Waste Aluminum Cans as Effective Electrodes for Acid Red 18 Dye Removal *via* Electrocoagulation: Parametric Effects, Kinetic and Modeling Studies

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ABSTRACT: *The widespread use of aluminum-based food packaging materials has significantly contributed to an increase in aluminum waste generation, the majority of which ends up in landfills. To address this issue, the current study attempted to recycle Waste Aluminum Cans (WAC) by converting them into an effective electrode for the treatment of Acid Red 18 (AR18) dye via electrocoagulation (EC). Chemical pre-treatment was used for the de-coating of WAC before its application in the EC process. A parameter study was then carried out in a batch monopolar EC cell with two chemically pre-treated WAC electrodes connected to an external DC Power supply to study the effects of current density (10 - 30 mA/cm²), initial pH (3 - 11), and initial dye concentration (50 - 250 mg/L) up to 30 min of reaction time. The best-operating conditions were found to be at a current density of 25 mA/cm², an initial pH of 6.8 (original pH of dye) and an initial dye concentration of 100 mg/L with a nearly completed decolorization of 99.4 %. The kinetic model of the various current densities was well-fitted by the first-order reaction, with R^2 values ranging from 0.8955 to 0.9914. The mathematical model for the decolorization rate of AR18 dye was successfully developed based on the reaction kinetics and empirical models. The predicted data was in good agreement with the experimental data to validate the developed mathematical model. The characterization analysis of the flocs confirmed that the main dye removal mechanisms were through charge neutralization, coagulation, and adsorption of dye onto the $Al(OH)_3$ flocs. In conclusion, the WAC was successfully utilized as an effective electrode for the decolorization of AR18 dye via the EC process.*

KEYWORDS: *Electrocoagulation; Aluminum cans; AR18 dye; Removal efficiency; Kinetic; Empirical model.*

INTRODUCTION

The textile industry consumes huge amounts of freshwater contributing to the generation of large quantities of wastewater containing high organic and inorganic pollutants including dyes, surfactants, solvents, heavy metals, salts, etc. [1]. The total dyes consumption in the textile industry worldwide was estimated at over 10,000 tonnes yearly with azo dyes being the largest contributor [2]. Azo dyes are one of the anionic groups of dyes and considered the most difficult to treat due to their high water solubility producing very bright colors in water, quite stable towards the light and oxidizing agents and resistance to the degradation under the conventional biological treatment [2–4]. Furthermore, under the anaerobic conditions, it has been reported that the azo dyes' molecules could be reduced to form aromatic amines which are colorless, toxic and carcinogenic [5]. Thus, the effluents containing azo dyes are necessary to be treated properly prior to the discharge into the environment [4,6].

Recently, electrocoagulation (EC) process has received remarkable attention in treating textile dye wastewater due to its simplicity in design and operation yet offering high removal efficiency, low reaction time and sludge production as compared to chemical coagulation [7,8]. The EC process is also highly practical for replacing inefficient conventional technology with a more effective treatment system [9]. The electrode material is considered the heart of the EC process as it governs the electrochemical reactions [10]. Typically, aluminum (Al) and iron (Fe) materials have been widely used as electrode materials as these materials are readily available, non-toxic, have high electro dissolution rates and effective in treating various pollutants using the EC process. In most of the studies reported in the literature, the Al electrode was proven to demonstrate better pollutant removal efficiency as compared to the Fe electrode [1,11,12]. However, the cost of Al is higher than that of Fe [13].

As Al generally shows superior performance in treating various pollutants, most of the EC related studies use chemical reagent grade Al, which is produced by mining Al-based minerals, such as bauxite [14]. The production of new commercial-grade Al requires high energy consumption due to the mining and manufacturing processes which lead to the wastage of energy as well as causing extensive environmental damage. Furthermore, the use of commercial Al electrodes as sacrificial anodes during the EC process required frequent replacement and thus increased the cost of the electrode materials. As an alternative to commercial Al, Waste Aluminum Cans (WAC) are easily accessible, abundant, and appropriate sources of recycling material that could be beneficial for both economic efficiency and environmental considerations. It was reported that approximately 1.5 million tons of waste are created worldwide each year through the disposal of aluminium cans that occupy landfills [15]. In recent years, many researchers have embarked on the exploitation of WAC as a raw material in the preparation of adsorbent [14], catalyst [16–19], nanomaterial [20], alum [21], aluminum air-battery [22] as well as for hydrogen generation [23]. However, there are very limited works done on the utilisation of WAC as an effective electrode in the electrochemical process for the removal of dye pollutants from wastewater.

In our previous work, the applicability of the WAC in the removal of Acid Red 18 (AR18) dye via the EC process has been explored and the dye removal performance was compared with the commercial electrodes [24]. The findings of the previous work concluded that WAC performed better than the commercial one due to its better alloying elements with higher Mg composition that contributed to the higher dissolution of metal ions and thus enhanced the dye removal efficiency. Due to its superior performance, the effects of the parameters (such as current density, initial pH, initial dye concentration etc.) that influence the dye removal efficiency also deserve further investigation. Taking into account the significant influence of current density on controlling the EC's efficiency, previous researchers proposed an empirical model using classical kinetics law to correlate the relationship between the current density and the rate of pollutant removal through the EC process [1]. However, the proposed model has not been fully simulated to further confirm its validity. Thus, the novelty of this work lies in the development and validation of an empirical model for the removal rate of AR18 dye by the EC process using WAC electrodes.

The purpose of this study was to investigate the effects of operational parameters on process behavior and to determine the best conditions for the removal of AR18 dye from aqueous solution via the EC process. The experimental runs were performed in a batch monopolar EC cell using chemically pre-treated WAC electrodes. A kinetics and modeling study using *ode45* of MATLAB

Table 1: Characteristics of the AR18 dye.

Chemical structure	Molecular formula	Molecular weight (g/mol)	λ_{max} (nm)
	$C_{20}H_{11}N_2Na_3O_{10}S_3$	604.48	507

function was then performed at various current densities to develop and validate the empirical model for the rate of AR18 dye removal. Besides, SEM-EDX analysis was also conducted on the generated flocs to elucidate the main removal pathway of the AR18 dye. Furthermore, the residual level of Al after the EC process was determined to ensure the quality of the treated water in compliance with Malaysian's industrial effluent discharge standards.

