Electrochemical Degradation of Textile Effluent Using Novel Ozone Generating Sn-Sb-Ni Anodes

[Taner YONAR* and Özge SİVRİOĞLU]

Abstract- The application of Sn-Sb-Ni electrodes for the treatment of waste streams is promising for ozone production by electrolysis of water because of their stability and over potential for the oxygen evolution reaction. These series of anodes have high electrochemical ozone generation potential at ambient conditions (apprioximately 40% current efficiency). But the usinng and testing of these novel anodes for real wastewater are too limited in literature. Titanium mesh substrate coated with Sn-Sb-Ni alloy was used as anode immersed in wastewater at room temperature with platinised titanium cathode. Five operational parameter ssuch as: initial dye concentration, pH, COD, applied voltage/current and the contact time were evaluated for the ozonation process. Experimental findings revealed that after 30 min the degradation efficiency of dye and COD could reach upto 99% and 98% respectively at pH 3 and temperature of 25°C as the optimum conditions.

Keywords- Elelctrochemical ozone gerenartion, textile wastewater, COD, colour

I.   Introduction
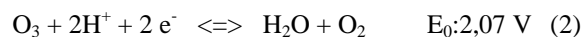
Textile dyehous effluents usualy generates primarily high amount of coloured and organic waste contents. These pollutants creates aesthetic and toxic problems on water bodies. Strict discharge regulations and public demand of color-free effluent dictate a colour removal process applications for industries [1]. Traditional processes including physico-chemical and bilogical stages can not treat colour content of textile industry [2]. From these reason different treatment alternatives are getting attention for treating coloured and toxic content of textile wastewater in last two decades.

Electrochemical treatment of synthetic dyestuff was studied in literature widely and 80-95% COD and colour removal efficiencies reported [3,4,5]. During these studies diffrent types of anodes were used. In last years, Sn-Sb-Ni/Ti anodes shows superior performance on electrochemical ozone generation studies [6]. But the testing of these anodes on synthetic or real wastewater samples are too limited in literature. [7,8,9,10,11,12].

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Current technology in ozone production utilizes several techniques [13] but in situ ozone can be generated by following technologies: (i) Corona discharge (dielectric barrier discharge); (ii) UV irradiation (photochemistry) and (iii) Electrochemical ozone production (electrolysis of aqueous solutions) [9,14]

Corona process, which is the traditional way to produce ozone, utilizes electrical discharges. In this process ozone is generated by passing dry oxygen or air through a high energy electric field, which oxygen is converted into ozone, generated an AC high voltage applied across plate and ground electrodes covered by dielectric [13,14,15]. For the efficiency of ozone generation ($O_2 + O \longrightarrow O_3$) in Corona discharge following factors are important; (i) oxygen source, (ii) gas temperature and (iii) presence of impurities in the gaseous phase [10]. The second type of ozone generation is UV irradiation at 185 nm but ozone concentration is lower and enery consumption is higher than corona discharge. Also periodic replacement of UV lamps makes additional expenses [12]. And the third type ozone generation is electrochemical process where water is used as electrolyte and at anode and cathode water dissociates into hydrogen and oxygen (See Eqs. 1-3) [16]. Ozone is generated at the anode surface and it competes with O_2 evolution cause it always occurs during electrochemical ozone generation since it is thermodinamically favorable [17,18] (See Eq. 4):
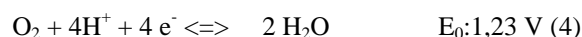
Anode Reaction

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

$$O_3 + 2H^+ + 2\ e^- \iff H_2O + O_2 \qquad E_0{:}2{,}07\ V \quad (2)$$

Cathode Reaction

$$2H^+ + 2e^- \longrightarrow H_2 \qquad\qquad\qquad (3)$$

Oxygen Evolution

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

Electrode materials and the reactor design affects the efficiency of electrochemical ozone generation also current efficiency can be influenced by electrode morphology, cell configurations, current density, electrolyte, anodic potential, and temperature [12]. Among these factors anodic material is one of the most important parameter cause it must be carefully chosen to achieve appreciable ozone evolution with considerable efficiency. It must have a high over potential to prohibit the oxygen evolution and be stable to strong anodic polarization in the electrolyte. Several anode materials have been investigated, Pt, DSA, Au, Pd, PbO_2, SnO_2, boron doped diamond (BDD) and glassy carbon are some of them [13]. It can be clearly seen from the literature that Pt and PbO_2 anodes have shown higher current efficiency 6.5-35 % at low temperature and 13% at room temperature respectively. It's notable that Sn-Sb-Ni/Ti anodes have shown the highest efficiency about <36.5 at room temperature [20]. On the other hand, durability of Sn-Sb-Ni/Ti anodes are relatively higher and price are lower

