

Electrochemical Removal of Cefazolin from Aqueous Media by Novel Composite Anodes: Effects of Electrolytes and Operating Parameters

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Received: 29 July 2021 / Accepted: 29 September 2021 / Published: 10 November 2021

In this study, we aimed to investigate the capability of novel stable Ni-based anodes with platinized titanium cathodes to eliminate cefazolin antibiotics from aqueous media. For this purpose, different types of electrolytes were compared, and potassium chloride was found to be the optimal electrolyte for promoting the elimination of antibiotics, even at low concentrations. Thus, it may be possible to obtain higher removal efficiencies with real water/wastewaters, even without the addition of extra electrolytic chemicals, assuming the water being treated includes chloride ions. A pH of 7, which is the neutral pH value of the aqueous solution containing antibiotics, was defined as the optimal pH value as it provided the highest removal efficiencies. Thus, it may be possible to operate the process more easily and more economically by working at neutral pH values, as no additional chemical costs are incurred due to pH adjustment. Moreover, more efficient results were obtained at lower current densities with this anode in comparison to other studies on the electrochemical treatment of antibiotics in the literature. As a result of this study, electrochemical oxidation with Sb-doped SnO₂ anodes was found to be very useful and successful for the removal of cefazolin from water in terms of both removal efficiency and cost effectiveness.

Keywords: Cefazolin, Electrochemical oxidation, Nickel-based anode, Platinized cathode, Electrolyte, Current density

1. INTRODUCTION

Pharmaceuticals are one of the most important pollutants that have a negative effect on the environment and health of living organisms, and they have been found to contaminate both water and soil environments [1-3]. There are many sources that lead to the spread of these synthetic chemicals

into the environment, such as the discharge of metabolized and unmetabolized drugs from humans and livestock passing through sewage systems and discharges from pharmaceutical industries, hospitals, and veterinary processes. Some of these pharmaceuticals are absorbed completely in the living body of the target organisms, while up to 70% of the others are excreted into the environment with either incomplete or no degradation, remaining in an active form. A large amount of pharmaceuticals can also be released into the receiving environment by applying them to the land as fertilizer [4, 5]. Antibiotics are considered the most significant types among all other pharmaceuticals (antipyretics, painkillers, antiseptics, etc.) because of their vast usage in medicine (human and veterinary) and the occurrence of microorganism resistance and bioaccumulation in the environment [3, 6, 7].

In the early 1980s, some concerns about antibiotics began to emerge regarding their presence in the environment. After several years, the existence of several types of antibiotics found in rivers was reported by Watts et al. (1983) [8]. Antibiotics in groundwaters, surface waters, landfills and wastewaters have recently been reported [9-11]. Consequently, the World Health Organization (WHO) declared that the development of antibiotic resistance genes is one of the most critical environmental threats due to the presence of low concentrations of antibiotics [12-15] throughout the environment. These toxic organic pollutants are discharged into sewage systems with/without treatment, reaching wastewater treatment plants [16, 17]. However, the removal of antibiotics from wastewater with conventional treatment processes (activated carbon, air stripping, membrane filtration, etc.) is not efficient enough due to the transference of contaminants from one phase to another without complete degradation [18-20]. Therefore, these antibiotic residues enter the receiving environment through discharges or sludge wastes [21-24].

The beta-lactam group of antibiotics had a higher rate of usage than other antibiotic classes, having highly effective results in therapeutic medicine [25-28]. For these reasons, in this study, the removal of cefazolin (CFZ) antibiotics, which have the highest rate of usage among beta-lactam group antibiotics, was investigated [29, 30]. Many methods have been proposed to eliminate these antibiotics from aquatic environments, such as coagulation [31-34], Fenton processes, ultraviolet oxidation (UV) [35], and activated sludge and advanced treatment processes such as carbon nanotubes, nanofiltration [36], electrochemical processes [37, 38], etc. However, in recent years, many researchers have shown great interest in electrochemical processes (electrochemical oxidation, electrocoagulation, electroflotation, etc.) to eliminate organic contaminants from wastewater because these methods have shown positive results in the destruction of toxic organic compounds (pesticides, etc.) [39-41].

Electrooxidation reactions can occur in two ways in aqueous solution: i) direct electrooxidation and ii) indirect electrooxidation [42-44]. Organic compounds are degraded on the anodic surface by a direct electrochemical oxidation process [45, 46], whereas they are mineralized with electrogenerated oxidants (hypochlorite ions and peroxodisulfate) during indirect processes [47-49].

Electrochemical oxidation plays an important role in the mineralization of antibiotics and does not allow the formation of extra waste products [50]. Several materials are used in the production of anodes, which are used for electrochemical processes [4]. To improve oxidation efficiency and avoid potential disadvantages, new anode materials that have been investigated include platinum (Pt), titanium oxide (TiO₂), graphite, boron-doped diamond (BDD), glassy carbon, activated carbon, β -PbO₂, IrO₂/Ti, Sn/Sb/Ni, etc. [51-53]. However, most of these materials are not suitable due to their

toxicity, instability, and high costs. In contrast to the aforementioned materials, Sb-doped SnO₂-Ni anodes successfully solved these problems. Additionally, these anodes have shown very promising results in the case of ozone production and electrochemical oxidation [54, 55]. The most important advantage of Sn/Sb/Ni-Ti anodes in ozone production is their low voltage operation. On the other hand, the possibility of ozone production in the liquid and gas phases is high, and there is no need for any input, such as dry, moisture-free air or pure oxygen [55]. Due to electrochemical ozone generation with these anodes, the electrodes must be stable and remain stable at a voltage of 1.51 V (ozone formation voltage). Other anodes are inhibited by oxygen formation at a voltage of 1.23 V after a while because they are not so stable, or the stability at 1.51 V is provided only at low temperatures [56]. However, the fact that these stable anodes have been used almost negligibly in the removal of various pollutants presents a serious gap in the literature.

Therefore, the removal of cefazolin antibiotics from aqueous solution using novel stable nickel-based anodes by tin/antimony/nickel (Sn/Sb/Ni) with a platinized titanium cathode was investigated in this study. For this purpose, the effect of different types and doses of electrolytes (potassium chloride: 250–1500 mg/L, sodium chloride and sodium sulfate: 1000–2500 mg/L), pH (in the range of 3–9), and current density values (10–50 mA/cm²) on the electrochemical process efficiencies was investigated. This study is unique because there are no such studies on the treatment of CFZ antibiotics with these anodes. However, removal studies of organic contaminants from water with these anodes are limited to only a few in the literature. Furthermore, the most important advantage of Sn/Sb/Ni-Ti anodes is their low voltage operation. Electrochemical oxidation of CFZ with Sn/Sb/Ni anodes requires a shorter reaction time, provides complete mineralization and does not require extra pH adjustment steps.

This study was conducted at Bursa Uludag University, Environmental Engineering Department, Wastewater Research Laboratories, between 2018 and 2020.

