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# Electro-Oxidation Treatment for Turbidity in Pistachio Processing Industry Wastewater (PPIW)

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**Abstract** - In this study, it was investigated removal of turbidity from Pistachio Processing Industry Wastewater (PPIW) by electrooxidation. Electro-oxidation was established using Ti/Pt anodes and stainless steel cathodes in batch mode. Experimental parameters were selected as stirring speed, initial pH value and supporting electrolyte species. Removal fraction and energy consumption was calculated using experimental results of electro-oxidation of PPIW using Ti/Pt DSA type anode and stainless steel cathodes. The highest removal fraction was obtained as 0.85 at pH: 5.3 (natural), no stirring and 0.5 M NaCl supporting electrolyte concentration. Whereas, energy consumption was obtained as 203.5 kW-h/m<sup>3</sup> at same experimental conditions.

*Keywords:* Electro-oxidation; Ti/Pt anode; Pistachio Processing Industry Wastewater (PPIW); Support electrolyte; Initial pH

## 1. Introduction

Type and concentration of pollutants which was released the result of human activity as a result has increased along with the industrial revolution of increasing industrialization and has become more complex. Especially, these waste waters which were given to receiving environment the uncontrolled pollute clean water supply. Therefore, these wastewaters should be treated before discharge to the receiving environment [1].

There are many traditional methods which were used in wastewater treatment. The traditional technologies can be sorted such as biological processes [2] and physicochemical processes, which include: membrane filtration [3], ion exchange [4], chemical precipitation [5], chemical oxidation [6], adsorption [7], reverse osmosis [8] and electro-dialysis [9]. Electro-oxidation is relatively new treatment method when compared with conventional treatment methods [1].

Electro-oxidation is process with the help of using insoluble anode material either organic contaminations can be degradation completely or conversion to the less toxic intermediates can be biodegraded [10, 11]. As the anode material is used various types of anodes such as BDD [12], Ti/Pb<sub>2</sub> [13], Ti/RuO<sub>2</sub> [14], Ti/IrO<sub>2</sub> [15], Ti/SnO<sub>2</sub> [16], Ti/Pt [17] and platinum [18]. Electro-oxidation process takes place in two ways including direct and indirect. While organic pollutants can be degraded as adsorb to anode surface by direct electro-oxidation, indirect electro-oxidation can degrade organic pollutant via electro-generated oxidants (e.g., hydroxyl radical OH• [19], chlorine, hypochlorite [20], hydrogen peroxide [21], ozone [22] and  $S_2OS_2$ -[23]).

Electro-oxidation has been applied successfully high organic pollution containing wastewater such as textile industry [24-26], tannery [13, 27], distillery [28], landfill [10, 29], paper mill [30], olive mill [31] and drug [32].

In this study, the effect of turbidity removal from Pistachio Processing Industry Wastewater (PPW) which contains high containing organic pollution was investigated. Experimental parameters were studied as wastewater stirring speed, the effect of initial pH of the wastewater and supporting electrolyte types. As the anode material DSA type Ti/Pt and as the cathode material stainless steel plate were used in batch mode. Depending on the applied current density, turbidity removal fraction was examined at specific time intervals.

#### 2. Material and Methods

The batch experimental setup is schematically shown in Fig.1. The monopolar electro-oxidation consists of approximately an 800 mL electrochemical glass-made batch reactor with five Ti/Pt anodes and five stainless steel plate cathodes. The length and width of each electrode is 100 mm and 60 mm, respectively. The total effective electrode surface areas of anode and cathode are 2000 cm<sup>2</sup>. The distance between electrodes was selected as 5 mm. The applied voltage was kept constant by means of a power supply (Chroma 6204P-40-120). During the experiments, pH, conductivity and temperature of wastewater samples were measured by a pH-meter (WTW-340i). Every experiment was performed at the room temperature.



Fig. 1: Experimental set up (1. DC power supply, 2.Ti/Pt anode, 3.Stainless steel cathode, 4. Wastewater, 5. Magnet, 6. Magnetic stirrer).

