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ELECTROCHEMICAL ELIMINATION OF METHYLENE BLUE DYE USING CARBON CLOTH MATERIAL

(Penghapusan Elektokimia Pewarna Biru Metilena Menggunakan Bahan Kain Karbon)

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Abstract

The effectiveness of the electrochemical technique to remove methylene blue (MB) from its aqueous solution was demonstrated in the current investigation. Various electrodes were used to explore the electrochemical process namely: aluminium (Al), copper (Cu) and carbon cloth (CC) as anode while the cathode was carbon cloth to select the highest removal%. Carbon cloth was selected as the best electrode due to its high efficiency for removal of MB dye compared to others. The effects of applied voltage, electrolysis time, and sodium chloride were investigated to identify the optimal conditions. Response surface approaches were used, however, to fully conceptualize how the factors interacted and get the best methylene blue dye elimination percentage using the electrochemical process. Rate constants ranged between 0.163 and 0.345 min^{-1}, demonstrating that high-rate constant accompanied pseudo first order kinetics, which was the dominating model throughout the investigation with high applied voltage and NaCl amount. Consumption energy was considered and measured; it was 0.104 Wh/mg at the maximum value applying 5 V referring that high consumption energy followed by high applied voltage. Utilizing response surface methodology (RSM), the electrochemical operating factor was optimized. The influence of NaCl addition rate, treatment time, and applied voltage were analysed using the optimum model derived from Box-Behnken Design (BBD), which was quadratic with MB removal (R^2 = 0.9447).

Keywords: methylene blue, electrochemical process, carbon cloth anode, energy consumption, pseudo first order kinetics

Abstrak

Keberkesanan teknik elektrokimia untuk mengeluarkan metilena biru (MB) daripada larutan akueusnya telah ditunjukkan di dalam kajian semasa. Pelbagai elektrod digunakan untuk meneroka proses elektrokimia iaitu: aluminium (Al), kuprum (Cu) dan kain karbon (CC) sebagai anod manakala katod adalah kain karbon untuk memilih penyingkiran tertinggi%. Kain karbon dipilih sebagai elektrod terbaik kerana kecekapannya yang tinggi untuk menanggalkan pewarna MB berbanding yang lain. Pemalar kadar berjulat antara 0.163 dan 0.345 min^{-1}, menunjukkan bahawa pemalar kadar tinggi mengiringi kinetik tertib pertama pseudo, yang merupakan model yang mendominasi bagi penyiasatan dengan penggunaan voltan tinggi dan jumlah NaCl. Penggunaan tenaga telah dipertimbangkan dan diukur; ia adalah 0.104 Wh/mg pada nilai maksimum menggunakan 5 V merujuk tenaga penggunaan tinggi diikuti dengan voltan gunaan tinggi. Dengan menggunakan kaedah permukaan tindak balas (RSM), faktor pengendalian elektrokimia telah dioptimumkan. Pengaruh kadar penambahan NaCl, masa rawatan, dan voltan gunaan dianalisis menggunakan model optimum yang diperolehi daripada Reka Bentuk Box-Behnken (BBD), iaitu kuadratik dengan penyingkiran MB (R^2 = 0.9447).

Kata kunci: metilena biru, proses elektrokimia, kain karbon anod, penggunaan tenaga

Introduction

It is very well known that harmful dyes are the main source of water contamination then it is considered as environmental issue concern [1]. Dyes in different names and applications are the dominant source for threaten water bodies as it is used in a variety of industries, including tanneries, paper mills, textile, leather, plastics, painting, food preserve, and pharmaceuticals [2-5]. Dyes are caused cancer and it is also participated to harm human health and animal. Their impact also extends to threaten aquatic life and environment [6-9].

The main constituent of textile industrial effluent is dyes, so it was characterised as high oxygen demand and resistant to biological treatment. Consequently, it requires extra treatment process which is tertiary treatment process [10]. One of these dyes is methylene blue which is water soluble, and it used in acid-base titrations and biological stains [11, 12, 9]. As seen in Figure 1, methylene blue is an organic chloride salt that contains 3,7-bis(dimethyamino)phenothiazine-5-ium.

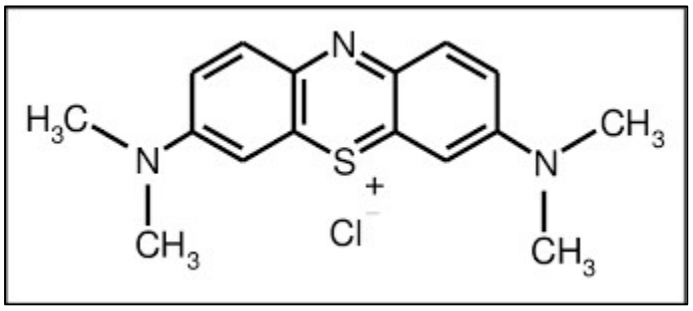

Figure 1. Chemical structure of methylene blue dye

The method most frequently employed to eliminate colour from aqueous solutions is electrochemical elimination. In contrast to other processes like photocatalysis, adsorption, membrane filtration, and reverse osmosis, the electrochemical process is simple to use, highly effective, technologically advanced, and safe. Other treatment methods like reverse osmosis, adsorption, and photocatalytic degradation were said to have certain drawbacks, such as the length of time needed for dye removal, issues with secondary pollutants, and a high cost of operation. The technologies have not shown to be particularly efficient or advantageous from an economic standpoint in eliminating colour from dye effluent [13]. However, the high prices and insufficient degradation of photocatalysis, Fenton-like processes, and ozonation processes continue to be a barrier [14]. Photocatalysis, one of the most advanced oxidation technologies, is one

of the most efficient processes because it uses an efficient semiconductor under UV/visible light irradiation and doesn't need additional chemicals or oxidants (atmospheric oxygen) to start the reaction. It is most likely among the AOPs with the highest efficiency and lowest cost [15]. The adsorption technique, on the other hand, is one of the successful methods that have been used to remove methylene blue dye due to its low cost, high efficiency, and simple operation. However, these treatment methods demand time and considerable effort to be effective [16].

