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Comparison of Different Anodes and Investigation of Energy Consumption on Electrooxidation COD and Turbidity Removal Efficiency of Paper Industry Wastewater: The Effect of Support Electrolyte Type and Concentration

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Abstract – In the studies, different experimental settings were investigated for the treatment of wastewater from the paper industry using the electrooxidation method, one of the electrochemical treatment methods in the batch system. In the 2000 mL volume jacketed glass reactor used for the treatment of wastewater from the paper industry, 4 anodes and 4 cathodes sieve type plates with dimensions of 7 cm x 10 cm were positioned at 0,5 cm intervals, and 1200 mL wastewater was used in the tests. Coated sieve type $Ti/IrO_2/RuO_2$ and Ti/Pt electrodes were used as the anode material and uncoated sieve type Ti electrodes as the cathode material in the electrooxidation tests. The active anodic wet surface area of all plates was calculated as 1078 cm^2. In the trials, the removal efficiency of pollutant parameters such as COD (Chemical Oxygen Demand) and turbidity; The effects of supporting electrolyte types and concentrations such as $NaNO_3$, Na_2SO_4, NaCl and KCl were investigated. According to the results obtained, for both anode types ($Ti/IrO_2/RuO_2$ and Ti/Pt); wastewater natural pH (~7.5) was the most effective pH value at 400 rpm mixing speed, 18.55 mA/cm^2 was the most effective current density, 0.50 M NaCl was the most effective supporting electrolyte type and concentration. 73.20% COD and 97.50% turbidity for $Ti/IrO_2/RuO_2$ anode at optimum conditions; For Ti/Pt anode, 52.96% COD and 95.38% turbidity removal efficiencies were obtained. While the energy consumption value for the $Ti/IrO_2/RuO_2$ anode was calculated as 154.08 kW-hour/kg COD, it was obtained as 312.05 kW-hour/kg COD for the Ti/Pt anode.

Keywords – Electrooxidation, Wastewater Treatment, Ti/Pt Anode, $Ti/IrO_2/RuO_2$ Anode, Turbidity

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 COD and turbidity removal in electrooxidation method; When $Ti/IrO_2/RuO_2$ anode and Ti/Pt anode are used, the effects of support electrolyte types and concentrations such as $NaNO_3$, Na_2SO_4, NaCl and KCl without supporting electrolyte were investigated. At the same time, energy consumption values were calculated for both types of anodes.

II. Materials and Method

In the studies, the treatment of paper industry wastewater was carried out with the electrooxidation method, which is one of the electrochemical treatment processes in the batch system. In order to investigate the effect of supporting electrolyte type and concentration on the removal of COD and turbidity from paper industry wastewater by electrooxidation method, 1200 mL wastewater was used as the wastewater volume in the experiments using $Ti/IrO_2/RuO_2$ and Ti/Pt anodes.

4 anode and 4 cathode sieve type plates of 7 x 10 cm dimensions 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. In the study, $Ti/IrO_2/RuO_2$ and Ti/Pt electrodes were used as anode material, and uncoated sieve type Ti electrodes were used as cathode material. The active anodic wet surface area was calculated as 1078 cm^2. A direct current power source was used to power the apparatus and a magnetic stirrer was used to continuously agitate the solution. A constant temperature water circulator was also used to maintain control over the leaving water temperature. Figure 1 shows the electrooxidation reactor.

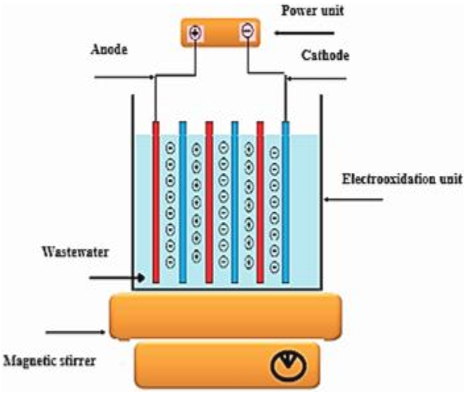

Fig. 1 Electrooxidation reactor

Removal efficiencies and energy consumptions for both anode types were calculated with the help of the equations given below.

