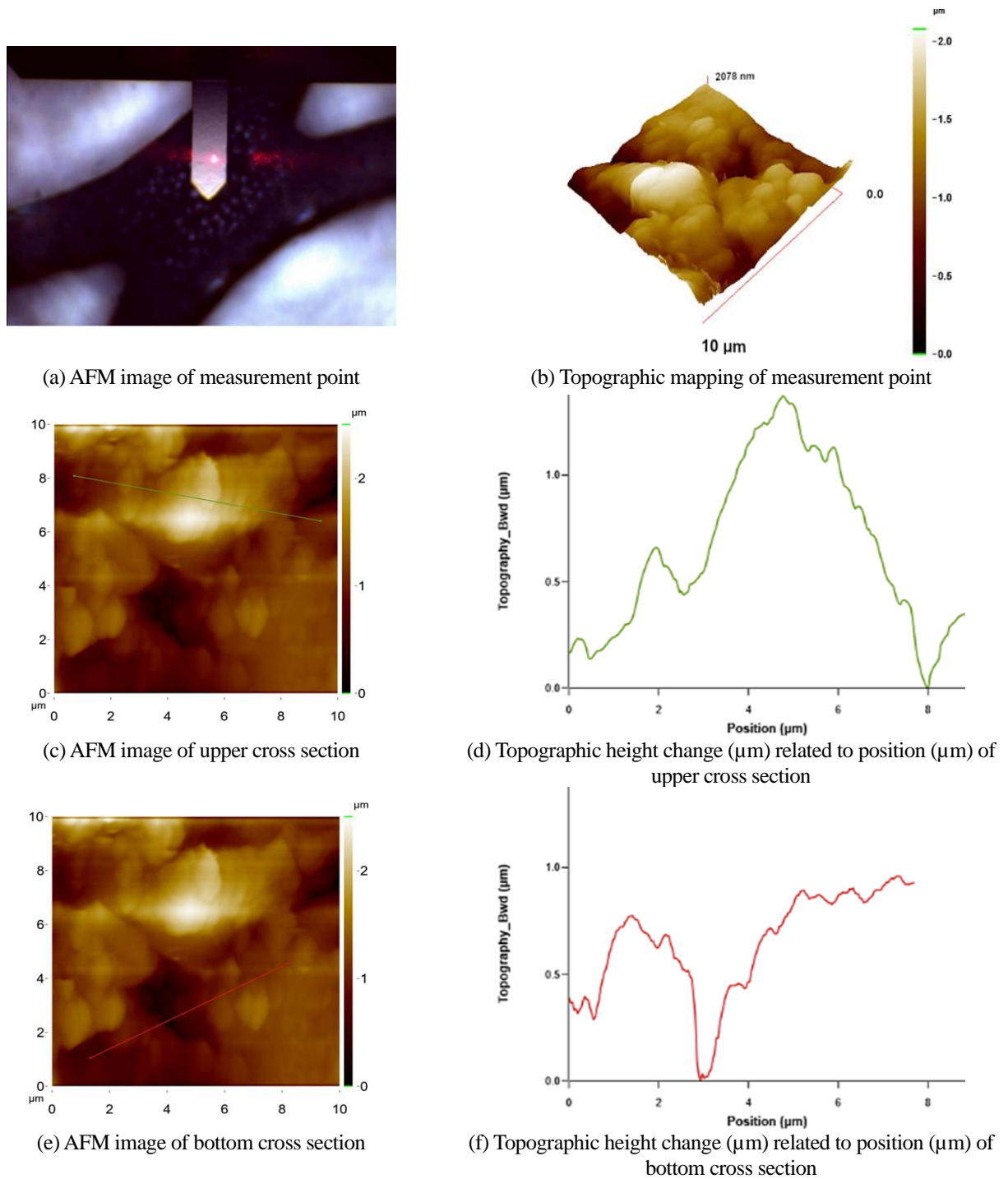


Fig. 4 AFM images and analyzes of the intersection on surface of the used anode

revealed that the anode surface was generally solid and smooth, although there were some cracks on the surface ranging in size from 1-10 μm . In addition, it was concluded that, the formation of these cracks could cause gradual inhibition of the anode during the electrochemical process. Qian *et al.* (2019) reported that the Ti substrate surface pretreated with Ti/SnO₂-Sb₂O₃/PbO₂ anode has a crusty and irregular shape, which is predicted to occur as a result of oxalic acid application. Thus, they stated that it would be beneficial to add SnO₂-Sb₂O₃ and PbO₂ as interlayers and active layers in order (Qian *et al.* 2019).

In addition, Figs. 3 and 4 show the AFM images showing the topographical height changes during the electrochemical oxidation process on the anodes. It was observed that, there is a difference between the used and unused anode plates in terms of topographic height. While topographic height differences tend to increase in parallel at the unused anode; some irregularities were observed in the (a) upper section and (b) lower section on the used anode, which is thought to be due to the ion transfer in the solution. However, it is known that the physicochemical properties of the anodes are directly related to the preparation methods. Composition ratios, particle size,

