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Investigation of the effect of supporting electrolyte type and pH parameters on electrooxidation color removal from Direct Blue 86

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Abstract – In this study, color removal and electrical consumption from Direct Blue 86 (DB86) dyestuff, commonly used in the textile industry, were investigated using the electrooxidation method. A jacketed glass reactor with a volume of 2000 mL was preferred for the electrooxidation process. Five anode and five cathode electrodes with dimensions of 70 x 100 mm were used. $Ti/IrO_2/RuO_2$ was chosen as the anode material, and stainless steel (plate type) electrodes were preferred as the cathode. The effects of the supporting electrolyte type and pH parameters on color removal were investigated. NaCl, KCl, $NaNO_3$, and Na_2SO_4 were used as supporting electrolytes. Experiments were conducted at pH 3, 5, 7, 9, and 11 with an applied current density of 0.325 mA/cm^2. The results showed that KCl as the supporting electrolyte provided the highest color removal efficiency with 99.76%. The optimum pH value was found to be pH 9. The minimum energy consumption was calculated as 3.39 $kW\text{-}h/m^3$ for pH 11. Based on the obtained results, it was concluded that the electrooxidation method is effective in color removal and can be preferred due to its ease of use and process control advantages.

Keywords – Direct Blue 86, Electrooxidation, Color Removal, pH, Supporting Electrloyte Type

I. INTRODUCTION

Textile industries consume significant amounts of water and employ a diverse range of synthetic dyes to color textile fibers, leading to the release of large volumes of wastewater [1]. The textile industry is a massive water-consuming sector [2, 3]. Furthermore, due to characteristics as oxidative chemicals, permanent color, low biodegradability, and alkalinity, the waste water produced in this industrial sector is regarded as a relevant cause of pollution [4]. The textile industry is one of the greatest generators of liquid effluent pollutants, due to the high quantities of water used in the dyeing processes. It is estimated that 280,000 tonnes of textile dyes are discharged in such industrial effluent every year worldwide [5, 6] The treatment of raw wastewaters from the textile and dyestuff industries is extremely challenging because these wastewaters consist of various structurally different dyes (e.g., azo, direct, disperse, reactive, etc.), metals (e.g., copper, lead, cadmium, mercury, nickel, cobalt, etc.), surfactants, solvents, salts, dye fixing agents, and intermediates [6, 7, 8]. The presence of dyestuff in nature, especially due to its toxic and carcinogenic effects, is highly dangerous for living organisms. Therefore, it is crucial to remove dyestuff from wastewater [9]. Various methods such as adsorption [10], membrane filtration [11], chemical coagulation and fenton oxidation [12] , and ozonation [13] are utilized for the removal of dyestuff from wastewater. For the treatment of organic contaminants, electrochemical techniques are frequently touted as appealing options because of their adaptability, simplicity of use, efficiency, and lower cost [14]. The electrode material is just one of many variables that affects how effective the electrochemical reaction is. Because of their mechanical resilience, low cost, and effective scale-up in the electrochemical industry, metallic oxide electrodes with RuO_2 and IrO_2 are frequently employed in environmental electrochemistry [15]. Ti/SnO_2 –IrO_2 , Ti/Sb – SnO_2 , Ti/SnO_2 –Sb_2O_5 – RuO_2 , Ti/Ta_2O_5–IrO_2 , Ti/RuO_2 –IrO_2 and Ti/TiO_2 –IrO_2 , boron doped diamond (BDD), carbon and graphite are some of the materials used in electrooxidation processes in water treatment studies [16]. The electro-oxidation efficiency is influenced by multiple factors including current density, anode type, pH, and the type and concentration of electrolyte (i.e., ionic compound) employed in the process [17, 18].

More intense oxidizing conditions are frequently required for electrochemical remediation, and highly oxidizing species as OH, Cl_2, and O_3 are electro generated. This can be achieved by altering the supporting electrolyte (NaCl) or the electrode material (SnO_2, PbO_2, BDD) [19]. Electrochemical processes like electroflotation, electrocoagulation, and electrooxidation have received a lot of interest recently. They are appealing because they require less chemicals and are simple to use [16].

In this study, it was aimed to investigate the effect of supporting electrolyte type and pH parameters affecting color removal by electrooxidation method from Direct Blue 86, one of the dyestuffs commonly used in the textile industry, and the electricity consumption of the system.

