KINETIC STUDY ON CELESTINE BLUE DYE REMOVAL USING ELECTROCOAGULATION METHOD

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Abstract: This research investigates the efficiency of the Celestine Blue dye removal from wastewater by electrocoagulation (EC) method using iron (Fe) electrodes through a batch electrolytic cell. Various operating parameters such as effect of the amount of electrolyte, voltage, amount of energy consumed, and kinetic studies have been studied on the dye removal efficiency of wastewater. Based on the results, without considering energy consumption, 6 V presents the best performance as 100 % removal efficiency obtained in 5 minutes using 1.0 g of sodium chloride (NaCl), pH of 7 and 10 ppm of Celestine blue solution. If energy consumption is considered, at 2 V, 0.6 g of NaCl yields optimum condition with removal efficiency of 41.99 % and low energy consumption of 1.65 kWh/m3 at pH 7 and 10 ppm of Celestine Blue dye solution. Characterization of dye solution after electrocoagulation using atomic absorption spectroscopy confirmed that there is significant presence of excess iron that is not used in the reaction. The dye removal rate is described well using second order kinetic model.

I. INTRODUCTION

In Malaysia, especially in the East Coast of Peninsular Malaysia and Sarawak, textile industry has contributed significantly to the economic growth due to the high demand of the local and abroad. However, the textile industry is one of the major industrial water users that consumes large amount of water ranging from 73 m3 to 167 m3 per ton of product during the dyeing process that leads to the contaminated outflow caused by the dye residuum [1]. The pollutants in the effluent contains strong colour, high pH, high chemical oxygen demand (COD), high biological oxygen demands (BOD), high total suspended solid (TSS) and high salt contents that pose serious environmental issues. The discharge of dye-contained wastewater creates an aesthetically undesirable aqueous environment that affects the penetration of sunlight for the photosynthetic and biological activity of the aquatic living organisms. Some of the dyes are also carcinogenic, mutagenic and toxic to human and aquatic life [2]. On top of that, since dyes are aromatic compounds, they are highly stable against light, oxidants and biological degradation, which complicates the treatment process as the dye reduction, will be difficult [3]. Currently, there are few conventional methods being practiced by the industries such as chemical coagulation, Fenton reagent, electro-kinetic coagulation, membrane filtration, oxidation processes and biological treatments [4,5]. Nonetheless, these existing treatments are not efficient, time consuming, costly and difficult. For example, chemical coagulation and ozone oxidation studies are not able to reduce the COD and colour of the wastewater. Chemical processes like Fenton reagent, electro-kinetic coagulation, electro-oxidation and membrane filtration produces large amount of sludge [6,7]. Advanced oxidation processes using ultraviolet/hydrogen peroxide (UV/H2O2), ozonation and photo-catalysis are economically unfeasible to treat wastewaters. Not only that, chemical oxidation uses chlorine and photochemical method releases toxic by-products and chemicals [8]. Biological treatments are also ineffective as most of the dyes are toxic to the microorganisms that inhibit biological degradation process [9]. Recently, electrocoagulation (EC) technology has been classified as an efficient and simple method to treat wastewater due to extensive successful application in other industries such as restaurant wastewater, metal plating wastewater, potable water treatment, tar sand and oil shale wastewater and urban wastewater [10]. Electrocoagulation has been classified as a preferable method over the others due to good quality effluent, simple treatment mechanism, low energy consumption, low formation of sludges and low dissolved solids [11]. Electrocoagulation is an electrochemical process comprised of removal mechanism of coagulation, adsorption, precipitation and flotation. Electrocoagulation can remove the colour, COD, turbidity and other suspended solids successfully with low energy consumptions, low cost and low sludge formation [12]. Furthermore, an additional benefit of EC is the ability to combine with another process, for example, EC/electrooxidation, EC/electro-fenton, EC/Solar Photocatalytic, EC/Anaerobic process and more [13]. Electrocoagulation method (EC) is an electrochemical process that applies direct current (DC) to the electrodes, normally iron or aluminium, which are dipped into the electrolytic solution containing the wastewater to be treated. At anode, metal cations are dissolved through oxidation process and hydrogen and hydroxyl ions are released at cathode through water reduction. The metal cations tend to combine with hydroxyl ions to form metal hydroxide which eventually neutralizes the suspended particles in the water by forming monomeric and polymeric hydroxo complex species [14]. The gases (H2, O2) produced at the cathode gives floatation effect, separating pollutants to the floc-foam layer on water surface [14]. The pollutants in the wastewater can be removed either through complexation or electrostatic attraction later by the remaining Fe(OH)n (s) which acts the