2. MATERIAL and METHODS

2.1. Chemicals, solvents and materials

The major material used for anode preparation was a titanium screen substrate with a size of 2.5 cm x 2.5 cm (3Ti7-077FA, Dexmet, USA). A 5 x 5 cm platinized titanium electrode (NRK Electrochem, Cornwall, UK) was provided (DuPont Corp., USA) and applied as the cathode. Potassium chloride (KCl), sodium chloride (NaCl), tin(IV) chloride pentahydrate (SnCl₄.5H₂O), hydrochloric acid (HCl), sulfuric acid (H₂SO₄), ethanol (C₂H₅OH), methanol (CH₃OH), formic acid (CH₂O₂), and oxalic acid (C₂H₂O₄) were provided by Merck (Darmstadt, Germany). Nickel oxide (NiO) and antimony(III) oxide (Sb₂O₃) were provided by Alfa Aesar (Kandel, Germany) and Merck (Darmstadt, Germany), respectively. All of these chemicals had a purity of ≥ 98% and were used directly without any further purification. Ultrapure water (Millipore Milli-Q, 18 MΩ cm) was used to prepare all of the solutions. A cefazolin antibiotic standard was provided by Sigma–Aldrich (Missouri, USA).

2.2. Experimental procedure

Sb-SnO₂-Ni anodes (2.5 cm x 2.5 cm) and platinized titanium cathodes were placed in a glass beaker. The reactor configuration used in the experiments is shown in Fig. 1. The electrochemical reaction procedure was carried out with an anode with a Sn/Sb/Ni molar ratio of 500/8/2. Kurt (2020) previously reported the electrochemical removal of cefaclor from water using an anode with a Sn/Sb/Ni molar ratio of 500/8/1 [57]. A magnetic stirrer was used to homogenize the aqueous antibiotic solution throughout the experiment. A DC (direct current) power supply was used, and the voltage used in the study varied between 3 V and 4 V. The distance between the anode and cathode was maintained at 1–2 cm. Zhi et al. (2017) stated that the $t_{1/2}$ values increased from 5.7 min to 19.1 min and the reaction constants decreased from $8.7 \times 10^{-2} \text{ min}^{-1}$ to $3.4 \times 10^{-2} \text{ min}^{-1}$ with increasing the distance between the anode and cathode from 0.5 cm to 2.5 cm, and tetracycline degradation was achieved with a Sb-doped SnO₂ anode [58].

Aqueous antibiotic solutions were prepared at 20–225 °C with a concentration of 50 mg/L for CFZ antibiotics. Elmolla ve Chaudhuri (2011) investigated UV/TiO₂/H₂O₂ oxidation of amoxicillin and 138 mg/L and 84 mg/L cloxacillin in pharmaceutical industrial wastewater [59]. Trovo et al. (2011) studied the photo Fenton oxidation of 50 mg/L amoxicillin antibiotics from synthetic wastewater [60].

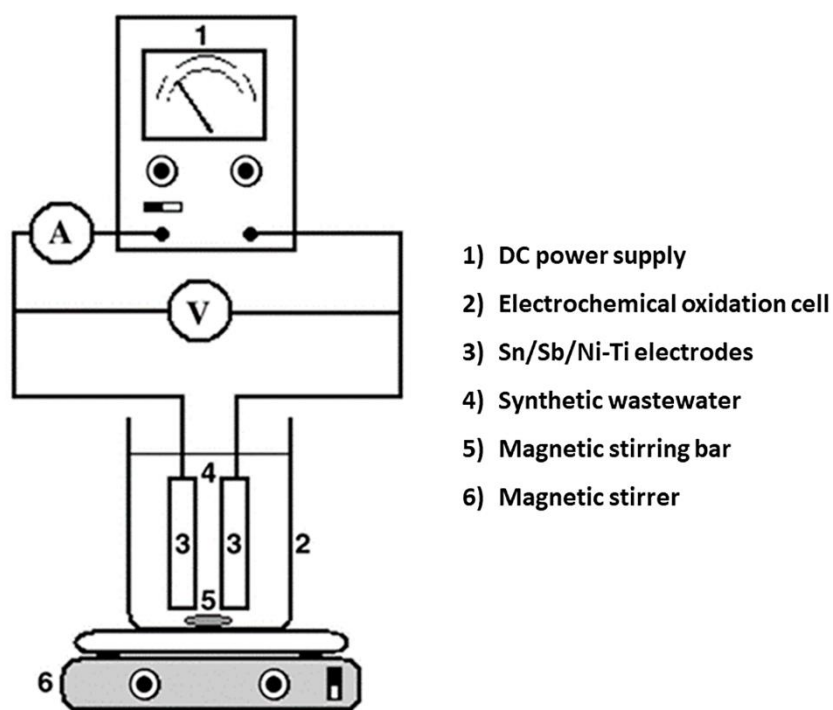


Figure 1. Configuration of the electrochemical reactor

2.3. Analytical measurements

Total organic carbon (TOC) analyses were performed by a total organic carbon analyser (TOC-L, Shimadzu, Kyoto, Japan). Analytical measurements of CFZ in the samples were made with ultra-

performance liquid chromatography (UPLC) and a photodiode array (PDA) detector (Thermo Scientific, Massachusetts, USA) at 254 and 272 nm wavelengths. A C-18 column with a size of 50 x 2.1 mm and 1.9 μm (Hypersil GOLD) was used for UPLC processes. The column temperature was adjusted to 35 $^{\circ}\text{C}$. The MeOH:H₂O ratio of the mobile phase was 40:60 (v/v) (0.1% formic acid in water). Additionally, it was studied at a flow rate of 0.2 mL min⁻¹. COD analyses were performed according to the APHA (2005) Standard Methods [61]. A Cyber Scan 500, Thermo Scientific (Massachusetts, USA) pH metre was used for the pH measurements. All of the measurements were performed in triplicate.

High-performance atomic force microscopy (HpAFM) (Nanomagnetics, Oxford, UK) was used in tapping mode with a 256 x 256 pixel solution. Scanning electron microscopy (SEM) (Quanta-250 FEG, Czech Republic) and energy dispersive spectroscopy (EDS) (EDAX Team) were used to monitor the surface of the anodes.

3. RESULTS AND DISCUSSION

3.1. Comparison of different electrolyte types

Different inorganic ions are commonly found in the environment in various water matrices and wastewaters. Thus, in this study, cefazolin oxidation was performed with the anions in antibiotic solution (containing Cl⁻ and SO₄⁻² ions). However, electrolyte (salt) type and dose (NaCl, Na₂SO₄, and KCl) positively affect electrochemical oxidation reactions by increasing conductivity [57, 62-64]. In these reactions, chloride gas is generated; thus, an excessive amount of hypochlorous acid is generated, which is a significant oxidant that is produced with the addition of chloride-containing electrolytes [65]. However, the addition of extra salt may cause an increase in cost and may be hazardous to the environment. Sivrioğlu and Yonar (2016) investigated COD and color removal from textile wastewater using Sn/Sb/Ni-Ti anodes. Although better efficiency was obtained at high NaCl concentrations, a 1 g/L NaCl concentration was chosen as the optimum salt dose due to environmental and high cost problems that the excess use of salt may later cause [66].

A comparison of the effects of NaCl, Na₂SO₄, and KCl addition on COD, TOC and CFZ removal with the Sn/Sb/Ni-Ti anode (500/8/2) (pH 7, 50 mA/cm²) is shown in Fig. 2. However, KCl addition positively affected the removal efficiencies, even at lower concentrations, especially for COD removal.

According to Fig. 2, a considerable decrease in TOC and CFZ was observed for NaCl addition, and a similar trend was observed in an even shorter time for KCl addition. According to Fig. 2, there was a significant decrease in TOC and CFZ with NaCl addition and similar removal rates in a very short time with KCl addition. KCl (750 mg/L) was identified as the optimum electrolyte parameter and dose as it provided more successful treatment conditions in even shorter times in comparison to other electrolyte types and doses. However, due to the lower voltage conditions, higher efficiencies could not be obtained at 250 and 500 mg/L KCl doses.