II. MATERIALS AND METHOD

Tablo 1. Features of DB86

DB 86	CAS No.	Molecular Formula	Molecular Weight
	1330-38-7	$C_{32}H_{14}CuN_8Na_2O_6S_2$	780.16

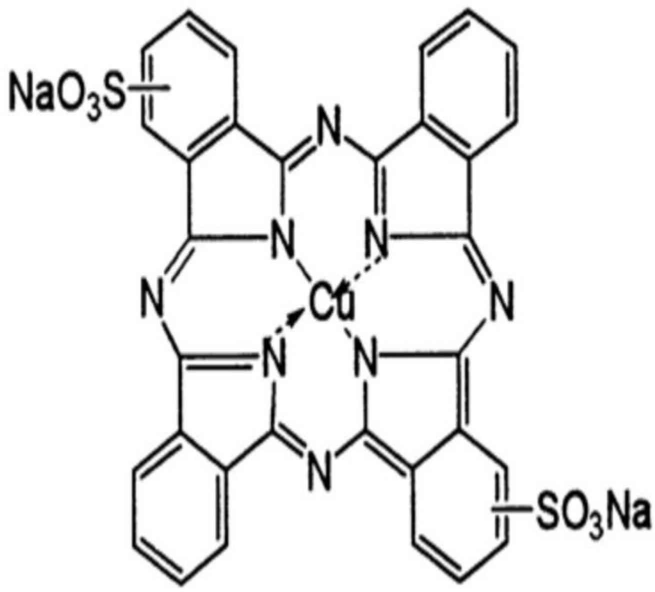

Figure 1. Chemical structure of Direct Blue 86

A. *Electrooxidation system installation*

A jacketed glass reactor with a volume of 2000 mL was utilized in the electrooxidation process. The electrode plates had dimensions of 70 x 100 mm, resulting in a total surface area of 3080 cm^2. The approximate wet surface area of all the plates was calculated to be 2464 cm^2. For the anode, a $Ti/IrO_2/RuO_2$ electrode of DSA type was used, while a stainless steel plate-type cathode was chosen. In the reactor vessel, a monopolar configuration was established by connecting five anode electrodes and five cathode electrodes in parallel, with a separation distance of 5 mm between each electrode. Voltage and current measurements were performed using a digital power supply unit of the brand "Control Unit PE280." Mixing inside the reactor was achieved with a magnetic stirrer of the brand "Yellowline MST." The system operated with a direct current power source, and the wastewater solution was continuously mixed using the magnetic stirrer. Color determination was carried out using a photometer of the brand "Lovibond." Parameters such as pH, temperature, conductivity, current, voltage, and color were examined.

B. *Experimental Procedure*

Experiment was conducted at a temperature of 25°C with a current density of 0.325 mA/cm^2, stirring speed of 200 rpm, initial concentration of 250 mg/L, and a total experiment time of 60 minutes. A 5 mL sample was taken from a 1000 mL stock solution and transferred to plastic tubes. In total, 8 samples were taken at specific time intervals, including the beginning, the 5th minute, the 10th minute, the 15th minute, the 20th minute, the 30th minute, the 45th minute, and the 60th minute. The temperature, conductivity, and pH values of each sample were checked, and a color determination was made by transferring them into glass sample tubes and measuring 10 mL.

C. Calculation

When calculating the color removal efficiency;

Removal efficiency;

$$\eta(\%) = \left(\frac{C_0 - C_e}{C_0}\right) x100$$

Where; C_0: Initial concentration, mg/L

C_e: final concentration, mg/L

Energy consumption;

$$\left(\text{kW} - \text{h/ m}^3\right) = \frac{V \times I \times t}{v}$$

Where, V (Volt) is the potential difference, I (ampere) is the current intensity, t (hour) is the time, and v (m^3) is the wastewater volume.

III. Results

3.1. Effect Of Supporting Electrolyte Type On Color Removal

It was proposed that raising the ionic strength of the treated water by adding supporting electrolytes leads the double layer to compress [20]. Experiments were conducted using different supporting electrolytes, including NaCl, KCl, $NaNO_3$, and Na_2SO_4, at an initial concentration of 250 ppm, a current density of 0.325 mA/cm^2, a temperature of 25°C, natural pH of wastewater, and a stirring speed of 200 rpm. The color removal efficiencies for KCl, NaCl, $NaNO_3$, and Na_2SO_4 electrolytes were calculated as 99.76%, 98.73%, 80.57%, and 56.42%, respectively, based on the obtained results. In their study, Li et al. reported achieving 100% efficiency in color removal from Reactive Blue 19 dye using NaCl as the supporting electrolyte, while obtaining 60% efficiency when using Na_2SO_4 [21]. In their study, Keyikoglu et al. found that NaCl and KCl as supporting electrolytes were more efficient in color removal in electrochemical treatment compared to other electrolytes [22].