coagulant agents [11]. The generation of $Fe(OH)n$ (s) can be in the form of divalent and trivalent that highly dependent on the pH and potential of the aqueous medium [15]. The mechanisms of the aforementioned process are as below by using iron electrode:

Anode:	$4 Fe (s) \rightarrow 4 Fe^{2+} (aq) + 2 e^-$	(1)
Alkaline Condition:	$Fe^{2+} + 2 OH^- \rightarrow Fe(OH)_2$	(2)
Cathode:	$4 Fe^{2+} + O_2 + 2 H_2O \rightarrow 4 Fe^{3+} + 4 OH^-$	(3)
Acidic Condition:	$2 H_2O + 2e^- \rightarrow H_2 + 2 OH^-$	(4)

During the electrocoagulation process, the degradation of the dyes can be categorized into two groups depending on the location where the oxidation takes place. The groups are direct oxidation and indirect oxidation. The direct oxidation takes place when the pollutants in the solution migrate near the surface of the electrode, and oxidation occur by adsorbing on the surface [16]. On the other hand, indirect oxidation generates oxidants from agents such as chlorine, hydroxide ions, hypochlorite and hydrogen peroxide which usually originated from the electrolytes used [18]. The reaction between the generated chlorine/hypochlorite/hypochlorous acid and the dye molecule promotes the decolourization process and it only takes place in the presence of sodium chloride as chlorine can degrade the dyes in the solution quickly electrochemically and the reaction is irreversible due to the strong oxidative activity [16]. To investigate from different perspective, another oxidizing species also can be produced during electrocoagulation when H_2O_2 are produced at the cathode. Hydroxyl radicals (OH•) are produced from the H2O2 through a series of chemical reaction that helps to remove the pollutants in the solution [15]. Therefore, the primary objective of this study is to study the treatment of the dye contaminated wastewater using electrocoagulation method using iron (Fe) electrode and to evaluate the influence of different operational parameters (voltage and amount of electrolyte) on the process efficiency. The optimum condition with low energy consumption and best dye removal rate has been figured.

II. MATERIALS AND METHOD

2.1. Materials
Celestine Blue, ($C_{17}H_{18}ClN_3O_4$), sodium chloride (NaCl) and nitric acid (HNO3) was obtained from Sigma-Aldrich and the dye solution is prepared as an acting textile wastewater for experimental purpose. The chemicals are of analytical reagent grade and no purification was made. The experiments were conducted in a batch electrolytic cell by using 800 ml of Celestine Blue dye solution. The temperature (room condition), pH (7) and initial concentration (10 ppm) of the dye were maintained constant throughout all the experiments.

2.2. Experimental Procedure
In this study, the objective is to determine the behaviour of

dye removal at higher voltage that ranges from 2 V – 10 V and the results are obtained at every 5 minutes. The schematic diagram of the electrocoagulation system is shown in Figure 1.

