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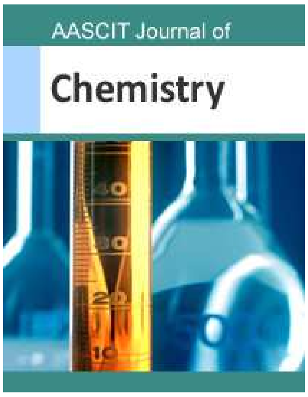

Effect of Operational Parameters on the Removal of Azo-2-Naphthol Dye on Aluminium Electrodes by Electrocoagulation

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Abstract
1-Phenylazo-2-naphthol (PAN) was subjected to electrocoagulation using a 0.3 A d.c electrolytic cell in ethanol. Rapid electrocoagulation of PAN in ethanol was observed within 15 minutes of electrolysis time. The effects of electrocoagulation time, initial pH and initial dye concentration on the decolourization of dye have been explored. The solution with higher concentration, 1.0 % (w/v) showed decolourization efficiency of 77 % compared to 0.1 % (w/v) which had decolourization efficiency of 73 %. Decolourization was faster in the more concentrated solution of PAN. The effective colour removal % (EC_R) has been evaluated and this indicate the amount of dye removed per unit of time. The results of pH studies indicated the pH of 5.5 as the optimum pH for the decolourization of PAN on aluminium electrodes in aqueous ethanol.

1. Introduction

One important electrochemical technique which has found extensive application in the effective removal of a variety of unwanted dissolved particles and suspended matters from aqueous solution by electrolysis is electrocoagulation. It has been a very useful alternative for clarifying and decolourizing certain solution containing unwanted dissolved substances or suspended matter. Electrocoagulation is capable of fractionating a number of organic substances in efficient manner by electrochemically coagulating some of them while leaving other components in solution [1]. This technique has been used to clarify food wastewater [2-3], industrial wastes containing cyanide and heavy metals [4-6], industrial wastewater containing organic pollutants [7], tar-sand and oil-shale wastewater [8], portable water [9-10], dye-containing textile wastewater [11-13] and phosphate-containing sewage [14-15]. It has also been successfully utilized in the removal of colour from tea effluent [16], removal of colour of spent wash [17], decolourization of methyl orange wastewater [18], purification of wastewater from gelatin production plant [19], denitrification [20], removal of Cr(VI) from polluted solutions [21], arsenic removal [22], boron removal [23] and removal of acid dye from aqueous solution [24]. Electrocoagulation has been used as a purification step in the isolation of a few natural products from crude plant extracts [25-27].

The efficiency of electrocoagulation in the pretreatment of polluted water has been determined [28]. The acidity of the solution is an important parameter that affects the whole performance of electrocoagulation processes [29-32]. The major steps in electrocoagulation processes include: electrolytic reactions at electrode surfaces, formation of coagulant in situ that initiate the coagulation process and adsorption of pollutants on coagulants [33-34]. With aluminum electrodes, the following reactions occur at the electrodes [35].

Anode reaction:

$$Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^{-} \quad (1)$$

Cathode reaction:

$$2H_2O_{(l)} + 2e^{-} \rightarrow H_{2(g)} + 2OH^{-}_{(aq)} \quad (2)$$

Al^{3+} and OH^- ions generated during the electrochemical reaction react to form various monomeric and polymeric species and transform into $Al(OH)_3$ [36]. The $Al(OH)_3$ flocs capture the dye molecules present in the solution by precipitation and adsorption.

An azo dye has been chosen for this study. This is because azo compounds constitute one of the largest classes of industrially synthesized organic compounds [37] and are extensively used as dye [38].

In this paper, the efficiency of electrocoagulation treatment using aluminum electrodes to remove azo-2-naphthol dye from solution has been studied. The effects of various parameters such as time of electrocoagulation, initial dye concentration and initial pH on dye removal efficiency have been appraised. Also, different integral linearized kinetic models have been investigated.