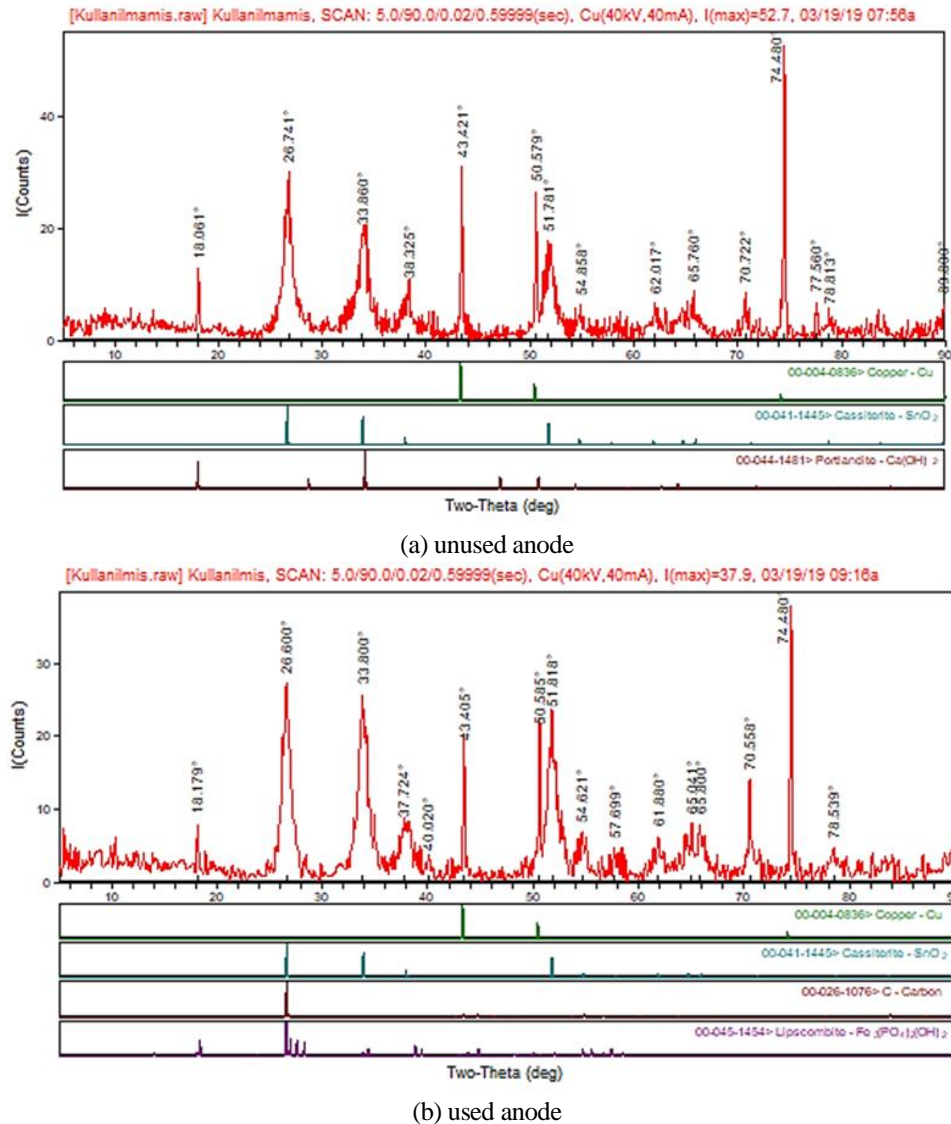


Fig. 5 XRD analysis of the intersections on surface of the anode

surface structure, specific surface area and bonding force directly affect the anode performance (Shmychkova *et al.* 2019).

Fig. 5 shows the XRD results of unused and used Sn/Sb/Ni-Ti anodes. Thus, XRD results stated in this figure confirmed the other EDS findings. It was observed that surface of the used anodes is filled with carbon and salts ($\text{Fe}_3(\text{PO}_4)_2(\text{OH})_2$), which are the other ion types found in the solution.

3.2 The anode stability

The stability of the anode is very important when electrochemical oxidation and ozone generation are used in the acidic environment of antibiotic containing solutions at high anodic potential. The stability of the Sn/Sb/Ni anode was evaluated by taking SEM images before (Fig. 1a) and after (Fig. 1b), AFM images before (Fig. 3) and after (Fig. 4) and XRD results before (Fig. 5a) and after (Fig. 5b)

NaCl and KCl electrolytes were used for electro-

oxidation reactions of cefalexin (Basiriparsa and Abbasi 2012, of electrochemical oxidation of cefalexin. Observation and comparison of SEM and AFM images and XRD results showed that it was not occurred too much change on the surface of the electrode even after 300 h of electrolysis. Thus, according to the results, it was determined that the anode material was not corroded to a large extent. Additionally, it was concluded that the removal efficiencies were very high for almost all the time and conditions.

3.3 Comparison and evaluation of NaCl and KCl electrolyte addition

According to the researchers, salt (electrolyte) concentration and type (NaCl, KCl) effect the electrochemical oxidation processes positively by increasing the conductivity. In this regard, Cl^- anion is particularly important as an inorganic ion, commonly found in aquatic environment and wastewaters. For this reason, Christensen

