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Effect of Nickel Concentration on Ozone Production using Nickel-Antimony Doped Tin Oxide for Wastewater Treatment

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Abstract: Nickel-antimony doped tin oxide (NATO) catalyst has greatly considered its capability to treat high organic matter and eliminate colour in wastewater as palm oil mill wastewater with electrochemical ozone generation. This study presents the optimal Ni content of NATO and its properties to enhance ozone generation. The NATO anodes were fabricated by dip-coating, varying the Ni content between 0.5% and 5%. The key findings show that all anodes showed a single phase of rutile structure with the cracked mud on the surface. The binding energies of the $Sb3d_{3/2}$ peak at 540.48 eV and 541.58 eV agree with Sb^{3+} and Sb^{5+}, respectively. The optimal ozone current efficiency of 37% at the current density of ca. 0.22 A cm^{-2} in 0.5 M H_2SO_4 at 2.7V was obtained on the NATO anode with 2% Ni content calcined at 700 °C. The palm oil mill wastewater treatment had the efficiency of decolourisation TOC and COD removal increased with increasing electrolysis time. The colour removal efficiency achieved was more than 85% for a reaction time of 15 min. The efficiency of TOC and COD removal was reached ca. 80% in 20 min. The overall results appeared that NATO with electrochemical ozone generation could be employed to treat palm oil mill wastewater with high efficiency due to •OH and O_3.

Keywords: Palm Oil Mill Wastewater; Ni-Sb/SnO_2; Ozone; Electrochemical

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1. Introduction

Advanced oxidation processes (AOPs) have been extensively applied to water and wastewater treatment to eliminate organic substances and hazardous and toxic pollutants before treatment with conventional methods [1]. The mechanism of AOPs is based on hydroxyl radicals with high potential oxidation (2.87eV) [2]. AOPs technology consists of ozonation, UV/H_2O_2, photocatalytic oxidation, electro-oxidation and Fenton's oxidation [3]. Ozone is a powerful oxidizing agent. The most common method of generating ozone on the industrial scale is using Cold Corona Discharge (CCD) and the electrochemical generating of ozone. The latter has many potential advantages, including low voltage operation and the possibility of generating high concentrations of ozone in the gas and liquid phases with high current efficiency [4]. The water electrolysis can produce through a 6-electron process at an anode ($E^o = 1.51$ V).

Several electrode materials have been studied concerning ozone activity and selectivity over many years, including graphite, glassy-carbon, platinum, boron-doped diamond (BDD) and Ni/Sb-SnO_2 (NATO) [5]. Recently, it has been reported that the applicability of the NATO electrodes was employed for the degradation of refractory pollutants, decolourisation, microorganisms removal and decomposition of organic compounds [6] [7]. Wang and co-workers [7] reported that the 4-chlorophenol (4-CP) was degraded using a NATO anode via an electrochemical process. It has been suggested that Ni co-doped Sb-SnO_2 could produce •OH radicals that can form ozone without organic molecules. Zakaria and Christensen (2014) [6] and Maneelok et al. (2018) [8] have reported complete decolourisation of Reactive Blue 50 (RB50) Dye solution due to the destruction of the anthraquinone moiety using NATO anode at 2.7V. Furthermore, Sun and co-workers (2015) [9] reported that co-doping of Ce-Ni into Sb-SnO_2 can enhance phenol degradation and TOC removal as well as electrocatalytic activity and service life due to the changes in the concentration of oxygen vacancies in the lattice of SnO_2 and the generation of reactive oxygen species (ROS) in the solution for indirect oxidation. With respect to previous studies, a novel material as NATO could enhanced the degradation of toxic organic compounds. However, most of studies above were investigated on synthetic wastewater, of which the composition was simple. While the real wastewater always contained organics, complex inorganics, solid and microorganisms [10]. Thus, the applicability of NATO anodes in real wastewater as Palm oil mill wastewater (POW) was investigated.