Removal efficiency: $$\eta\ (\%) = \left(\frac{C_0 - C_e}{C_0}\right) \times 100 \qquad (1)$$

Energy consumption: $$W\left(\frac{kW\text{-}hr}{m^3}\right) = \frac{V \times I \times t}{v} \qquad (2)$$

Given in the equations, C_0: initial pollutant concentration in wastewater (mg/L), C_e: pollutant concentration remaining in wastewater at time t (mg/L), W: energy consumption value (kW-hr/m^3), V: potential difference in the system (Volt), I: applied current strength (A), ν: total solution volume in the reactor (m^3) t: time (Minute) , is expressed as.

Figure 2 illustrates the experimental configuration.

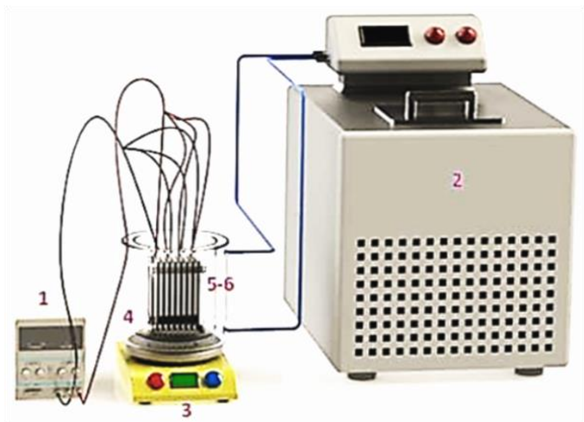

Fig. 2 Experimental configuration
(1. Direct current power unit, 2. Constant temperature water circulator, 3. Magnetic stirrer, 4. Glass reactor, 5. Ti cathode, 6. Ti/Pt and $Ti/IrO_2/RuO_2$ anode)

III. RESULTS

A. Effect of Supporting Electrolyte Type on Removal Efficiency

The effect of supporting electrolyte types such as $NaNO_3$, Na_2SO_4, NaCl and KCl, which are used as support electrolytes in studies using $Ti/IrO_2/RuO_2$, at 0.50 M concentrations, during the reaction for 180 minutes, at pH≈7.5, at 18.55 mA/cm^2 current density. and 400 rpm mixing speed, and the removal efficiencies of COD and turbidity parameters are plotted in Figures 3.

COD removal efficiencies for wastewater medium without supporting electrolyte and NaCl, KCl, Na_2SO_4, $NaNO_3$ were obtained as 19.62%, 73.20%, 70.14%, 32.82%, and 43.79%, respectively. Turbidity removal efficiencies were obtained as 97.50%, 96.18%, 95.00%, 92.50% and 89.00%, respectively.

It is seen that the purification efficiency of supporting electrolytes containing chlorine, such as NaCl and KCl, is higher than other supporting electrolytes.

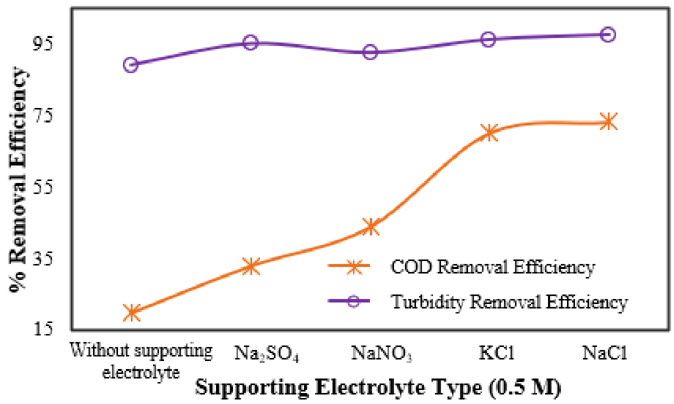

Fig. 3 The effect of supporting electrolyte type on COD and turbidity removal efficiency when $Ti/IrO_2/RuO_2$ anode is used

In studies using Ti/Pt as the anode type, the COD removal efficiencies for wastewater medium without supporting electrolyte and for NaCl, KCl, Na_2SO_4, $NaNO_3$ are respectively; 25.74%, 52.96%, 53.85%, 32.58%, 39.53% were obtained. Turbidity removal efficiencies were obtained as 95.38%, 93.64%, 90.00%, 92.31% and 84.29%, respectively. In support electrolytes containing chlorine in its structure, the purification is higher than other supporting electrolytes. The results are shown in Figure 4.