EXPERIMENTAL SECTION

Chemicals

Analytical grade of AR18 dye (>99 % purity), sulphuric acid (H_2SO_4) (95-98 % purity), hydrochloric acid (HCl) (37 % purity), sodium hydroxide (NaOH) and sodium chloride (NaCl) were obtained from Merck. All the chemicals were used as received. Table 1 shows the characteristics of the AR18 dye. A stock solution of AR18 dye at 1 g/L was prepared and it was diluted to obtain the desired initial concentrations in the range of 50 – 250 mg/L. Deionized water (Milipore Mili-Q system) was used to prepare all the solutions.

Pre-treatment of the WAC electrodes

The collected WACs from the student's hostel in the Universiti Sains Malaysia were cut into T-shape dimensions as described in the previous study [24]. They were then subjected to the chemical pre-treatment to remove the paint and epoxy coating on the outer and inner walls of the waste material. The chemical pre-treatment was done by immersing the WAC into concentrated H_2SO_4 for 8 min and then washed thoroughly with deionized water. The pre-treated WAC was then air-dried and used in the batch EC experiment. The elemental composition of the pre-treated WAC electrodes obtained from the EDX analysis is shown in Table 2.

Table 2: The elemental composition of the pre-treated WAC electrodes.

Element	Weight, %
C	10.32
O	3.81
Mg	1.24
Al	83.78
Mn	0.86
Totals	100.00

Batch EC system

Batch monopolar EC experiments were conducted to investigate the effect of operating parameters on the decolorization of AR18 dye as well as to determine the optimum conditions for the process. The experiments were carried out in a 1.1 L rectangular reactor as shown in Fig. 1. Two pieces of pre-treated WAC were used as electrodes and placed at the center of the cell with a gap of 0.5 cm between them. The area of each electrode immersed into the dye solution was 7 cm (W) x 6 cm (H) with an effective surface area of 84 cm^2 (both sides). The electrodes were connected with external wires to a DC Power supply (Dazheng PS - 305D, 0 - 5 A, 0 - 30 V) to provide the required current during the experiment.

The AR18 dye solution with a volume of 800 mL was initially fed into the EC cell. Then, the operational conditions (current density, initial pH and initial concentration) for each experimental run were set according to the parameter conditions as listed in Table 3. The solution was continuously stirred with a magnetic stirrer (Topolino, IKA) at medium speed during the experiment to acquire a homogeneous solution. All the experiments were carried out at a constant reaction time of 30 min, a NaCl dosage of 2 g/L and a room temperature of 25±1 ºC. During the EC process, the change of pH was monitored

Table 3: The operational conditions of the batch EC experiment.

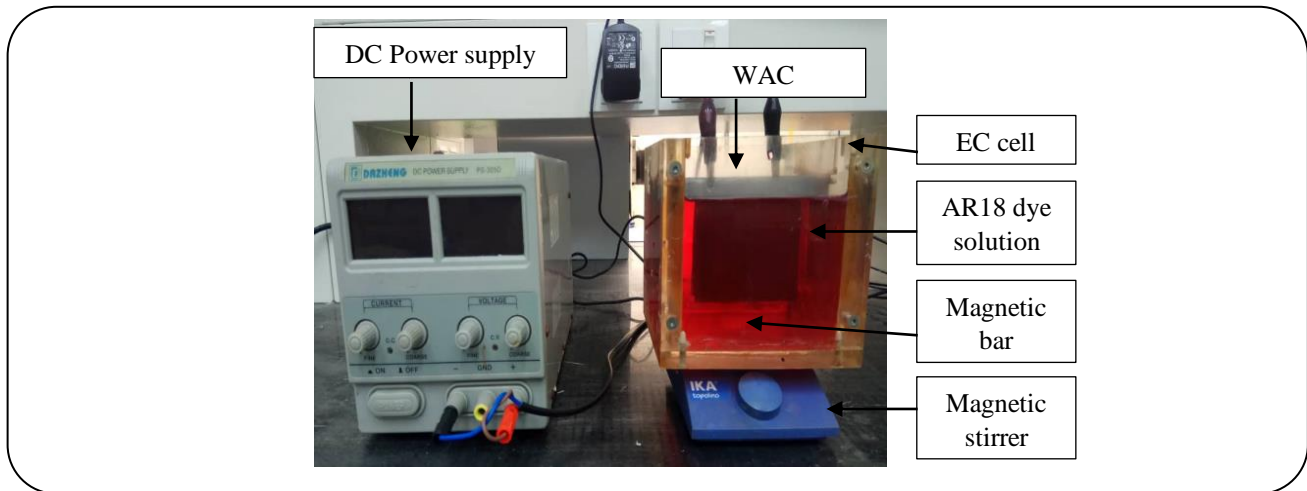| Parameter study	Operating Conditions		
	Current density (mA/cm²)	pH	Initial concentration (mg/L)
Current density and time	10-30	6.8	100
Initial pH	25	3 - 11	100
Initial dye concentration	25	6.8	50-250

Fig. 1: Batch monopolar EC system for the treatment of AR18 dye.

using a pH meter (Eutech pH2700, Thermo Scientific, Singapore) and samples of the treated wastewater were taken every 5 min. The samples were then filtered using a 0.45 μm Whatman filter paper prior to its color measurement. After the EC process, the treated water was filtered using a vacuum filtration pump to collect the produced flocs for subsequent drying in an oven at 105 ℃ overnight. The flocs samples were weighed before and after the drying process to determine the amount of generated floc. Each experimental run was conducted in duplicate and the average dye removal efficiency was calculated to ensure reproducibility with variations ±5 % as shown by the error bar in each figure.