than other ozone generating anode configurations. But the testing of these anodes on real textile wastewater can not be detected by authors in accessed literature.

The aim of this study is to investigate the treatment efficiency of new anode configuration (Ti mesh anode coated with Co-Sn- $SnCl_4$) on real textile wastewater. Color and COD has been selected as target pollutant because of their importance for textile effluent.

II.   Experimental

A. *Chemicals*

$SnCl_4.5H_2O$ (Alfa Aeser), Sb_2O_3 (Merck), HCl (Merck), H_2SO_4 (Merck), ethanol (Merck), oxalic acid (Merck) were used without further purification. All solutions were prepared by using Millipore Milli-Q (18MΩ cm) water. Wastewater samples were collected from the treatment plant of a fabric dyeing textile industy,Bursa, Turkey The textile wastewater samples were collected from an equalisation tank of a textile dyeing factory treatment plant. Environmental caharacterization of collected sample given in Table 1.

TABLE I. ENVIRONMENTAL CHARACTERIZATION OF RAW HAND-PRINTED TEXTILE EFFLUENTS

Parameter	Unit	Value
COD	mg/l	2320± 40
Suspended Solids	mg/l	120 ± 20
NH_4-N	mg/l	42±1.6
Free chlorine	mg/l	<0.1
Total chromium	mg/l	<0.1
Sulphur	mg/l	<0.1
Sulphide	mg/l	<0.2
Phenol	mg/l	<0.1
pH	-	7.2
Condcutivity	mS/cm	2,25
Colour[a]	1/cm	1.02

a. Absorbance at 610 nm (SM 2120 C)

Electrode preparation (Coating)

Ti mesh substrates (Dexmet, USA) (2.5 x 2.5 cm) were treated in 10% boiling oxalic acid for half an hour, sonicated with distilled water for 10 minutes 3 times by using ultrasonic bath and dried naturally in room temperature. The Ti-mesh electrodes were dip coated by pyrolysis solution consists of Sn-Sb-Ni in the molar ratio of 500:8:0,5. The electrode was doped into solution and it was dried in an oven at 105ºC for 15 min. In the final heating step electrodes were And then annealed in preheated furnace for 15 min at 520ºC. The coating cycle was repeated 15 times. In the final heating step electrodes were annealed for 75 minute. A 5.0 cm x 5.0 cm platinized titanium electrode (NRK Electrochem) was used as cathode.
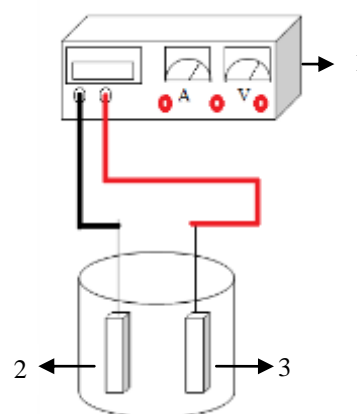

Figure 1. Experimental setup used in electrochemical ozone generation: (1) power supply (2)anode, ,(3) cathode

Analyses

Electrochemical ozone generation and ozonation of textile industry wastewater were carried out using the experimental set up presented in Fig 1.

All the experiments were performed in an undivided cell with volume 250 ml. pH was measured using a pH meter (Cyberscan 10). COD measurements were also carried out to investigate the mineralization according to closed reflux, titrimetric method. The electric current was provided by a programmable DC power supply (Extech Instruments-382280).

The removal efficiencies of the parameters evaluated and was determines by using Eq. (5) as follows:

Removal (%)=((C_0 - C_t) / C_0) x 100   (5)

In this equation C_0 and C_t are concentrations of dye absorbtion and COD, at initial and any

reaction time respectively. The energy consumption per unit COD removed (E_{COD}) was calculated accoring to Eq. (6).