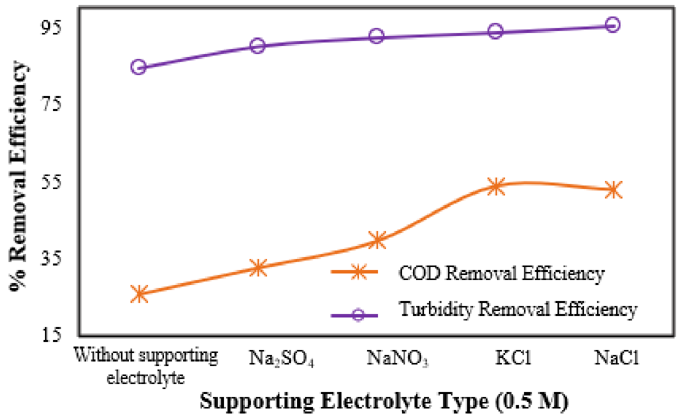

Fig. 4 The effect of supporting electrolyte type on COD and turbidity removal efficiency when Ti/Pt anode is used

One of the most important parameters affecting electrooxidation is the presence of electrolyte in the environment. Because salt in the environment will increase conductivity as well as increase indirect electrooxidation [19]. As can be seen, when $Ti/IrO_2/RuO_2$ and Ti/Pt anodes are used, the highest purification efficiencies for COD and turbidity pollution parameters were achieved in the NaCl salt type. The catalytic activity of chlorine ion in the structure of NaCl and KCl supporting electrolyte types, which have the highest removal efficiencies, facilitated the breakdown of impurities in wastewater [20], [21], [22]. A similar situation is supported by studies in the literature [23], [24], [25].

The results obtained in experiments investigating the effect of supporting electrolyte type on energy consumption are shown in Figure 5.

In studies using $Ti/IrO_2/RuO_2$ anode as anode type; In the presence of NaCl, which was chosen as the optimum supporting electrolyte type, it was concluded that 154.08 kW-hour/kg COD (565.5 kW-hour/m^3).

In studies using Ti/Pt anode as anode type; It was concluded that 312.05 kW-hour/kg COD (697.5 kW-hour/m^3) was obtained when NaCl, which was selected as the optimum supporting electrolyte type, was used after 3 hours of electrolysis.

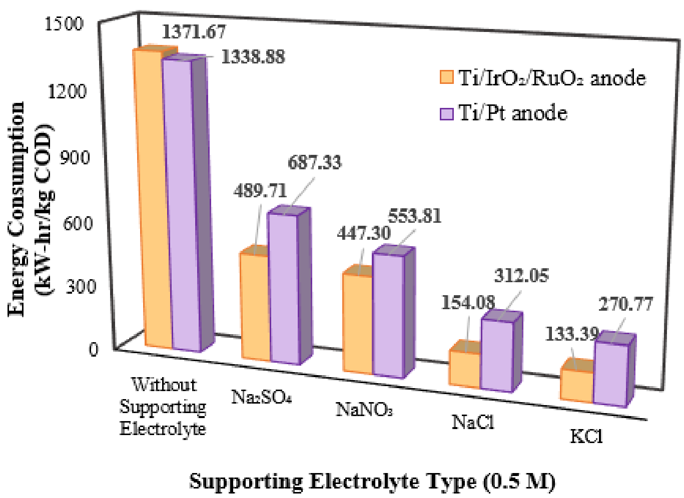

Fig. 5 Effect of supporting electrolyte type on energy consumption for both anodes ($Ti/IrO_2/RuO_2$ and Ti/Pt)