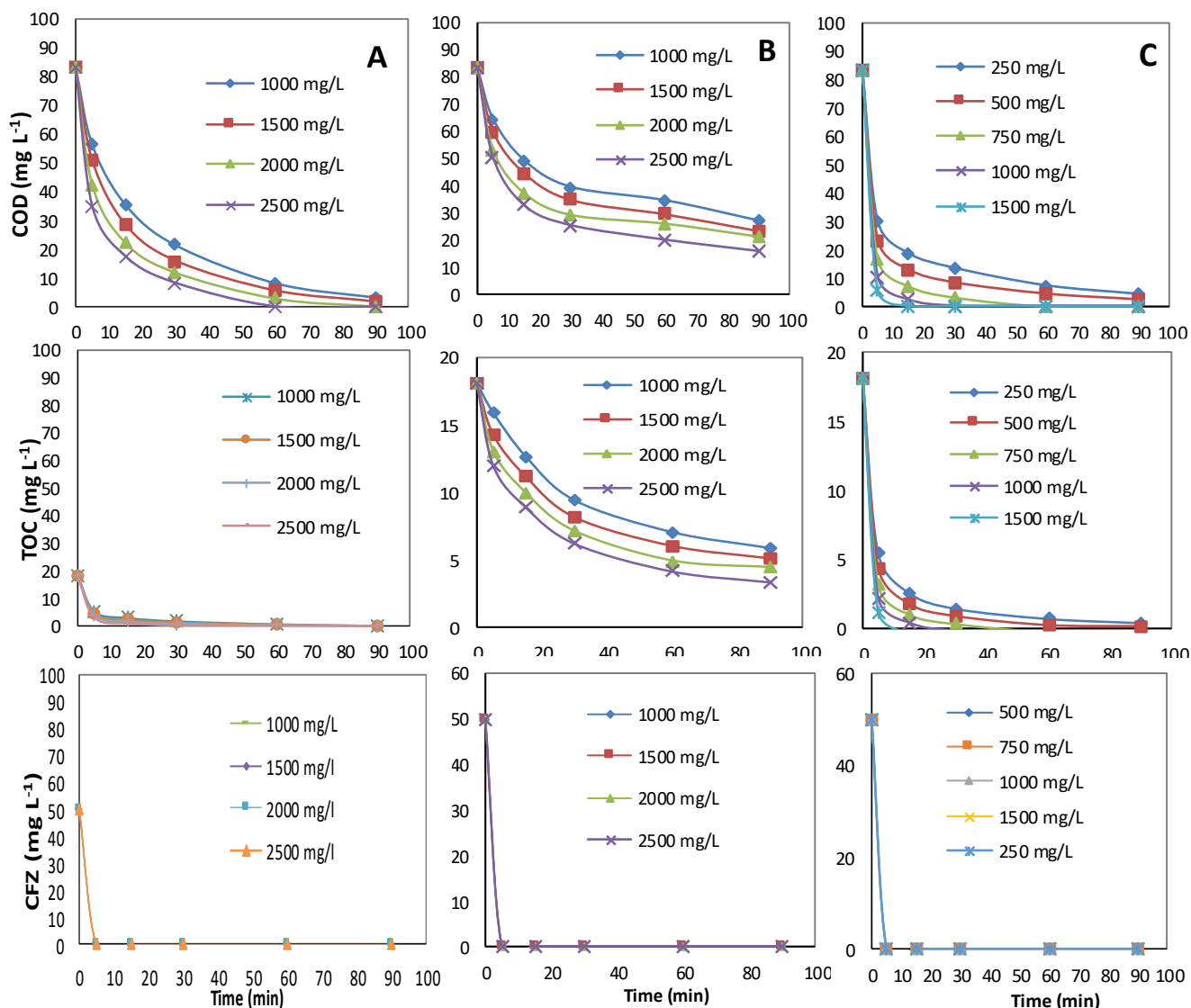


Figure 2. Comparison of the effect of electrolyte type and concentration on COD, TOC and CFZ removal with the Sn/Sb/Ni anode (500/8/2) A) with NaCl concentration, B) with Na₂SO₄ concentration and C) with KCl concentration (pH 7, 50 mA/cm²)

Furthermore, the COD values reached below 0.5 mg/L in just 30 min with 750 mg/L KCl. Although higher efficiencies could be obtained with excess salt, the most effective dose was determined to be 750 mg/L for the KCl parameter, as the excess use of chemicals (salts) may increase the cost and create environmental risks. However, when carried out with 1000 mg/L NaCl addition, the process provided 80.77% COD removal and a decrease in TOC to below 1 mg/L in just 60 min, and CFZ was consumed completely in just 5 min. Furthermore, a sufficient removal efficiency could not be obtained with Na₂SO₄ addition. The vast majority of COD and TOC remained untreated. According to Miyata et al. (2005), electrochemical oxidation occurs at the surface of the anode as direct oxidation with the addition of Na₂SO₄, while the reactions occur in aqueous solution with sodium hypochlorite and potassium hypochlorite as indirect processes. Hai et al. (2020) explored the electrooxidation of

sulfamethoxazole with a boron-doped diamond (BDD) anode and stainless-steel cathode. The complete removal of SMX, 65.6% COD removal, 40.1% current efficiency, and 72 kWh kg/COD energy consumption rates were obtained with 0.1 M Na₂SO₄ after 3 hours of reaction at a 30 mA/cm² current density and pH 7 [67]. Miyata et al. (2011) studied the removal of oxytetracycline and chlortetracycline with a Ti/IrO₂ anode and NaCl and Na₂SO₄ additions [68]. Each of the oxytetracycline and chlortetracycline concentrations decreased from 100 mg/L to <0.3 mg/L in 30 min with NaCl addition, while each concentration decreased to lower than 0.5 mg/L within 6 h with Na₂SO₄ addition.

Kurt (2020) investigated the oxidation of cefaclor with an anode with a Sn/Sb/Ni molar ratio of 500/8/1 and found that KCl positively affected the electrochemical oxidation process, even at low concentrations [57].

Thus, according to the results of this study, it may be possible to obtain higher removal efficiencies with real water/wastewater samples, even without the addition of extra electrolytic chemicals, assuming that the samples primarily include Cl⁻ ions.

3.2. Kinetic evaluation

To obtain pseudo-first-degree kinetics during the electrochemical oxidation of CFZ, the kinetic coefficient was determined from the slope of the curve formed according to the formulation stated below:

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

k_d : Pseudo-first-degree CFZ removal rate constant (1 min⁻¹).

However, COD reduction was much clearer than a conventional parameter; thus, the COD parameter was considered and evaluated as the major parameter for this study.