$E_{COD}= (E_{Cell} \, I \, t) / (V \, \Delta COD)$ (6)

where E_{cell} is the energy consumption in kWh/gCOD; E_{Cell} is the average cell voltage in volt, I is the current in A and t is the electolysis time in hours, V is the solution volume in L and ΔCOD is the experimental COD decay in mg/L.

III.   Results and Discussion

A. *Effect of Sodium Chloride concentration*

The effect of sodium chloride (NaCl) concentration on removal of colour and COD from textile wastewater was tested in varied concentrations of 0.5 g L^{-1}–2 g L^{-1} (at constant current 50 mA/cm^2 and pH=7.2). Salt content is playing a crucial role for electrochemical processes to increase the conductivity of treated wastewater [21,22]. Textile dyestuff solution includes high amount of salt (40-100 g/L) as a catalyst during the dyeing process [23]. Salt

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concentration is reduced with the addition of freshwater for washing and cleaning stages of fabrics. But, at the end of the dyeing and finishing processes, textile wastewater still includes high enough amount of salt content for electrochemical processes. Sn-Sb-Ni anodes has well known and high ozone generation capacity [6,24].   But high amount of salt generates another important oxidant chlorin gas and hypochloric acid [22].   On the other hand, salt addition generates additional operational cost and environmental pollution problem for most low conductivity including waste streams. From these reasons, textile wastewater is very fit for treating with electrochemical processes from the reason of high salt content.

As seen in the Fig.2 and Fig.3, increasing NaCl concentrations positively affect COD and colour removal efficiencies.
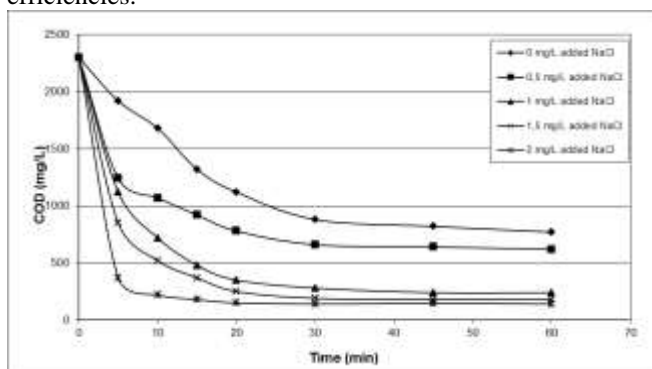

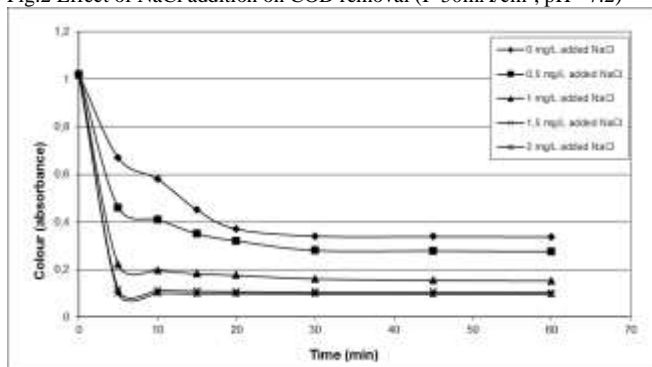Fig.2 Effect of NaCl addition on COD removal (I=50mA/cm^2, pH= 7.2)

Fig.3 Effect of NaCl addition on colour removal (I=50mA/cm^2, pH= 7.2)

At constant current pH vallues salt eddition shown important amount of COD colour removal. These results were determined witout any rpimary treatment or purification process/processes. Actually, no salt added samples has shown satisfying results. Following electrochemical oxidation process, other treatment processes can be applied untill discharge standards. But, the authors aimed to catch discharge standards with the application of electrochemical oxidation process. The addition of 1 g/L NaCl results 86% COD and 90% colour removal efficiencies. These removal efficiencies are good enogh for Turkish Discharge Standards for evaluated textile industry. Increasing amount of salt did not affect COD and colour removal efficiencies dramatically. On the other hand, increasing salt content reduces voltage of electrochemical stystem. But added salt content create a further environmental problen in future for discharging of treated waste streams. From these reasons 1

g/L NaCl addition choosen as optimum for tested wastewater in this study.