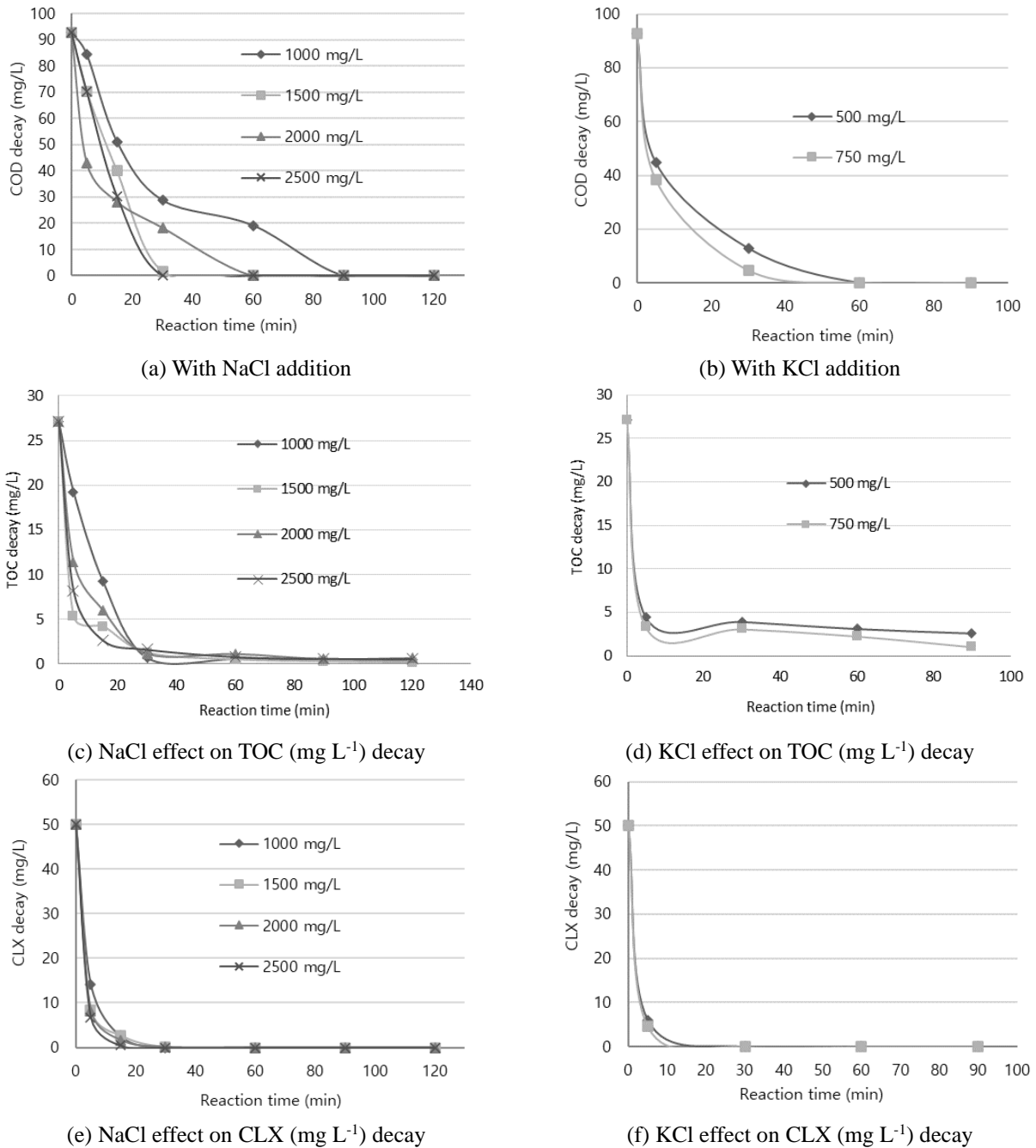


Fig. 6 Comparison the effect of NaCl and KCl addition ($I: 50 \text{ mA cm}^{-2}$, $\text{pH } 7$)

et al. 2013). Chlorine gas and hypochloric acid are other significant oxidants that are produced as a result of high amount of salt addition (Pillai and Gupta 2016). Cl_2 (chlorine) gas occurs at the surface of anode, to able to generate hypochlorous acid (HOCl). In addition to this, it could be possible elimination of radical ($\bullet\text{OH}$) scavengers (HCO_3^- and CO_3^{2-} ions) at acidic pH values. Furthermore, occurrence of chlorine gas and hypochlorite ions effect positively degradation of organics at alkaline conditions (Deng and Englehardt 2007). However, addition of extra salt may cause environmental issues and increase the cost. In Fig. 6 (a) and (b) it is seen the comparison the effect of NaCl and KCl addition on operating parameters (COD, TOC and CLX) respectively.

NaCl effect on the process was evaluated between 1000 and 2500 mg L^{-1} concentrations ($\text{pH } 7$ and 50 mA cm^{-2} current density). According to the graph in Fig. 6 (a), CLX degradation trend with NaCl was similar to the oxidation with KCl electrolyte. However, it was observed differences in COD removal and TOC mineralization rates. It was obtained higher removal rates with KCl addition than with the NaCl addition in shorter times and with less electrolyte addition need.

Effect of KCl concentration (mg L^{-1}) on operating parameters were evaluated for 500 and 750 mg L^{-1} values, at $\text{pH } 7$ and 50 mA cm^{-2} current density. However, up to 500 mg L^{-1} concentration, electrochemical oxidation efficiency couldn't be detected for the reason of lower voltage and