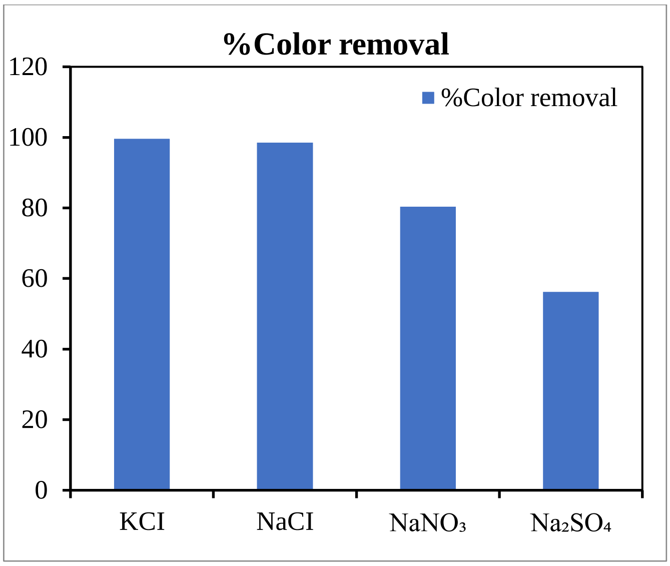

Figure 2. Effect of supporting electrolyte type on color removal

3.2. Effect of Support Electrolyte Type on Energy Consumption

Supporting electrolytes are primarily used to give the solution a particular amount of conductivity during electrochemical reactions. The solution's ohmic resistance decreases when electrolytes are added to boost conductivity. Reduced resistance between the electrodes allows for less electrical energy to be used [23].Through decreasing the cell voltage, supporting electrolytes have a direct impact on the rate of metal dissolution and energy consumption [24, 25]. The energy consumption values obtained from one-hour experiments for each supporting electrolyte are as follows: 3.39 kW-h/m^3 for KCl, 3.72 kW-h/m^3 for 5 mM NaCl, 3.81 kW-h/m^3 for 5 mM $NaNO_3$, and 3.84 kW-h/m^3 for 5 mM Na_2SO_4. According to the data, Na_2SO_4 electrolyte has the highest energy usage. As KCl is the most effective electrolyte, it uses the least amount of energy.

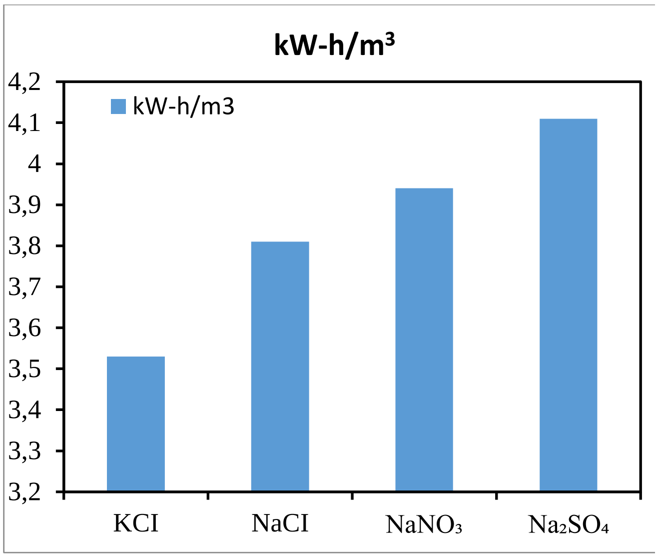

Figure 3. Effect of support electrolyte type on energy consumption

3.3. Effect of pH on Color Removal

In order to examine the effect of pH on decolorization, it was carried out at a current density of 0.325 mA/cm^2, a stirring speed of 200 rpm, using 5 mM supporting electrolyte concentration, 250 mg/L dyestuff concentration, NACI supporting electrolyte and a temperature of 25°C. As a result of the studies carried out for the pH parameter, the color removal efficiencies for pH 3, 5, 7, 9, 11 were calculated as 98.73%, 97.32%, 98.40%, 98.85%, and 90.69%, respectively.