B. *Effect of initial pH*

For electrochemical oxidation processes, pH has an important role. The effect of pH tested between 3-9 at constant density 50mA/cm^2 and 1 g/L NaCl concentration. In the acidic range, COD and colour removal efficiencies higher than basic range removal efficiencies (Fig. 3). In acidic range, ozone generation capacity of Sn-Sb-Ni anodes are dominant [6,24]. Another imporant oxidizing agent, chlorin gas, is produced at acidic pH range on anode surface. At this pH range chlorine gas generates hypochloric acid. On the other hand, COD and colour removal efficiencies may also dominated by hydroxyle radicals, which is generated by ozone at anode surface and hydrogen peroxide at cathode surface under these conditions instantly. But, it is not possible to determine most effective or dominant oxidizing agent for a real wastewater studies.

3,4,5 and 6 pH removal efficiencies were too similar for both COD and colour removal. But, neutral pH values shown slightly lower removal efficiencies than acidic pH values (3%). These results are also supported by literature [25].   Acidic and basic pH regions could support the treatment of organics, theoretically. In acidic conditions hydroxyle radical (generated on anode surface) scavengers (HCO$_3^-$ and CO$_3^-$) can be eleminated and removal of organics can be increased. Alcaline conditions can also support the removal of organics parallel to chlorine gas and hypochlorite ion production [26,27]. Although, acidic pH values shown slightly better COD and colour (Fig.4 and 5) removal efficiencies, 7,2 natural pH of samples were chosen as optimum pH for further experiments to avoid extra operational cost for pH adjustment.
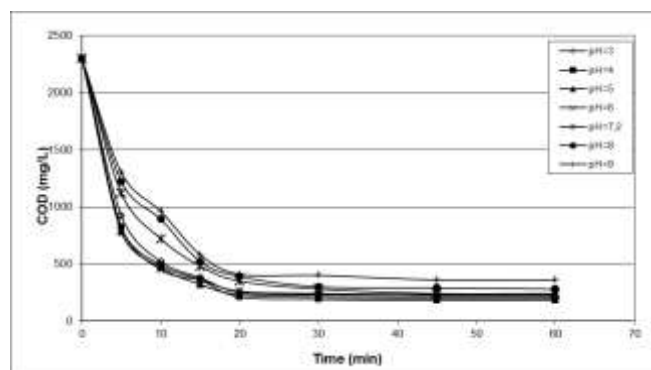

Fig.4 Effect of pH on COD removal (I=50mA/cm^2, NaCl add.=1 g/L)

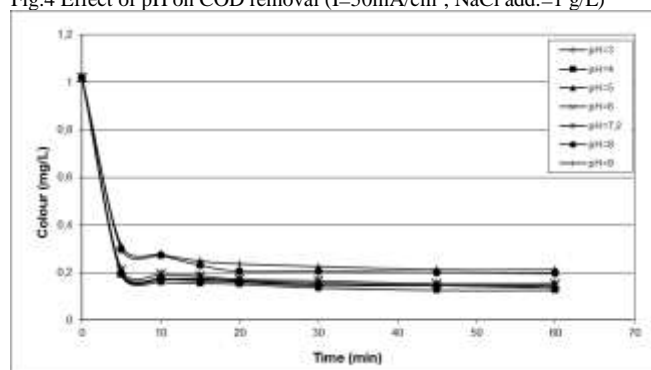Fig.5 Effect of pH on colour removal (I=50mA/cm^2, NaCl add.=1 g/L)

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As it can be seen from both Fig 4 and Fig.5 effect of pH on the electrochemical treatment of textile effluent cannot be detected. Acidic and neutral pH values have shown slightly better results than basic conditions. Briefly, effect of pH on the electrochemical treatment of real textile wastewater is too limited and not so clear in literature. For further studies, the authors will be concentrated on the understanding of effect of pH on the electrochemical removal of COD and colour from textile effluent.