The water cycle is so necessary to contaminant removal from wastewater's water system. Regarding the rigid structure of dyes, its removal from wastewater requires many steps for this purpose thus it is considered big challenge task. As we know, the main steps in wastewater treatment system are pretreatment, physical, chemical, and biological processes are reflected in the primary, secondary, and tertiary treatments, respectively according to the type of wastewater plant and target pollutants. As reported previously, conventional wastewater plants are ineffective for degradation dyes or other resistant-organic pollutants from water, resulting in other by-products more toxic than the parent compounds [17, 18]. Consequently, to avoid the issues that are linked with the conventional wastewater treatment plants, the application of advanced oxidation processes (AOPs) is the observed indication [19, 20]. These active degradation processes are able to be produced more effectively using an oxidizing agent like ozone or hydroxyl radicals to clean up the organic pollutant. After biological treatment, advanced oxidation processes can be used to get rid of the recalcitrant organic pollutants that are resistant toward the biodegradation treatment as well as to reduce the content of residual organic species.

Among the AOPs technologies such as ozonation treatment process [21], photocatalytic degradation process [22, 23], and sono-photocatalytic oxidation process [24] and electrochemical degradation process which is one of the promising technologies for its ability in remediation of organic pollutant compounds [25, 26]. Electrochemical degradation process is a promising technology due to its various benefits, which include its low cost, easy to operate, environmental compatibility and safe [20]. Anode material has interested property to assess the efficiency of electrochemical degradation method and it is considered a critical factor for this purpose [27]. However, two types of electrochemical reactions, direct and indirect electrochemical oxidation process as reported in details [28]. Electrochemical oxidation process may vary depending on the working principle. When it starts with pollutants degradation by anodic electrodes attracting the pollutants towards the anode. Following this Principle is called Direct electrochemical oxidation. On the other hand, it may be carried out by eliminating the compounds in the bulk solution concomitantly with active and strong oxidation agents like chlorine and hypochlorite [29]. Preparation of chlorine, chloride, and hypochlorite is according to the following equations:

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (1)$$

$$Cl_2 + H_2O \rightarrow H^+ + Cl^- + HOCl \quad (2)$$

$$HOCl \leftrightarrow H^+ + ClO^- \quad (3)$$

The main disadvantage in direct anode oxidation is that weaking the activity of the anode surface through fouling leading [30]. However, indirect anode oxidation is the most common for treatment of organic pollutants using boron-doped diamond (BDD) as anode [31], mixed metal oxide electrodes [32, 33] and graphite-PVC composite [34]. One of the most used electrode materials for the treatment of contaminants is BDD anode, but its high cost participates to avoid its wide application. Other materials have long-term stability issue, low degradation efficiency depending on the pollutant substrate. The most important characteristic of electrochemical oxidation process is that anodes must exhibit good evolution of oxygen to make the efficiency of electrochemical process less and the consumption of energy is high during the electrochemical process of wastewater treatment process [35].

Some process parameters were affecting electrochemical performance including electrolyte amount, applied voltage and electrolysis time. These factors were optimized conventionally by carrying a set of experiments for each factor to ensure higher

efficiency with lowest costs [36]. The literature showed that the classic optimization not effective enough to balance the optimization between the different operational factors, but treat each factor separately, but it requires a long time and effort to manually integrate between the factors [37, 38]**.** In order to facilitate the overlapping of optimal factors, a multivariable statistical technique was commonly used, which replaces the traditional methods with higher efficiency, reduces operating expenses and guarantees shorter treatment times [39]. A statistical method called response surface methodology (RSM) may be followed to study higher number of variables with lower number of experiments [40]**.** It was applied by [41] in electrocoagulation and electro-Fenton optimization for POME removal with iron and aluminium electrodes. This study aims to (i) investigate the optimum combination of electrodes (Anode – Cathode) for MB removal with electrochemical method, (ii) to optimize the most influencing factors including electrolyte amount, applied voltage and electrolysis time using response surface methodology-BBD design to achieve maximum MB dye removal efficiencies.

Materials and methods

Reagents and chemicals

Pure standards (≥98%) of methylene blue (CAS no. 61-73-4) was bought at Sigma-Aldrich (St. Louis, MO). The provider of deionized water (DIW) was EASYPure RODI (Thermo Fisher Scientific, Waltham, MA). UV-visible spectrophotometer was used for sample analysis. Copper (CAS No. 7440-50-8) sheet with 0.25 mm of thickness and 99.98% trace base metal was purchased from Merck.

Standard methylene blue dye preparation

Methylene blue stock solution (1000 mg/L) was diluted in de-ionized water and kept at 4 °C. By varying the amount of NaCl (Merck, Germany) added to MB solutions, the conductivity could be changed.

Set up of electrochemical process

A Pyrex glass vessel (100mL) was used for all analysis/A Pyrex glass electrochemical cell (reactor) was placed on top of a magnetic stirring block. Electrochemical cell setup, as shown in Figure 2.

The electrochemical cell was a glass container involved two electrodes for degradation of methylene blue at normal conditions: 1.0 atm and 20±2 ℃. The working electrode (anode) and the counter electrode (cathode) were carbon cloth in dimensions of 1cm × 1cm (1 cm^2). The gap between two electrodes was kept constant of 2 cm and both connected to the DC power supply which is working at fixed current in all electrochemical experiments. The concentration of dye was 10 mg/L in deionised water, it was prepared from the stock solution (1000 mg/L) after serial dilutions. Different concentrations of the electrolyte (NaCl) were infused into the mixture then was stirred at 500 rotation per minute under magnetic stirred device to ensure complete mixing and distribution of dye and salt in the solution. At each treated sample the corresponding current between the electrodes was recorded as well as the temperature was also monitored. The collected samples were directly analysed and the methylene blue degradation rate was measured in terms of reducing colour removal of dye at wavelength of 660 nm using UV-Visible spectrophotometry, and the range scan is between 400 to 800 nm. Three applied voltages of 2, 3 and 5 V were tested in electrochemical removing of methylene blue at fixed NaCl amount of 0.5g.