Palm oil mill wastewater treatment is crucial. In terms of composition, POW is a complex liquid consisting of macromolecules, such as polysaccharides, lipids, proteins, and many monocyclic and polymeric aromatic molecules with typically the chemical oxygen demand (COD) of 15,000-100,000 mg/L, biochemical oxygen demand (BOD) of 10,000-43,750 mg/L, pH of 3.4-5.2, oil and grease of 8 g/l, suspended solids of 20 g/l, and total solids of 40 g/l [11]. Several treatment methods for POW have been proposed, such as adsorption, electrocoagulation, photocatalytic oxidation, ultrafiltration and conventional method as aerobic and anaerobic treatment [12]. Alternatively, the electrochemical process was considered to overcome the drawbacks of traditional and wastewater treatment technologies due to its simplicity in operation, no chemical addition required, and less sludge production [13]. Thus, this research focused on the palm oil mill wastewater treatment by using electrochemical ozone generation at NATO electrodes while investigating the effect of Ni content on the performance of the NATO anodes concerning electrocatalytic activity and the active site for ozone generation. The surface properties of NATO anodes were carried out, and the ozone generation by the electrochemical process for POW treatment was evaluated.

2. Materials and Methods

2.1 Synthesis method

The electrode preparation and dip-coating synthesis to fabricate Nickel-Antimony doped Tin Oxide anodes (NATO) were adapted from Christensen et al. (2014) [6] and Maneelok et al. (2018)[8]. The precursor solutions contained $SnCl_4.5H_2O$, $SbCl_3$ and $NiCl_2.6H_2O$ in the mole ratio Sn:Sb:Ni of 500: 8: x, where x represents the Ni content with varying doping levels at 0.5, 1, 2, 3, 4, and 5. All chemicals were dissolved in ethanol. The titanium substrates were dipped in the catalyst solution and were then calcined in a furnace at 700 ^{o}C for 1 hour. The electrodes were allowed to cool in the air, after which they were weighed.

2.2 Analytical method

The NATO anodes were characterised by structure, morphology and chemical composition. The determination of structure was carried out by X-ray diffraction (XRD). Scanning Electron Microscope (SEM), Energy Dispersive X-ray Spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS) were employed to observe the morphology and chemical composition, respectively. The electrochemical oxidation process measured the generation of ozone. 3 cm^3 of 0.5M H_2SO_4 was utilised as an electrolyte. A 0.64 cm^2 Pt-Ti mesh was employed as a cathode. Both electrodes were comprised of the cuvette cell and placed in the cuvette holder in a UV spectrophotometer. A reference spectrum was collected with the potential at 2.7V for the 30s. The steady-state absorbance at 258 nm was used to calculate the current efficiency, assuming an extinction coefficient of 3000 M^{-1} cm^{-1} [5]. The current efficiency of ozone (%CE) was calculated from:

$$\eta = 58.A_{O3} / Q$$

Where A is the ozone absorbance and Q is the charge passed

2.3 Wastewater collection and characterisation

The Palm oil mill wastewater was collected from the final anaerobic tank of Palm Oil Company, Nakhon Si Thammarat, Thailand. The samples were preserved in the fridge with a temperature of less than 4 °C. Decolourisation experiments were carried out using the NATO anodes at 2.7V as a function of electrolysis time (0.5, 5, 10, 15 and 30 min). M/NATO anode was employed with a 0.64 cm^2 Pt/Ti mesh as a cathode in a quartz cuvette cell placed in the spectrophotometer. During the experiment, the current and absorbance was recorded. Decolourization was determined from the absorbance of the 383 nm band [14] in the ratio A/A_0. Palm oil mill wastewater was analysed for COD using the Closed Reflux, Titrimetric Method (5220C) [15]. The high-temperature combustion method (5310B) was used to measure TOC. The Palm oil mill wastewater remediation was evaluated from the measurements of COD and TOC as follows:

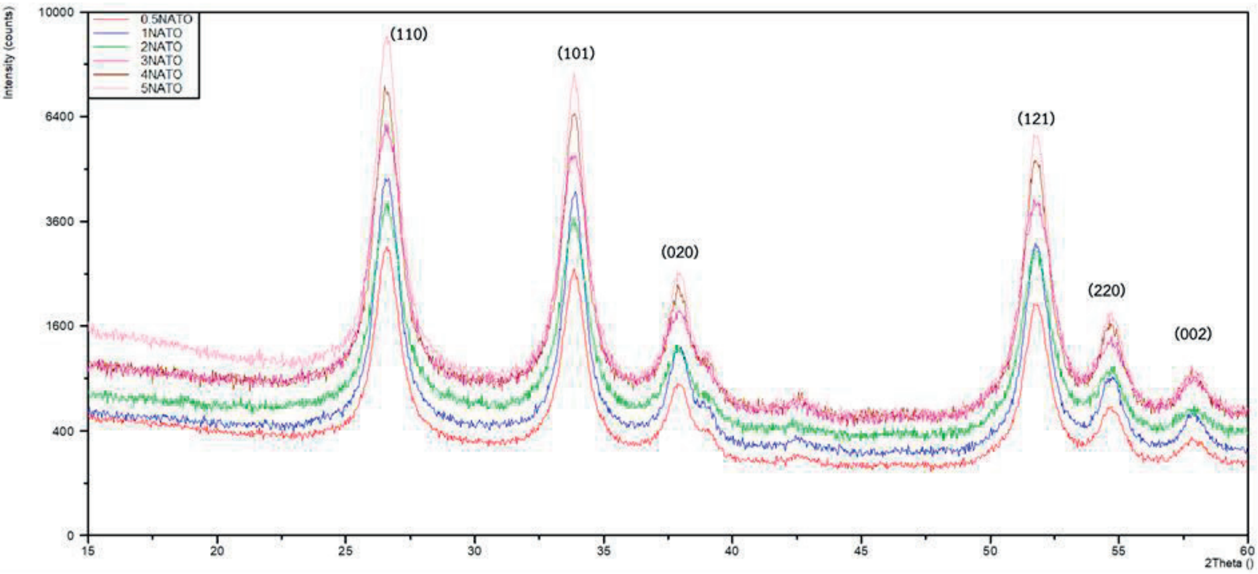
$$COD, TOC = \frac{100\times(C_i - C_t)}{C_i}$$

Where C_i is the concentration of COD and TOC before treatment and C_t the COD and TOC after a time t [10]

3. Results and Discussion

3.1 The electrode surface characterisation

The prepared NATO electrodes calcined at 700 °C with different Ni content of Sn:Sb:Ni in a mole ratio of 500:8:x where x is 0.5-5 presents the Ni content. Figure 1 shows the XRD pattern of NATO with different Ni loading. It can be seen that the result of XRD patterns in all samples shows the single crystalline phase of the rutile structure. The crystal structures is the space group (SG): $P4_2/mnm$ and the unit cell parameter are the values of: a = b = 0.4738 nm and c = 0.3187 nm [4]. Regarding the peak position of all the XRD patterns, they (2θ = 26.6, 33.8, 37.9, 51.8, 54.7 and 57.9°) were attributed to 110, 101, 020, 121, 220, 002 planes of SnO_2. Hence, the patterns of all products agreed well with the reflection of a single phase of "SnO_2; Tin Oxide; Cassiterite, syn; Q: S; 00-041-1445" obtained from the crystallographic database ICSD 39173. No characteristic impurity was detected. When comparing the SnO_2 pattern with other research [8, 9]. It was found that the diffraction peaks of all products were quite the same as the position peaks of those. Regarding the effect of Ni content, there is no effect of Ni content up to 5%Ni on the structure. This suggests that the addition of nickel and antimony to tin oxide did not change the crystal structure, suggesting that Ni and Sb replaced Sn ion in the lattice of SnO_2. It can be explained that the ionic radius of Sb^{3+} and Sb^{5+} is 0.76 A° and 0.60 A°, respectively. Ni^{2+} and Ni^{3+} ionic is ca. 0.69 A° and 0.72 A°, respectively whilst the ionic radius of Sn^{4+} is 0.69 A° [9]. Hence, the Sb^{5+} and Ni^{2+} ions could substitute Sn^{4+} ions in the bulk of the lattice. The Sb^{3+} and Ni^{3+} ions might be placed at the surface [16].



Figures 1. The XRD patterns of the NATO samples were calcined at 700 ºC with various Ni content from 0.5%Ni to 5% Ni.