The electrocoagulation experiment was carried out in a 1 L beaker by immersing the two iron electrodes with dimension of 5 cm x 13.6 cm x 2 cm vertically with the support of retort stand and clamp to hold the electrodes in place. The electrodes were connected to a direct current (DC) power supply (Instek, Model: GPS – 3030DD). Before starting the experiment, an initial sample is taken, and the experiment is started by stirring the solution continuously at 4 rpm by using a magnetic stirrer. At every interval of 5 minutes over minutes, samples were withdrawn from the beaker containing dye solution and filtered using filter paper (Whatman, 110 mm). Then, the absorbance of the solution is measured using Uv-Vis Spectrophotometer (HACH model, DR 5000). The remaining concentration of dye after treatment is determined by using calibration graph plotted between absorbance and concentration of dye. The unconsumed iron concentration in dye solution after electrocoagulation is determined using atomic absorption spectroscopy (AAS). By using the change in absorbance value, the dye removal efficiency is expressed in percentage by using the formula below:

$$\text{Removal rate of dye \%} = \frac{C_0 - C_f}{C_0} \times 100\% \qquad (1)$$

where;

C_0 = initial absorbance of dye solution
C_f = final absorbance of dye solution

1 – Beaker
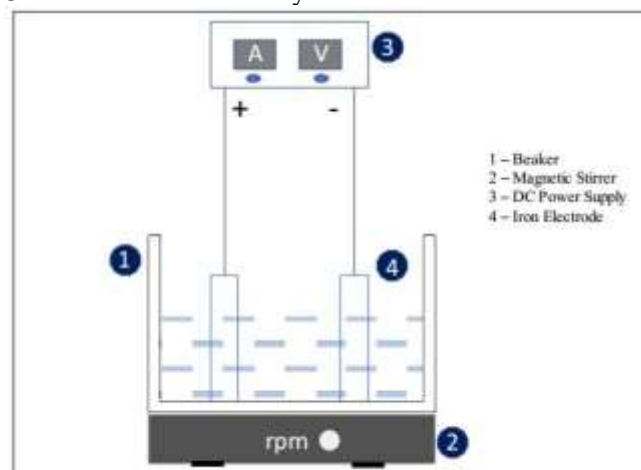2 – Magnetic Stirrer
3 – DC Power Supply
4 – Iron Electrode

Figure 1. Schematic Basic Electrocoagulation Set up

III. RESULTS AND DISCUSSION

In this study, three set of experiments were carried out to identify the optimized condition for dye removal in the solution at constant Celestine Blue dye concentration of 10 ppm, pH 7 and at room temperature. The objective of study is to determine the effect of voltage at higher range (2 V – 10 V) and effect of sodium chloride (0.2 g – 1.0 g) on the trend of dye removal efficiency at an interval of 5 minutes for 15 minutes length of time. The experiments conducted include:

- Effect of Voltage (i.e. 2 V, 4 V, 6 V, 8 V and 10 V) and amount of electrolyte (1.0 g)
- Effect of the Amount of Electrolyte (i.e. 0.2 g, 0.4 g, 0.6 g, 0.8 g and 1.0 g NaCl) at fixed voltage of 2 V
- Effect of the Amount of Electrolyte (i.e. 0.2 g, 0.4 g, 0.6 g, 0.8 g and 1.0 g NaCl) at fixed voltage of 10 V

The concentration of the dye in the solution at each time interval was determined based on the calibration graph constructed as shown in Figure 2.
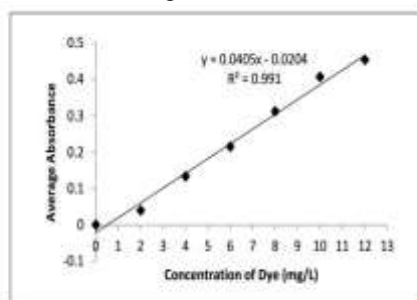

Figure 2. Graph of Calibration Curve for Different Concentration of Celestine Blue Dye