The influence of sodium chloride concentration (0.1, 0.3 and 0.5g) on the electrochemical removal of methylene blue (10 mg/L) using CC as anode at fixed 5 V was investigated. All absorbance measurements of methylene blue dye are converted into concentration using a linear calibration curve (R^2 = 0.996).

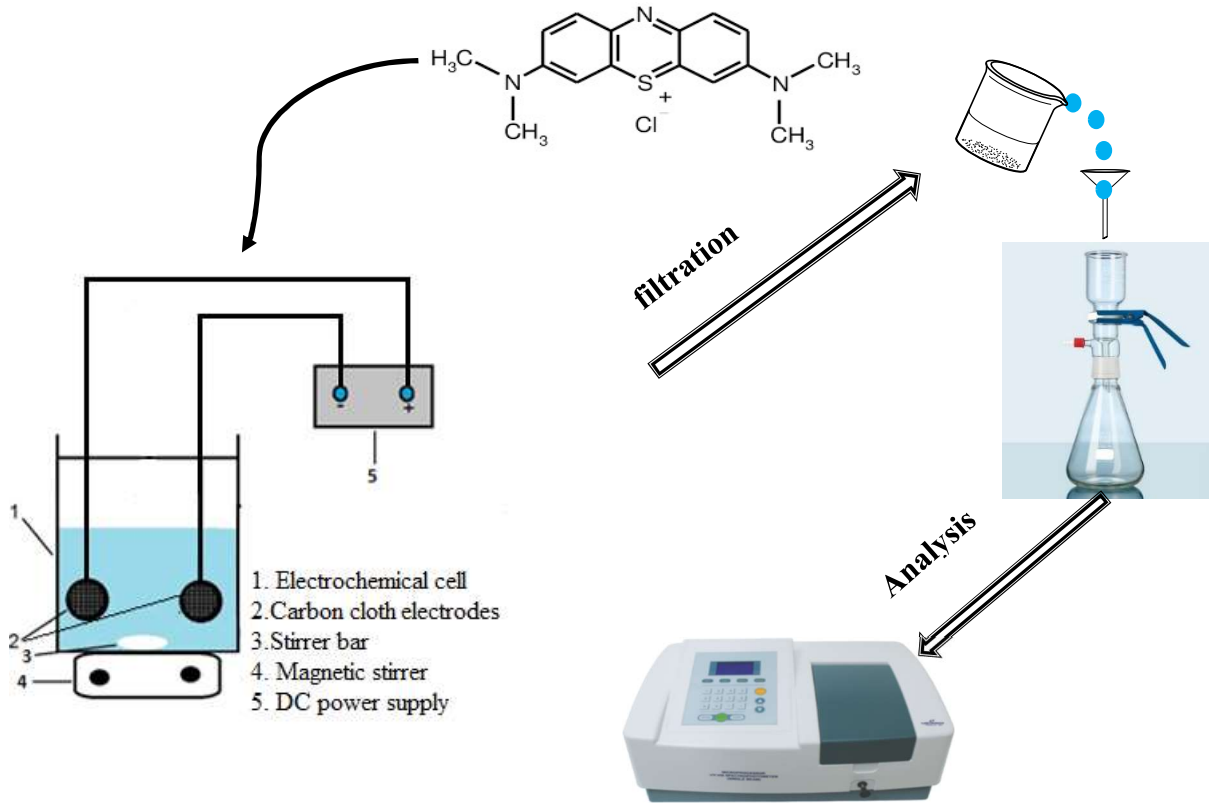

Figure 2. Electrochemical cell setup

Morphology and electrochemical characterizations of carbon cloth

The morphology and electrochemical characterizations of carbon fabric were investigated using powder X-ray diffraction (XRD, GBC MMA XRD), high-resolution transmission electron microscopy (HR-TEM, model: JEOL JEM-2011) and field emission scanning electron microscopy (FESEM, JEOL JSM-7500FA). The acceleration voltage is 15 kV and the beam current is 700 pA. All samples after treatment were analysed using U-visible spectrophotometer under maximum wavelength of 668 nm.

Box-Behnken design

Three parameters have been investigated on elimination of methylene blue dye using three-level Box-Behnken Design (BDD) namely: electrolyte amount, applied voltage and electrolysis time. Table 1 present the three parameters with their values which were processed in 45 runs and 9 centre points. The total number of experiment sets were calculated using the following equation [40]**:**

$$N = 2K(K-1) + C_0 \quad (4)$$

where C_0 is the number of a central point and K is the number of factors. The statistical studies were conducted using the Design Expert regression tool (Version MINITAB statistical software package).

Table 1. Levels and ranges of independent variables

Variable	Factors	Level		
(unit)	X	-a	0	+a
NaCl amount (g)	A	0.1	0.3	0.5
Applied voltage (V)	B	1	3	5
Electrolysis time (min)	C	4	8	12

Results and Discussion

The results presented here could introduce the efficiency of electrochemical degradation of MB via producing an active species that are strong oxidants (ClO^-). One of these active species was chloride which is presented in wastewater or added to the wastewater. Through an oxidation process at the anode electrode, these chloride ions can be converted into active chlorine (Cl_2, HOCl, and ClO). These oxidants have a long-life time to achieve the required oxidation of methylene blue dye.