The typical SEM and EDX images of the 5NATO electrode calcined at 700ºC, as represented by the cross on the electrode, are shown in Figure 2. It can be seen from Figure 2(a) that the electrode morphology showed the smooth, cracked mud structure resulting from mechanical tension and stress inside the coating. These could occur from the dopant, the plasticity of the coating, and the difference between the thermal expansion coefficients of the Ti substrate and the coating [17]. Despite the change in nickel concentration, it is clear that the morphology of all anodes is quite the same. However, It has been reported that the Sb and Ni content can affect morphology. Wang et al.(2013) [18] reported that a NATO catalyst with a high nickel content and low antimony concentration appeared to display a smooth surface. The EDX spectra of 5NATO electrodes calcined at 700 ºC at the cross are shown in Fig. 2(b). It can be seen from the figures that Sn, Sb and O were detected but no Ni due to the limitations of the instrument. However, the element Sn, Sb, Ni, O and Ti in term of weight percentage show the percentage of nickel were observed.

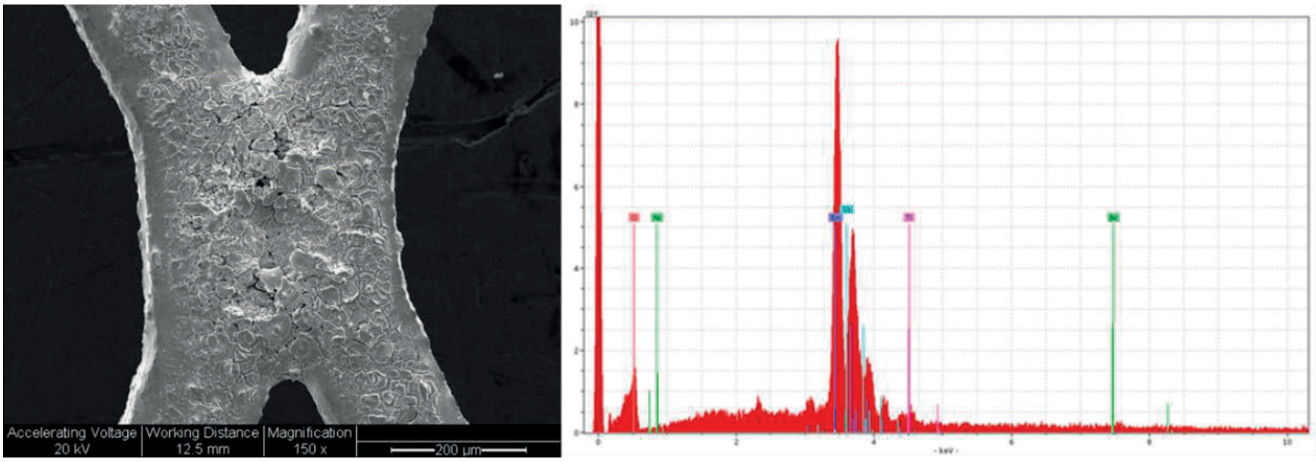


Figure 2.(a) A typical SEM image and **(b)** EDX spectra of 5NATO anode calcined at 700 ºC: magnification x 150 and scale bar = 200 μm

The broad scan XPS spectrum clearly shows photoelectric peaks that correspond to Sn, Sb and O; however, no Ni peak was observed at the surface of the NATO. Figures 3(a) and (b) show the spectrum of

Sn3d and Sb3d states for 0.5NATO anode calcined at 700 °C, respectively. As can be seen from the figures, the spin-orbital of the Sn3d peak of all the samples split into $Sn3d_{3/2}$ and $Sn3d_{5/2}$, with a symmetric peak shape component that was fitted at a binding energy of 495.5 and 487.9 eV, respectively. A good fit was obtained between the experimental and calculated data, which leads to assigning the state of Sn^{4+} within Sb-SnO_2 in agreement with the literature [16]. No chemical shift of the Sn3d state was observed after doping with Sb and Ni, and the separation distance between $Sn3d_{3/2}$ and $Sn3d_{5/2}$ peaks of both samples is equal to 8.4 eV, which agrees with Babar et al.(2011) [19]. They had detected a gap of ca.8.5 eV between the $Sn3d_{3/2}$ and $Sn3d_{5/2}$ peaks.