The concentration of AR18 dye solution was determined using a double beam UV-Visible spectrophotometer (Shimadzu 1800, Japan) at a maximum wavelength of 507 nm. The AR18 dye removal efficiency is calculated using Eq. (1):

$$\text{Removal Efficiency, \%} = \frac{C_0 - C_t}{C_0} \times 100\% \qquad (1)$$

Where,
C_0 = initial dye concentration (mg/L) and
C_t = dye concentration at a time, t (mg/L)

Operational cost

The estimation of the operational cost is usually based on the electrical energy, chemical and electrode consumption used during the EC process. In this work, the cost of electrode consumption was neglected since the WAC electrodes used were made from waste material. The Electrical Energy Consumption (EEC) and operating cost are calculated using Eq. (2) and Eq. (3), respectively [25].

$$\text{EEC, (kWh/m}^3) = \frac{V \times I \times t}{v} \qquad (2)$$

Where;
V = applied voltage (V)
I = current (A)
t = time (h)
v = volume of dye solution (m³)

$$\text{Operating cost, (\$)} = a \times EEC + b \times CC \qquad (3)$$

Where;
a = electrical city price (US$/kWh)
b = chemical unit price (US$/kg)
EEC = electrical energy consumption (kWh/m³)
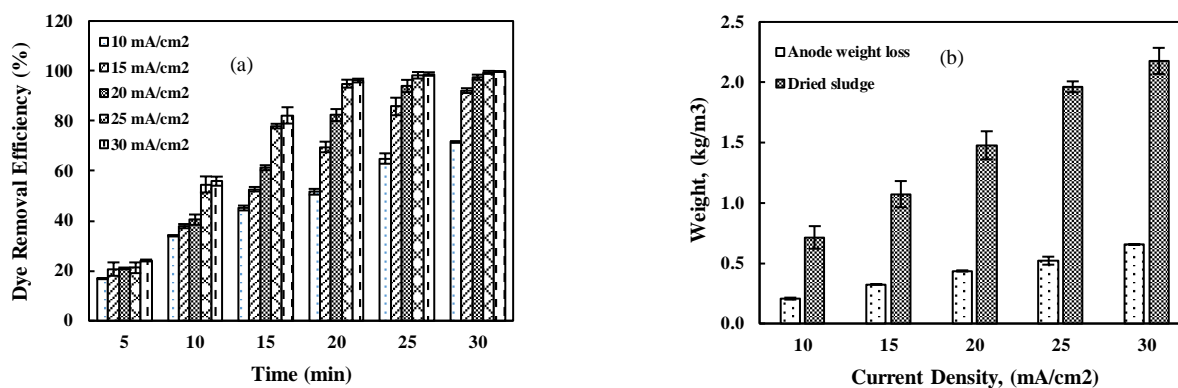CC = chemical consumption (kg/m³)

Fig. 2: Effects of current density on (a) dye removal efficiency using WAC electrode and (b) anode weight loss and dried sludge produced by the EC process. (Initial pH=6.8, initial dye concentration=100 mg/L, NaCl=2 g/L, IED=0.5 cm, time=30 min).

The electrical cost was US$ 0.077/kWh based on the rates and tariffs in Malaysia throughout June 2022 [26] while the price for NaCl was US$ 0.16/kg.

Analytical methods

The surface morphology and the elemental composition of WAC floc were examined using a scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectroscopy (EDX) facility (Quanta 450 FEG, FEI, Netherlands) operated at an accelerating voltage of 5 kV. The concentration of Al ions in the treated water was evaluated using an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) (ICAP 7600, Thermo Scientific, USA).

RESULTS AND DISCUSSION
Effect of current density and reaction time on the AR18 dye removal efficiency

Current density is one of the most critical parameters in controlling the electrochemical reaction rate, as it affects the coagulant production rate and the size of the bubbles generated, which affected the growth of flocs in the EC process [27]. The current per area of the electrode, which determines the amount of metal ions, such as Al^{3+} or Fe^{2+} ions, released from the electrodes represented the current density. In this study, current density was varied between 10 to 30 mA/cm² at a constant initial pH of 6.8, initial dye concentration of 100 mg/L and 30 min of reaction time to determine the optimum current density and reaction time for AR18 dye removal. Fig. 2 (a) shows that the percentage removal of AR18 dye gradually increased as the current density and reaction time were increased.

The lowest AR18 dye removal of 71.6 % was obtained at a minimum current density of 10 mA/cm² within 30 min of reaction time. Meanwhile, the highest AR18 removal of 99.8 % was achieved at a maximum current density of 30 mA/cm². The results were consistent with the theory of Faraday's law. As the current density and reaction time were increased, more Al would dissolve from the anode electrode into the solution as the amount of dissolved metal is directly proportional to the quantity of electric current passing through the electrolyte solution [28]. Meanwhile, hydroxyl ions and hydrogen bubbles were generated from the reduction of water at the cathode resulting in the availability of more Al hydroxyl polymers that were finally transformed into $Al(OH)_3$ coagulant for the enmeshment and/or adsorption of the dye molecules (sweep flocculation). Accordingly, an increase in the current density and the reaction time produced more $Al(OH)_3$ coagulant causing more formation of flocs in the solution which significantly enhanced the dye removal efficiency. The finding was consistent with work reported by *Amani-Ghadim et al.* [29] who claimed that the sweep flocculation mechanism was mainly dependent on the dosage of coagulant produced during the EC process, especially in neutral pH conditions.

Furthermore, current density also has a significant effect on the weight loss of anode electrode as well as the dried sludge production as illustrated in Fig. 2 (b). The weight loss of anode and dried sludge production per treated dye solution were observed to increase progressively from 0.21 to 0.65 kg/m³ and 0.71 and 2.18 kg/m³, respectively as the current density was increased from 10 to 30 mA/cm² at 30 min of reaction. The results
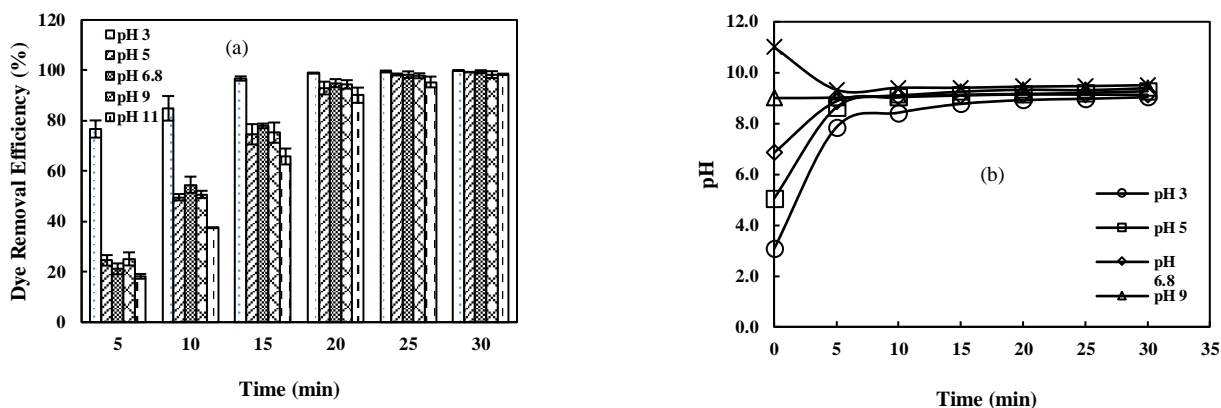
Fig. 3: (a) Effects of initial pH on dye removal efficiency by WAC electrode and (b) Changes in the solution pH during the EC process at different initial pH. (Current density= 25 mA/cm^2, initial dye concentration=100 mg/L, NaCl=2 g/L, IED=0.5 cm, time=30 min).