Selection of electrode materials

Cu-CC, CC-CC, and Al-CC electrode material combinations were employed under the conditions of 5 volt for 20 minutes with 0.5g NaCl serving as the support electrolyte. Based on Figure 3, full elimination of MB (100%) was obtained using CC-CC electrode after 10 min; meanwhile, MB removal in terms of Cu-CC and Al-CC was 20% and 54%, respectively after 16 min. According to the statistical analysis, the electrode materials significantly affect the removal of MB (P= 0.05), according to the results. A report claims that copper anode material was an excellent option for the treatment of organic pollutants due to its antibacterial qualities, ease of ionization, high conductivity, and low toxicity [42, 43, 44].

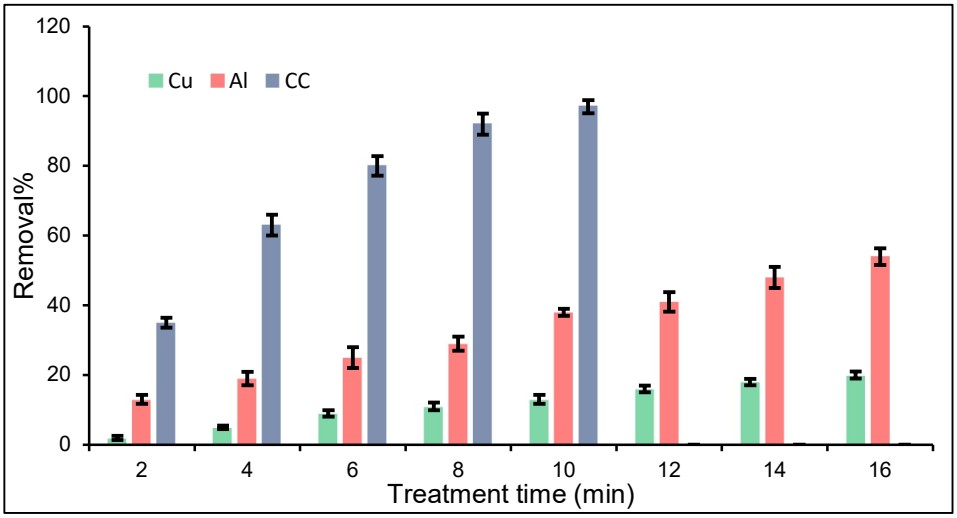

Figure 3. Selection of anode materials based on the removal% of methylene blue under these conditions: 5 V, 100 mL of solution, 5 mg/L of dye and 0.5 g NaCl

However, it was found experimentally that copper was easily corroded. In addition, the literature also showed that coper has low removal capability of MB which does not exceed (28%) [45]. As opposed to that, Al and carbon clothes were widely available with relatively low costs [46]. Furthermore, carbon clothes showed higher efficiency than Al in MB removal. The literature also supports this disadvantage of Al electrocoagulation used for POME removal with Al electrodes, the results indicated that only 42.94% of COD treated [47]. In addition, carbon clothes provide higher chemical stability, and better electrical conductivity [48]. Treatment of wastewater from poultry butcheries revealed that COD removal was 76% using graphite as anode [49]. Accordingly, the optimum electrodes combination used in this study were CC-CC based on methylene blue removal efficiency and stability of the electrolysis [50].

According to the previous report, MnO_2 based on a Pt electrode exhibited 90% removal of MB dye at the optimum conditions: pH =8, current density of 7 mA/cm^2, and supporting electrolyte of 0.05 mol/L [51]. From this point, Carbon cloth electrode exhibited a very good elimination% as shown from Figure 3.

To support the results above, characterization of carbon cloth has been investigated. The SEM image in Figure

4a, showed that the carbon cloth consists of a microstructure of embedded beam rods, this is a fictitious, two-dimensional artificial network made of organized tissue, where each fiber has a smooth surface and a constant 8.5 mm diameter. In addition, one of the characteristics of carbon cloth was that its fabric has excellent mechanical strength, flexibility, as well as high conductivity. Clear lattice fringes with 0.24 nm and 0.47 nm d-spacing, which correspond to (002) and (100) planes, are seen in Figure 4b. The pattern of electron diffraction (SAED) in the selected area, which demonstrates the crystalline nature of the porous carbon clothing, is shown in Figure 4c. However, the composition of the carbon cloth with the percentage has been included in Figure 4 d. It was observed that carbon is the major element in the sample. Consequently, the ease with which electrons and ions can approach the active surface is advantageous as it facilitates a rabid reaction producing higher power performance.

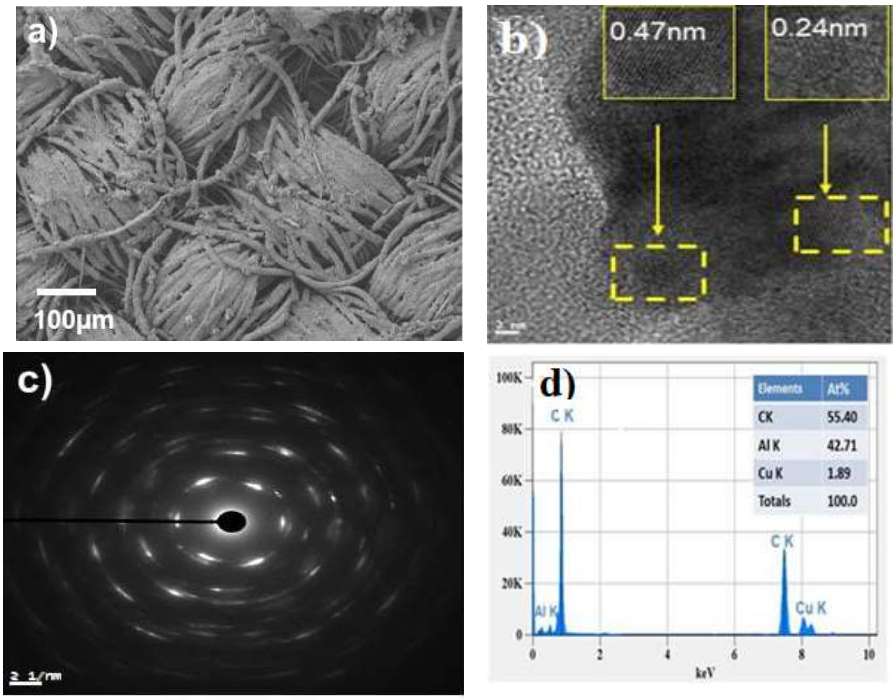

Figure 4. Characterization of carbon cloth: (a) SEM image, (b) TEM images at different magnifications of the carbon cloth (c) corresponding SAED pattern and (d) EDS analysis data for carbon cloth

