

Application of Electrooxidation Technology in the Treatment of Paper Industry Wastewater: The Effect of pH and Current Density

Baybars Ali Fil¹, Cansu Elgün^{1*} and Süleyman Uzuner¹

¹Environmental Engineering Department, Balıkesir University, Türkiye

*(cansuelgun_1996@hotmail.com) Email of the corresponding author

Abstract – In the studies, the treatment of wastewater from the paper industry using the electrooxidation method one of the electrochemical treatment methods in the batch system was explored under various experimental settings. 4 anodes and 4 cathodes sieve type plates with dimensions of 7 cm x 10 cm were placed at 0,5 cm intervals in the 2000 mL volume jacketed glass reactor used for the treatment of wastewater originating from the paper industry, and 1200 mL wastewater was used in the experiments. In the electrooxidation experiments, coated sieve type Ti/Pt electrodes were used as the anode material, and uncoated sieve type Ti electrodes were used as the cathode material. The active anodic wet surface area was calculated as 1078 cm². Removal rates of pollutant parameters such as color and SS (Suspended Solids) in the experiments; The effects of wastewater initial pH value and current density parameters were investigated. According to the results obtained, for Ti/Pt anode type; Wastewater natural pH (~7.5) was determined as the most effective pH value at 400 rpm mixing speed, and 18.55 mA/cm² was determined as the most effective current density. For Ti/Pt anode in optimum conditions; 96.92% Suspended Solids and 96.12% color removal efficiencies were obtained.

Keywords – Wastewater Treatment, Electrooxidation, Paper Industry Wastewater, Suspended Solids, Ti/Pt Anode

I. INTRODUCTION

Water supplies quickly run out due to industrialization's increased demand for drinking and utility water as well as the rapid population rise. In both wealthy and developing nations, industrial activities need large volumes of water. These wastewaters, which are produced as a result of water consumption, must be treated and then disposed in compliance with the proper discharge criteria to the receiving environment.

Since wastewater is typically dumped into receiving habitats like lakes and seas, which are located closest to industry, the pollution they produce has very significant and detrimental impacts, such as upsetting the ecological balance in these areas. Industries including paper, textile, chemistry and food that are located in or close to communities heavily pollute the surrounding environment [1]. Before being discharged, industrial wastewater should be treated by methods such as chemical coagulation, flotation, adsorption, biological treatment and electrochemical treatment methods.

The amount of wastewater and pollution load resulting from production in the paper industry is considerably higher than in other industries. Contaminations originating from the paper industry largely depend on the raw materials used in production, additional additives and the production process [2].

The most commonly used methods for the treatment of paper industry wastewater are adsorption [3], [4], chemical oxidation [5], [6] and biological [7], [8] are purification methods.

Turbidity caused by the presence of suspended solids (SS) and colloidal particles in the paper industry wastewater cannot be removed by classical methods such as filtration and conditioning [9]. Due to these disadvantages, the use of electrochemical methods should be preferred in the treatment of paper industry wastewater. Electrooxidation, which is one of the electrochemical methods; graphite [10], [11], coated titanium [12], [13], platinum [14], [15], boron-coated diamond [16], [17] is based on the direct or indirect oxidation of organic materials using an insoluble anode material [18].

In this study, the treatment of paper industry wastewater by electrooxidation method, which is one of the electrochemical treatment methods in batch system, was investigated. For this purpose, optimum SS and color removal in electrooxidation

method; The effects of current density and initial wastewater pH were investigated when Ti/Pt anode was used.

II. MATERIALS AND METHOD

In the studies, the treatment of industrial wastewater obtained from the paper industry was carried out by electrooxidation method, which is one of the electrochemical treatment processes in the batch system. 1200 mL wastewater was used for experiments with Ti/Pt anode in order to investigate suspended solids and color removal from paper industry wastewater by electrooxidation method.

4 anodes and 4 cathodes sieve type plates with dimensions of 7 cm x 10 cm were placed at 0,5 cm intervals in the 2000 mL volume jacketed glass reactor used for the treatment of wastewater originating from the paper industry, and 1200 mL wastewater was used in the experiments. In the study, Ti/Pt electrodes were used as the anode material and uncoated sieve type Ti electrodes were used as the cathode material. Active anodic wet surface area is calculated as 1078 cm². A direct current power supply was used to provide electricity to the apparatus, and a magnetic stirrer was used to continually agitate the solution. A constant temperature water circulator was also used to maintain control over the temperature of the effluent.