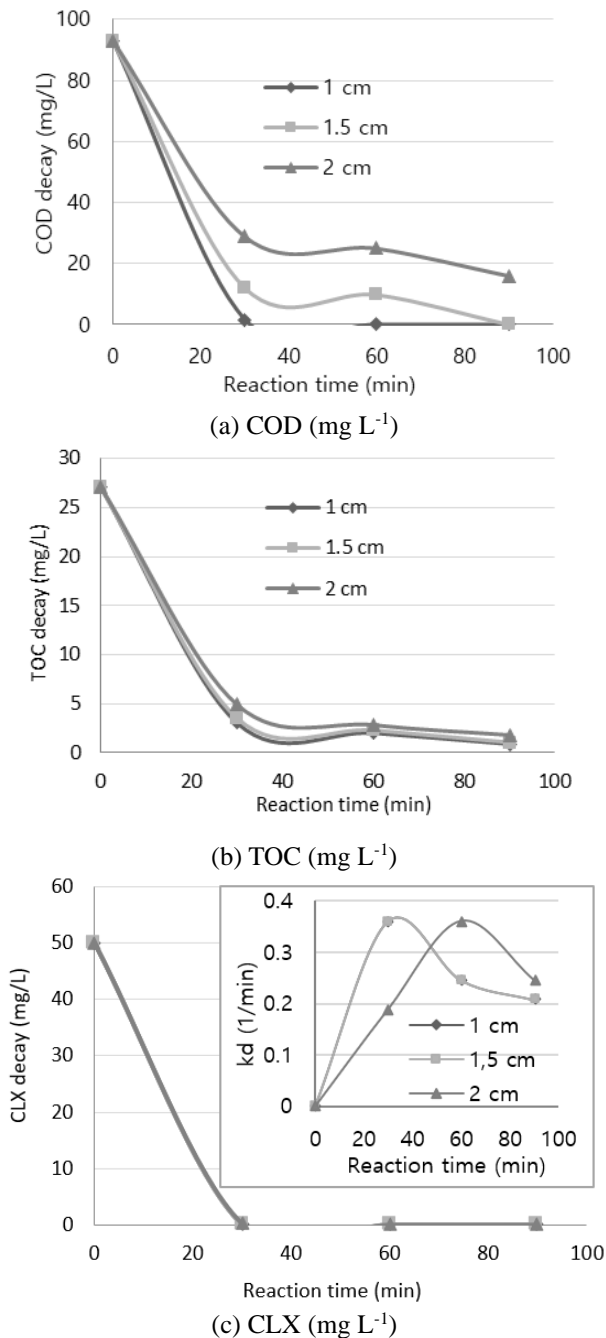


Fig. 7 Effect of anode-cathode distance (750 mg/L KCl, pH: 7, I: 50 mA/cm²)

current, while more than 750 mg L⁻¹ KCl conc. was not chosen to study to avoid extra cost.

COD graphs were clearer compared to other operating parameter (TOC and CLX) results and thus, COD was chosen as major parameter to evaluate study results. According to the graphs in Fig. 6 (d) the best efficiencies were obtained for 750 mg L⁻¹ KCl addition after 60 min reaction (COD was almost completed) with the conditions of I: 50 mA cm⁻², at pH 7. Optimum salt type and conc. was found as 750 mg L⁻¹ KCl for electrochemical oxidation of CLX with Sn/Sb/Ni: 500/8/1 anode. To obtain the reaction kinetics for CLX degradation, pseudo-first degree (k_d)

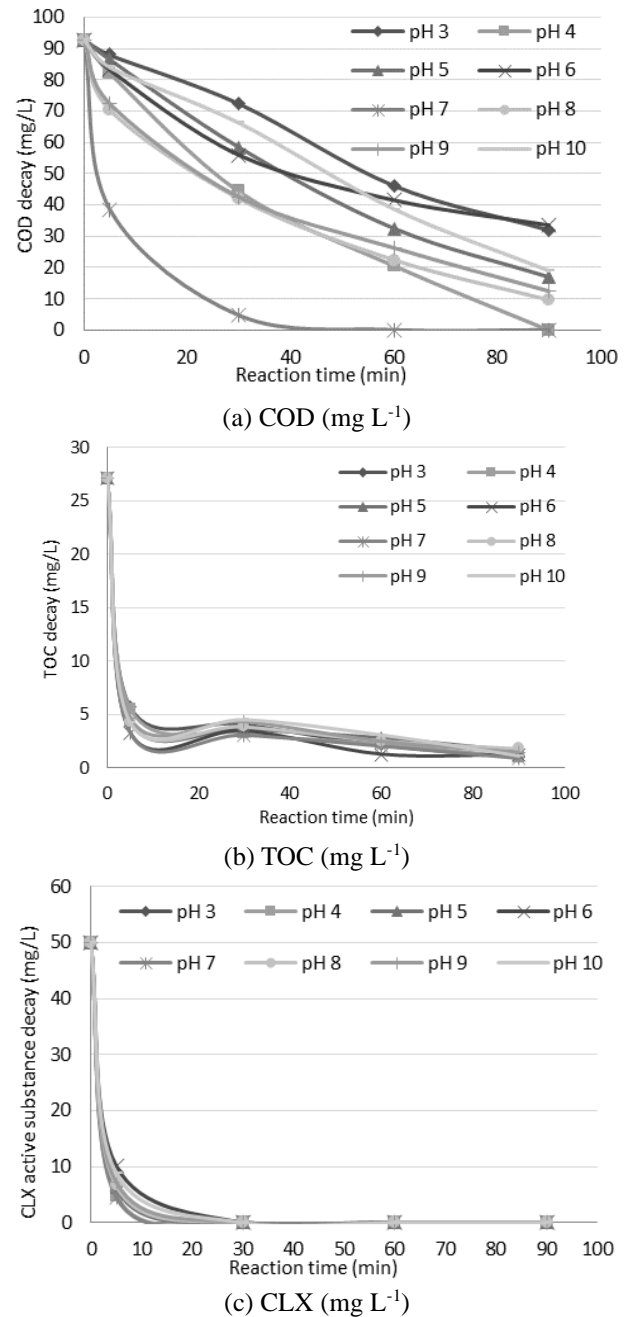


Fig. 8 Effect of pH (750 mg/L KCl, I: 50 mA/cm²)

values were calculated to show more clearer results and verify of other analysis results. According to the kinetic evaluation it was seen that KCl addition affected the electrochemical oxidation reactions significantly, due to the increase of conductivity and occurring of chloride gas thus, hypochloric acid (Pillai and Gupta 2016). Thus, it was decided to study with KCl for further analysis.