The composition and phase purity of the carbon fabric were examined using the XRD pattern of the pure carbon cloth, as shown in Figure 5. The (002) and (100) planes of the carbon cloth substrate may be responsible for the acute and powerful diffraction peaks seen at 26 and 43.

Electrocoagulation modelling and optimization

Depending on the MB removal rate from the contaminated aqueous solution, the optimized operational factors of the electrochemical process were studied using three factor and three level BBD. The developed model was not much differing from the predicted values as the regression coefficient was (R^2 = 0.9447) with nine (9) center points. The experimental data for MB removal illustrated in Table 2 were then investigated and studied using analysis of variance (ANOVA). Using the values of P and F, a clear induction to the influence of an operational factor. Practical experiments have shown that using P and F values, the significance of the factors can be predicted with 95% accuracy. Higher significance obtained with a lower P (F Prob) value and a higher F value [52].

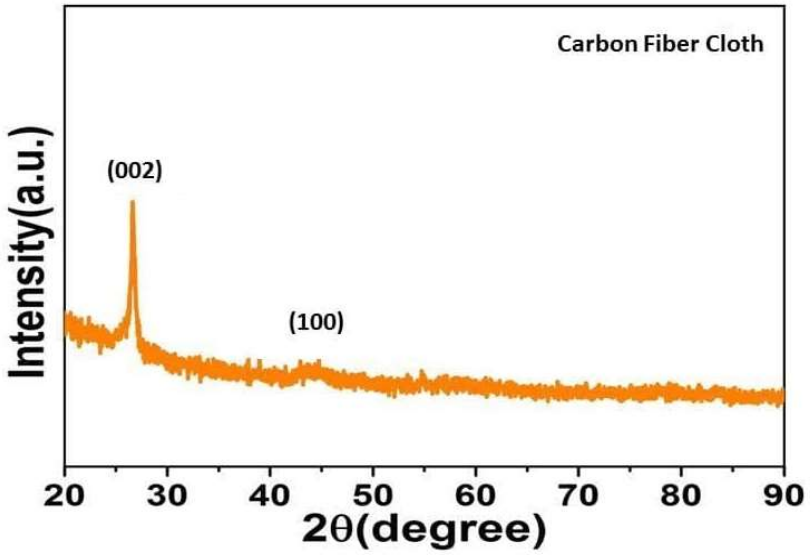

Figure 5. XRD Patterns of carbon cloth electrode

ANOVA findings showed that the F value for methylene blue dye elimination was high values, that means developed mathematical method exhibited good significance represented through preferred relationship between the response and external circumstances. Most model P values are less than 0.05, indicating that the mathematical models generated were significant. In addition, adjusted R^2 of the developed model is lower than R^2 (adjusted R^2 0.9305 < R^2 0.9447) which indicates the model has good quality. The effect of electrolyte amount (A), effect of applied voltage (B) and effect of electrolysis time (C) (p <0.05) are significant to remove MB dye.

In one reported paper, the removal of methylene blue dye was provided through a three-dimensional electrochemical process. It was observed that, through central composite design, the electrolysis time and applied voltage are the most significant factors in responses. However, initial concentration and pH factors are not significant [53].

In case of interaction factors, both interactions between (AC) and (BC) are significant meanwhile for the interaction between (AB) has no significant effect to remove MB dye. To find the relationship between each operational factor and the others, multiple regression analysis was carried out from BBD experiments. MB removal was modelled as a function of (time, electrolyte amount, and voltage) using second order polynomial equation as illustrated in (Equation 5):

$$R\% = -3.1 - 43.5\,A + 3.73\,B - 2.26\,C + 69.1A^2 + 0.108\,B^2 - 0.114\,C^2 + 6.88\,AB + 8.96 + 1.458\,BC \quad (5)$$

To evaluate the significance of each element and its relationships on treatment efficacy (%), Figure 6 shows the plot of the normal probability of the uniform effects with p = 0.05. The plot is divided into two different regions, (positive on the right side, and negative on the left side). The factors marked with red squares indicate their importance.

Table 2. The analysis of variance (ANOVA) for the second-order regression model

Source	DF	*F*-value	*P*-value	Remarks
Model	9	66.48	0.000	Significant
Linear	3	188.53	0.000	
A	1	103.51	0.000	
B	1	416.92	0.000	
C	1	45.16	0.000	
A^2	1	1.12	0.297	
B^2	1	0.03	0.870	
C^2	1	0.49	0.490	
AB	1	1.20	0.280	
AC	1	8.17	0.007	
BC	1	21.64	0.000	
Error	35			
Lack-of-fit	3	294.85	0.000	Significant
Pure error	32			
Total	44			

