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Evaluation of the Efficiency of $Ti/IrO_2/RuO_2$ Anode in COD Removal from Paper Industry Wastewaters by Electrooxidation Method

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Abstract **–** In the research, the electrooxidation method of the electrochemical treatment methods in the batch system was explored a variety of experimental conditions for the treatment of wastewater from the paper sector. 4 anodes and 4 cathodes sieve type plates with dimensions of 7 cm x 10 cm were positioned at 0,5 cm intervals in the 2000 mL volume jacketed glass reactor used for the treatment of wastewater from the paper industry, and 1200 mL wastewater was used in the testing. 4 coated $Ti/IrO_2/RuO_2$ electrodes of the sieve type were used as the anode material and 4 uncoated Ti electrodes of the sieve type were utilized as the cathode material in the electrooxidation of effluent from the paper industry. In the experiments, the removal rate of the COD (Chemical Oxygen Demand) pollutant parameter; The effects of supporting electrolyte types and concentrations such as KCl, NaCl, $NaNO_3$, and Na_2SO_4, and parameters such as initial pH value and current density of wastewater without supporting electrolyte were investigated. According to the results obtained; In the experiments conducted at the natural pH value of wastewater, 18.55 mA/cm^2 was the most effective current density, 0.50 M NaCl was the most effective supporting electrolyte type and concentration. The COD removal rate at the best conditions (37.11 mA/cm^2 current density) was 90.62%. In optimum conditions; 73.20% COD removal efficiency has been achieved.

Keywords – $Ti/IrO_2/RuO_2$ anode, electrooxidation, wastewater treatment, COD removal, paper industry

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 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].

This study investigated into the electrooxidation method, one of the electrochemical treatment methods used in batch systems, for treating effluent from the paper sector. For this purpose, optimum COD removal in electrooxidation method; When $Ti/IrO_2/RuO_2$ anode is used, the effects of supporting electrolyte types and concentrations such as $NaNO_3$, Na_2SO_4, NaCl and KCl without supporting electrolyte, wastewater initial pH value and current density were investigated.

II. Materials and Method

In the experiment, the electrooxidation method one of the electrochemical treatment procedures in the batch system was used to treat the wastewater from the paper industry. In order to investigate the effect of supporting electrolyte type and concentration, wastewater initial pH value and current density on COD removal by electrooxidation method from paper industry wastewaters, 1200 mL wastewater was used as wastewater volume in the experiments using $Ti/IrO_2/RuO_2$ anode.

4 pieces of 7 x 10 cm anode and 4 cathode sieve type plates were placed at 0.5 cm intervals in the jacketed glass reactor with a volume of 2000 mL used for the treatment of wastewater originating from the paper industry. In the study, uncoated sieve type Ti electrodes were used as the cathode material and $Ti/IrO_2/RuO_2$ electrodes were used as the anode material. The active anodic wet surface area was calculated as 1078 cm^2. A direct current power supply was used to power the device 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.

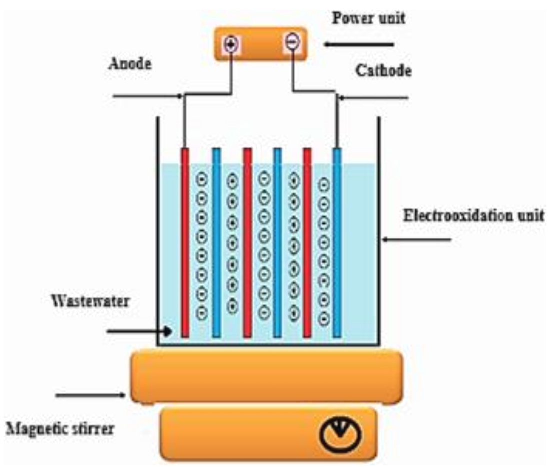

Fig. 1 Electrooxidation reactor

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

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

Energy consumption: $W\left(\frac{kW\text{-}hr}{m^3}\right) = \frac{V \times I \times t}{v}$ (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), t: time (Minute), I: applied current strength (A), ν: total solution volume in the reactor (m^3), is expressed as.

III. Results And Discussion

A. *The Effect of Supporting Electrolyte Type on COD 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 parameters are plotted in Figures 2.

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.

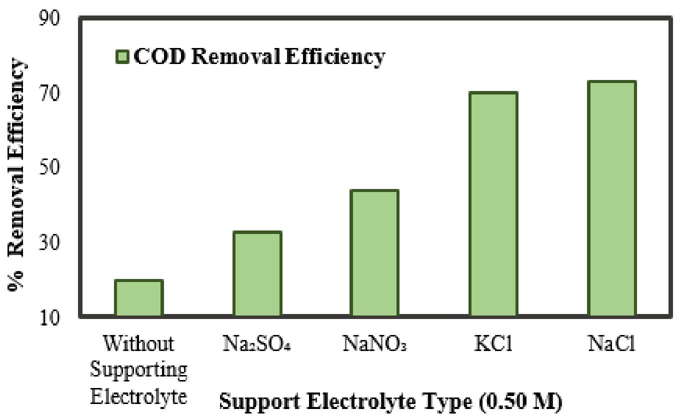

Fig. 2 Effect of SET on COD removal efficiency when $Ti/IrO_2/RuO_2$ anode is used

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 $Ti/IrO_2/RuO_2$ anode 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].

B. *The Effect of Support Electrolyte Concentration on COD 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 3.

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.