3.1. Effect of Voltage on Dye Removal Efficiency

Voltage is usually taken into consideration in electrocoagulation process instead of current in the laboratory or pilot studies as voltage can be easily adapted to large-scale treatment and widely used compared to applied current. To study the effect of voltage, assays with 2 V, 4 V, 6 V, 8 V, and 10 V is applied to the electrochemical system at pH of 7, with a supporting electrolyte of 1.0 g sodium chloride (NaCl) and 10 ppm of initial concentration of Celestine Blue dye used. As can be seen from Figure 3, at 15 minutes, maximum dye removal of 100 % has been achieved from 6 V to 10 V, 78.25 % is observed at 4 V and 44.23 % at 2 V. This indicates that highest removal efficiency is achieved at high amount of voltage supplied as anode dissolution is enhanced at high voltages. At 2 V and 4 V, the dye could not be completely removed due to the less formation of oxidizing agent such as hypochlorite ions and hydroxyl radicals, hence the dye is not able to be removed completely within a short period of time [18]. At 6 V, 8 V and 10 V, the current passed in the electrocoagulation system is sufficient to dissolute the anode into metal ions that can form metal hydroxide. The dye was fully removed 100 % at all voltages after 15 minutes except at 2 V and 4 V. In Figure 3, the graph also shows the amount of electrical energy needed for the electrocoagulation process and the corresponding percentage of dye removal at different voltage. It is concluded that the variation of voltage has a significant effect on the electrical energy consumption and dye removal efficiency. As the voltage increases from 2 V to 10 V, the electrical energy consumption increases from 28.5 kWh/m³ to 900 kWh/m³ which means that the least amount of energy is consumed at 2 V and highest amount of energy is consumed at 10 V. Without considering electrical consumption, 6 V presents the best performance as 100 % removal efficiency is obtained within 5 minutes. However, if energy consumption is assessed, 2 V with removal efficiency of 44.33 % is taken as the optimum voltage as only 28.5

kWh/m³ is required if compared to 6 V that consumes 226.13 kWh/m³. Therefore, it is deduced that 44.33 % is sufficing as least amount of energy as well as sodium chloride consumed relatively.
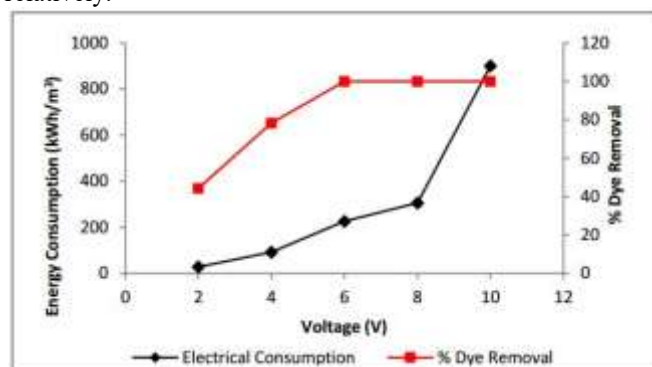

Figure 3. Graph of % Energy Consumption and % Dye Removal at Different Voltage using 10 ppm Celestine Blue solution at pH 7 and 1.0 g NaCl

3.2. Effect of Sodium Chloride on Dye Removal Efficiency

To evaluate the effect of the electrolyte in the solution on the dye removal efficiency, 0.2 g, 0.4 g, 0.6 g, 0.8 g and 1.0 g of sodium chloride (NaCl) were tested at two different voltages (2 V and 10 V) at pH 7 and initial Celestine blue dye concentration of 10 ppm. 2 V and 10 V were chosen to be studied in this part to evaluate the performance of dye removal at low voltage and high voltage using different amount of sodium chloride.