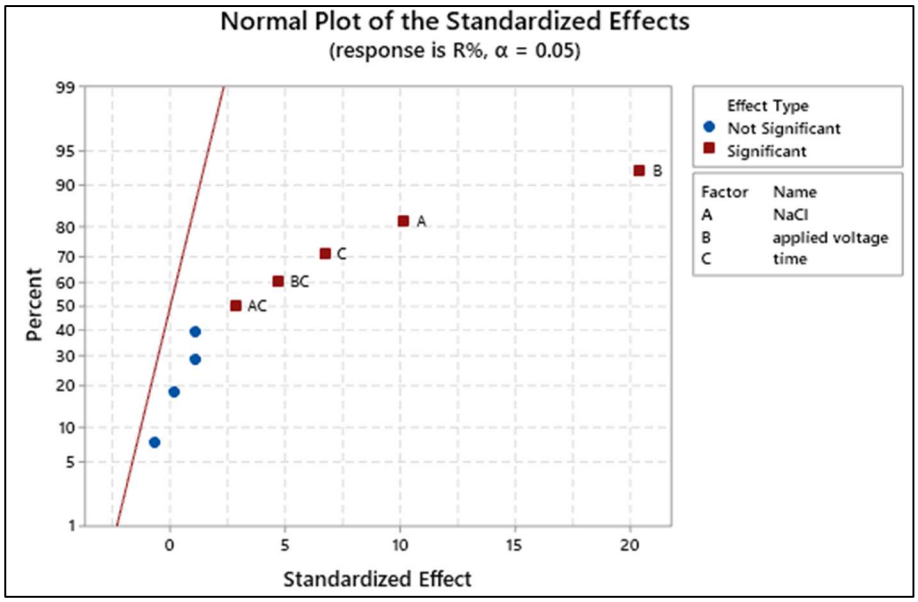

Figure 6. Plot of normalized probabilities for the impacts at p = 0.05 on removal% of MB dye

The relative importance of the individual and interaction effects was shown by the Pareto chart of the standardized effects in Figure 7. Student's t-test was used to confirm that the researched factors' impact was significantly higher than zero. The horizontal columns of a Pareto chart represented the importance of each effect. The lowest 95% confidence level statistically significant effect is shown by the vertical line (2.03) in the graph. Therefore, all values that are on the right side of the dashed line and are more than 2.03 (p = 0.05) are regarded as significant. The finding that MB removal is directly correlated with greater applied voltage, NaCl concentration, and treatment time is explained by the fact that raising these variables results in a sufficient amount of OCl^- acting as an oxidizing agent, directly assisting in the elimination of methylene blue. It is

noteworthy that the interaction between the factors (AC and BC) indicates a positive result associated with MB removal%. As a result, the effect of increasing NaCl or the applied effort relative to time leads to an increase in efficiency.

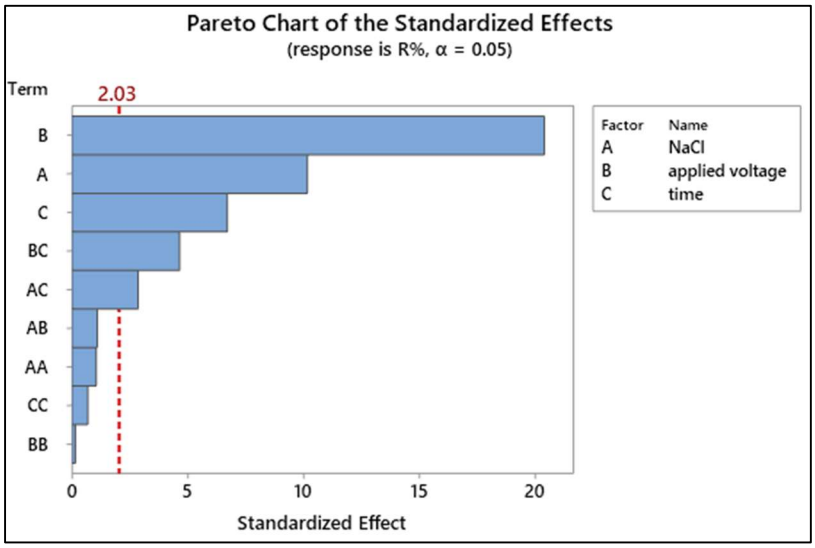

Figure 7. Chart demonstrating Pareto's standardized impacts on the percentage of removal of MB dye

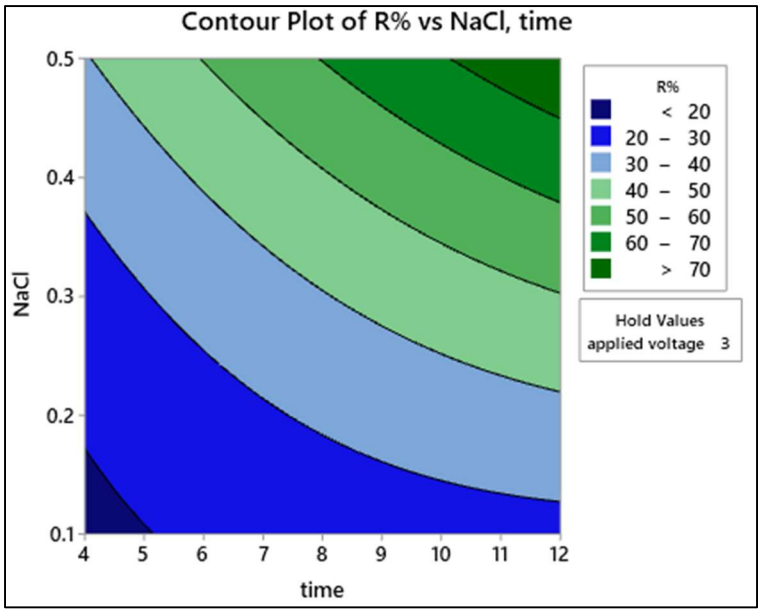

Figure 8. Contour response shows the relationship between the amount of NaCl vs electrolysis time on removal% of MB dye

It could be shown that the decolorization efficiency increases considerably with both NaCl amount and electrolysis time. In other words, increasing both NaCl amount and electrolysis time has positive impact on removal of MB dye. These results are supported by the contour plot given in Figure 8 as can be seen using 0.2-0.3g NaCl and 5-12 min of treatment time, the elimination% of MB was 20-30%. Increasing the amount of NaCl and the electrolysis time to 5 g and 10

min, respectively increases the elimination efficiency to >70%.