3.4 The effect of distance between anode and cathode

The optimum anode-cathode distance was obtained as 1 cm at the optimum conditions, due to obtain higher removal efficiencies (Fig. 7). Wang *et al.* (2018) evaluated tetracycline

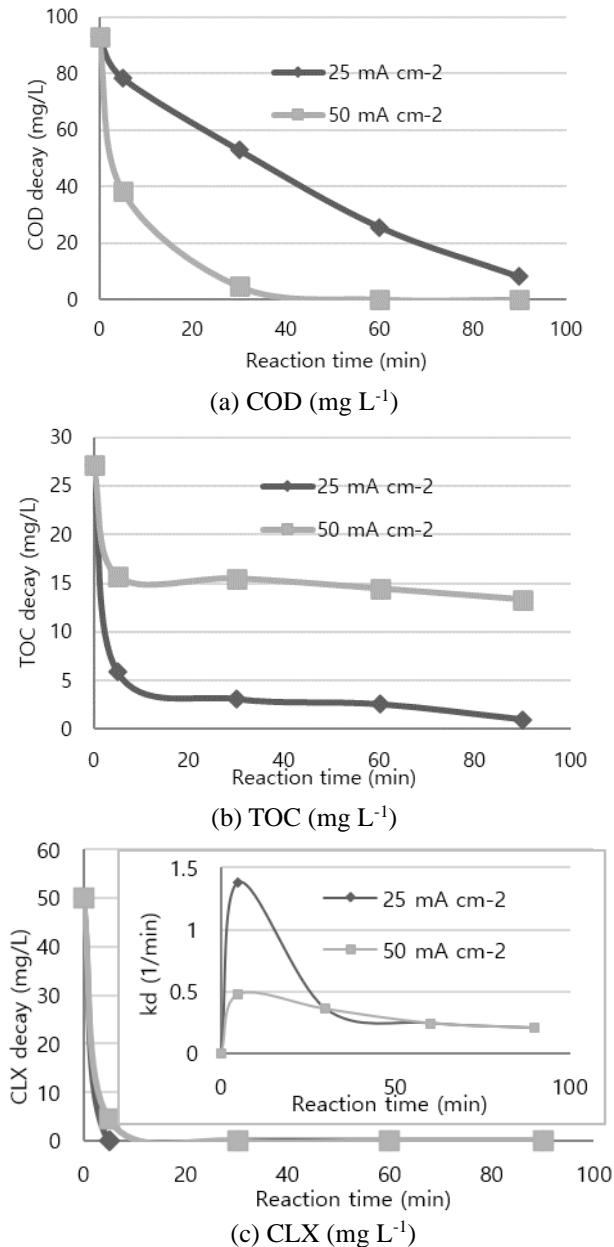


Fig. 9 Effect of current density (KCl conc.: 750 mg L⁻¹ and pH 7)

(TC) degradation with Ti/Ti₄O₇ anode and they saw that TC degradation efficiency had a negative correlation with the the anode-cathode distance. The *k_d* values significantly decreased from $(8.9 \pm 0.1) \times 10^{-2}$ to $(6.2 \pm 0.04) \times 10^{-2}$ min⁻¹ with the increase of anode-cathode distance from 5 to 25 mm, while the *t*_{1/2} values increased from 5.6 to 13.0 min (Wang *et al.* 2018). In the studies of Lin *et al.* (2013) similar results were observed in anodic oxidation of perfluorooctanoic acid and sulfamethoxazole. At shorter electrode distance, faster CLX electrochemical oxidation could be explained with more efficient electrolysis with shorter diffusion distance between the anode-cathode (Lin *et al.* 2013). However, very small electrode distances may cause operational difficulties in terms of potential for short circuits between the anode and cathode.

3.5 Initial pH

In this study, it was investigated the effect of pH values at the range of [3-10] on COD, TOC, and CLX decays. pH is one of the most important parameter affecting the electrochemical processes. Fig. 8 shows the effect of pH and according to the graphs in Fig. 8 COD was consumed completely just after 60 min at pH 7 with 750 mg L⁻¹ KCl and 50 mA cm⁻² current density. pH 7 was found as the optimum, due to have the highest removal efficiencies. Degradation rates were obtained more clearly for pH parameter than the other operating parameters.

Yonar *et al.* (2019) investigated electrochemical color removal from organized industrial district (OID) wastewater with Sn/Sb/Ni: (500/8/0.5) anode (Yonar *et al.* 2019). The affect of pH on COD and color removal was evaluated between 3-9 values (with no addition of NaCl, at 50 mA cm⁻² current density). COD and color removal efficiencies were higher at acidic conditions rather than the basic conditions. Better COD and color removal efficiencies could be obtained at acidic pH values, but neutral pH at 8.2 was chosen as the optimum pH value to avoid extra operational cost.