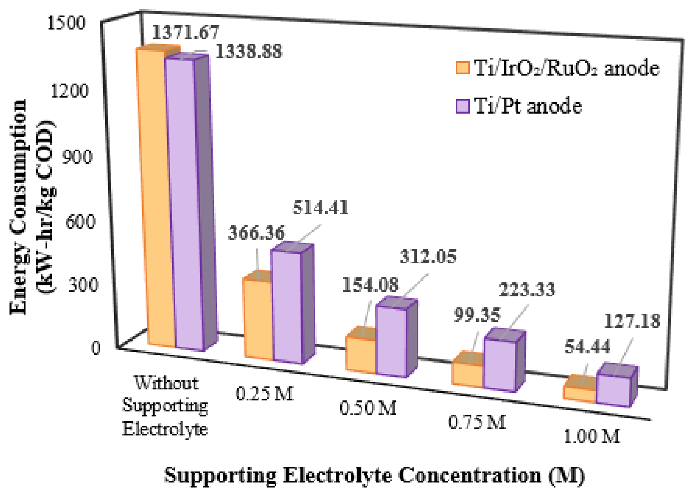

Fig. 6 The effect of supporting electrolyte concentration on COD and turbidity removal efficiency when $Ti/IrO_2/RuO_2$ anode is used

B. *Effect of Support Electrolyte Concentration on Removal Efficiency*

The effect of supporting electrolyte concentration on COD and turbidity treatment efficiencies in experiments performed using $Ti/IrO_2/RuO_2$ anodes, at concentrations ranging from 0.25 M to 1.00 M, during the reaction for 180 minutes, at a current density of 18.55 mA/cm^2 and at pH≈7.5 performed and the results are shown in the graph in Figure 6.

Considering the COD removal efficiencies, while the removal efficiency in the wastewater medium without supporting electrolyte was 19.62%, the removal efficiency for 0.25 M increased to 56.71%. The removal efficiency reached 73.20% when the support electrolyte concentration was 0.50 M, 76.08% at 0.75 M, and 79.43% at 1.00 M. Turbidity removal efficiencies were obtained as 94.00%, 97.50%, 98.33%, 99.23% and 89.00%, respectively, in the 0.25-1.00 M concentration range.

The increase in the support electrolyte concentration increases the removal efficiency relatively up to a certain concentration. However, 0.50 M was chosen as the optimum support electrolyte concentration, since there was no significant increase in the removal efficiencies at the support electrolyte concentration values above 0.50 M.

In experiments using Ti/Pt anode as anode type; In the absence of supporting electrolyte, the COD removal efficiency is 25.74% as a result of the electrolysis lasting for 3 hours, while the COD removal efficiencies when 0.25, 0.50, 0.75 and 1.00 M support electrolyte concentrations are; 41.73%, 52.96%, 54.38% and 57.33% were obtained. Turbidity removal efficiencies were found to be 90.00%, 95.38%, 96.43%, 97.69% and 84.29%, respectively.

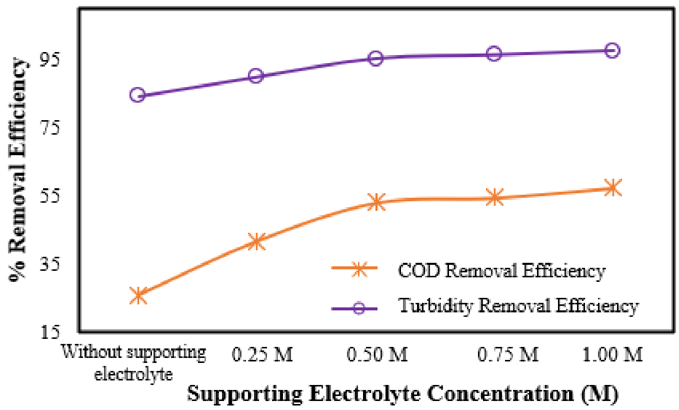

Fig. 7 The effect of supporting electrolyte concentration on COD and turbidity removal efficiency when Ti/Pt anode is used

Another important parameter for electrochemical treatment processes is the conductivity of wastewater [26]. In general, a high conductivity value means low resistance in the electrochemical cell and the process efficiency increases more [27]. While free chloride is the dominant oxidizing agent in acidic conditions, chlorine ions, hypochlorous and hydroxyl radicals are important in basic conditions [28]. When chloride ion is present in the environment as hypochlorite, indirect electrooxidation is positively affected [29], [30]. There are similar studies in the literature [31].