Figure 1 illustrates the experimental configuration.

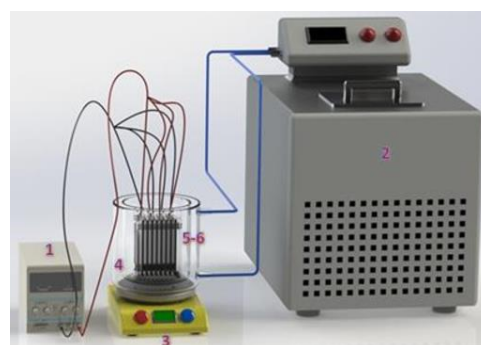


Fig. 1 Experimental Setup. (1. Direct current power supply, 2. Constant temperature water circulator, 3. Magnetic stirrer, 4. Glass reactor, 5. Uncoated Ti cathode, 6. Ti/Pt anode)

III. RESULTS

A. *Effect of Initial Wastewater pH on Removal Efficiency*

In the experiments using Ti/Pt anode, the initial pH value of the wastewater was adjusted

to the initial pH values ranging from 3 to 11 using sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH), and the optimum pH value was investigated. The effect of initial pH value on SS and color removal efficiencies; It was investigated in a reaction time of 3 hours, current density of 18.55 mA/cm^2 , type and concentration of 0.50 M NaCl support electrolyte, stirring speed of 400 rpm , and the results are shown in Figure 2 and Figure 3.

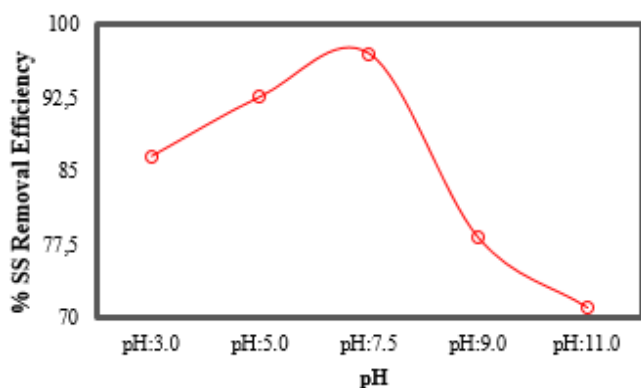


Fig. 2 The effect of initial wastewater pH value on SS removal efficiency when Ti/Pt anode is used.

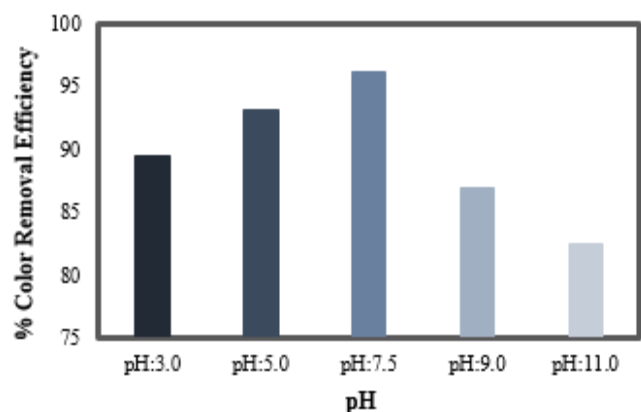


Fig. 3 The effect of initial wastewater pH value on color removal efficiency when Ti/Pt anode is used.

SS removal efficiencies for pH values 3, 5, 7.5, 9 and 11 were 86.47%, 92.56%, 96.92%, 78.13% and 71.00%, respectively, while color removal efficiencies were 89.40%, 93.04%, 96.12%, 86.86% and 82.38% were obtained.

More than 99% of active chlorine is found as ClO^- (hypochlorite) in basic environments, and more than 99% as $HClO$ (hypochlorous acid) in acidic environments [19]. In electrochemical processes, when chlorine ions are present in the environment, oxidation is generally in acidic conditions; The reason why it gives more effective results than basic or neutral conditions

is that hypochlorous acid is a stronger oxidant than hypochlorite. Previous studies also support that free chlorine is the dominant oxidizing agent in acidic conditions [20], [21]. Similar studies are available in the literature [22], [23], [13].