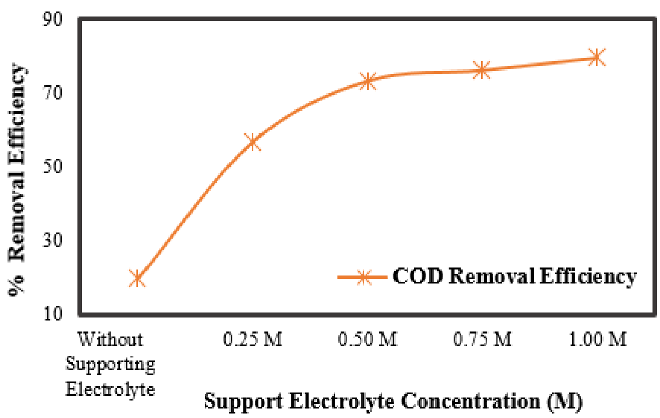

Fig. 3 Effect of SEC on COD removal efficiency when $Ti/IrO_2/RuO_2$ anode is used

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].

C. *The Effect of Wastewater Initial pH Value on COD Removal Efficiency*

In the trials where $Ti/IrO_2/RuO_2$ anode was used as the anode material, the initial pH value of the wastewater was examined between 3-11 and the optimum pH value was investigated. The effect of initial pH value on treatment efficiency; It was investigated between pH:3-11 for reaction times of 3 hours at a current intensity of 18.55 mA/cm^2, in 0.50 M NaCl supporting electrolyte type, at 400 rpm mixing speed. COD removal efficiencies are given in Figure 4.

COD removal efficiencies were obtained as 65.46%, 69.45%, 73.20%, 63.70% and 60.57% for pH values 3, 5, 7.5, 9 and 11, respectively.

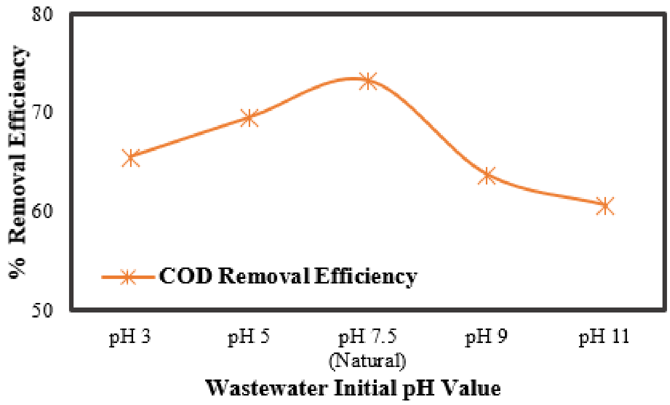

Fig. 4 Effect of wastewater initial pH value on COD removal efficiency when $Ti/IrO_2/RuO_2$ anode is used

More than 99% of active chlorine is found as hypochlorous acid (HClO) in acidic medium, and more than 99% of active chlorine is found as hypochlorite (ClO^-) in basic medium [32]. Because hypochlorous acid is a stronger oxidant than hypochlorous acid, electrochemical operations involving oxidation of chlorine ions typically provide better results in acidic settings than in basic or neutral ones. Previous research has shown that free chlorine is the main oxidizing agent in acidic environments. [28].

D. *The Effect of Current Density Applied on COD Removal Efficiency*

The effect of current density on the removal of polluting COD in paper industry wastewater in trials using $Ti/IrO_2/RuO_2$ anode material; 18.55;23.19;27.83;32.47;37.11 mA/cm^2 varying values at natural pH value of wastewater, 400 rpm mixing speed, 0.5 M NaCl support electrolyte in the presence of 3 hours reaction time and the data obtained are graphed in Figure 5.

COD removal efficiency was 73.20% for 18.55 mA/cm^2 current density, 77.98% for 23.19 mA/cm^2, 82.88% for 27.83 mA/cm^2, 87.22% for 32.47 mA/cm^2 and 90.62% for 37.11 mA/cm^2.

The results clearly show that; The increased current density significantly increased the treatment efficiency.

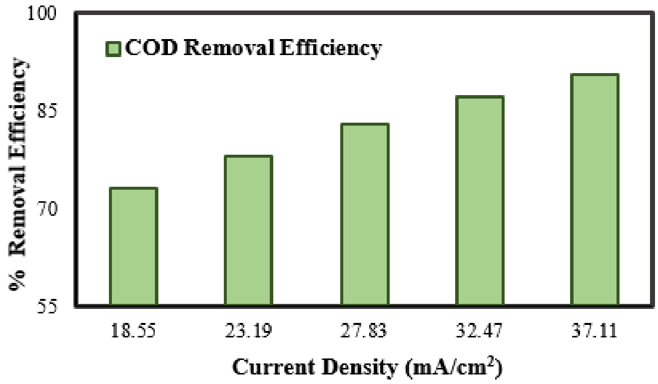

Fig. 5 Effect of current density on COD removal efficiency when $Ti/IrO_2/RuO_2$ anode is used

When controlling the rate of a reaction in electrochemical processes, the current density applied to each unit area of the electrode is preferable [30]. I. Faraday's law states that as the quantity of current grows, so will the amount of oxidized and reduced material in the electrodes. The creation of free chlorine during electrooxidation will grow concurrently with the increase in current density, which will indirectly aid in the breakdown of contaminants [33].
Similar findings can be found in the literature [16], [34], [35].

IV. 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.

Table 1. COD Removal Efficiency in Optimum Conditions

Anode type: $Ti/IrO_2/RuO_2$	
Optimal Conditions	**% COD Removal Efficiency**
Supporting Electrolyte Type and Concentration: 0.50 M NaCl pH: ≈ 7.5 (Natural) Current Density: 18.55 mA/cm^2 Temperature Value: 20±1ºC Mixing Speed: 400 rpm	73.20%

In the case of using $Ti/IrO_2/RuO_2$ anode as the anode type, in the optimum conditions; The COD removal efficiencies are shown in Figures. 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 and wastewater natural pH value (pH:≈7.5) for 73.20% COD removal efficiencies of were obtained.

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