3.6 Current Density Variation

Current density is another significant parameter affects the electrochemical degradation processes that has an active role in reaction kinetics (Deng and Englehardt 2007). Organic compounds are oxidized on anodic surface at lower current density values generally while, the oxidation process occurs in the solution at higher currents. Thus, current density value range was chosen between 10 – 50 mA cm⁻² for direct (anodic) electrooxidation, in this study (KCl conc.: 750 mg L⁻¹, pH 7). In almost all of the electrochemical processes, chloride ions concentration is found mainly depending on the current density (it remains constant or decreases beyond the degradation rate) (Giraldo *et al.* 2015). Optimum current density was determined as 50 mA cm⁻² having the highest removal efficiencies in shorter time (60 min). At higher current densities active oxidants occur increasingly in aqueous solution thus, the removal efficiencies increased generally. Fig. 9 shows the effect of current density on reaction control parameters (COD, TOC and CLX decay) and it can be seen from that, current density variation affected the reaction efficiencies highly (750 mg L⁻¹ KCl and pH 7).

Giraldo *et al.* (2015) applied anodic oxidation for the removal of oxacillin (OXA) with Ti/IrO₂ anode and it was obtained that, current density was the main variable effecting the OXA degradation (Giraldo *et al.* 2015). Current density increases increased the degradation rates highly and the best current density value was found as 30,25 mA cm⁻² for degradation of OXA with 0,225 mol L⁻¹ NaCl. Yonar *et al.* (2019) studied electrochemical oxidation of colored industrial wastewater with Sn/Sb/Ni anode (500/8/0.5) and current density parameter was observed as the most significant parameter (Yonar *et al.* 2019). The lowest energy consumption was seen between 10-25 mA cm⁻² of current density, while the highest energy consumption

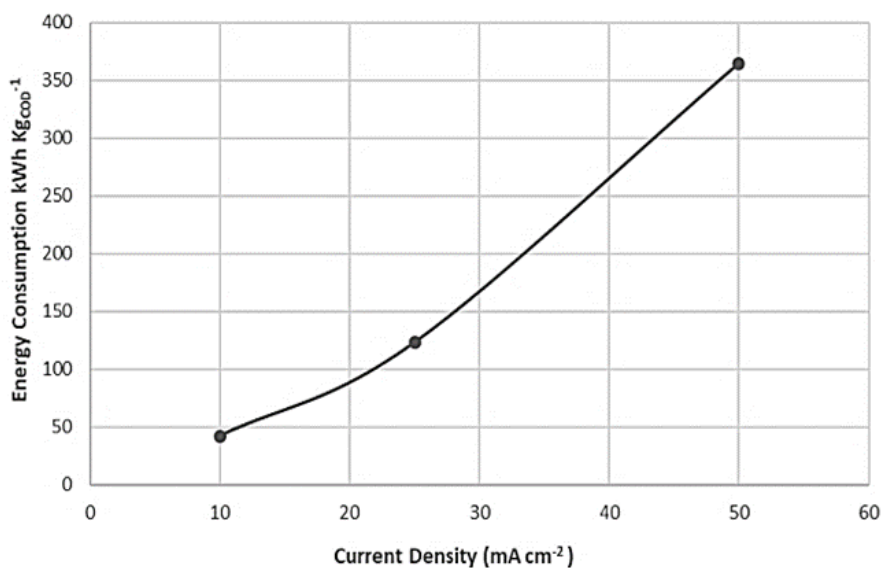


Fig. 10 Energy consumption rates according to the applied current density values

was 100 mA cm⁻² of current density. The optimum current density was found as 50 mA cm⁻².

Although higher current density values increase the removal efficiencies, they increase power consumption. A dramatic increase in energy consumption could be seen by with the current density increase in Fig. 10.

4. Conclusions

In this study, it was investigated the electrochemical oxidation of cefalexin by using new generation Sn/Sb/Ni-Ti anodes. It was obtained that, 750 mg L⁻¹ KCl was found as the optimum salt type and concentration for the electrochemical oxidation of CLX. pH parameter was found as the clearest parameter in the other operating parameters and pH 7 was found as the optimum. Thus, it could be possible to save costs by working at natural pH of the solution and it is easier and practical way to operate process. Current density variation affected reaction efficiencies highly. Optimum current density was found as 50 mA cm⁻² due to obtain the highest removal efficiencies in shorter time (60 min). Also, the observation and comparison of SEM and AFM images and XRD results showed that the anode material was not not corroded too much even after 300 h of electro-oxidation and the removal efficiencies were very high for almost all the time and conditions. According to the results of this study, electrochemical oxidation with new generation Sn/Sb/Ni-Ti anodes for CLX antibiotic removal was found very successful and applicable due to require less reaction time, less energy requirement (due to using direct current), complete mineralization, and doesn't require extra pH adjustment steps. For further studies in future, different antibiotic types should be studied with this anode and also with real wastewaters containing antibiotics without adding extra electrolyte assuming they contain ions (Na⁺, K⁺, Cl⁻ etc.) naturally and without pH adjustment step to test applicability of the process, in a better way. Thus, the studies should concentrate on anode stability with current

density and energy consumption, mostly to develop more stabil anode working with lower current and energy need.

Acknowledgments

The authors acknowledge the support of Bursa Uludag University Research Projects Department for this study (Project No. OUAP (MH)-2018/8).