were in agreement with the findings reported by other researchers [1,30]. Thus, to minimize the operating cost including the energy consumption, cost of electrodes and sludge disposal, a current density of 25 mA/cm^2 and a reaction time of 30 min were chosen for the subsequent study as they gave the highest removal of AR18 dye of 99.4 %. In fact, a current density greater than 25 mA/cm^2 was unnecessary since there was no significant difference obtained in the dye removal efficiency (>99 %). *Khosravi et al.* [31] also reported the optimum current density of 26 mA/cm^2 with a slightly lower AR18 dye removal efficiency of 89.5 % in 30 min.

Effect of pH on the AR18 dye removal efficiency

pH is also an essential parameter as it determines the predominance of coagulant species formed during the EC process [32]. Generally, the Al ions released from the anode oxidation were in the form of monomeric ions, Al hydroxo complexes and other various polymers over a wide range of pH. In order to investigate the effect of initial pH values on the dye removal efficiency, a series of batch experiments were performed at different initial pH from 3.0 to 11.0 at a constant current density of 25 mA/cm^2, an initial dye concentration of 100 mg/L and 30 min of reaction time. Results for the effect of initial pH on the removal efficiency of AR18 dye as a function of time and the changes in solution pH throughout the EC process are depicted in Fig. 3 (a) and (b), respectively.

In the first 15 min, it was observed that the highest removal efficiency was obtained at pH 3 with 96.8 % whereas the lowest was about 65.8 % at an initial pH of 11.

At low initial pH of 2 to 3, Al^{3+} and $Al(OH)^{2+}$ were the primary cationic soluble species that were formed in the solution [7,33]. This cationic species could interact strongly with the negatively charged AR18 dye ($-SO_3$ group) and destabilize the dye pollutant through a charge neutralization mechanism. This finding was consistent with the work reported by *Amani-Ghadim et al.* [29] as they concluded that the charge neutralization mechanism played a dominant role in highly acidic conditions (pH<4) and could achieve maximum removal efficiency in the early reaction time with low Al^{3+} concentration. Therefore, at the initial acidic pH, the major removal pathway was caused by the dye precipitation process via the charge neutralization mechanism while adsorption of the dye molecules by $Al(OH)_3$ flocs had a lesser effect [7].

Meanwhile, other monomeric and polymeric species could also be formed in the system such as $Al(OH)_4^-$, $Al_2(OH)_2^{4+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, etc. in the wide range of initial pH (4 < pH < 7) that finally converted into $Al(OH)_3$ flocs. At about neutral initial pH (pH > 6.5 to 9), most of the Al hydroxides precipitated due to the poor solubility of $Al(OH)_3$. In fact, the $Al(OH)_3$ coagulant in the generated flocs had large surface area which was responsible for the rapid adsorption of AR18 dye molecules [7]. Thus, the adsorption of the AR18 dye and/or enmeshment of dye onto $Al(OH)_3$ flocs could be the main removal mechanism. In contrast, at high pH conditions (pH > 9), the formation of soluble $Al(OH)_4^-$ ions predominated and thus, increased the ionic repulsion between $Al(OH)_4^-$ and negatively charged AR18 dye molecules. The repulsive interaction between the ions led

to an ineffective coagulation process between dye pollutants and Al flocs.

Furthermore, with an increase in the reaction time up to 30 min, all the experiments demonstrated almost complete decolorization within 98-100 % of dye removal efficiency. This is due to the fact that the initial solution pH gradually changed to the final pH of around 7 to 9, at this particular reaction time as illustrated in Fig. 3 (b). It was noted that the insoluble $Al(OH)_3(s)$ species generated by the EC process was stable at this range of pH thus enhancing the adsorption of the dye molecules. The $Al(OH)_3$ together with the AR18 dye would then be separated from the solution by either H_2 floatation or sedimentation. Therefore, it can be concluded that the optimum range for the initial pH to be applied in the EC process for the removal of AR18 dye was between 3 to 7 (acidic to neutral conditions). As the dye removal efficiency was almost similar after 30 min of reaction time, the original dye pH of 6.8 was selected to be used for further study since no chemical was needed to adjust the pH of the dye solution before the EC process.

Effect of initial concentration on the AR18 dye removal efficiency

Effect of different initial dye concentrations was investigated in the range of 50-250 mg/L at a current density of 25 mA/cm², an initial pH of 6.8 and 30 min of reaction time. The influence of initial dye concentrations on dye removal efficiency during the EC process is presented in Fig. 4. In the first 15 min of reaction, the dye removal efficiency showed a decreasing trend as the initial concentration was increased from 50 to 250 mg/L. This was because the amount of dye molecules available in the solution increased with an increase in the initial concentration of dye. Thus, the rate of adsorption decreased with increasing initial dye concentration due to the insufficient amount of the available $Al(OH)_3$ coagulant produced at the constant current density and reaction time [34]. *Shokri* [35] reported a similar observation in which the percentage of degradation was reduced from 99.0 to 68.5 % with an increase in the concentration of Acid orange 5 from 30 to 120 mg/L. However, with further progress of the reaction up to 30 min, almost complete dye removals were attained for all the initial concentrations with the removal efficiencies of up to 97 to 99 %. This was attributed to the adequate amount of $Al(OH)_3$ generated during
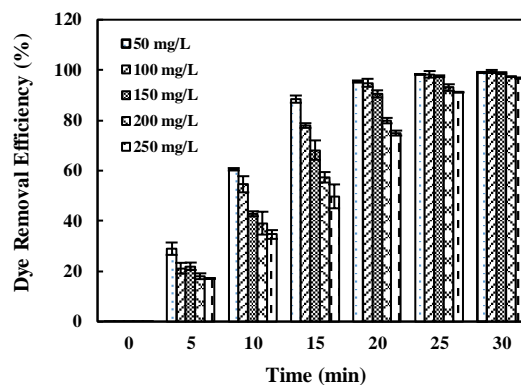