The turbidity removal fraction  $(\eta)$  is calculated as follows:

$$\eta = \frac{C_t}{C_0} \tag{1}$$

where;  $C_0$ : Initial concentration (mg/L);  $C_i$ : Concentration at t (mg/L) Specific energy consumption (SEC) per m3 of wastewater treated has calculated as follows;

$$SEC\left(\frac{kW - h}{m^3}\right) = \frac{V \times I \times t}{v}$$
<sup>(2)</sup>

Where; V: Cell voltage (v); I: Current (A); t: Time (h); v: Volume of wastewater (m<sup>3</sup>)

#### 3. Results and Discussion

#### 3.1. Effect of Stirring Speed

To investigate the effect of stirring speed on turbidity removal, electro-oxidation process was carried out using various stirring speed varying from 0 to 600 rpm at natural wastewater pH ( $\approx$ 5.3) and 5 mA/cm<sup>2</sup> for 5 h electrolysis time. The effect

of stirring speed can be deduced from Fig. 2. It was discovered that stirring speed had very little or no effect on the electrooxidation. At increasing stirring speed, the percentage removal increased at very little quantities. When stirring speed was increased from 0 to 400 rpm, removal fraction increased from 0.65 to 0.68. If the stirring speed is increased from 400 to 600 rpm, the removal fraction is reduced by about 0.47. Because stirring speed didn't removal efficiencies too much, the stirring speed was chosen 0 rpm because of energy consumption taking into consideration [33-35].



Fig. 2: Effect of stirring speed on the removal of turbidity.

### 3.2. Effect of Supporting Electrolyte Types

Effects of supporting electrolyte type on the turbidity removal by electro-oxidation was investigated at wastewater natural pH, 5 mA/cm<sup>2</sup> current density, 0.50 M supporting electrolyte concentration for 5h electrolysis time. Supporting electrolyte types were selected different salt types such as Na<sub>2</sub>SO<sub>4</sub>, NaNO<sub>3</sub>, NaCI and KCI which have a high solubility in aqueous media. The results were showed in Figure 3. As can be seen from the results, the presence of the supporting electrolyte in wastewater medium increased removal fraction significantly. Turbidity removal fraction was found to be 0.85 for NaCl, 0.79 for KCl, 0.72 for NaNO<sub>3</sub>, 0.70 for Na<sub>2</sub>SO<sub>4</sub> and 0.65 for no supporting electrolyte. Therefore, NaCl was chosen to be support electrolyte types on subsequent experiments [36, 37].

### 3.3. Effect of Initial Wastewater pH

It has been established that the influenced pH is of vital importance in the performance of many electrochemical processes. Also, that the initial pH of the electrolyte is one of the important factors affecting the performance of electrochemical process particularly on the performance of electro-oxidation process. In this study, turbidity removal fraction was determined in the pH range from 3 to 11. Figure 4 shows the influence of solution pH on turbidity removal. It shows that the turbidity removal fraction increased with pH until it reached to 5.3 (Natural), and after this point, further increase of pH, the removal fraction decreased. Maximum removal occurred at pH 5.3 value, thus pH = 5.3 (Natural) was the optimum pH [38-41].



Time (minute) Fig. 3: Effect of supporting electrolyte types on the removal of turbidity.



Time (minute)Fig. 4: Effect of supporting electrolyte types on the removal of turbidity.

#### 3.4. Energy Consumption

The effects of stirring speed on electrical energy consumption were given in Fig. 5. Results showed that with increasing stirring speed from 0 to 400 rpm electrical energy consumption decreases from 289.5 to 245.5 kW-h/m<sup>3</sup> wastewater at natural pH value ( $\approx$ 5.3) and 5 mA/cm<sup>2</sup> current density after 5 h reaction. When stirring speed was increased form 400 rpm to 600 rpm, energy consumption was increased as 69 kW-h/m<sup>3</sup>. At all stirring speeds, electrical energy consumption was higher form 400 rpm. It can be concluded the slowing down process of electron transfer in lower stirring speed. The centrifugal force on the electron transfer has been oppressing at higher stirring speeds. Therefore, energy consumption increased in over and 400 rpm under stirring speed [33].



Fig. 5: Effect of stirring speed on the energy consumption.

The energy consumptions for 0.5 M of NaCl, KCl, NaNO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub> and without supporting electrolyte were calculated to be 203.5, 182.5, 235, 221.5 and 296.5 kW-h/m<sup>3</sup>, respectively. When supporting electrolyte was added to wastewater, energy consumption was decreased because of amounts of ions in solution increasing. Figure 6 showed that the higher energy consumption was detected at without supporting electrolyte as 2965.5 kW-h/m<sup>3</sup>. But the smallest energy consumption values were obtained at NaCl and KCl supporting electrolyte types for 0.5 M initial concentration 203.5 and 182.5 kW-h/m<sup>3</sup>, respectively. This situation can be explained that both NaCl and KCl water is almost completely dissolved.