References

- Abbasi, M., Soleymani, A.R. and Parssa, J.B. (2014), "Operation simulation of a recycled electrochemical ozone generator using artificial neural network", *Chem. Eng. Res. Des.*, **92**(11), 2618-2625. <https://doi.org/10.1016/j.cherd.2014.02.027>.
- Aydin, S., Aydin, M.E., Ulvi, A. and Kilic, H. (2018), "Determination of antibiotics by SPE-LC-MS/MS in wastewater and risk assessment", *Adv. Environ. Res.*, **7**(3), 201-212. <http://doi.org/10.12989/aer.2019.7.3.201>.
- Basiriparsa, J. and Abbasi, M. (2012), "High-efficiency ozone generation via electrochemical oxidation of water using Ti anode coated with Ni-Sb-SnO₂", *J. Solid State Electrochem.*, **16**(3), 1011-1018. <https://doi.org/10.1007/s10008-011-1440-6>.
- Christensen, P., Lin, W., Christensen, H., Imkum, A., Jin, J., Li, G. and Dyson, C. (2009), "Room temperature, electrochemical generation of ozone with 50% current efficiency in 0.5 M sulfuric acid at cell voltages < 3V", *Ozone Sci. Eng.*, **31**(4), 287-293. <https://doi.org/10.1080/01919510903039309>.
- Christensen, P., Zakaria, K. and Curtis, T. (2012), "Structure and activity of Ni- and Sb-doped SnO₂ ozone anodes", *Ozone Sci. Eng.*, **34**(1), 49-56. <https://doi.org/10.1080/01919512.2012.639687>.
- Christensen, P.A., Zakaria, K., Christensen, H. and Yonar, T. (2013), "The effect of Ni and Sb oxide precursors, and of Ni composition, synthesis conditions and operating parameters on the activity, selectivity and durability of Sb-doped SnO₂ anodes modified with Ni", *J. Electrochem. Soc.*, **160**(8), H405-H413. <https://doi.org/10.1149/2.023308JES>.
- Cui, Y., Wang, Y., Wang, B., Zhou, H., Chan, K.-Y. and Li, X.-Y. (2009), "Electrochemical generation of ozone in a membrane