Fig. 4: Effects of initial dye concentration on dye removal efficiency by WAC electrode. (Current density=25 mA/cm², initial pH=6.8, NaCl=2 g/L, IED=0.5 cm, time=30 min)

the increased reaction time to adsorb most of the dye molecules. From this finding, it could be summarized that the EC process is an effective method capable of removing high concentrations of dye from the aqueous solution owing to the sufficient amount of the generated $Al(OH)_3$ coagulant. This was further assisted by the complex removal mechanisms during the EC process such as entrapment or enmeshment of dye onto the flocs.

Evaluation of the best operating conditions for the decolorization of AR18 dye

Based on the findings, the best operating conditions for removal of AR18 dye were at a current density of 25 mA/cm², an initial pH of 6.8 (original pH of dye), an initial dye concentration of 100 mg/L and 30 min of reaction time. At these conditions, the dye removal efficiency could be removed almost completely (99.4 %) after the EC process with a sludge production rate of 1.96 kg/m³ of the dye solution. The result obtained in this present study was comparable with the other reported EC studies (Table 4). The energy consumption and operating cost at the best-operating conditions were estimated to be 13.13 kWh/m³ and US\$1.33/m³, respectively. The operating cost was found to be significantly lower than that reported by *Bener et al.* [1], which is US\$1.5/m³ contributed by the use of waste material to eliminate the cost of electrodes. Furthermore, the easy availability and abundance of WAC are some of the additional benefits, indicating a promising future for the environmentally friendly EC-WAC process in AR18 dye removal from aqueous solutions.

Table 4: Performance of EC process for the treatment of various dyes using Al-based electrodes reported in the literature.

Electrode type	Type of dye	Optimum operating conditions	% Removal efficiency	References
WAC/WAC (Waste-based electrode)	AR 18	CD: 25 mA/cm^2 pH: 6.8 NaCl: 2 g/L Time: 30 min	99.4	Present study
Al-Al (Commercial electrode)	AR 18	CD: 26 mA/cm^2 pH: 4 NaCl: 1 g/L Time: 40 min	92.3	[31]
Al/Al (Commercial electrode)	Eriochrome Black	V: 7.0 V pH: 7 NaCl: 2g/L Time: 55 min	98.5	[36]
Al/Al (Commercial electrode)	Methylene blue	CD: 5 mA/cm^2 pH: 7 NaCl: 0.2 mol/L Time: 30 min	99.4	[33]
Al/Al (Commercial electrode)	Reactive Red 24	CD: 10 mA/cm^2 pH: 7.2 NaCl: 2.5 g/L Time: 35 min	97.9	[37]

*CD= Current Density, V=Voltage

The removal of AR18 dye by the EC process was also monitored by the spectrophotometry analysis. The UV-Vis absorption spectra of the AR18 dye before and after the EC process are presented in Fig. 5. The spectrum of AR18 dye mainly consists of two different peaks at wavelengths of 507 nm and 330 nm. The major peak at 507 nm could be ascribed to the chromophore containing azo linkage (-N=N-) which is responsible for the color of the dye, while the other peak at 330 nm is attributed to the aromatic (naphthalene) rings [38]. The results demonstrated that the peak at 507 nm diminished significantly over time which is consistent with the disappearance of the color of the treated solution (Fig. 5). The color of the treated solution gradually changed from red to colorless within 30 min indicating that the decolorization process involved the coagulation, adsorption and enmeshment of AR18 dye molecules onto the Al(OH)$_3$ flocs. Meanwhile, the absorbance at 330 nm declined to only ~55 % of its original value. This reveals that the EC process alone was not sufficient to eliminate all the organic compounds in the solution within 30 min. However, since there is no appearance of a new absorbance peak in the absorption spectrum, it can be concluded that there was no intermediate product formed during the EC process [39].
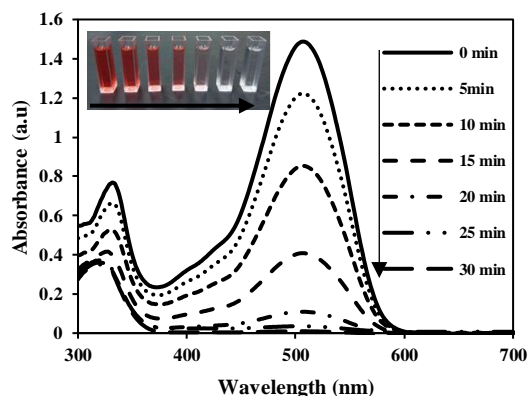

Fig. 5: Absorption spectra of AR18 dye during the EC process.

Kinetic and modeling study of AR18 dye at different current density

In this work, the mathematical model for AR18 dye removal was developed for capturing the effect of current density on dye concentration in a batch EC system. A hybrid model was considered in this study since the reaction kinetics model and empirical model were implemented. First-order and second-order reaction kinetics were analyzed and compared in determining the most accurate reaction kinetics order. Then, the function of kinetic constants with the selected order of reaction

Table 5: Kinetic parameters at different current densities (Initial dye concentration= 100mg/L, initial pH= 6.8, NaCl=2 g/L, IED=0.5 cm and reaction time= 30min).