C. *Effect of Current Density*

Current density is another important parameter for electrochemical processes controlling the reaction rate [27]. To detect the effect of current density on COD and colour removal from tested samples, 10-100 mA/cm^2 was applied (pH=7.2 and 1g/L NaCL). Increasing current densities increased the COD and colour removal effciencies. A possible reason to explain this situation is increasing generation of active oxidizing agent production under high current densities. Fig 6 and 7 shows the effect of current density on COD and colour removal efficiencies.
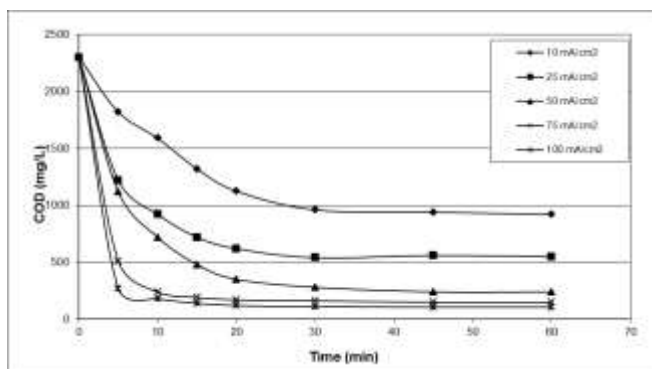

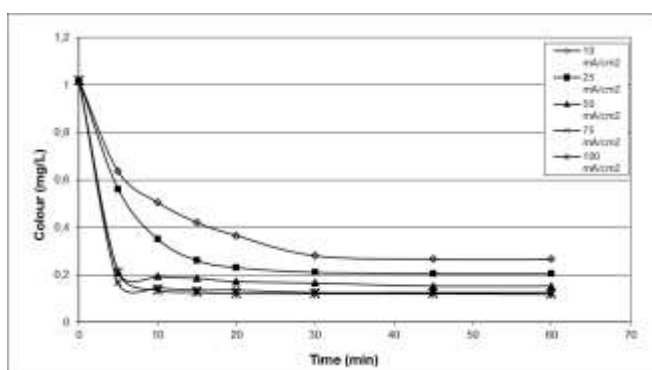Fig.6 Effect of Current Density on COD removal (pH=7.2, NaCl add.=1 g/L)

Fig.7 Effect of Current Density on COD removal (pH=7.2, NaCl add.=1 g/L)

According to Fig 6 and 7 lower current densities decreases the COD and colour removal efficiencies. 10 and 25 mA/cm^2 current density values also can not be reached discharge limits on COD. But, 50 and over current densities meet discharge limits on evaluated parameters. Over 50 mA/cm^2 current density values decreases hydraulic retention time value less than 10 mins. But increasing current density means increasing power consumption. To chose correct value for current density power cunsumption values calculated. As shown in Fig 8., increasing current density

increses power consumption dramatically. Consequently, according to power consumption calculations 50 mA/cm^2 current density is fit for evaluated wastewater.
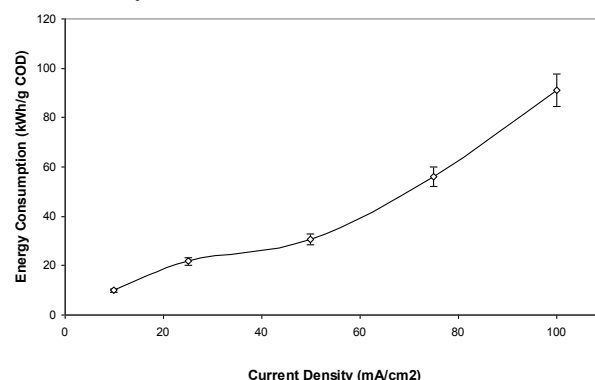

Figure 8. Power consumption values according to applied current density

IV. **Conslusions**

In this study, treatment of real textile wastewater by electrochemical oxidation using new series of Sn-Sb-Ni anodes. Consequently;

(1) COD and colour content of real textile dyeing factory wastewater decreased 90% and 94%, respectively.
(2) Salt addition positively affected the COD and colur removal efficiencies. Salt addition increased COD and colour removal efficiencies from 60% to 91%.
(3) All pH values tested to remove COD and colour content of wastewater samples have not been shown great differences. From this reason, natural pH of wastewater can be used as optimum pH value.
(4) Current density is strongly effecting COD and colour removal. But increasing current density values is also increasing power consumption dramaticaly.

Acknowledgement

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