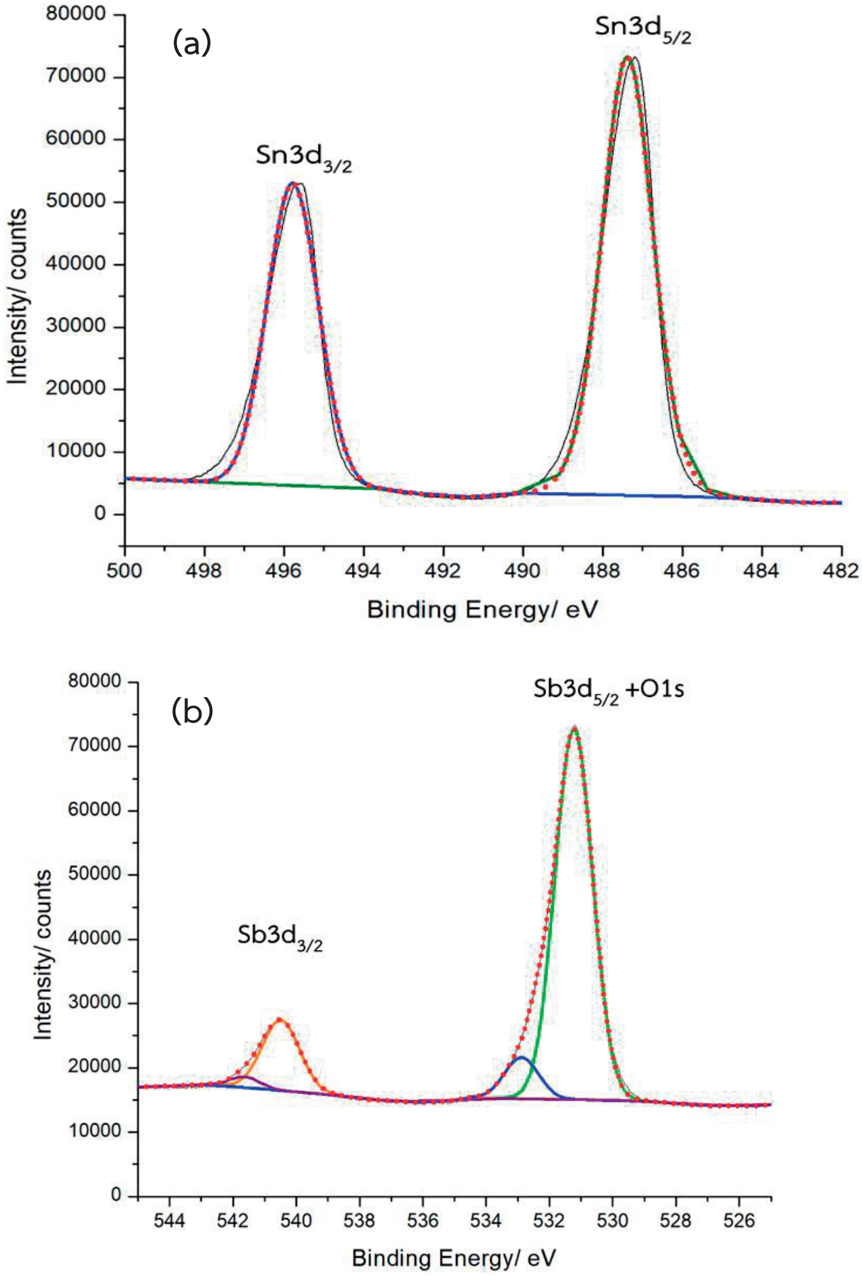


Figure 3. The fitting of the XPS spectra of the (a) Sn3d and (b) Sb3d peak of 0.5NATO electrode calcined at 700 °C: the dotted line is the raw data and the solid line is the synthesised curve and components.

As can be seen in figure 3(b), the binding energy of the $Sb3d_{3/2}$ was at 540.48 eV and 541.58 eV corresponding to Sb^{3+} and Sb^{5+}, respectively. The $Sb3d_{5/2}$ peak shows that the $Sb3d_{5/2}$ and O 1s region are dominated by the O 1s peak, which is broad and asymmetric, suggesting the other oxygen species contributions.

Peaks with binding energies in the range 530-531.5 eV in the spectra of metal oxides are commonly attributed to lattice oxygen species (MOx) [20]. Moreover, oxygen directly bonded to metals (M-O) gives increases to peaks in the range 530.0-532.0 eV, and metal hydroxides (M-OH) to peaks with binding energies of 531-533.5 eV [20]. Babar and co-workers (2011) [19] observed the XPS spectra of ATO thin film with binding energies between 530.45 and 530.57 eV were attributed to chemisorbed oxygen, along with a peak at 532 eV indicating M-OH.