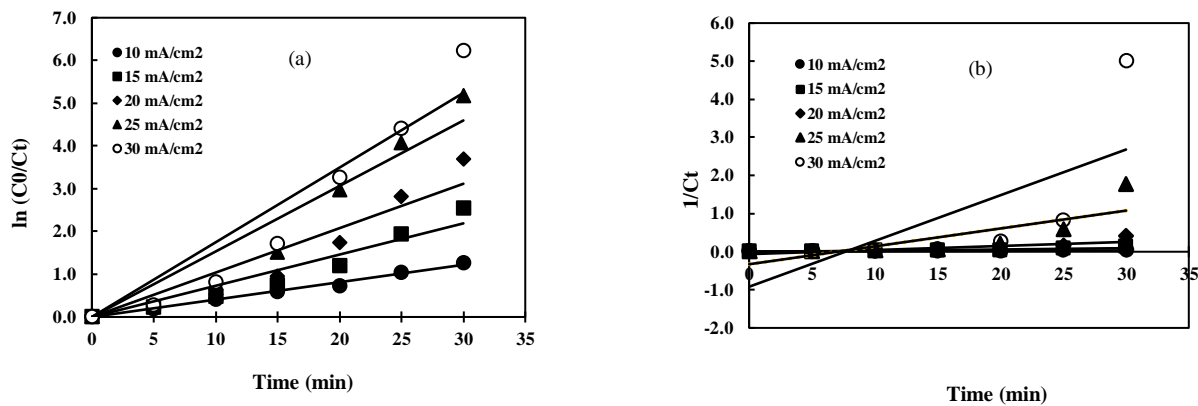| Current density, mA/cm^2	First-order reaction		Second-order reaction	
	k_1	R^2	k_2	R^2
10	0.0407	0.9914	0.0008	0.9410
15	0.0730	0.9207	0.0034	0.7508
20	0.1039	0.8955	0.0107	0.6604
25	0.1532	0.9229	0.0469	0.6152
30	0.1747	0.9068	0.1200	0.4969

Fig. 6: Kinetic study on the AR18 dye removal at different current densities using WAC electrodes (a) First-order reaction and (b) Second-order reaction. (Initial dye concentration= 100mg/L, initial pH= 6.8, NaCl=2 g/L, IED=0.5 cm and reaction time= 30min).

kinetics was described by using an empirical model. Finally, the developed mathematical model was validated experimentally.

The determination of the reaction kinetic model

The equation for first-order and second-order reaction kinetic models are given in Eqs. (4) and (5), respectively:

$$\frac{dC}{dt} = - k_1 C \tag{4}$$

$$\frac{dC}{dt} = - k_2 C^2 \tag{5}$$

Where; C is dye concentration in mg/L and t is the reaction time in min. Meanwhile, k_1 and k_2 denote the kinetic rate constants of the first-order and second-order reactions, respectively. The integration of Eqs. (4) and (5) give:

$$C_t = C_0 e^{-k_1 t} \tag{6}$$

$$\frac{1}{C_t} = \frac{1}{C_0} + k_2 t \tag{7}$$

Where; C_0 and C_t are the initial dye concentration and the dye concentration at time t, respectively. The first-order and second-order kinetic models were examined by plotting the graphs of ln (C_0/C_t) versus time and $1/C_t$ versus time, respectively as shown in Fig. 6. From the regression analysis, the correlation coefficient (R^2) and the kinetic rate constants obtained for both reaction kinetics models are listed in Table 5. Better fittings of experimental data to the first-order kinetic reaction with a higher regression coefficient for all the current densities in the range of 0.8955 to 0.9914 as compared to the second-order reaction are observed. Therefore, the first-order kinetics which had higher accuracy in R^2 was selected as the kinetic model of this system [35]. The reaction rate constants for the first-order kinetic model at current densities of 10, 15, 20, 25 and 30 mA/cm^2 were evaluated as 0.0407, 0.0730, 0.1039, 0.1532 and 0.1747 min^{-1}, respectively. Rate constants were observed to increase with increasing current density for both kinetic models and the results were consistent with the other reported works [1,40].
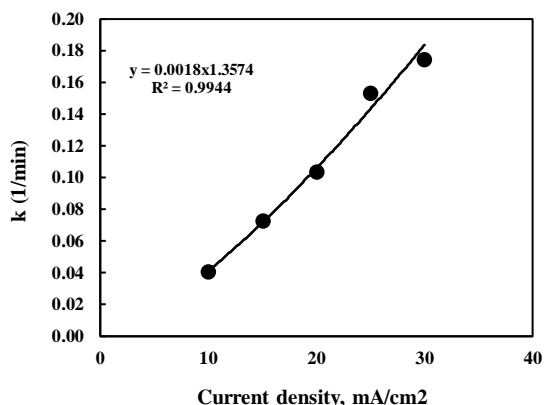
Fig. 7: *Relationship between reaction rate constants and current densities for the first-order kinetic reaction.*

An empirical model for kinetic constant

Since the first-order kinetic was chosen as the kinetic model, the function of the kinetic constants, k_1 as shown in Eq. (4), was then represented by the empirical model. The function of k_1 in terms of current density was approximated by the power equation [1] as in Eq. (8):

$$k_1 = \alpha * I^\beta \tag{8}$$

Where; k_1 is the rate constant in 1/min and I is the current density in mA/cm^2 and, β and α are the arbitrary constants. The nonlinear regression toolbox in Microsoft Excel was applied to estimate the arbitrary constants with an acceptable R^2. The relationship between reaction rate constants and current densities for the first-order kinetic reaction is illustrated in Fig. 7.

The result showed that the reaction rate constant can be modelled empirically by using a power-law equation with high confidence (R^2=0.9944) and it was expressed as follow:

$$k_1 = \left(0.0018 * I^{1.3574}\right) \tag{9}$$

Therefore, the rate of the decolorization of AR18 dye in Eq. (4) can be written as Eq. (10):

$$-\frac{dC}{dt} = \left(0.0018 * I^{1.3574}\right) \times C \tag{10}$$

Validation of the model developed

The model developed for the removal of AR18 dye by the EC process as in Eq. (10) was then further validated experimentally. The concentration of dye obtained from the experimental data was compared with the simulated data from Eq. (10). The ordinary differential equation formed was solved numerically by Runge Kutta 4th order technique via *ode45* of MATLAB function. The comparison results between the experimental and simulated data obtained from the developed model at different current densities are presented in Fig. 8 (a) – (d).