Table 1. Variation in pseudo-first-degree COD removal rate constant (k_d) with NaCl addition and Na₂SO₄ addition (pH 7, 50 mA/cm²)

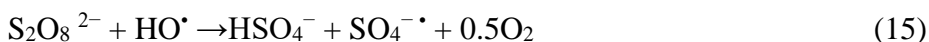
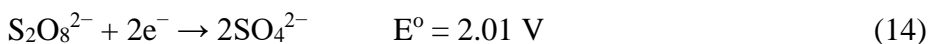
		Time (min)	Pseudo-first-degree kinetic rate constant (k_d) values (min ⁻¹)			
			1000 mg/L	1500 mg/L	2000 mg/L	2500 mg/L
With NaCl addition		5	0.0785	0.0994	0.1358	0.1743
		15	0.0570	0.0721	0.0884	0.1043
		30	0.0453	0.0558	0.0651	0.0772
		60	0.0386	0.0462	0.0565	0.3039
		90	0.0362	0.0453	0.2026	0.2026
With Na ₂ SO ₄		5	0.0515	0.0664	0.0909	0.1010
		15	0.0353	0.0419	0.0544	0.0625

addition	30	0.0251	0.0292	0.0354	0.0397
	60	0.0148	0.0173	0.0196	0.0238
	90	0.0126	0.0142	0.0154	0.0185

Table 2. Variation in the pseudo-first-degree COD removal rate constant (k_d) with KCl (pH 7, 50 mA/cm²)

	Time (min)	Pseudo-first-degree kinetic rate constant (k_d) values (min⁻¹)				
		250 mg/L	500 mg/L	750 mg/L	1000 mg/L	1500 mg/L
With KCl addition	5	0.2053	0.2554	0.3224	0.4198	0.5470
	15	0.0999	0.1248	0.1631	0.2421	1.2158
	30	0.0609	0.0772	0.1086	0.6078	0.6079
	60	0.0408	0.0498	0.3039	0.3039	0.3039
	90	0.0332	0.0404	0.2026	0.2026	0.2026

Variations in the pseudo-first-degree COD removal rate constant (k_d) with NaCl addition, Na₂SO₄ addition, and KCl concentration are provided in Table 1 and Table 2 to confirm other study results, and the calculations are sourced from Fig. 2 (COD decay with different electrolyte types, namely, NaCl, Na₂SO₄ and KCl). Thus, KCl affected the process efficiencies more positively than NaCl and Na₂SO₄ addition, even at lower concentrations. Qian et al. (2019) explored the effect of electrolyte addition on the electrooxidation of tetracyclines (tetracycline, oxytetracycline, and chlortetracycline) with a Ti/SnO₂-Sb₂O₃/PbO₂ anode. All of the antibiotic compounds were consumed completely within two hours with NH₃·H₂O-NH₄Cl. However, the removal efficiencies of these antibiotics were lower than 80% with Na₂HPO₄-NaH₂PO₄ addition, and 82.4%, 83.6% and 88.4% removal rates were obtained with Na₂SO₄ after 2 h [69]. Xie et al. (2017) stated that the removal rates of ofloxacin increased slightly with increasing Na₂SO₄ concentration from 0.005 M to 0.1 M. However, with increasing Na₂SO₄ dose to 0.5 M, the reaction rates dramatically decreased. This may be because sulfate ions cause persulfate formation at high potential values in an electrochemical process, which significantly scavenges hydroxyl radicals [70, 71]. The proposed scavenging mechanism reactions are stated below [71].



3.3. Variation in removal efficiencies with pH

The pH parameter has a very important impact on electrochemical oxidation processes since many radical chain reactions occur with the participation of protons [72]. The effect of pH values on the reaction control parameters COD, TOC, and CFZ was investigated in the pH range of 3–9. The effect of pH on the control parameters (KCl conc.: 750 mg/L and I: 50 mA/cm²) can be seen in Fig. 3. pH 7, which is the neutral pH value of antibiotic solution, was identified as the optimum as it achieves the highest removal efficiencies (Fig. 3). Working at natural pH values could make the process easier and cheaper to operate because there is no need for an extra pH adjustment step, thus avoiding additional chemical costs. However, after the 30 min electrochemical oxidation process, no significant changes were observed in the removal efficiencies, which was true for all the explored pH values. In a study by Kaur et al. (2018) with a Ti/RuO₂ anode, the removal of ofloxacin (OFL) occurred rapidly during the first 15 min of reaction, and after 30 min, there were no significant changes for any of the pH values investigated [75]. They found that higher removal efficiencies were observed with lower pH values. After just 30 min of electrooxidation, 88.6% OFL degradation was achieved at pH 2, while 68.6% OFL was degraded in 30 min at pH 9. However, in the pH range of 4–8, a 79% removal rate was achieved in approximately 30 min. At a pH value of 7, the COD concentration reached zero in just 30 min, TOC was mineralized almost completely (reaching 0.11 mg/L) after 15 min of reaction, and CFZ was consumed in just 5 min. Hai et al. (2020) investigated the effect of pH with a BDD anode for the removal of sulfamethoxazole at 3, 7 and 11 pH values and a current density of 30 mA cm⁻². Thus, higher removal efficiencies were obtained at neutral pH values than at pH 3 and 11 [67].

Jojoa-Sierra et al. (2017) evaluated the electrochemical degradation of norfloxacin antibiotics on Ti/IrO₂ anodes in various aqueous matrices at pH values of 3.0, 6.5, 7.5 and 9.0, with the most common inorganic ions being Cl⁻, HCO₃⁻, SO₄⁻² and NO₃⁻ in aquatic environments [73]. They found that destruction of norfloxacin is possible with both direct and indirect oxidation. However, nitrates had inhibitory effects on the process. Thus, the removal efficiencies of the process with chloride anions followed the pH value order of 9.0>7.5>6.5>3.0 (sourced from the anionic form of NOR). At alkaline pH values, the potential for chlorine gas and hypochlorite ion formation could support the removal of organic compounds [74, 75]. However, according to some researchers, acidic natural pH values could be efficient for electrochemical processes [64, 76]. Under acidic pH conditions, chlorine gas is exposed on the anodic surface as another significant oxidizing agent that is able to generate HOCl[·]. Moreover, elimination of hydroxyl radical scavengers (HCO₃⁻ and CO₃⁻) could be possible under acidic conditions.