3.2. Effect of Ni content on ozone generation

Figure 4 shows the current efficiencies and the current densities of the NATO anodes series as a function of the nickel content in the precursor solutions. As seen from the figure, the current efficiency of all NATO anodes showed the same behaviour: the current efficiencies increased steadily with increasing Ni content up to 2%Ni before decreasing Ni by doping Ni up to 5%. This might be due to an increase resistant to doping Ni. This result is in agreement with the work of Wang et al. (2006) [7] reported that the resistivities of Ni/Sb-SnO_2 electrodes effectively increased by a factor of ca.100 on doping with 1.0 at%Ni (from 0.2 Ωcm^{-1} for undoped Ni to 20 Ωcm^{-1} for 1 at.%Ni). Moreover, the current efficiency was decreased because the ratio of O_3 and O_2 active sites decreased with increasing Ni content. The optimum electrode was 2NATO calcined at 700 ^oC. The anode showed the highest current efficiency and density at ca. 37% and 0.22 A cm^{-2}, respectively. Wang et al.(2006) [7] and Shekarchizade and Amini (2011) [17] found that current efficiency decreased with Ni doping, with the optimum Ni concentration being ca. 0.2 at.%.

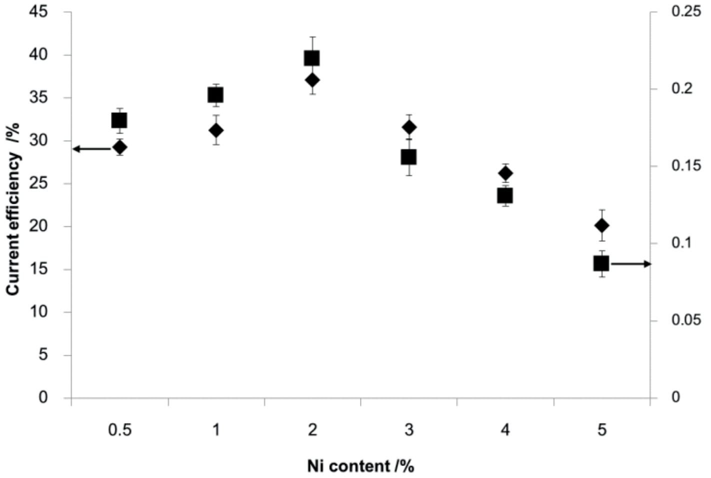


Figure 4. Plots of current efficiency and current density vs the nickel concentration in the precursor solution for the NATO series anodes of 0.5M H_2SO_4 at 2.7V.

3.3. Effect of ozone on degradation and decolourisation of POW

The properties of POW before and after the electrochemical ozone generation process by the 2NATO anode are summarized in Table 1. As can be observed from table 1, the pH increased after electrolysis due to hydroxide formation, and hence COD and TOC also decreased as a function of time.

Table 1. Characteristics of Palm oil mill wastewater after electrolysis for 30 minutes with electrochemical ozone generation process.

Parameter	Before ozonation	After ozonation
pH	5.14	5.87
COD (mg L^{-1})	8,540	1,238
TOC (mg L^{-1})	178.6	30.79

The effect of current density and ozone current efficiency on the removal of COD, TOC and colour from the POW was investigated on the 2NATO anode corresponding to the highest current efficiency. The experiment operated under the same conditions as in the previous section. Figure 5 shows removal efficiency for decolourisation, COD and TOC as a function of time. As may be seen, the absorbance decreased by ca. 80% in 10 min and ca. 90% in 25 min. COD and TOC removal in POW were achieved more than 80% after electrolysis for 15 min and 20 min, respectively. Regarding electrochemical ozone generation, it is generally assumed that water oxidation on NATO anodes involves the formation of OH radicals, which then react with dye molecules and toxic substant [21] :

$$H_2O \rightarrow OH\bullet + H^+ + e^- \quad (1)$$

A more detailed mechanism has been prepared by [21] .Firstly, water oxidation yields the adsorbed hydroxyl radical (•OH) according to equation (2) .This radical interacts with lattice oxygen at the surface yielding "active oxygen" MO_{x+1}, see reaction (3) .Finally, the MO_{x+1} reacts with the organic pollutant (R) according to reaction (4):