The results obtained in experiments investigating the effect of supporting electrolyte concentration on energy consumption are shown in Figure 8.

In experiments using Ti/IrO_2/RuO_2 anode as anode type; In the presence of 0.50 M NaCl, which was decided as the most appropriate value, it was calculated as 154.08 kW-hour/kg COD (565.5 kW-hour/m^3).

In experiments using Ti/Pt anode as anode type; When 0.50 M NaCl was used, it was concluded that 312.05 kW-hour/kg COD (697.5 kW-hour/m^3).

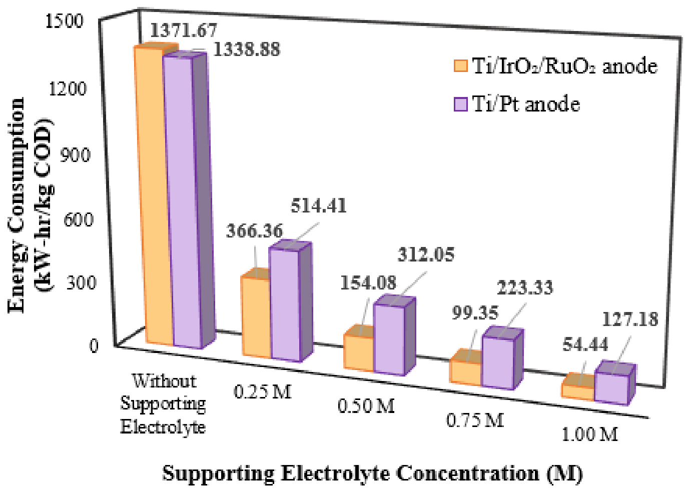

Fig. 8 Effect of supporting electrolyte concentration on energy consumption for both anodes (Ti/IrO_2/RuO_2 and Ti/Pt)

IV. DISCUSSION

A. *Effect of Supporting Electrolyte Type on Removal Efficiency*

For both anode types (Ti/IrO_2/RuO_2 and Ti/Pt); The results obtained from studies examining the effect of supporting electrolyte type on COD and turbidity removal efficiencies are compared in the graphics.

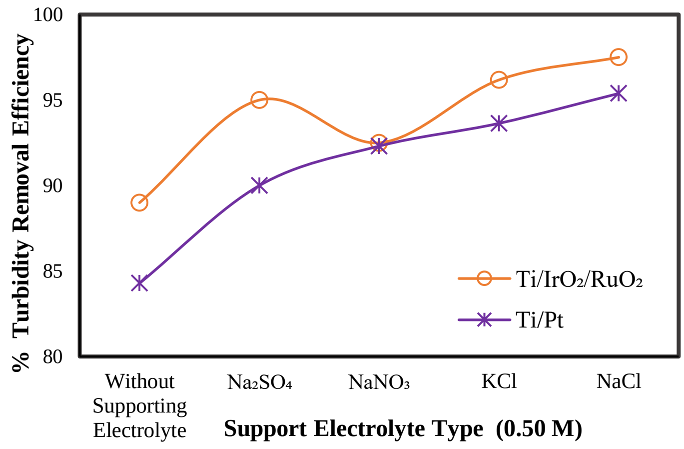

Fig. 9 Effect of SET on COD removal efficiency when Ti/IrO_2/RuO_2 and Ti/Pt anodes are used