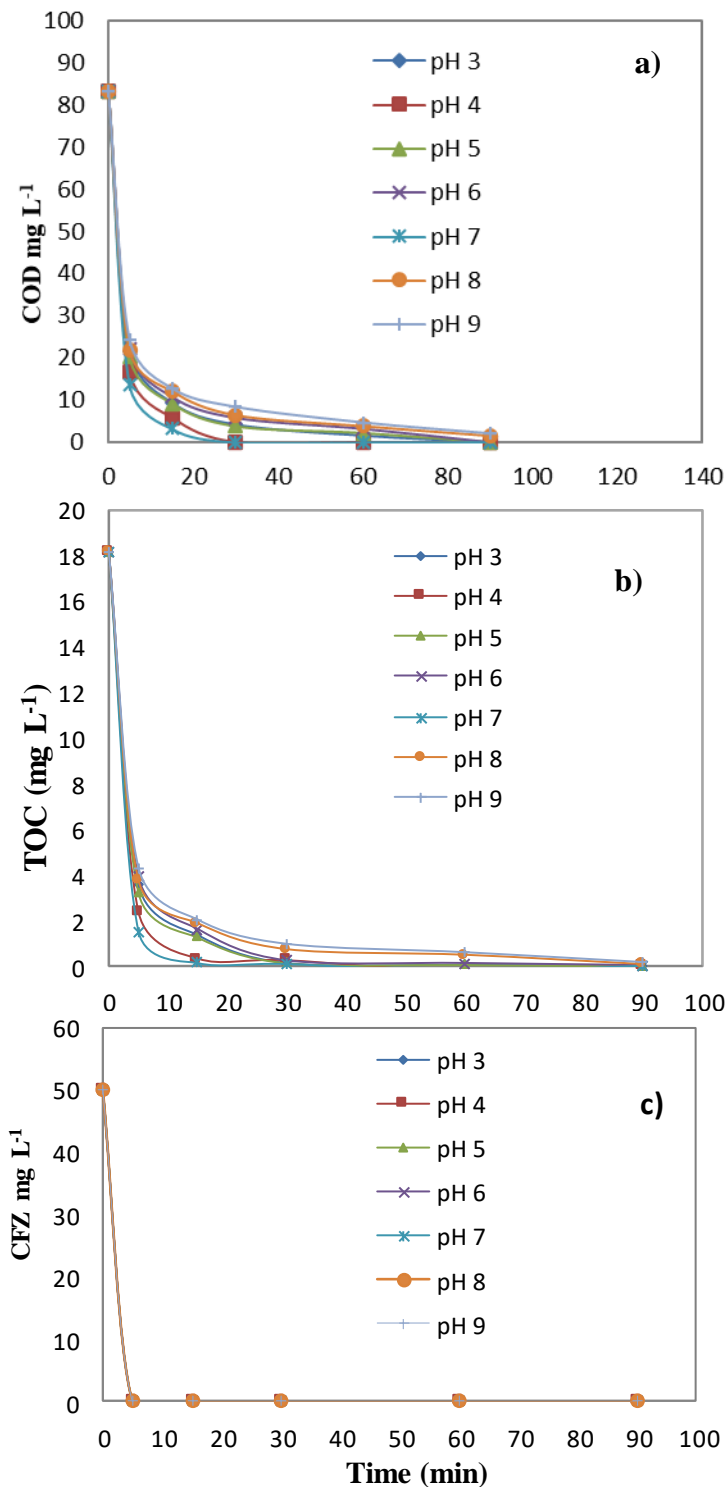


Figure 3. Effect of pH variation (KCl: 750 mg/L, I: 50 mA/cm²) on a) COD (mg/L), b) TOC (mg/L), and c) CFZ conc. (mg/L)

Esfandyari et al. (2019) investigated the degradation of cefazolin in hospital wastewaters with electrocoagulation using aluminum and iron electrodes. Cefazolin removal rates of 90.55, 91.92 and 90.56% were observed at 15 V in 30 min at pH values of 4, 7 and 9, respectively [77]. Esfandyari et al. (2020) studied electrocoagulation with aluminum and iron electrodes for the removal of cefazolin

antibiotics from hospital wastewaters and obtained 69.49%, 79.49%, and 86.67% removal efficiencies, respectively, for TSS (total suspended solids), COD, and cefazolin, at the optimal conditions of pH 7, 30 V and a 30 min reaction time [78]. El-Ghenymy et al. (2013) investigated sulfamethazine removal with an electro-Fenton process with a BDD anode. They observed that the removal rate of sulfamethazine reached 90% at pH 3.0. Dissolved organic carbon decreased at rates of 84%, 84%, 80% and 65% at pH values of 2, 4, 5 and 6, respectively [79]. Xie et al. (2017) stated that the degradation rate of ofloxacin increased from 0.029 min^{-1} to 0.054 min^{-1} with increasing pH from 4 to 11, and the power consumption also decreased from 6.10 kWh/m^3 to 3.98 kWh/m^3 . This may be due to the decrease in the reduction potential of hydroxyl radicals, which diminished from 2.74 V (pH 4) to 2.5 V (pH 11). With the maintenance of the applied potential and current density, the energy barrier decreases, and the valence band holes on the surface of the anode become more energetic, producing more hydroxyl radicals [80]. Wang et al. (2016) investigated the removal of ciprofloxacin with a Sb-doped SnO_2/Ti anode. According to their results, the removal rates (ciprofloxacin and COD removal rates) were greater at higher pH values, while the k_d (kinetic rate constant) and the current efficiency values were the highest at pH 3 [81]. Sivrioğlu and Yonar (2016) investigated the treatment of textile wastewater using a Sn/Sb/Ni-Ti anode. At pH 3, the COD and color removal rates were determined to be 98% and 99%, respectively. Although the natural pH (7.2) of the wastewater showed a slightly lower efficiency (3%) than acidic conditions, 7.2 was chosen as the best to avoid extra pH adjustment and chemical cost [66]. Yonar et al. (2019) explored the electrochemical oxidation of organized industrial district wastewaters in the pH range of 3–6 by using a new generation Sn/Sb/Ni-Ti anode and found that at neutral pH, removal efficiencies were slightly lower (3%) than those obtained at acidic pH values [82]. Kurt (2020) studied the electrooxidation of cefaclor with KCl as the electrolyte, and pH 7 was found to be the optimum for the electrochemical oxidation of cefaclor [57]. As seen from the results of other investigations, the pH parameter has a very important effect on antibiotic destruction by radiation ionization [83, 84]. The pH of the solution could affect the distribution of zwitterion antibiotic molecules and ions, in addition to the charge of the surface, which may create attraction/repulsion between different antibiotics and eventually affect the reaction efficiencies [85].

3.4. Effect of current density

In this study, the removal efficiency variation with current density variation between 10 and 50 mA/cm^2 at 750 mg/L KCl and pH 7 was studied. A value of 50 mA/cm^2 was found to be the optimum current density parameter, providing almost full mineralization after 30 min (TOC value decreased to 0.40 mg/L). The removal efficiencies generally increased with increasing current density, and active oxidants increasingly occurred in aqueous solution. Moreover, the current density parameter considerably affects the electrochemical reactions, playing an active role in reaction kinetics [75]. Fig. 4 shows the effect of the current density parameter on the COD, TOC and CFZ concentrations. According to the graphs in Fig. 4, current density variation considerably affected the reaction efficiencies in parallel for each parameter (COD, TOC and CFZ). The COD was consumed completely in just 60 min of reaction, TOC decreased to 0.40 mg/L in just 30 min, and CFZ was consumed

completely in 5 min at pH 7 with 750 mg/L KCl addition. It is known that organics are oxidized on the surface of anodes, mostly at lower current densities, whereas in this study, electrooxidation occurred in aqueous solution at higher current densities. The current density directly affects the electrochemical oxidation reaction and thus the efficiency [86]. However, it could be possible that oxygen increasingly occurs on the anode surface [87, 88] and may negatively affect the electrode [89].