Figure 9 showed the efficiency of applied voltage is higher than NaCl with electrolysis time in terms of removal of MB. However, it could be noted that the elimination% raises effectively with increasing of applied voltage and time. These results are supported by the contour plot given in Figure 9 as can be seen using 3-4 V within 12 min of treatment time, the elimination% of MB was 20-40%. Increasing the applied voltage to 5 V at same period of time increases the elimination efficiency to >80%.

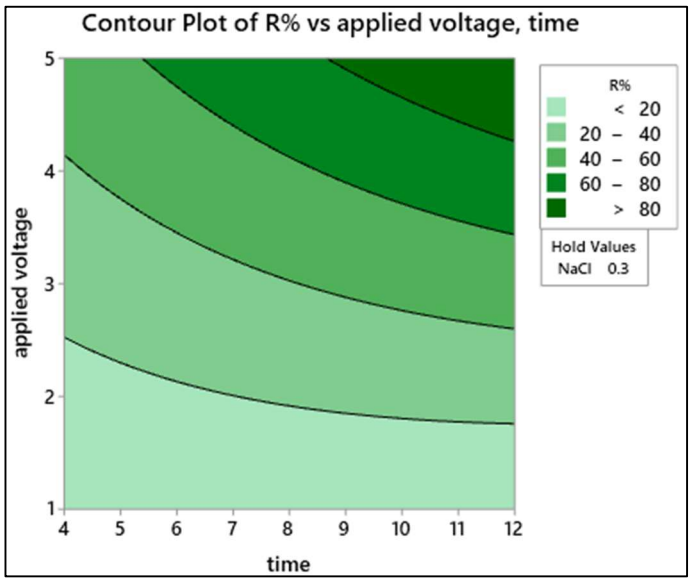

Figure 9. Contour response shows the relationship between applied voltage vs electrolysis time on removal% of MB dye

Electro-kinetics reaction

It was very well known from the results of RSM optimization that the interaction between "NaCl *vs* time" and "applied voltage *vs* time" are very significant so these two variables against time were considered in the present study. The linear time-course plot of Ln ([MB]t/[MB]0) in the elimination of MB tests in the presence of NaCl showed a pseudo-first order kinetics on the MB. The pseudo-first-order kinetic plot of MB elimination at 0.1, 0.3, and 0.5 g NaCl using 5 V is shown in an example in Figure 10. These graphs (0.988 R^2 0.99) were linear. For the experiments made possible by the applied voltage, comparable correlation coefficients were found. As a result, relative to the overall MB concentration, MB vanished at a pseudo-first-order rate for each trial. You can write the following equations:

$$-\frac{d[MB]_t}{dt} = K_{obs}[MB]_t \quad (6)$$

$$Ln\frac{[MB]_t}{[MB]_0} = -K_{obs}t \quad (7)$$

with [MB]t being the total residual concentration of MB and Kobs being the pseudo-first-order kinetic constant. Based on the slope of the linear time-course plot of Ln ([MB]t/[MB]0), Kobs was calculated for each experiment. Figure 10 displayed the profile of the methylene blue dye removal rate constant, or "Kobs," which was observed. Finding in Figure 10 showed that, under the conditions of 5 volts and 10 mg/L MB, the electrochemical elimination of MB dye followed pseudo-first order kinetics in the presence of all various NaCl concentrations. The rate range constants listed in Table 3 between 0.163 and 0.3451 min^{-1}. The rate constant that is measured at 0.3g NaCl is slightly lower than that of measured at 0.5g NaCl, the results were

0.3277 and 0.345 min^{-1}, respectively. This refers to an increase in NaCl amount would not significantly influence the MB degradation kinetics.

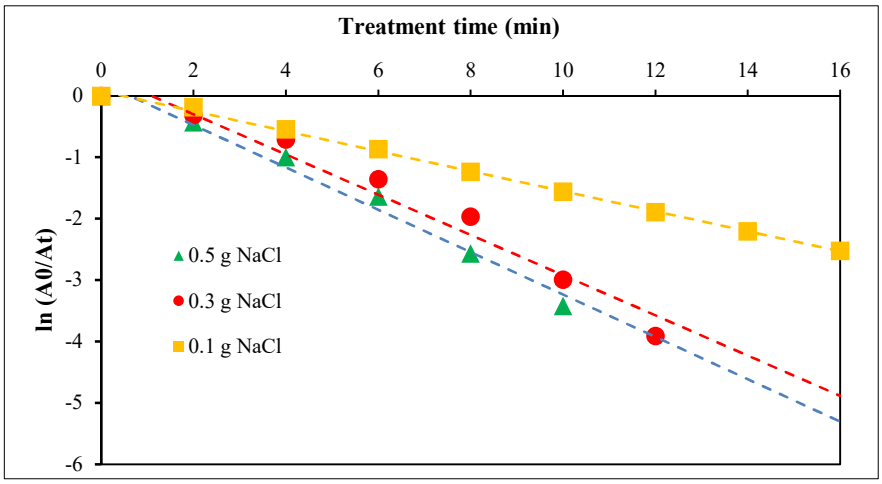

Figure 10. Impact of NaCl amount on rate constant at the following conditions: 5 volts, 10 mg/L MB, and 50 mL solution, of electrochemical degradation of MB

Table 3. Pseudo first-order rate constants for MB for various sodium chloride concentrations and voltage applications