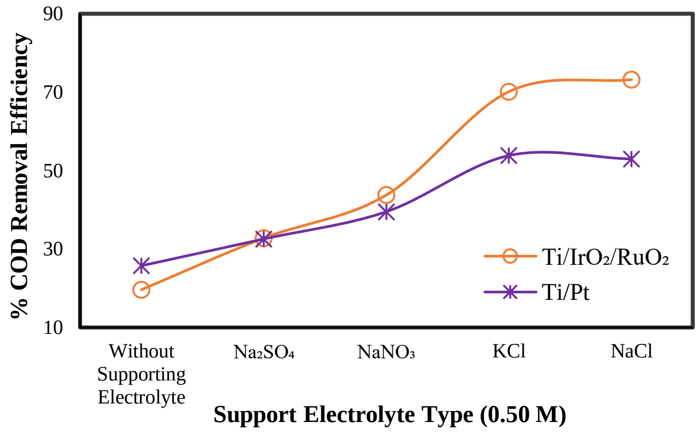

Fig. 10 Effect of SET on turbidity removal efficiency when Ti/IrO_2/RuO_2 and Ti/Pt anodes are used

The effect of supporting electrolyte type and concentration on energy consumption was examined in both anodes and the comparison of the graphs in Figure 5 and Figure 8 is shown.

B. *Effect of Support Electrolyte Concentration on Removal Efficiency*

For both anode types (Ti/IrO_2/RuO_2 and Ti/Pt); The results obtained from studies examining the effect of supporting electrolyte concentration on COD and turbidity removal efficiencies are compared in the graphics.

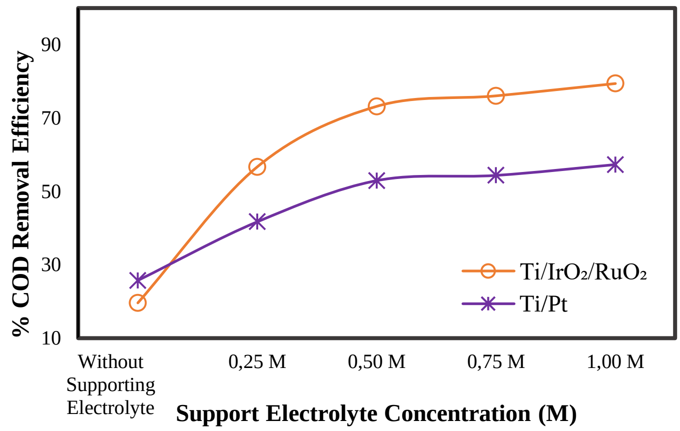

Fig. 11 Effect of SEC on COD removal efficiency when $Ti/IrO_2/RuO_2$ and Ti/Pt anodes are used

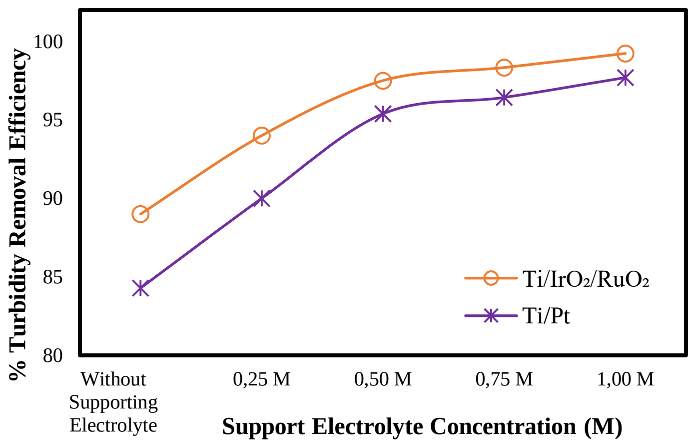

Fig. 12 Effect of SEC on turbidity removal efficiency when $Ti/IrO_2/RuO_2$ and Ti/Pt anodes are used

V. CONCLUSION

In the study, the treatability of the wastewater obtained from the paper mill using the electrooxidation method was examined and all the experiments were carried out in batch mode. The effects of system parameters on treatment efficiency were determined. The performance of the system was also determined by measuring different parameters such as COD and turbidity. Optimum results are obtained in the electrooxidation process; support electrolyte type and concentration and electrode type were selected.

In the case of using $Ti/IrO_2/RuO_2$ anode as the anode type, in the optimum conditions; The COD and turbidity removal efficiencies are shown in Figure 9-12. At the end of the 3-hour trial at 0.50 M NaCl supporting electrolyte type and concentration, 400 rpm mixing speed, 18.55 mA/cm^2 current density, wastewater natural pH value (pH:≈7.5), 73.20% COD and Turbidity removal efficiencies of 97.50% were obtained. At the same time, the energy consumption was found to be 154.08 kW-hour/kg COD (565.5 kW-hour/m^3) in the conditions mentioned.