The energy consumption rates at for pH:3, pH:4, pH:5.3 (natural), pH:7, pH:9, and pH:11 were calculated to be 187, 188, 193.5, 178, 166 and 155 kW-h/m<sup>3</sup>, for 5 h of electrolysis time, respectively. When considered the data in Figure 7, it can be stated that the lowest energy consumption rate is obtained with a pH 11 and energy consumption is reduced below and above of natural pH value of wastewater. This condition can be explained from the different conductivity of wastewater with different initial pH values. Total resistance of the system can be affected the specific conductivity of a wastewater medium [42]. When conductivity increases, wastewater resistance decreases. This decreasing in wastewater resistance can be reduce energy consumption.

#### 4. Conclusion

In the this paper, the electro-oxidation of PPIW was carried out using Ti/Pt DSA type anode under different stirring speeds, initial wastewater pH values and supporting electrolytes types. The stirring speed was determined to have no effect

on removal fraction. Treatment efficiency decreased in the above and below the value of the natural pH. The supporting electrolyte types in which was used (NaCl, KCl, NaNO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub>) were determined to be the most effective of NaCl. The energy consumption for all experimental conditions were calculated to be 314.5 kW-h/m<sup>3</sup> for the highest and to be 155 kW-h/m<sup>3</sup> for the lowest for 5 h electrolysis time.



Supporting electrolyte types

Fig. 6: Effect of supporting electrolyte types on the energy consumption.