2. Materials and Methods

2.1. General

In this work, all chemicals and reagents used were mainly of analytical grade. The compound of interest [1-phenylazo-2-naphthol (PAN)] was obtained as previously prepared from our past work [39]. The Aluminium plates used were sourced locally and GW Instek model DC power supply system was employed to provide the required Direct current. The absorbance was measured from a UV-Visible spectrophotometer (UV-780c).

2.2. Preparation of Sample Solutions for Electrocoagulation

PAN was dissolved in ethanol to obtain the concentrations, 0.1 and 1.0 % (w/v). The solution was scanned through 200-800 nm wavelengths using UV-Visible spectrophotometer to obtain the wavelength of maximum absorption. The absorption maximum λ_{max} for the dye solution in ethanol was 400 nm.

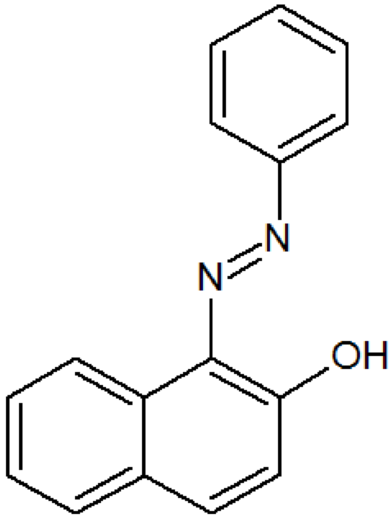
2.3. Electrocoagulation Procedures

The aluminum plates used were 12 x 4 cm in dimension. The two plates were placed 3 cm apart and immersed 5.5 cm into each sample solution (250 mL) contained in a 400 mL beaker. A magnetic plate stirrer with Teflon bar rotating at a velocity of 500 rpm was used to effect agitation of the solution throughout the duration of the experiment. The supporting electrolyte used in this experiment was sodium chloride (0.5 g). The Direct current (0.3 A, 24 V) was passed through the solution via the two aluminium electrodes. The measurement of colour of the dye samples before the electrocoagulation was done by means of a UV-Visible spectrophotometer, and at 15 minutes interval over a 2-hour period of electrolysis, aliquots of the solution (4 mL) were withdrawn, centrifuged and the absorbance of the supernatant solution measured at the wavelength corresponding to the absorption maximum for the dye solution. The resultant data obtained were used to construct electrocoagulation curves.

For pH studies, PAN was dissolved in aqueous ethanol (50% v/v) to obtain a concentration of 1.0 % (w/v). pH probe was inserted and the pH was adjusted to the required value (3-11) using 0.1 M HCl and 0.1 M NaOH for the acid and alkaline range respectively.

3. Results and Discussion

Electrocoagulation curves for 0.1 % (w/v) and 1.0 % (w/v) of PAN (1) in ethanol were plotted as a function of absorbance versus electrolysis time.



1

Compound (1). 1-Phenylazo-2-naphthol (PAN).

PAN coagulated rapidly within the first 15minutes of electrocoagulation in the solvent used. Such rapid electrocoagulation had been noted to occur with compounds having two adjacent phenolic hydroxyl groups which seem to be particularly prone to coagulation by a metal ion, probably by complexation [1]. PAN has similar arrangement suitable for coagulation by a metal ion. The position of the azo and hydroxyl groups is consistent with such observation and azo group has been known to possess excellent donor properties which enable them to be used in coordination chemistry [40]. This rapid coagulation was observed for both concentrations of PAN studied as shown in Fig. 1.