$$MO_x + H_2O \rightarrow MO_x(\bullet OH) + H^+ + e^- \quad (2)$$

$$MO_x(\bullet OH) \rightarrow MO_{x+1} + H^+ + e^- \quad (3)$$

$$MO_{x+1} + R \rightarrow MO_x + RO \quad (4)$$

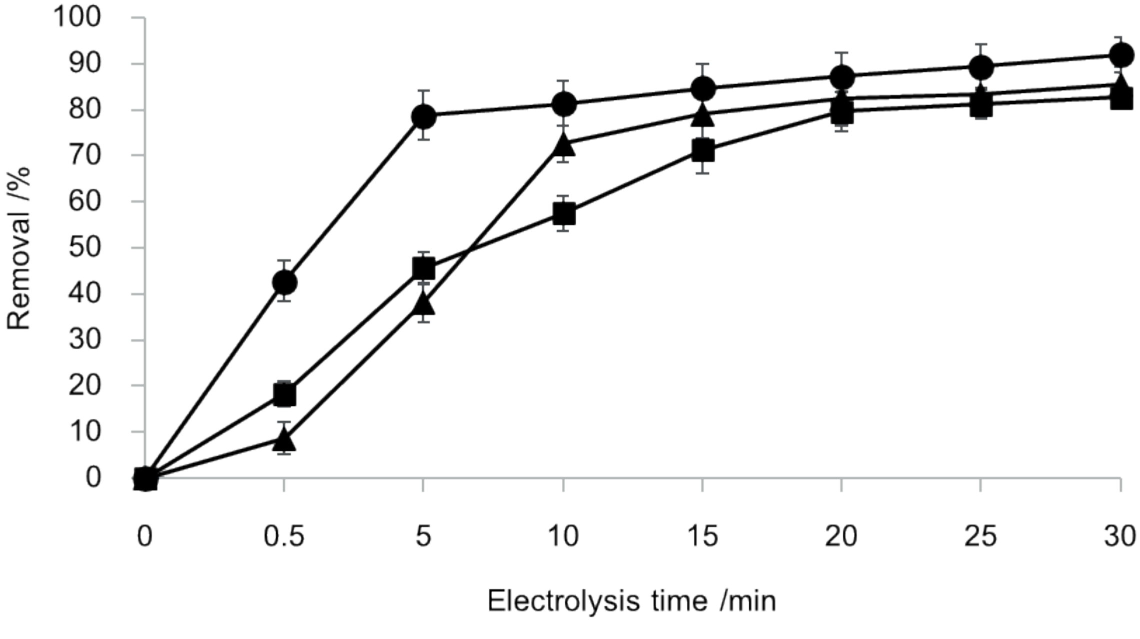


Figure 5. Plots of the removal of (●) colour, (▲) COD and (■) TOC removal of POW as a function of time at 2.7 V using 2NATO anode.

4. Conclusions

NATO anodes were prepared by dip-coating method with various Ni doping levels to investigate electrochemical ozone generation and their surface properties. Furthermore, the anodes were employed to examine the electrocatalytic activities for decolourisation and degradation of organic pollutants in POW. The XRD characterisation shows a single phase of rutile structure. Sb and Ni are substituted into the SnO_2 lattice, suggesting that Sb^{3+} ions at the surface of the crystallites provide the active sites for oxygen adsorption. The morphology of all NATO showed the cracked mud structure due to mechanical tension and stress inside the coating. The element composition of NATO anodes shows Sn, Sb, Ni, O and Ti. For the chemical oxidation state, it was found that the peaks at 495.5 eV and 487.7 eV of the 0.5NATO are attributed to the Sn^{4+} state. The binding energy of the $Sb3d_{3/2}$ was at 540.48 eV and 541.58 eV, corresponding to Sb^{3+} and Sb^{5+}, respectively. The current efficiency and density increased with doping Ni up to 2%, then decreased gradually with increasing Ni content up to 5% due to its resistance. The optimum current efficiency of ca. 37% and current density of 0.22 A cm^{-2} were observed for the 2NATO. Decolourisation and degradation of POW, the colour removal was achieved ca. 80% in 10 min. The performance of COD and TOC reduction increased with increasing ozonation time. The efficiency of COD removal increased linearly up to > 80% after electrolysis for 15 min and 20 min for TOC. Hence, a higher electrochemical oxidation rate is observed at higher current densities due to more elevated ozone and hydroxyl radicals production.

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