Results demonstrated a good agreement between the experimental and the predicted data for various current densities with R^2 values in the range of 0.8402 to 0.9941. The R^2 values exhibited higher values of > 0.90 at the lower current density (10 and 15 mA/cm^2) as compared to the higher current density (20 and 25 mA/cm^2) with $R^2 \sim$ 0.84. Slightly lower R^2 values at higher current density were caused by the deviation of the experimental values from the predicted ones at 5 to 20 min of reaction time in which the experimental results seem to be higher than the one predicted by the model. The deviation between the model and the experimental result could be attributed to the accumulation of error in the regression task to represent the relationship between kinetic constant and various current densities as well as to determine the coefficients of the equation. However, with a further increase of the reaction time to more than 25 min, the model prediction was observed to lie close to the experimental data for all the current densities to indicate that the maximum rates of dye removal were achieved within this reaction time. Therefore, it can be concluded the validated model (Eq. 10) in this present study could be used to predict the decolorization rate of AR18 dye using the EC process satisfactorily.

SEM-EDX analysis of the produced floc after EC treatment

SEM-EDX analysis was conducted to examine the surface morphology and elemental composition of generated WAC floc from the EC process at the optimum conditions. Fig. 9 (a) and (b) exhibit the surface morphology of WAC flocs at different magnifications of 500 x and 5000 x, respectively. Meanwhile, the EDX result of the produced WAC floc is illustrated in Fig. 9 (c). The SEM images suggest that the generated flocs consisted of non-uniform shapes with micrometer-sized particles and it was mostly amorphous in nature [31,41,42]. According to the EDX analysis, O was identified as the predominant element in the WAC floc with a composition of 62.79 %, followed by Al at 31.82 %. This was attributed to the formation of Al(OH)$_3$ as a coagulant that was responsible
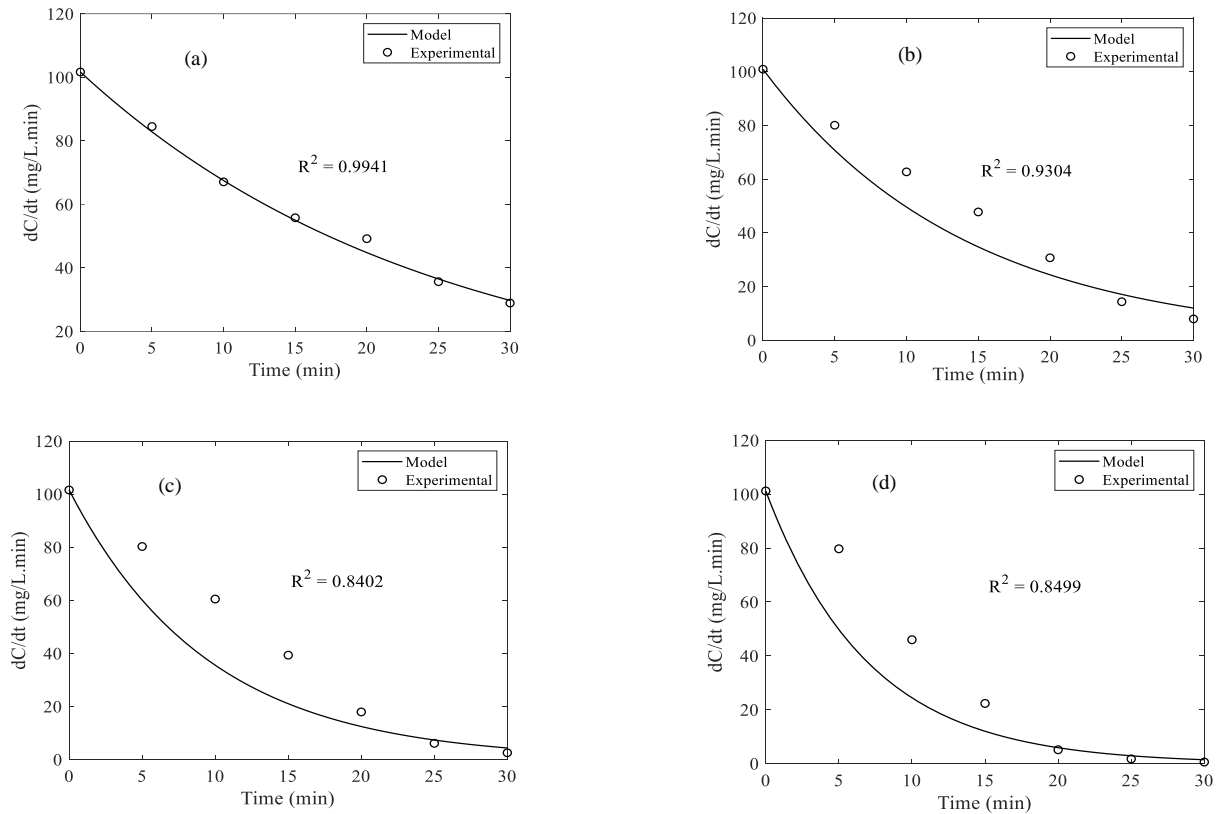
Fig. 8: Comparison between experimental and the predicted data of AR18 dye removal rate with time at different current density (a) 10 mA/cm², (b) 15 mA/cm², (c) 20 mA/cm² and (d) 25 mA/cm² (Initial dye concentration=100 mg/L, initial pH=6.8, NaCl=2 g/L, IED=0.5 cm and reaction time= 30min).

for the coagulation and rapid adsorption of AR18 dye molecules [43]. The presence of Mg at a composition of 0.27 % was as expected because Mg was used as one of the alloying elements in the WAC material, whereas the existence of Na and Cl were due to the use of NaCl as a supporting electrolyte. Meanwhile, the S component was also noticed in the floc sample with a composition of 0.38 % to indicate the occurrence of electrostatic attraction between the negatively charged sulfonic groups of AR18 dye with the positively charged Al coagulant, thus confirming the adsorption of dye molecules onto the produced flocs. A similar conclusion was reported by *Mollah et al.* [42], who assumed that the removal of Orange II dye was caused by physisorption onto the floc surfaces through the presence of S, Al, Na, Cl and O components detected from EDS analysis. Thus, it can be concluded that most of the dye molecules coagulated to form floc and this floc was removed from the solution through floatation of H_2 bubble or sedimentation. Meanwhile, the residual dye could

be adsorbed on the floc or being entrapped between floc particles to further increase the removal efficiency.