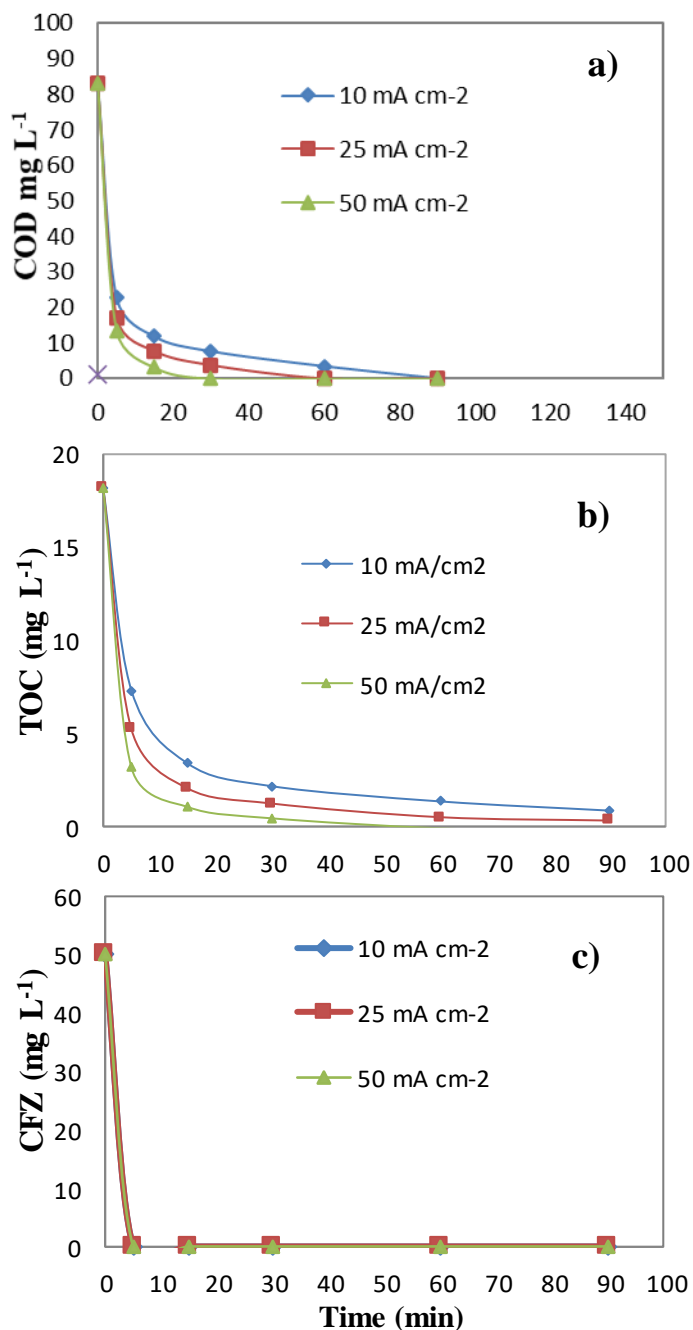


Figure 4. Effect of current density on a) COD (mg/L), b) TOC (mg/L), and c) CFZ conc. (mg/L) (KCl: 750 mg/L, pH 7)

Xie et al. (2017) explored OFL removal with a SnO₂-Sb/FR-PbO₂ anode with a Na₂SO₄ concentration of 0.05 M. The electrooxidation rate increased significantly with increasing current density. However, at a current density of 50 mA/cm², the energy consumption increased from 3.78 kWh/m³ to 6.74 kWh/m³ [80]. Kitazono et al. (2017) reported that the reaction rate constant of chlortetracycline increased with increasing current density with a Ti/PbO₂ anode because of higher OH· production [90]. Eleoterio et al. (2013) observed that COD removal efficiencies increased as the current density increased (from 10 to 100 mA/cm²) with dimensionally stable anodes (DSAs) (Ti/Ru_{0.3}Ti_{0.7}O₂, Ti/Ru_{0.3}Sn_{0.7}O₂, and Ti/(RuO₂)_{0.8}(Ta₂O₅)_{0.2}) for wastewater containing sulfamethoxazole and trimethoprim [91]. Dirany et al. (2010) reported that at lower current densities, oxidation reactions predominantly occurred at the anode; furthermore, at higher current values, sulfamethoxazole was mostly degraded in aqueous solution using a Pt/BDD anode [92]. Hai et al. (2020) studied the removal of sulfamethoxazole with a BDD anode, and SMX was completely degraded after 1 hour of electrochemical reaction at a 45 mA/cm² current density, while it was degraded after 3 h at 15 and 30 mA/cm² current density values [67]. Haidar et al. (2013) investigated sulfachloropyridazine decomposition with a BDD anode; thus, they observed that the reaction time needed for complete degradation decreased with increasing current density [93]. Moreira et al. (2014) reported that trimethoprim oxidation occurred faster at higher current densities with boron-doped or platinum anodes [94]. Jara et al. (2007) investigated the electrochemical oxidation of ofloxacin and lincomycin from wastewaters and found that kinetic rate constants increased with increasing current density [95]. Dirany et al. (2010) explored the electrooxidation of sulfamethoxazole from water with Pt and BDD anodes and carbon felt cell cathodes [92]. With the Pt anode, sulfamethoxazole (SMX) was decomposed in 7, 15, 30 and 60 min at 400, 300, 120 and 60 mA current values, respectively. TOC mineralization of 91% was obtained at 300 mA after 600 min. Due to the synergistic effect of hydroxyl radicals forming at the anode and aqueous solution, the amount of ·OH was larger at the anode and the aqueous solution with the BDD anode. Complete destruction of SMX occurred in 15, 20 and 25 min at 200, 120 and 60 mA, respectively. Furthermore, nearly complete mineralization (>95%) was achieved with the BDD anode. However, SMX oxidation did not accelerate at higher currents (450 mA), which could be due to parasitic reactions occurring at the cathode: H₂ evolution and ·OH self-destruction on the anodic surface. This can be attributed to the predominance of competition for oxidant production and oxygen formation on the surface of the anode at higher current densities, as indicated in the following reaction [96, 97]:



However, although BDD anodes have shown satisfying results for antibiotic removal, they have a high capital cost and are not as practical as Sn/Sb/Ni-Ti anodes [98]. In contrast to BDD anodes, Sn/Sb/Ni-Ti anodes are cost-effective. Applying Sn/Sb/Ni-Ti anodes, a 37% current efficiency could be reached at room temperature [63]. In this respect, Sb-doped SnO₂ anodes are advantageous due to their cost efficiencies and practical application. In a study conducted by Zakaria and Christensen (2014), 1000 mg/L Reactive Blue 50 dye fed to a membrane electrochemical electrode

reactor system was 100% removed within 5 minutes with a platinized titanium cathode and Sn/Sb/Ni anode. Qian et al. (2019) reported that the degradation of tetracycline antibiotics was lower than 2% within 2 h without power with SnO₂-Sb₂O₃ and PbO₂-doped Ti anodes, which indicates that the adsorption of antibiotics on the anode could be negligibly low. The removal rates of tetracyclines increased progressively with increasing current density, and they reached 98.1%, 97.6% and 99.5% at 15 mA/cm² in 2 hours for tetracycline (TC), oxytetracycline (OTC) and chlortetracycline (CTC), respectively. However, the removal rates of tetracycline, oxytetracycline and chlortetracycline were 79.5%, 82.0% and 90.3% at 5 mA/cm², respectively [69].

Zhi et al. (2017) stated that the degradation of tetracycline (TC) increased with increasing current density with a Ti/SnO₂-Sb anode. At a current density in the range of 5–25 mA/cm², the kinetic reaction constants increased from 3.6×10⁻² min⁻¹ to 7.8×10⁻² min⁻¹, while the half-life (t_{1/2}) decreased from 15.9 min to 5.3 min [58]. Yonar et al. (2019) reported electrochemical color removal from wastewater with a Sn/Sb/Ni-Ti anode, and they observed that the current density parameter was the most important parameter affecting the reaction efficiencies. Energy consumption of 0.6 kWh gCOD⁻¹ was obtained at 10–25 mA cm⁻² current density values, which was the lowest, while energy consumption of 9.12 kWh kgCOD⁻¹ was attained at a current density of 100 mA cm⁻², which was the highest value. They found the optimum current density to be 50 mA cm⁻² [82]. Kurt (2020) investigated the anodic oxidation of cefaclor with a Sn/Sb/Ni anode and platinized titanium cathode. A current density of 50 mA cm⁻² was found to be the best value [57]. Sivrioğlu and Yonar (2016) investigated COD and color removal from textile wastewater using Sn/Sb/Ni-Ti anodes. They obtained more efficient results at lower current densities (50 mA/cm²) [66].