B. Effect of Current Density Applied on Removal Efficiency

In experiments using Ti/Pt anode as anode type, the effect of current density on SS and decolorization efficiencies was carried out at 0.50 M NaCl support electrolyte type and concentration, $pH \approx 7.5$, mixing speed of 400 rpm , and reaction time of 3 hours. The effect of current density on SS and color removal efficiencies 18.55 ; 23.19 ; 27.83 ; 32.47 ; It was examined at 37.11 mA/cm^2 values and the results are shown in Figure 4 and Figure 5.

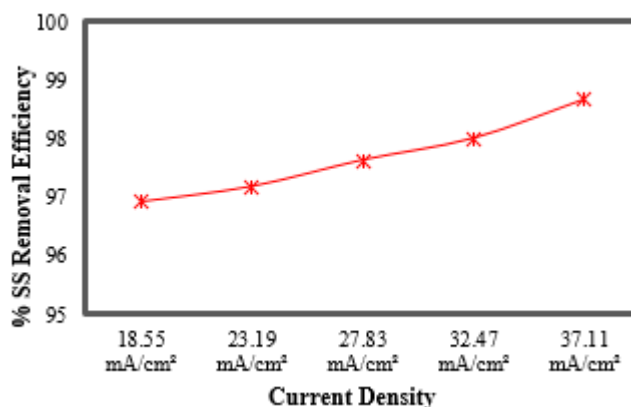


Fig. 4 The effect of applied current density on SS removal efficiency when Ti/Pt anode is used.

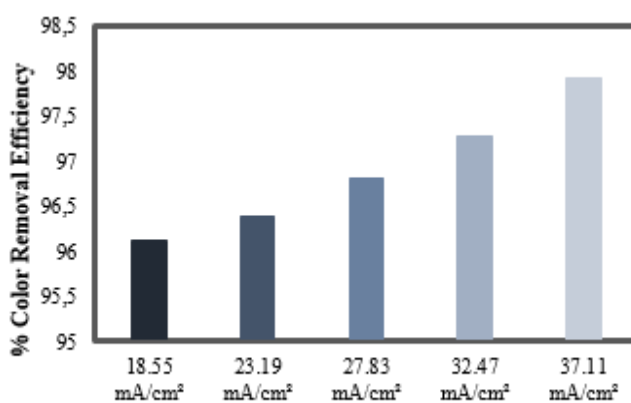


Fig. 5 The effect of applied current density on color removal efficiency when Ti/Pt anode is used.

Current densities are 18.55 ; 23.19 ; 27.83 ; 32.47 ; At 37.11 mA/cm^2 , SS removal efficiencies were obtained as 96.92%, 97.19%, 97.63%, 98.00% and 98.67%, respectively. Color removal efficiencies were observed as

96.12%, 96.40%, 96.81%, 97.29% and 97.92%, respectively.

In electrochemical processes; The applied current density is extremely important to control the reaction effect [24], [25]. It is stated in similar studies that the electrooxidation method is used that the flow density causes effective results in the oxidation and removal of organic substances in wastewater and the treatment of industrial wastewater [26]. Studies with similar results with the trials are available in the literature [27], [28], [29].

IV. DISCUSSION

A. Effect of Initial Wastewater pH on Removal Efficiency

Table 1. Effect of initial wastewater pH retention removal permanence.

Anode type: Ti/Pt		
Wastewater initial pH value	SS(%)	COLOR(%)
pH 3	86.47	89.40
pH 5	92.57	93.04
pH 7.5 (Natural)	96.92	96.12
pH 9	78.13	86.86
pH 11	71.00	82.36

As can be seen from the results, it has been determined that the highest treatment efficiency for SS and color parameters is at pH:7.5, which is the natural pH value of wastewater. According to the results obtained from the experiments when Ti/Pt anode was used, the natural pH value of the wastewater (pH≈7.5) was preferred as the initial pH value of the wastewater.

B. Effect of Current Density Applied on Removal Efficiency

Table 2. The effect of applied current density on removal efficiency.