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# References

- [1] B. A. Fil, R. Boncukcuoğlu, A. E. Yilmaz, and S. Bayar, "Electro-Oxidation of Pistachio Processing Industry Wastewater Using Graphite Anode," *Clean*, vol. 42, no. 9, pp. 1232–1238, 2014.
- [2] C. Guomin, Y. Guoping, S. Mei, and W. Yongjian, "Chemical industrial wastewater treated by combined biological and chemical oxidation process," *Water Sci. Technol.*, vol. 59, no. 5, pp. 1019-1024, 2009.
- [3] S. Šostar-Turk, I. Petrinić, and M. Simonič, "Laundry wastewater treatment using coagulation and membrane filtration," *Resour. Conserv. Recy.*, vol. 44, no. 2, pp. 185–196, 2005.
- [4] M. D. Víctor-Ortega, J. M. Ochando-Pulido, G. Hodaifa, and A. Martinez-Ferez, "Final purification of synthetic olive oil mill wastewater treated by chemical oxidation using ion exchange: Study of operating parameters," *Chem. Eng. Process.*, vol. 85, pp. 241-247, 2014.
- [5] S. H. Lee, J. Iamchaturapatr, C. Polprasert, and K. H. Ahn, "Application of chemical precipitation for piggery wastewater treatment," *Water Sci. Technol.*, vol. 49, no. 5-6, pp. 381-388, 2004.
- [6] M. Dias-Machado, L. M. Madeira, B. Nogales, O. C. Nunes, and C. M. Manaia, "Treatment of cork boiling wastewater using chemical oxidation and biodegradation," *Chemosphere*, vol. 64, no. 3, pp. 455-461, 2006.
- [7] F. T. Ademiluyi, S. A. Amadi, and N. J. Amakama, "Adsorption and Treatment of Organic Contaminants using Activated Carbon from Waste Nigerian Bamboo," *J. Appl. Sci. Environ. Manage.*, vol. 13, no. 3, pp. 39-47, 2009.
- [8] K. Ghasemipanah, "Treatment of ion-exchange resins regeneration wastewater using reverse osmosis method for reuse," *Desalin. Water Treat.*, vol. 51, no. 25-27, pp. 5179-5183, 2013.
- [9] R. F. Dalla Costa, C. W. Klein, A. M. Bernardes, and J. Zoppas Ferreira, "Evaluation of the electrodialysis process for the treatment of metal finishing wastewater," *J. Braz. Chem. Soc.*, vol. 13, pp. 540-547, 2002.
- [10] Y. Deng and J. D. Englehardt, "Electrochemical oxidation for landfill leachate treatment," *Waste Manage.*, vol. 27, no. 3, pp. 380-388, 2007.
- [11] F. Çiner and Ö. Gökkuş, "Treatability of Dye Solutions Containing Disperse Dyes by Fenton and Fenton-Solar Light Oxidation Processes," *Clean*, vol. 41, no. 1, pp. 80-85, 2013.
- [12] X. Zhao, Y. N. Hou, H. J. Liu, Z. M. Qiang, and J. H. Qu, "Electro-oxidation of diclofenac at boron doped diamond: Kinetics and mechanism," *Electrochim. Acta*, vol. 54, no. 17, pp. 4172-4179, 2009.
- [13] L. Szpyrkowicz, S. N. Kaul, R. N. Neti, and S. Satyanarayan, "Influence of anode material on electrochemical oxidation for the treatment of tannery wastewater," *Water Res.*, vol. 39, no. 8, pp. 1601-1613, 2005.
- [14] I. D. d. Santos, J. C. Afonso, and A. J. B. Dutra, "Electrooxidation of Phenol on a Ti/RuO2 anode: effect of some electrolysis parameters," J. Braz. Chem. Soc., vol. 22, no., pp. 875-883, 2011.
- [15] M. Miyata, I. Ihara, G. Yoshid, K. Toyod, and K. Umetsu, "Electrochemical oxidation of tetracycline antibiotics using a Ti/IrO2 anode for wastewater treatment of animal husbandry," *Water Sci. Technol.*, vol. 63, no. 3, pp. 456-461, 2011.
- [16] M. Quiroz, S. Reyna, and J. Sánchez, "Anodic oxidation of pentachlorophenol at Ti/SnO2 electrodes," J. Solid State Electrochem., vol. 7, no. 5, pp. 277-282, 2003.
- [17] M. A. Abdel Rahim and H. B. Hassan, "Titanium and platinum modified titanium electrodes as catalysts for methanol electro-oxidation," *Thin Solid Films*, vol. 517, no. 11, pp. 3362-3369, 2009.
- [18] S. Malkhandi, A. Bonnefont, and K. Krischer, "Strictly potentiostatic current oscillations during bulk CO electrooxidation on platinum in the presence of inhibiting anions," *Electrochem. Commun.*, vol. 7, no. 7, pp. 710-716, 2005.
- [19] J. Naumczyk and M. Kucharska, "Tannery Wastewater Treatment by Anodic Electrooxidation Coupled with Electro-Fenton Process," *Environ. Prot. Eng.*, vol. 37, no. 3, pp. 47-54, 2011.
- [20] J. Naumczyk, L. Szpyrkowicz and F. Zilio-Grandi, "Electrochemical treatment of textile wastewater," *Water Sci. Technol.*, vol. 34, no. 17, pp. 17-24, 1996.
- [21] E. Brillas, R. M. Bastida, E. Llosa, and J. Casado, "Electrochemical destruction of aniline and 4-chloroaniline for wastewater treatment using a carbon-PTFE O2-fed cathode," J. Electrochem. Soc., vol. 142, no. 6, pp. 1733–1741, 1995.
- [22] S. Stucki, H. Baumann, H. J. Christen, and R. Kotz, "Performance of a pressurized electrochemical ozone generator," *J. Appl. Electrochem.*, vol. 17, no. 4, pp. 773–778, 1987.
- [23] A. Tsitonaki, B. Petri, M. Crimi, H. Mosbaek, R. L. Siegrist, and P. L. Bjerg, "In Situ Chemical Oxidation of Contaminated Soil and Groundwater Using Persulfate: A Review," *Crit. Rev. Env. Sci. Tec.*, vol. 40, no., pp. 55-91, 2010.