Analysis of the treated water

The Al ions concentration remaining in the treated solution was then examined using ICP-OES analysis. From the results, it was found that the residual Al concentration in the treated water was 4.1 ppm. Hence, it can be concluded that the EC process using WAC electrode was safe since it produced lower residual concentration of Al than the maximum permissible limit for the industrial effluent set at 10 ppm and 15 ppm for Standard A and Standard B, respectively as stated in the Malaysian's Fifth Schedule of Environmental Quality (Industrial Effluent) Regulation 2009 [44].

CONCLUSIONS

WAC was a good candidate to be converted into electrodes for the treatment of AR18 dye via the EC process.

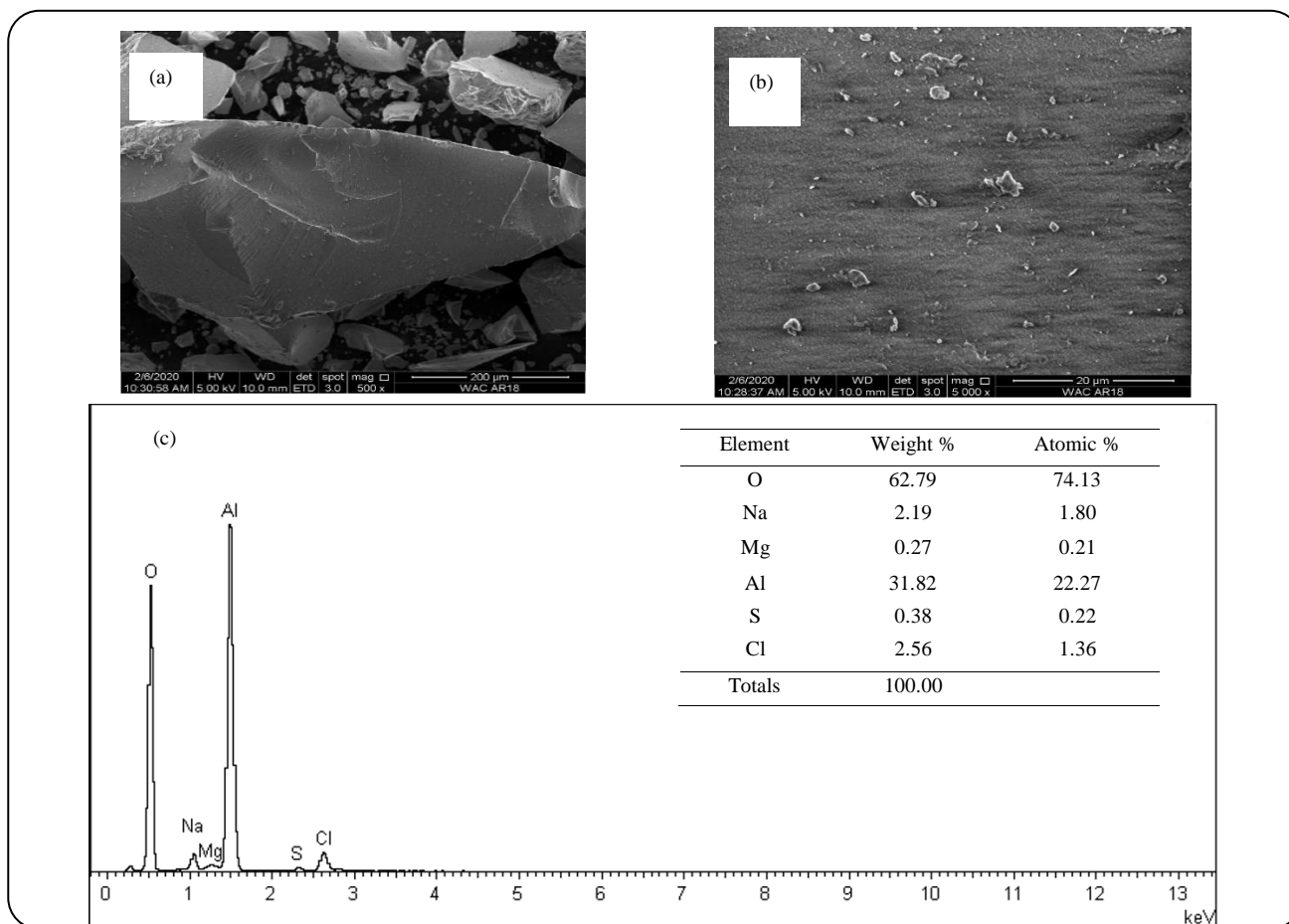| Element	Weight %	Atomic %
O	62.79	74.13
Na	2.19	1.80
Mg	0.27	0.21
Al	31.82	22.27
S	0.38	0.22
Cl	2.56	1.36
Totals	100.00	

Fig. 9: SEM-EDX images of WAC floc produced in the EC process at different magnifications of (a) 500 x, (b) 5000 x and (c) EDX analysis results.

The WAC required only a simple chemical pre-treatment step to eliminate the outer and inner coatings prior to its application as electrode in the EC process. The optimum conditions for the batch EC process using the chemically pre-treated WAC were found to be at a current density of 25 mA/cm^2, a pH of 6.8 (original pH of dye) and an initial dye concentration of 100 mg/L for 30 min of reaction time with the highest dye removal efficiency of 99.4 %. Higher current density would lead to higher removal efficiency and lower reaction time. However, the optimization of this parameter was essential as too high of current density (> 25mA/cm^2) would cause high sludge production, energy consumption and an excess of Al^{3+} ion concentration remaining in the treated wastewater. Besides, pH control of the solution was also crucial as it influenced the main dye removal mechanism in the EC process. Under acidic to neutral pH conditions (pH 3-7), the removal pathway of the dye was through coagulation via charge neutralization mechanism followed by the adsorption as well as entrapment of the AR18 dye onto the generated flocs. The dye removals at various current densities fit a first-order kinetic model quite accurately. Subsequently, the mathematical model for the rate of decolorization of AR18 dye was successfully developed as well as validated using Runge Kutta 4th order technique via *ode45* of MATLAB function. Overall, it could be concluded that WAC was a potential electrode to be used as an alternative to the commercial ones due to its availability, high efficiency and being environmentally friendly. Low Al^{3+} ion was also observed to remain in the treated solution which was in accordance with the Malaysian's industrial effluent discharged standards.

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