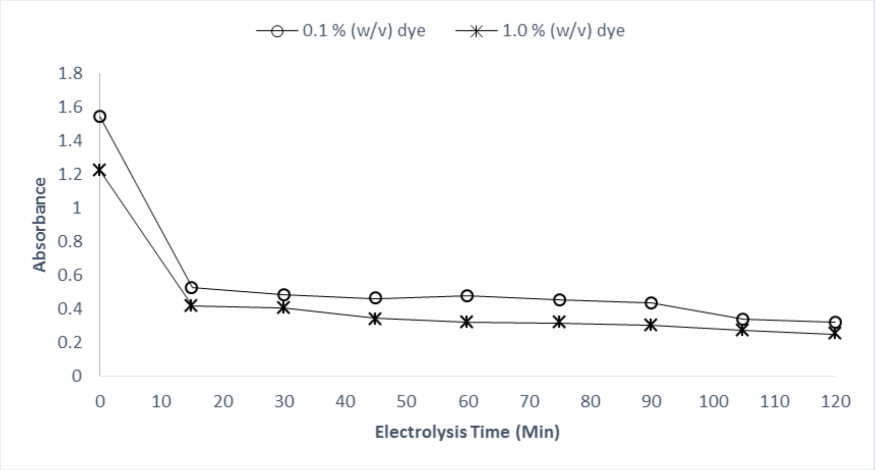


Fig. 1. *Plots of absorbance vs electrolysis time for 0.1 % (w/v) and 1.0 % (w/v) of PAN in ethanol.*

3.1. Effect of Electrocoagulation Time on Color Removal

Fig. 2 presents the relationship between colour removal efficiency and electrocoagulation time. The electrocoagulation time has influence on the colour removal efficiency of dye. Colour removal (%) was determined using the absorbance data according to Eq. (3) and this was plotted against electrocoagulation time.

$$\text{Colour removal (\%)} = (1\ \ A_t/A_o) \times 100 \qquad (3)$$

Where A_o and A_t are absorbance values at time zero and t (taken every 15 min) respectively. According to the results obtained, 66 % colour removal efficiency was achieved after the first 15 min of electrocoagulation time and after 120 min of operating time, about 77 % decolourization was achieved for PAN at 1.0 % (w/v) whereas for 0.1 % (w/v), 66 % decolouration was also obtained in the first 15 minutes and 73 % after 120 minutes of electrocoagulation time. The inability to achieve a decolourization efficiency greater than 90 % may be attributed to hydrogen bonding which may affect electrocoagulation process. PAN has substituents that are capable of hydrogen bonding especially with hydrogen bond donor (HBD) solvent such as ethanol. Significant contributions of hydrogen bond donor acidity (HBD) and hydrogen bond acceptor basicity (HBA) to solute-solvent interaction of PAN in ethanol had been evaluated [39].