Based on the results in Figure 4, at 2 V, highest dye removal of 44.33 % is obtained using 1.0 g NaCl and lowest removal efficiency of 22.58 % using 0.2 g of NaCl at 15 minutes. The dye removal efficiency increases with increasing amount NaCl used which proves that NaCl plays a significant role in improving the performance of dye removal. It is noticed the usage of higher amount of NaCl, for example 0.6 g, 0.8 g and 1.0 g of NaCl yield better results because high mass transport of the chloride ions to the surface of the anode produces more chlorine/hypochlorite that causes the rate of removal also to increase significantly. Hypochlorite is an oxidizing agent that promotes decolorization and dye removal efficiency in electrocoagulation system [19]. Hence, since 1.0 g of NaCl yield better performance at 15 minutes with a dye removal efficiency of 44.33%, it is chosen as the optimum condition at 2 V. On the other hand, based on the study by using the same condition at 10 V, it is deduced that the dye removal efficiency have improved significantly as shown in Figure 5 when it is compared to the results obtained at 2 V previously. This is because at higher amount of voltage, the production of OH- and high coagulant dissolution induce faster and better removal efficiency [20]. It is noticed that the highest removal efficiency of 96.66 % has been achieved using 0.4 g of NaCl at 15 minutes.

Figure 4 and Figure 5 also illustrates the electrical energy consumption for different number of electrolytes (NaCl) at voltage 2 V and 10 V respectively. Based on the graph, at 2

V, the highest dye removal efficiency of 44.33 % is attained by using 1.0 g of NaCl with moderate amount electrical energy of 2.99 kWh/m^3. However, since the removal efficiency between 0.6 g of NaCl and 1.0 g NaCl is close to each other, 0.6 g NaCl is the chosen as best condition at 2V with lower energy consumption of 1.65 kWh/m^3. On the contrary, at 10 V, energy consumption also increases with the amount of NaCl but the increment in energy consumed is significantly higher whereby it reaches 31.88 kWh/m^3 for best removal efficiency condition which is by using 0.4 g of NaCl. Hence, to make consideration from the perspective of cost saving, chemical usage saving and the energy consumption, it is deduced that the optimum condition of this study is offered at 2 V using 0.6 g of sodium chloride with removal efficiency of 41.99 % and energy consumption of 1.65 kWh/m^3.
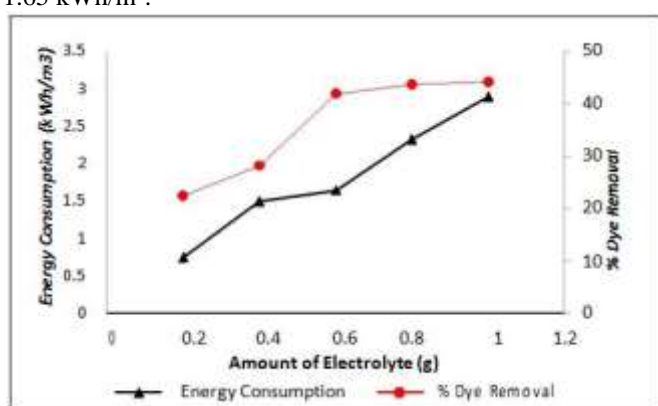

Figure 4. Graph of Energy Consumption and % Dye Removal using Different Amount of Electrolyte, 2 V, 10 ppm Celestine Blue, pH 7
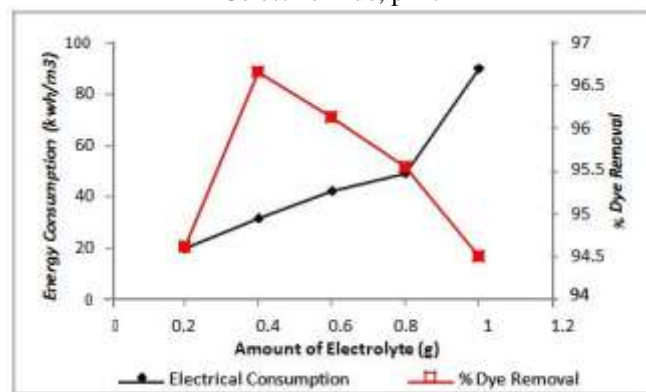

Figure 5. Graph of Energy Consumption and % Dye Removal using Different Amount of Electrolyte, 10 V, 10 ppm Celestine Blue, pH 7