NaCl Amount	**Effect of Sodium Chloride**		
(g)	**Equation**	**R^2**	**K_{obs} (min^{-1})**
0.1	y=0.163x+0.079	0.9981	0.163
0.3	y=-0.3277x+0.3579	0.9633	0.3277
0.5	y=-0.3451x+0.2156	0.9814	0.3451
Applied Voltage	**Effect of Applied Voltage**		
(volt)	**Equation**	**R^2**	**K_{obs} (min^{-1})**
1*	-	-	-
3	y = 0.1916 x+0.1256	0.9943	0.1916
5	y=0.3451x +0.2156	0.9814	0.3451

* There were not suitable results to be built

Kinetic study has been represented according to equations 5 and 6 so the profile plot confirmed that methylene blue dye has pseudo first-order kinetics as predominant at all applied voltage as shown in Figure 11. However, Table 4 provides a list of the reaction rate constants, K_{obs}. As we know, high applied voltage resulted quick elimination of MB dye then the rate constant could be large. On the other hand, the low applied voltage indicated that very slow removal of MB then it requires extra time to achieve the purpose. From Table 4**,** the reaction rate constants were 0.1916 and 0.3451 min^{-1} at 3 V and 5 V, respectively while it was not recorded for 1 volt as there is no significant removal.

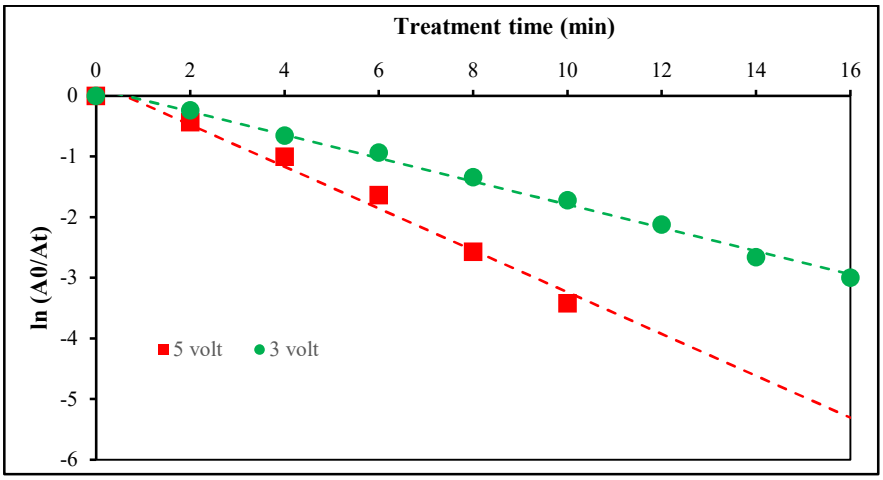

Figure 11. Impact of applied voltage on rate constant of electrochemical degradation of MB under these conditions: 0.5 g NaCl, 10 mg/L MB and 50 mL solution

Table 4. Energy consumption values of MB after electrochemical degradation process at 50 mL of 10 mg/L MB

Time	Energy consumption (Wh/mg)					
	1 V	3 V	5 V	0.1 g NaCl	0.3 g NaCl	0.5 g NaCl
2	0.0333	0.0285	0.0571	0.0392	0.0370	0.0571
4	0.0296	0.0250	0.0634	0.0317	0.0392	0.0634
6	0.0333	0.0295	0.0750	0.0344	0.0400	0.0750
8	0.0444	0.0324	0.0869	0.0375	0.0465	0.0869
10	0.0444	0.0365	0.1041	0.0421	0.0526	0.1041
12	0.0470	0.0409	-	0.0470	0.0612	-
14	0.0491	0.0451	-	0.0524	-	-
16	0.0561	0.0505	-	0.0579	-	-
18	0.06	-	-	-	-	-
20	0.0666	-	-	-	-	-
Average	0.0464	0.0360	0.0773	0.0428	0.0461	0.0773

Consumption energy

In electrochemical degradation process, when the removal% is high at short time then no consumption energy was observed. The energy consumption is calculated according to the equation 8:

$$EC = \frac{VI\Delta t}{\Delta\,[MB]} \qquad (8)$$

Where EC is the energy consumption in Wh/mg, I the current intensity (A), V the electrical potential (volt), t the treatment time (h) and [MB] the reduced mass of MB (mg).

However, the average consumption energy was 0.0428 Wh/mg in the presence of 0.1 g NaCl while it was 0.0773 Wh/mg in the presence of 0.5g NaCl even though it was similar to 0.3g NaCl as presented in Table 4. However, 0.3g NaCl exhibited results of 0.0461 Wh/mg which close to the results of 0.1g NaCl. As is well known, high applied voltage consumes high energy to achieve the electrochemical degradation of organic pollutants, so the present study was focused on this concept. Naturally, high applied voltage led to increased energy consumption. According to one previous study [53], greater applied voltages are linked to increased energy consumption and electrode corrosion. For this reason, in the current study, we concentrated on having the lowest energy consumption and best electrode

stability possible. All the consumption energy was calculated according to equation 7. The maximum average consumed energy was 0.0773 Wh/mg using 5 V while the lowest average consumption energy was 0.036 Wh/mg using 3 V as presented in Table 4. In light of this discovery, 5 volts was chosen as the ideal applied voltage for more research.

Conclusion

Electrochemical degradation process of methylene blue from its aqueous solution was carried out in this present work. Effect some independent variables such as amount of NaCl, applied voltage and electrolysis time was designed by using BDD software on removal% of MB. According to the mathematical method and BDD design plots, the most significant factors on removal% were NaCl amount (A), applied voltage (B) and electrolysis time (C). The interaction factors BC and AD, however, were equally important. On the other hand, unlike AB, the other interaction was not significant. The findings demonstrated that under the impact of sodium chloride and applied voltage, MB was removed in 10–20 minutes. Throughout the investigation, pseudo first order kinetics predominated. The rate constant, however, varied from 0.163 to 0.345 min^{-1}. In the current study, consumption energy was also considered; its range was 0.0366 to 0.104 Wh/mg.

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