- [24] G. Bhaskar Raju, M. Thalamadai Karuppiah, S. S. Latha, D. Latha Priya, S. Parvathy, and S. Prabhakar, "Electrochemical pretreatment of textile effluents and effect of electrode materials on the removal of organics," *Desalination*, vol. 249, no. 1, pp. 167-174, 2009.
- [25] W. Miled, H. A. Said, and S. Roudesli, "Decolorization of high polluted textile wastewater by indirect electrochemical oxidation process," *J. Textile App. Technol. Manage.*, vol. 6, no. 3, pp. 1-6, 2010.
- [26] M. Das and K. G. Bhattacharyya, "Oxidative Degradation of Orange II Dye in Water with Raw and Acid-Treated ZnO, and MnO2," *Clean*, vol. 41, no. 10, pp. 984-991, 2013.
- [27] S. Sundarapandiyan, R. Chandrasekar, B. Ramanaiah, S. Krishnan, and P. Saravanan, "Electrochemical oxidation and reuse of tannery saline wastewater," *J. Hazard. Mater.*, vol. 180, no. 1-3, pp. 197-203, 2010.
- [28] P. Piya-Areetham, K. Shenchunthichai, and M. Hunsom, "Application of electrooxidation process for treating concentrated wastewater from distillery industry with a voluminous electrode," *Water Res.*, vol. 40, no. 15, pp. 2857-2864, 2006.
- [29] A. Urtiaga, A. Rueda, A. Anglada, and I. Ortiz, "Integrated treatment of landfill leachates including electrooxidation at pilot plant scale," *J. Hazard. Mater.*, vol. 166, no. 2-3, pp. 1530-1534, 2009.
- [30] T. Zayas, M. Picazo, and L. Salgado, "Removal of Organic Matter from Paper Mill Effluent by Electrochemical Oxidation," *J. Water Resource Prot.*, vol. 3, no. 1, pp. 32-40, 2011.
- [31] U. T. Un, U. Altay, A. S. Koparal, and U. B. Ogutveren, "Complete treatment of olive mill wastewaters by electrooxidation," *Chem. Eng. J.*, vol. 139, no. 3, pp. 445-452, 2008.
- [32] R. H. Patil, R. N. Hegde, and S. T. Nandibewoor, "Electro-oxidation and determination of antihistamine drug, cetirizine dihydrochloride at glassy carbon electrode modified with multi-walled carbon nanotubes," *Colloid Surface B*, vol. 83, no. 1, pp. 133-138, 2011.
- [33] N. Bensalah, M. A. Q. Alfaro, and C. A. Martínez-Huitle, "Electrochemical treatment of synthetic wastewaters containing Alphazurine A dye," *Chem. Eng. J.*, vol. 149, no. 1–3, pp. 348-352, 2009.
- [34] S. Bayar, Y. Ş. Yıldız, A. E. Yılmaz, and Ş. İrdemez, "The effect of stirring speed and current density on removal efficiency of poultry slaughterhouse wastewater by electrocoagulation method," *Desalination*, vol. 280, no. 1-3, pp. 103-107, 2011.
- [35] V. Khandegar and A. K. Saroha, "Electrochemical Treatment of Distillery Spent Wash Using Aluminum and Iron Electrodes," *Chinese J. Chem. Eng.*, vol. 20, no. 3, pp. 439-443, 2012.
- [36] H. S. Awad and N. A. Galwa, "Electrochemical degradation of Acid Blue and Basic Brown dyes on Pb/PbO2 electrode in the presence of different conductive electrolyte and effect of various operating factors," *Chemosphere*, vol. 61, no. 9, pp. 1327-1335, 2005.
- [37] N. A. Ghalwa, H. M. Abu-Shawish, M. Hamada, K. Hartani, and A. A. H. Basheer, "Studies on Degradation of Diquat Pesticide in Aqueous Solutions Using Electrochemical Method," *American J. Anal. Chem.*, vol. 3, no. 2, pp. 99-105, 2012.
- [38] L. Gu, B. Wang, H. Ma, and W. Kong, "Catalytic oxidation of anionic surfactants by electrochemical oxidation with CuO-Co2O3-PO43- modified kaolin," *J. Hazard. Mater.*, vol. 137, no. 2, pp. 842-848, 2006.
- [39] J. Bandara, P. T. Wansapura, and S. P. B. Jayathilaka, "Indium tin oxide coated conducting glass electrode for electrochemical destruction of textile colorants," *Electrochim. Acta*, vol. 52, no. 12, pp. 4161-4166, 2007.
- [40] H. Ma, Q. Zhuo, and B. Wang, "Electro-catalytic degradation of methylene blue wastewater assisted by Fe2O3-modified kaolin," *Chem. Eng. J.*, vol. 155, no. 1–2, pp. 248-253, 2009.
- [41] A. J. B. Dutra, I. D. Santos, and J. C. Afonso, "Behavior of a Ti/RuO(2) anode in concentrated chloride medium for phenol and their chlorinated intermediates electrooxidation," Sep. Purif. Technol., vol. 76, no. 2, pp. 151-157, 2010.
- [42] A. E. Yılmaz, R. Boncukcuoğlu, M. M. Kocakerim and E. Kocadağistan, "An empirical model for kinetics of boron removal from boroncontaining wastewaters by the electrocoagulation method in a batch reactor," *Desalination*, vol. 230, no. 1–3, pp. 288-297, 2008.