- electrode assembly cell with convective flow”, *J. Electrochem. Soc.*, **156**(4), E75-E80. <https://doi.org/10.1149/1.3072686>.
- Deng, Y. and Englehardt, J.D. (2007), “Electrochemical oxidation for landfill leachate treatment”, *Waste Manage.*, **27**(3), 380-388. <https://doi.org/10.1016/j.wasman.2006.02.004>.
- Federation, W.E. and Association, A.P.H. (2005), *Standard methods for the examination of water and wastewater*, Washington DC, U.S.A.
- Giraldo, A.L., Erazo-Eraza, E.D., Flórez-Acosta, O.A., Serna-Galvis, E.A. and Torres-Palma, R.A. (2015), “Degradation of the antibiotic oxacillin in water by anodic oxidation with Ti/IrO₂ anodes: evaluation of degradation routes, organic by-products and effects of water matrix components”, *Chem. Eng. J.*, **279**, 103-114. <https://doi.org/10.1016/j.cej.2015.04.140>.
- Gonçalves, A.G., Órfão, J.J. and Pereira, M.F.R. (2012), “Catalytic ozonation of sulphamethoxazole in the presence of carbon materials: catalytic performance and reaction pathways”, *J. Hazard. Mater.*, **239**, 167-174. <https://doi.org/10.1016/j.jhazmat.2012.08.057>.
- Isarain-Chávez, E., Baró, M.D., Rossinyol, E., Morales-Ortiz, U., Sort, J., Brillas, E. and Pellicer, E. (2017), “Comparative electrochemical oxidation of methyl orange azo dye using Ti/Ir-Pb, Ti/Ir-Sn, Ti/Ru-Pb, Ti/Pt-Pd and Ti/RuO₂ anodes”, *Electrochimica Acta*, **244**, 199-208 <https://doi.org/10.1016/j.electacta.2017.05.101>.
- Kurt, A. and Yonar, T. (2016), “Endokrin bozucu antibiyotik bileşiklerinin UV/H₂O₂ prosesi ile taguchi deneysel dizaynına göre aritilabilirliği”, *Afyon Kocatepe Üniversitesi Fen Ve Mühendislik Bilimleri Dergisi*, **17**(2), 854-860. <https://doi.org/10.5578/fmbd.57594>.
- Letti, C.J., Costa, K.A., Gross, M.A., Paterno, L.G., Pereira-da-Silva, M.A., Morais, P.C. and Soler, M.A. (2017), “Synthesis, morphology and electrochemical applications of iron oxide based nanocomposites”, *Adv. Nano Res.*, **5**(3), 215. <https://doi.org/10.12989/anr.2017.5.3.215>.
- Lin, H., Niu, J., Xu, J., Li, Y. and Pan, Y. (2013), “Electrochemical mineralization of sulfamethoxazole by Ti/SnO₂-Sb/Ce-PbO₂ anode: kinetics, reaction pathways, and energy cost evolution”, *Electrochimica Acta*, **97**, 167-174. <https://doi.org/10.1016/j.electacta.2013.03.019>.
- Mompelet, S., Le Bot, B. and Thomas, O. (2009), “Occurrence and fate of pharmaceutical products and by-products, from resource to drinking water”, *Environ. Int.*, **35** (5), 803-814. <https://doi.org/10.1016/j.envint.2008.10.008>.
- Parsa, J.B. and Abbasi, M. (2012), “Application of in situ electrochemically generated ozone for degradation of anthraquinone dye Reactive Blue 19”, *J. Appl. Electrochem.*, **42** (6), 435-442. <https://doi.org/10.1007/s10800-012-0417-1>
- Petrović, M., Hernando, M.D., Díaz-Cruz, M.S. and Barceló, D. (2005), “Liquid chromatography–tandem mass spectrometry for the analysis of pharmaceutical residues in environmental samples: A review”, *J. Chromatography A*, **1067**(1-2), 1-14. <https://doi.org/10.1016/j.chroma.2004.10.110>.
- Pillai, I.M.S. and Gupta, A.K. (2016), “Anodic oxidation of coke oven wastewater: multiparameter optimization for simultaneous removal of cyanide, COD and phenol”, *J. Environ. Manage.*, **176**, 45-53. <https://doi.org/10.1016/j.jenvman.2016.03.021>.
- Qian, S., Liu, S., Jiang, Z., Deng, D., Tang, B. and Zhang, J. (2019), “Electrochemical degradation of tetracycline antibiotics using a Ti/SnO₂-Sb₂O₃/PbO₂ anode: Kinetics, pathways, and biotoxicity change”, *J. Electrochem. Soc.*, **166**(6), E192. <https://orcid.org/0000-0003-1879-9378>.
- Shmychkova, O., Luk’yanenko, T., Dmitrikova, L. and Velichenko, A. (2019), “Modified lead dioxide for organic wastewater treatment: Physicochemical properties and electrocatalytic activity”, *J. Serbian Chem. Soc.*, **84** (2), 187-198. <https://doi.org/10.2298/JSC180712091S>.
- Souza, F., Quijorna, S., Lanza, M.R.d.V., Sáez, C., Cañizares, P. and Rodrigo, M. (2017), “Applicability of electrochemical oxidation using diamond anodes to the treatment of a sulfonylurea herbicide”, *Catalysis Today*, **280**, 192-198. <https://doi.org/10.1016/j.cattod.2016.04.030>.
- Tran, N., Drogui, P., Nguyen, L. and Brar, S.K. (2016), “Electrooxidation–ultrasonication hybrid process for antibiotic chlortetracycline treatment”, *J. Environ. Eng.*, **142**(5), 04016011. [https://doi.org/10.1061/\(ASCE\)EE.1943-7870.0001088](https://doi.org/10.1061/(ASCE)EE.1943-7870.0001088).
- Trovo, A.G., Nogueira, R.F.P., Agüera, A., Fernandez-Alba, A.R. and Malato, S. (2011), “Degradation of the antibiotic amoxicillin by photo-Fenton process–chemical and toxicological assessment”, *Water Res.*, **45**(3), 1394-1402. <https://doi.org/10.1016/j.watres.2010.10.029>.
- Vergili, İ., Kaya, Y., Gönder, Z. and Barlas, H. (2005), “İlaç aktif maddelerinin sucul çevrede bulunuşları, davranışları ve etkileri”, *Türk Sucul Yaşam Dergisi*, **4**, 284-291.
- Wang, J., Zhi, D., Zhou, H., He, X. and Zhang, D. (2018), “Evaluating tetracycline degradation pathway and intermediate toxicity during the electrochemical oxidation over a Ti/Ti4O7 anode”, *Water Res.*, **137**, 324-334. <https://doi.org/10.1016/j.watres.2018.03.030>.
- Wang, Y.H. (2006), “Electrochemical generation of ozone on antimony and nickel doped tin oxide”, *Degree of Doctor of Philosophy*, The university of Hong Kong, honk Kong.
- Weist, K. and Högberg, L.D. (2016), “ECDC publishes 2015 surveillance data on antimicrobial resistance and antimicrobial consumption in Europe”, *Eurosurveillance*, **21**(46). <https://doi.org/10.2807/1560-7917.ES.2016.21.46.30399>.
- Wirzal, M.D.H., Yusoff, A.R.M., Zima, J. and Barek, J. (2013), “Degradation of ampicillin and penicillin G using anodic oxidation”, *Int. J. Electrochem. Sci.*, **8**, 8978-8988.
- Yonar, T., Shakir, F. and Kurt, A. (2019), “Investigation of electrochemical color removal from organized industrial district (OID) wastewater treatment plants using new generation Sn/Sb/Ni-Ti anodes”, *Global Nest J.*, **21** (2), 106-112. <https://doi.org/10.30955/gnj.002696>.
- Zhi, D., Qin, J., Zhou, H., Wang, J. and Yang, S. (2017), “Removal of tetracycline by electrochemical oxidation using a Ti/SnO₂-Sb anode: Characterization, kinetics, and degradation pathway”, *J. Appl. Electrochem.*, **47**(12), 1313-1322. <https://doi.org/10.1007/s10800-017-1125-7>.

CC

Abbreviations

CLX	cephalexin
COD	chemical oxygen demand, mg L ⁻¹
C	concentration of CLX for reaction time (mg L ⁻¹)
Co	initial CLX concentration (mg L ⁻¹)
NaCl	sodium chloride, mg L ⁻¹
KCl	potassium chloride, mg L ⁻¹
Sn/Sb/Ni-Ti	Tin/Antimony/Nickel-Titanium

UV	ultraviole
PbO ₂	lead dioxide
BDD	boron doped diamond
NiO	nickel (II) oxide
Sb ₂ O ₃	antimony (III) oxide
C ₂ H ₅ OH	ethanol
HCl,	hydrochloric acid
CH ₂ O ₂ ,	formic acid
C ₂ H ₂ O ₄ ,	oxalic acid
H ₂ SO ₄ ,	sulphuric acid
UPLC	ultra performanced liquid chromatography
SEM	scanning electron microscope
EDS	energy dispersive spectroscopy
OID	organized industrial district
OXA	oxacillin
•OH	hydroxyl radical
cm	Anode-cathode distance
mA cm ⁻²	Current density
PDA	photo diode array detector
V	cell volume, L
I	current value, amperes
E _{COD}	energy consumption, kWh kg ⁻¹ COD
ΔCOD	amount of COD removed between start and finishing time, kg L ⁻¹
k _d	pseudo-first degree CLX removal constant, 1 min ⁻¹
t	reaction time (min)