Anode type: Ti/Pt		
Applied current density	SS(%)	COLOR(%)
18.55 mA/cm ²	96.92	96.12
23.19 mA/cm ²	97.19	96.40
27.83 mA/cm ²	97.63	96.81
32.47 mA/cm ²	98.00	97.29

37.11 mA/cm ²	98.67	97.92
--------------------------	-------	-------

From the results obtained, it is seen that it is a natural situation that the removal efficiency increases as the current density increases. In addition, since the wear on the anodes will increase as the current density increases, this will prevent the long-lasting use of the anodes. Therefore, considering the problems that may be encountered at high current density and the cost, the current density with the optimum removal efficiency was determined as 18.55 mA/cm² in the experiments performed with Ti/Pt anode materials.

V. CONCLUSION

In the study, when Ti/Pt anode was used as the anode type, SS and color removal efficiencies were investigated under the conditions considered optimum. At the end of the 3-hour trials at 0.50 M NaCl supporting electrolyte type and concentration, 400 rpm mixing speed, 18.55 mA/cm² current density, wastewater natural pH value (pH: ≈7.5), 96.92% SS and Color removal efficiencies of 96.12% were obtained.

ACKNOWLEDGMENT

We would like to thank Balıkesir University Engineering Faculty Environmental Engineering Department Laboratory for making the experiments happen.

REFERENCES

- [1] B. A. Fil. Treatment of Pistachio Processing Wastewater by Electrooxidation Method,. PhD Thesis, Ataturk University, Erzurum, 2014.
- [2] B. Özçelep. Advanced treatment of paper industry wastewater by membrane processes,. PhD Thesis, Istanbul Technical University, İstanbul., 2009.
- [3] C. Das and L. N. Patnaik, "Removal of lignin by industrial solid wastes,"*Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management*, vol. 4, pp. 156-161, 2000.
- [4] A. R. Shawwa, D. W. Smith and D. C. Sego, "Color and chlorinated organics removal from pulp mills wastewater using activated petroleum coke,"*Water Res*, vol. 35, pp. 745-749, 2001.
- [5] S. Verenich, A. Laari and J. Kallas, "Wet oxidation of concentrated wastewaters of paper mills for water cycle closing,"*Waste Management*, vol. 20, pp. 287-293, 2000.
- [6] M. M. Hassan and C. J. Hawkyard, "Decolourisation of aqueous dyes by sequential oxidation treatment with ozone and Fenton's reagent,"*Journal of Chemical Technology & Biotechnology: International Research in Process, Environmental & Clean Technology*, vol. 77, pp. 834-841, 2002.