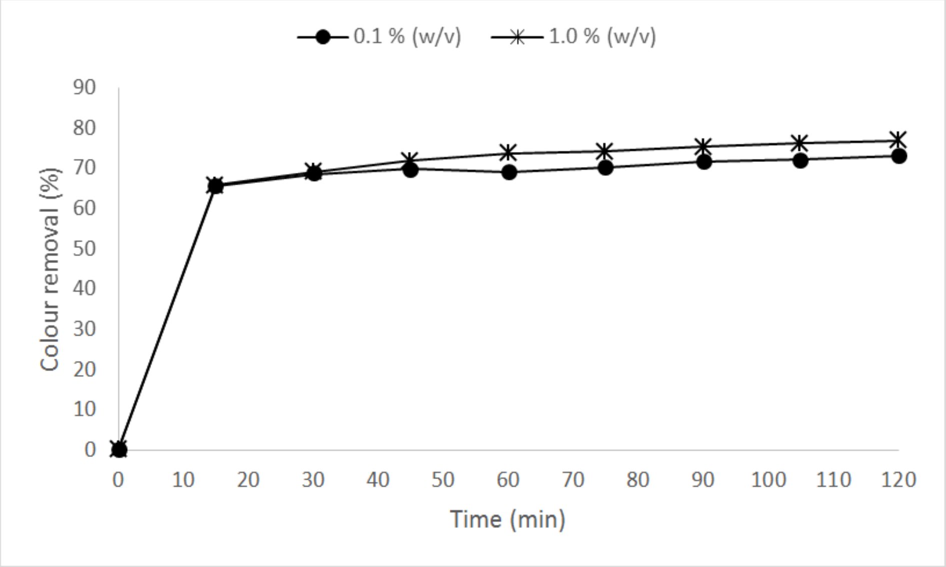


Fig. 2. *Effect of electrolysis time on colour removal efficiency.*

In order to understand clearly the colour removal efficiency of dye, the effective colour removal % (EC_R) was evaluated by subtracting the colour removal (%) between the time intervals (15 min). EC_R shows the percentage of dye colour that was removed in every 15 min and this is presented in Fig. 3. It can be seen that within the first 15 min interval, 66 % of the colour was removed. Subsequently, dye colour removal was very minimal from 3 % down to 0.62 % within the same time frame. This also shows that the amount of colour removed per 15 min interval was not constant throughout the electrocoagulation process.

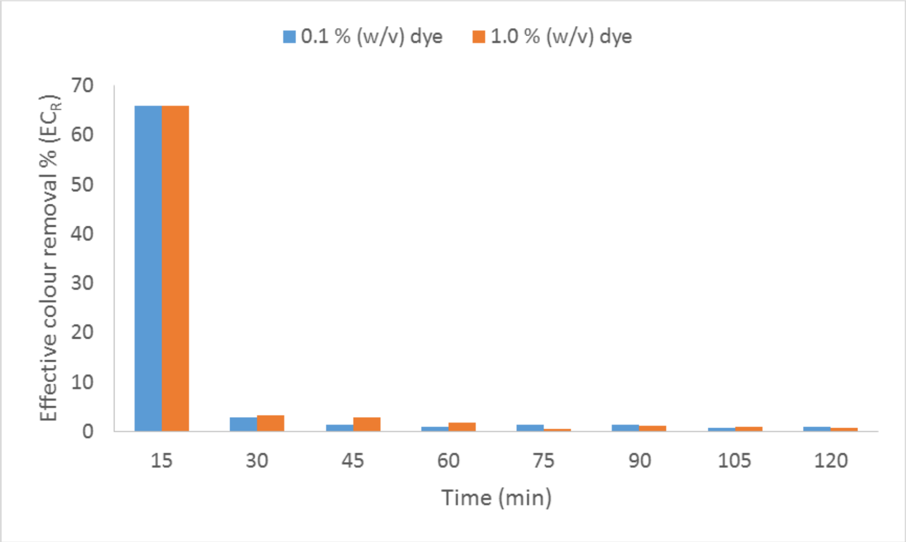


Fig. 3. *Effective colour removal % (ECR) of dye per 15 min interval at different concentrations.*

3.2. Effect of Initial Dye Concentration

The effects of initial dye concentration on the removal efficiency of colour with time are shown in Fig. 4. It can be seen that at 0.1 % (w/v) dye concentration, 65.78 % decolourization efficiency was achieved within the first 15 min compared to 65.85 % decolourization recorded for 1.0 % (w/v) of dye. A difference of 0.07 % in decolourization efficiency could be considered minimal during the first 15 min of operating time. But after 120 min of the operating time investigated for the electrocoagulation study, 77.02 % decolourization was evaluated for 1.0 % (w/v) of dye compared to 73.1 % for 0.1 % (w/v). A difference of 3.9 % efficiency in decolourization of dye is significant showing that the colour removal efficiency was higher for 1.0 % (w/v) initial dye concentration compared to 0.1 % (w/v) concentration, for all the time intervals evaluated.