When Ti/Pt anode is used as the anode type, under optimum conditions; The COD and turbidity removal efficiencies are shown in Figure 9-12. Under optimum conditions, 52.96% COD and 95.38% turbidity removal efficiencies were obtained. At the same time, the energy consumption was found to be 312.05 kW-hour/kg COD (697.5 kW-hour/m^3) in the conditions mentioned.

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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. Sundarapandiyan, 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. Urtiaga 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] B. A. Fil, C. Elgün, S. A. Cihan, S. Günaslan, A. E. Yılmaz, "Investigation of Nickel Removal from Heavy Metal Containing Industrial Wastewater by Electrocoagulation Method,"*Journal of Electrochemical Science and Technology*, vol., pp. 7, 2022.
[19] N. A. Ghalwa, H.M Abu-Shawish, F. R. Zaggout, S. M. Saadeh, A. R. Al-Dalou and A. A. Abou Assi, "Electrochemical degradation of tramadol hydrochloride: Novel use of potentiometric carbon paste electrodes as a tracer,"*Arabian Journal of Chemistry*, vol. 7(5), pp. 708-714, 2014.
[20] C. Comninellis, "Electrocatalysis in the Electrochemical Conversion/Combustion of Organic Pollutants for Waste-Water Treatment, "*Electrochimica Acta*, vol. 39(11-12), pp. 1857-1862, 1994.
[21] J. Iniesta, J. Gonzalez-Garcia, E. Exposito, V. Montiel and A. Aldaz, "Influence of chloride ion on electrochemical degradation of phenol in alkaline medium using bismuth doped and pure PbO_2 anodes,"*Water Research*, vol. 35(14), pp. 3291-3300, 2001.
[22] M. T. Karuppiah and G. B. Raju, "Anodic Degradation of CI Reactive Blue 221 Using Graphite and $IrO_2/TaO_2/RuO_2$ Coated Titanium Electrodes,"*Industrial & Engineering Chemistry Research*, vol. 48(4), pp. 2149-2156, 2009.
[23] H. S. Awad and N. A. Galwa, "Electrochemical degradation of Acid Blue and Basic Brown dyes on Pb/PbO_2 electrode in the presence of different conductive electrolyte and effect of various operating factors,"*Chemosphere*, vol. 61(9), pp. 1327-1335, 2005.
[24] 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 Journal of Analytical Chemistry*, vol. 3(2), pp. 99, 2012.
[25] P. Canizares, B. Louhichi, A. Gadri, B. Nasr, R. Paz, M. A. Rodrigo and C. Saez, "Electrochemical treatment of the pollutants generated in an ink-manufacturing process,"*Journal of Hazardous Materials*, vol. 146(3), pp. 552-557, 2007.
[26] C. Elgün. Treatment Of Paper Industry Wastewater by Electrooxidation Method,. Master's Thesis, Balikesir University, Balikesir., 2022.
[27] G. R. P. Malpass, D. W. Miwa, D. A. Mortari, S. A. S. Machado and A. J. Motheo, "Decolorisation of real textile waste using electrochemical techniques: Effect of the chloride concentration,"*Water Research*, vol. 41(13), pp. 2969-2977, 2007.
[28] 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.
[29] A. Fernandes, A. Morao, M. Magrinho, A. Lopes and I. Goncalves, "Electrochemical degradation of C. I. Acid Orange 7,"*Dyes and Pigments*, vol. 61(3), pp. 287-296, 2004.
[30] P. Piya-Areetham, K. Shenchunthichai and M. Hunsom, "Application of Electrooxidation Process for Treating Concentrated Wastewater From Distillery İndustry with a Voluminous Electrode,"*Water Research*, vol. 40(15), pp. 2857-2864, 2006.
[31] D. Rajkumar and K. Palanivelu, "Electrochemical Treatment of İndustrial Wastewater,"*Journal of Hazardous Materials*, vol. 113(1-3), pp. 123-129, 2004.