3.5. SEM images of the anodes

The electrodeposition conditions of Ni/Sb-SnO₂, applied current, reaction time, etc., may have important effects on the composition and crystal orientation of the anode surface and thus the anode performance [99]. Typical scanning electron microscopy images (×50, bar = 500 μm) of Sn/Sb/Ni-coated Ti anodes with a Sn/Sb/Ni molar ratio of 500/8/2 are shown in Fig. 5 at ×50 magnification for clean and contaminated (used) anodes. There were cracks on the clean anode, especially on the intersection points of the mesh, that could have been the result of thermal shocking while cooling after the heating process in an oven [65, 100, 101]. In contrast, a filled and raised surface was observed for the anode that may have resulted from ions formed via direct oxidation at lower current values with NaSO₄ addition [68] and sourced from carbon and Fe₃(PO₄)₂(OH)₂ salts passing from the aqueous solution. Zhi et al. (2017) explored the destruction of tetracycline antibiotics with Ti/SnO₂-Sb anodes, and they used the sol-gel technique to coat the anode. The SEM images revealed that the anode surface was generally firm and smooth, even though there were some cracks ranging in size from 1–10 μm. Additionally, they found that the formation of those cracks may cause gradual inhibition of the anode during the electrochemical process [58]. Qian et al. (2019) reported that the surface of the pretreated Ti substrate of a Ti/SnO₂-Sb₂O₃/PbO₂ anode is nonuniform and scabrous, which may be a

result of processing by oxalic acid. Thus, they stated that it could be practicable to load $\text{SnO}_2\text{-Sb}_2\text{O}_3$ and PbO_2 as interlayers and active layers, respectively [69].

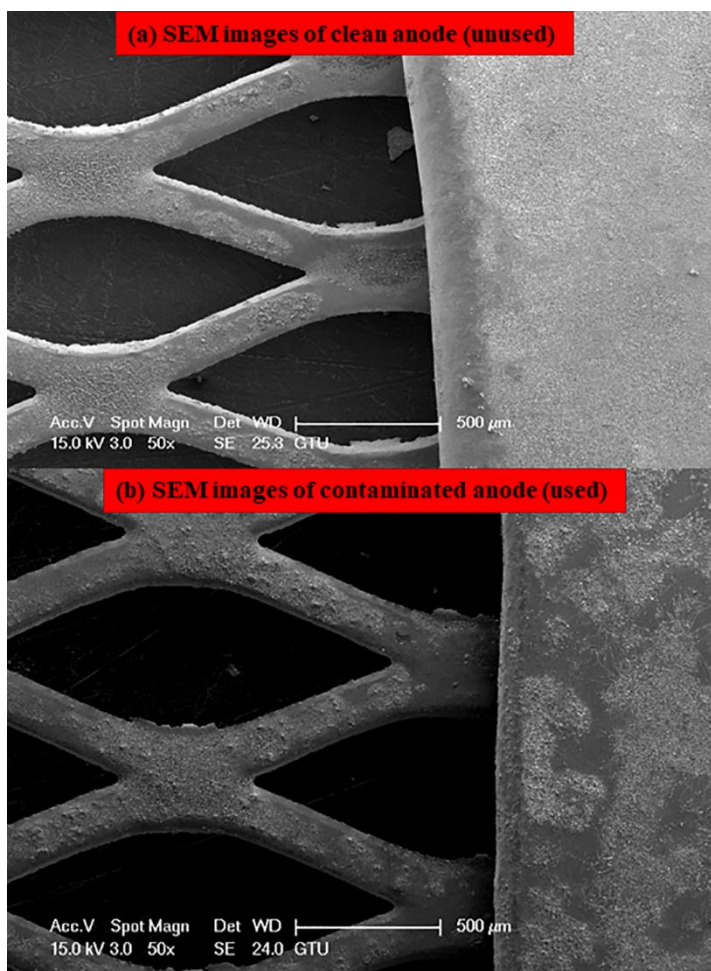


Figure 5. Typical SEM images ($\times 50$, bar = 500 μm) of Sn/Sb/Ni-coated Ti anodes with a Sn/Sb/Ni molar ratio of 500/8/2: (a) clean anode (unused) and (b) contaminated anode (used)

Fig. 6 and Fig. 7 show AFM images of the clean (unused) and contaminated (used) anodes for upper and bottom cross sections of the meshes, from which topographic height changes can be observed. There were significant differences between the clean and used anodes in terms of topographic height changes. However, it is known that the physicochemical properties of anodes are directly affected by their preparation methods. The particle size, composition ratios, structure of the surface, bonding force and specific surface area directly affect the anode performance [71]. Irregularities were observed on the used anode compared to the clean anode, which may be due to the passing of ions and carbon molecules from the aqueous solution (mostly direct oxidation).