- [7] K. Rajeshwari, M. Balakrishnan, A. Kansal, K. Lata and V. Kishore, "State-of-the-art of anaerobic digestion technology for industrial wastewater treatment," *Renewable and sustainable energy reviews*, vol. 4, pp. 135-156, 2000.
- [8] A. Raj, M. K. Reddy and R. Chandra, "Decolourisation and treatment of pulp and paper mill effluent by lignin-degrading *Bacillus* sp.," *Journal of Chemical Technology & Biotechnology: International Research in Process, Environmental & Clean Technology*, vol. 82, pp. 399-406, 2007.
- [9] E. Terrazas, A. Vázquez, R. Briones, I. Lázaro and I. Rodríguez, "EC treatment for reuse of tissue paper wastewater: Aspects that affect energy consumption," *J Hazard Mater*, vol. 181, pp. 809-816, 2010.
- [10] M. Sathish and R. P. Viswanath, "Electrochemical degradation of aqueous phenols using graphite electrode in a divided electrolytic cell," *Korean J Chem Eng*, vol. 22, pp. 358-363, 2005.
- [11] S. Sundarapandiyam, R. Chandrasekar, B. Ramanaiah, S. Krishnan and P. Saravanan, "Electrochemical oxidation and reuse of tannery saline wastewater," *J Hazard Mater*, vol. 180, pp. 197-203, 2010.
- [12] W. P. Kong, B. Wang, H. Z. Ma and L. Gu, "Electrochemical treatment of anionic surfactants in synthetic wastewater with three-dimensional electrodes," *J Hazard Mater*, vol. 137, pp. 1532-1537, 2006.
- [13] I. D. Santos, J. C. Afonso and A. J. B. Dutra, "Behavior of a Ti/RuO₂ anode in concentrated chloride medium for phenol and their chlorinated intermediates electrooxidation," *Sep Purif Technol*, vol. 76, pp. 151-157, 2010.
- [14] D. Fino, C. Jara, G. Saracco, V. Specchia and P. Spinelli, "Deactivation and regeneration of Pt anodes for the electro-oxidation of phenol," *J Appl Electrochem*, vol. 35, pp. 405-411, 2005.
- [15] E. A. Carbonio, R. Nagao, E. R. Gonzalez and H. Varela, "Temperature effects on the oscillatory electro-oxidation of methanol on platinum," *Phys Chem Chem Phys*, vol. 11, pp. 665-670, 2009.
- [16] A. Anglada, A. Urriaga and I. Ortiz, "Pilot Scale Performance of the Electro-Oxidation of Landfill Leachate at Boron-Doped Diamond Anodes," *Environ Sci Technol*, vol. 43, pp. 2035-2040, 2009.
- [17] J. R. Dominguez, T. Gonzalez, P. Palo and J. Sanchez-Martin, "Anodic oxidation of ketoprofen on boron-doped diamond (BDD) electrodes. Role of operative parameters," *Chem Eng J*, vol. 162, pp. 1012-1018, 2010.
- [18] A. Fil B, Elgün C., Cihan S, A., Günaslan S., Yılmaz A, E., "Investigation of Nickel Removal from Heavy Metal Containing Industrial Wastewater by Electrocoagulation Method," *Journal of Electrochemical Science and Technology*, vol., pp. 7, 2022.
- [19] Y. G. Feng, D. W. Smith and J. R. Bolton, "Photolysis of aqueous free chlorine species (NOCl and OCI-) with 254 nm ultraviolet light," *J Environ Eng Sci*, vol. 6, pp. 277-284, 2007.
- [20] M. Gotsi, N. Kalogerakis, E. Psillakis, P. Samaras and D. Mantzavinos, "Electrochemical oxidation of olive oil mill wastewaters," *Water Res*, vol. 39, pp. 4177-4187, 2005.
- [21] Y. Li, R. Ehrhard, P. Biswas, P. Kulkarni, K. Carns, C. Patterson, R. Krishnan and R. Sinha, "Removal of Waterborne Particles by Electrofiltration: Pilot-Scale Testing," *Environ Eng Sci*, vol. 26, pp. 1795-1803, 2009.
- [22] L. Gu, B. Wang, H. Z. Ma and W. P. Kong, "Catalytic oxidation of anionic surfactants by electrochemical oxidation with CuO-Co₂O₃-PO₄³⁻ modified kaolin," *J Hazard Mater*, vol. 137, pp. 842-848, 2006.
- [23] H. Z. Ma, Q. F. Zhuo and B. Wang, "Electro-catalytic degradation of methylene blue wastewater assisted by Fe₂O₃-modified kaolin," *Chem Eng J*, vol. 155, pp. 248-253, 2009.
- [24] P. H. Chang, Y. H. Huang, C. L. Hsueh, M. C. Lu and G. H. Huang, "Treatment of non-biodegradable wastewater by electro-Fenton method," *Water Sci Technol*, vol. 49, pp. 213-218, 2004.
- [25] 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, pp. 2857-2864, 2006.
- [26] M. Panizza and G. Cerisola, "Olive mill wastewater treatment by anodic oxidation with parallel plate electrodes," *Water Res*, vol. 40, pp. 1179-1184, 2006.
- [27] A. Anglada, A. Urriaga, I. Ortiz, D. Mantzavinos and E. Diamadopoulos, "Boron-doped diamond anodic treatment of landfill leachate: Evaluation of operating variables and formation of oxidation by-products," *Water Res*, vol. 45, pp. 828-838, 2011.
- [28] S. H. Lin, C. T. Shyu and M. C. Sun, "Saline wastewater treatment by electrochemical method," *Water Res*, vol. 32, pp. 1059-1066, 1998.
- [29] I. Linares-Hernandez, C. Barrera-Diaz, B. Bilyeu, P. Juarez-GarciaRojas and E. Campos-Medina, "A combined electrocoagulation-electrooxidation treatment for industrial wastewater," *J Hazard Mater*, vol. 175, pp. 688-694, 2010.