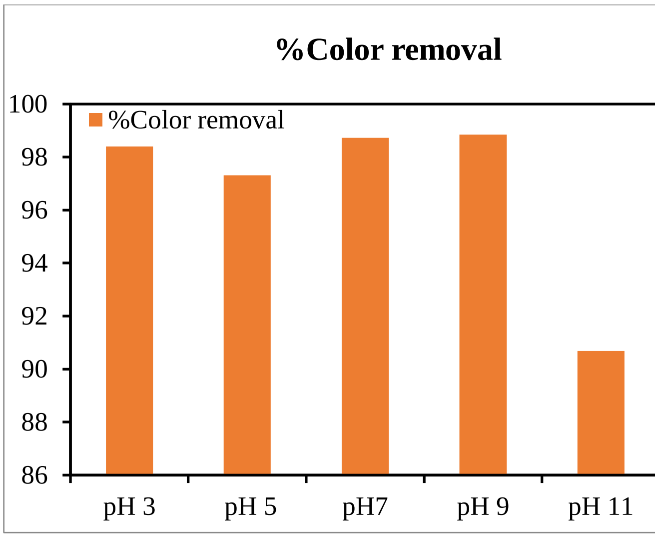

Figure 4. Effect of pH on color removal

3.4. Effect of pH on Energy Consumption

One of the important parameters in the electrooxidation process is pH. The values obtained from studies conducted to examine the effect of initial pH are respectively found as pH 11<3<5<9<7. Since no electrolyte is added to the wastewater at its natural pH, the highest consumption is achieved at the natural pH. Therefore, the use of supporting electrolyte is crucial in electrochemical treatment.

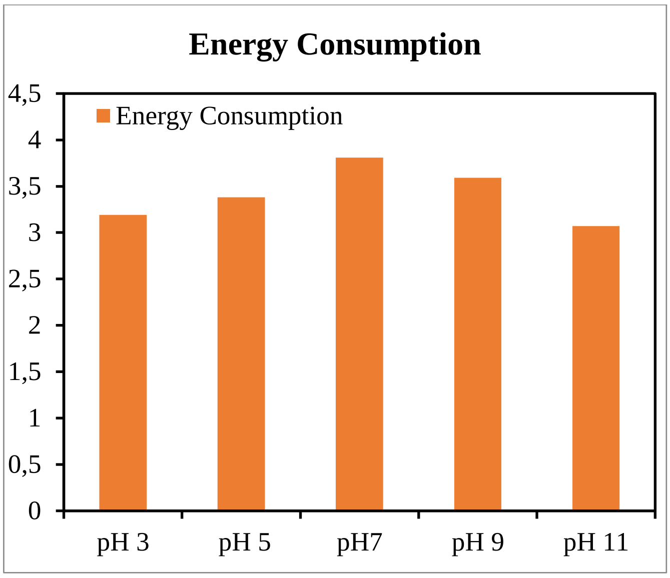

Figure 5. Effect of pH on energy consumption

IV. DISCUSSION

Synthetic dye wastewater containing hazardous substances can pose a threat to receiving environments and the organisms inhabiting them, necessitating their treatment and discharge into receiving bodies after purification. Although conventional treatment methods are employed for color removal of these substances, they have certain disadvantages such as excessive sludge formation and high costs. Electrochemical treatment methods, particularly the electrooxidation process, are preferred due to their operational ease and ability to achieve higher efficiency at lower costs, with minimal post-process sludge generation. In this study, the electrooxidation process was chosen among various electrochemical methods. The effects of different supporting electrolytes and initial pH on color removal from Direct Blue 86 dye were investigated, and the optimal operating conditions were determined for both parameters. The results obtained indicated high efficiency and usability of the electrochemical treatment method. Determining the electricity consumption of the system, which is an important operational parameter in electrochemical treatment methods, is necessary for cost considerations. Optimization of electricity consumption is required for systems with high energy consumption.

V. CONCLUSION

It has been observed that the electrochemical oxidation process is highly efficient in the removal of color from Direct Blue 86 dye. Among the process parameters, the type of supporting electrolyte and initial pH value are important factors in electrochemical treatment processes. In this study, it was found that KCl and NaCl, among different types of supporting electrolytes, achieved the highest efficiencies in color removal. The effect of initial pH value on electrooxidation was determined by conducting experiments at pH 3.5, 7, 9, and 11, and it was found that pH 9 was the most efficient pH. The energy consumption, which is an important aspect of electrochemical treatment, was also examined, and it was observed that the highest energy consumption occurred at the natural pH of the wastewater.

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