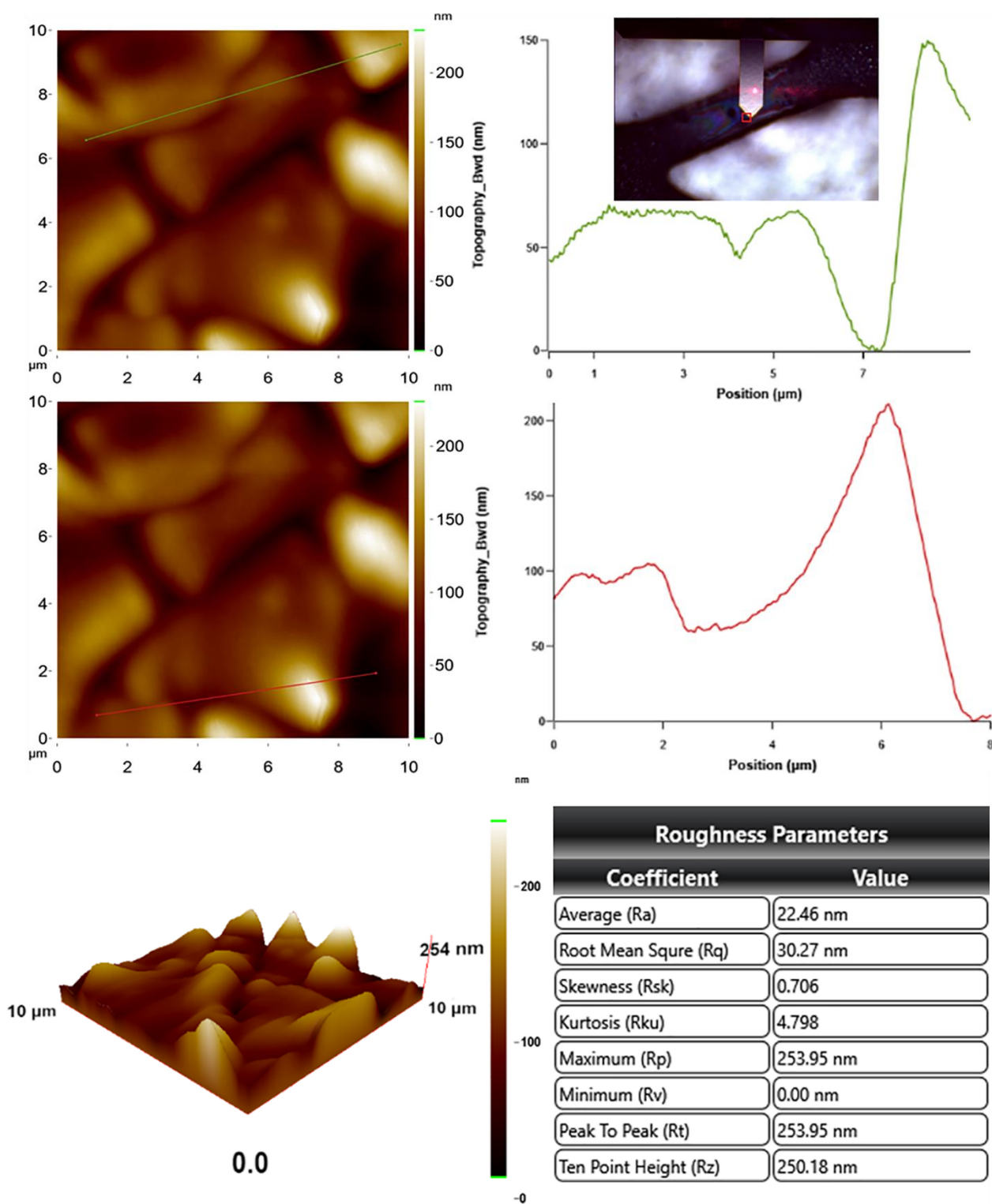


Figure 6. AFM images of the Sn/Sb/Ni-coated Ti anode with a Sn/Sb/Ni molar ratio of 500/8/2 for clean anodes (unused): upper cross section and bottom cross section of the mesh

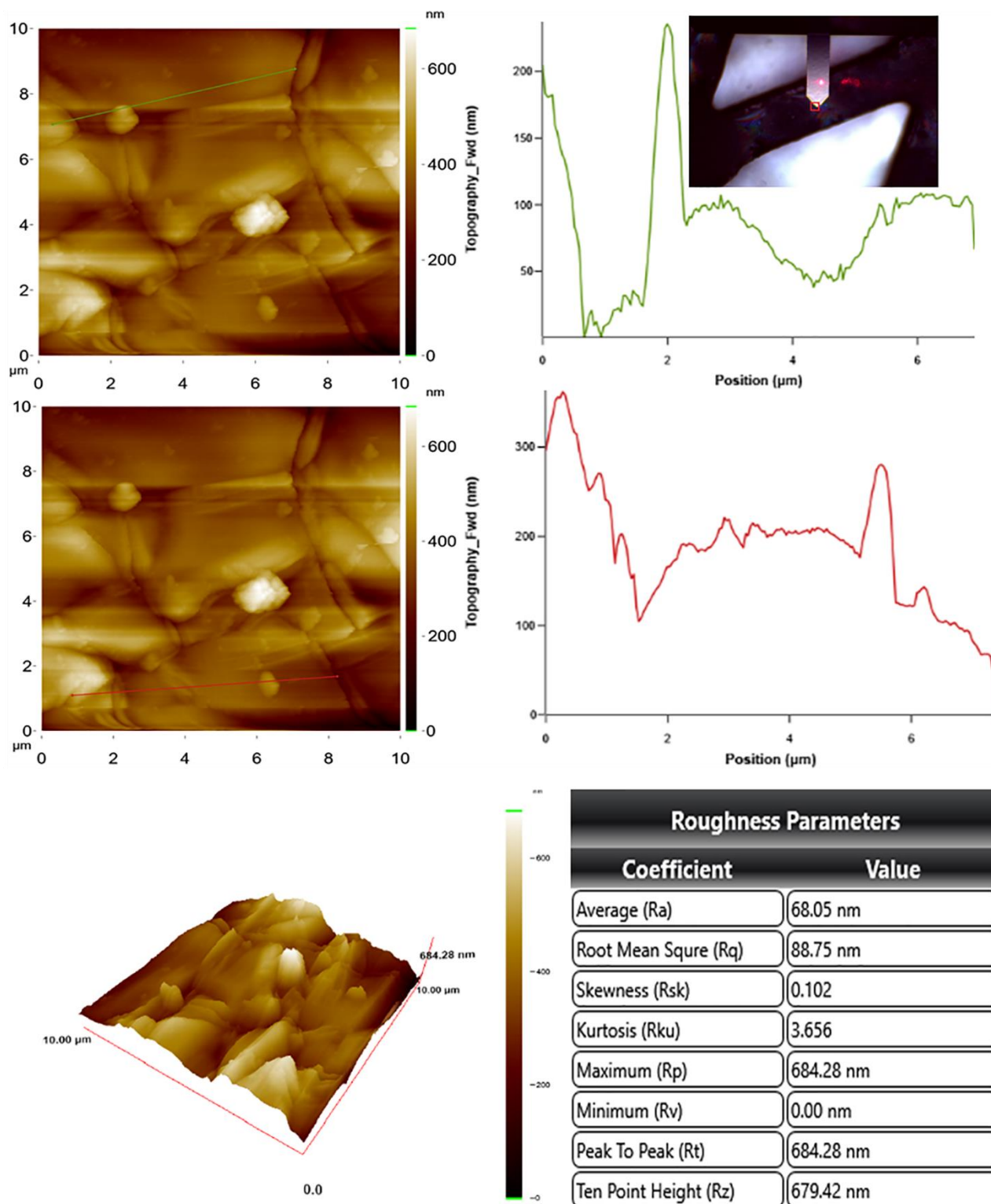


Figure 7. AFM images of the Sn/Sb/Ni-coated Ti anode with a Sn/Sb/Ni molar ratio of 500/8/2 for the contaminated anode (used): upper cross section and bottom cross section of the mesh

4. CONCLUSIONS

In this study, the removal of cefazolin antibiotics with a novel stable Sb-SnO₂ composite anode was investigated. Three control parameters, electrolyte type and concentration, pH, and current density, were evaluated. Comparison of different types of electrolytes, NaCl, Na₂SO₄ and KCl, was performed for 100–2500 mg/L (NaCl and Na₂SO₄) and 250–1500 mg/L (KCl) concentration ranges. KCl was found to be the optimum electrolyte type affecting the electrochemical reactions the most, even at lower doses than the other electrolytes. Thus, according to the obtained results, it was assumed that it could be possible to reach higher removal efficiencies with real water/wastewater samples (assuming they include Cl⁻), even without the addition of extra electrolytic chemicals. pH 7, the neutral pH value of aqueous solution, was determined to be the best value as it provided higher removal efficiencies. Therefore, it could be possible to operate the process more easily and more economically by working at natural pH values, as there is no need for additional chemicals and extra pH adjustment steps. The removal efficiencies generally increased with increasing current density because active oxidants increasingly occurred at higher values. The best current density value was 50 mA/cm², providing full mineralization after just 30 min. In our study, more efficient results were obtained at lower current densities (50 mA/cm²) with the Sn/Sb/Ni anode than with the other types of anodes used in most of the studies on the electrochemical treatment of antibiotics. Consequently, electrochemical oxidation processes with Sb-doped SnO₂ anodes were found to be very useful and applicable in terms of achieving higher removal efficiencies and having a low cost for the degradation of cefazolin antibiotics in water.

ACKNOWLEDGEMENTS

The authors thank the Bursa Uludag University Research Projects Department for their support (project no. OUAP(MH)-2018/8).

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