3.3. Iron Content in Dye Solution after Electrocoagulation

During electrocoagulation process, the amount of current supplied to the system must be regulated so that the quantity of metal oxidized can be controlled to prevent any iron residual in the final effluent. This is because, at higher voltages, the anodic dissolution is rapid and this cause large release of ferric ions into solution which perhaps unconsumed and entrained in the solution [13]. Table 1 shows the results obtained from atomic absorption

spectroscopy analysis (AAS) which was conducted to identify iron traces in the residual solution after electrocoagulation process for several samples. It is evident that there are some traces of iron in the solution after electrocoagulation process which is believed to be from iron electrode used as shown in Table I. These iron traces are the excessive ferric ions produced from significant anodic dissolution that has not been used in the reaction to remove the dyes. Based on Table 1, the concentration of ferric ion is higher at higher amount of voltage and sodium chloride used and this justifies the aforesaid hypothesis.

Table 1. Conditions of Sample and Iron Content

Sample Number	Experiment Condition	Concentration of Iron (ppm)
UNK -001	1.0 g NaCL, 10 V, 10 ppm dye solution	1.79
UNK-002	0.6 g NaCl, 2 V, 10 ppm dye solution	0.37
UNK-003	0.3 g NaCl, 10 V, 10 ppm dye solution	2.52

a. Measured from atomic absorption spectroscopy

3.4. Kinetic Study

In this part, kinetic study has been studied for zero order, first order and second order reaction kinetics to determine the best correlation coefficient (R2) that fits best for the results obtained at 1 V. The kinetics graph plotted are for condition 1 V and 1.0 g of NaCl and the respective correlation coefficient for each order is shown below.

Zero Order	$A = A_o - kt$	$R^2 = 0.6154$	(14)
First Order	$\ln A = \ln A_o - kt$	$R^2 = 0.7358$	(15)
Second Order	$\frac{1}{A} = \frac{1}{A_o} kt$	$R^2 = 0.8117$	(16)

Where A, A$_0$, k and t are the final concentration of dye, initial concentration of dye, reaction rate constant and reaction time respectively. The experimental date and model data are usually analysed based on the closeness of the correlation coefficient (R2). Comparatively, the R2 value of the pseudo-second order kinetic is the highest for all the rate of dye removal using different amount of sodium chloride as shown in Figure 6. Hence the removal rate of dye is described well using second order kinetics.
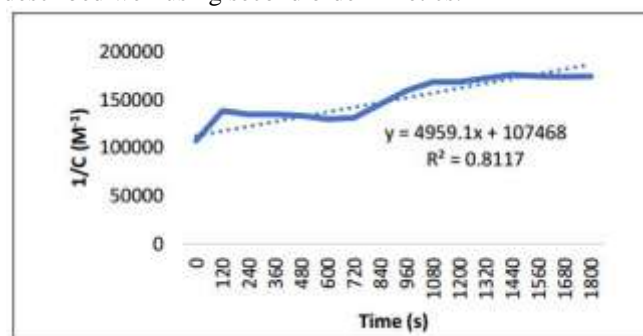

Figure 6. Second order against the time for dye removal using Fe electrodes. Initial concentration of dye = 10 mg/L, volume of the solution = 800 ml, voltage of 1 V, pH= 7.0, NaCl concentration = 1.0 g

IV. CONCLUSION

In conclusion, the wastewater effluent containing dye of the textile industry is a major challenge for most of the textile industries nowadays. In depth analysis of dye removal trend and behaviour at high voltages (i.e. 2 V, 4 V, 6 V, 8 V and

10 V) and using different amount of NaCl using electrocoagulation method has been studied. Based on the results from experiments, it is deduced that the optimum condition of this study is offered at 2 V using 0.6 g of sodium chloride with removal efficiency of 41.99 % and energy consumption of 1.65 kWh/m^3 by considering from the perspective of cost saving, chemical usage saving and the energy consumption. The dye removal rate is described well using second order kinetic model. Characterization of dye solution after electrocoagulation using atomic absorption spectroscopy reveals that there is significant presence of iron.

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