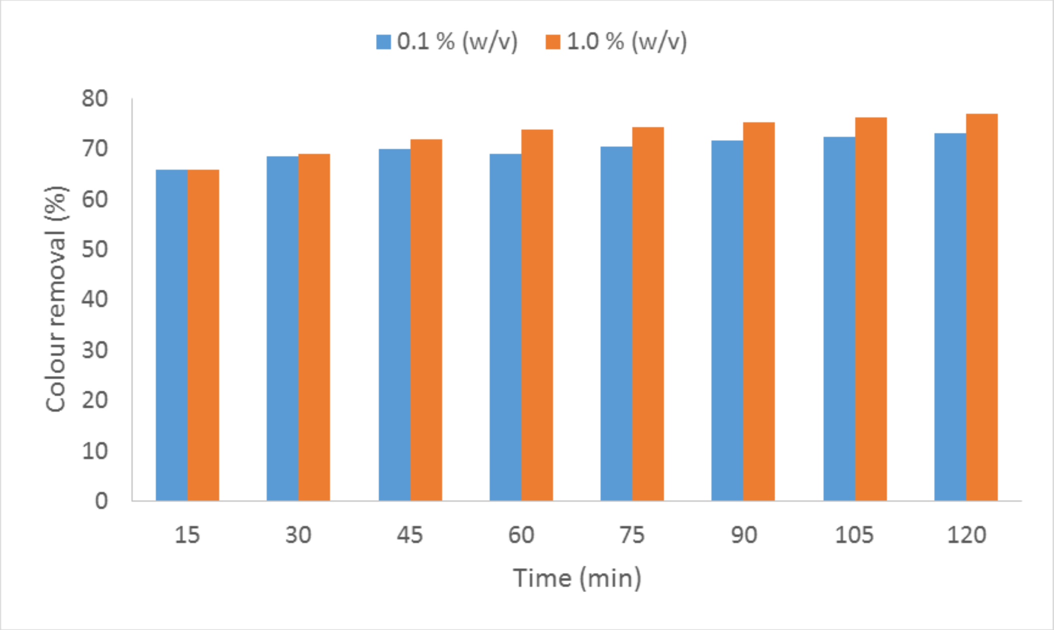
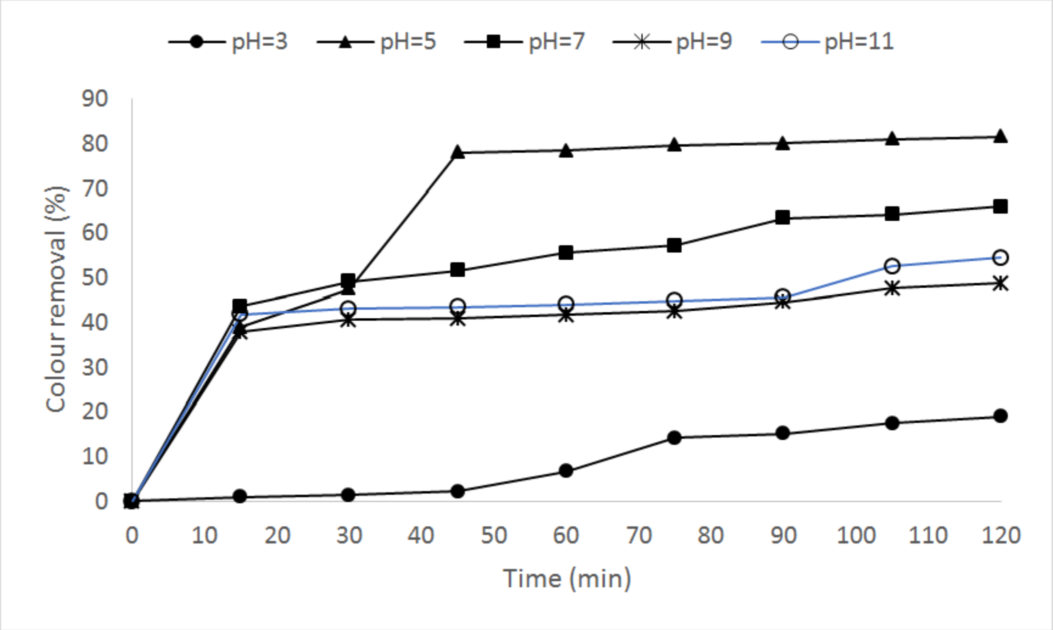


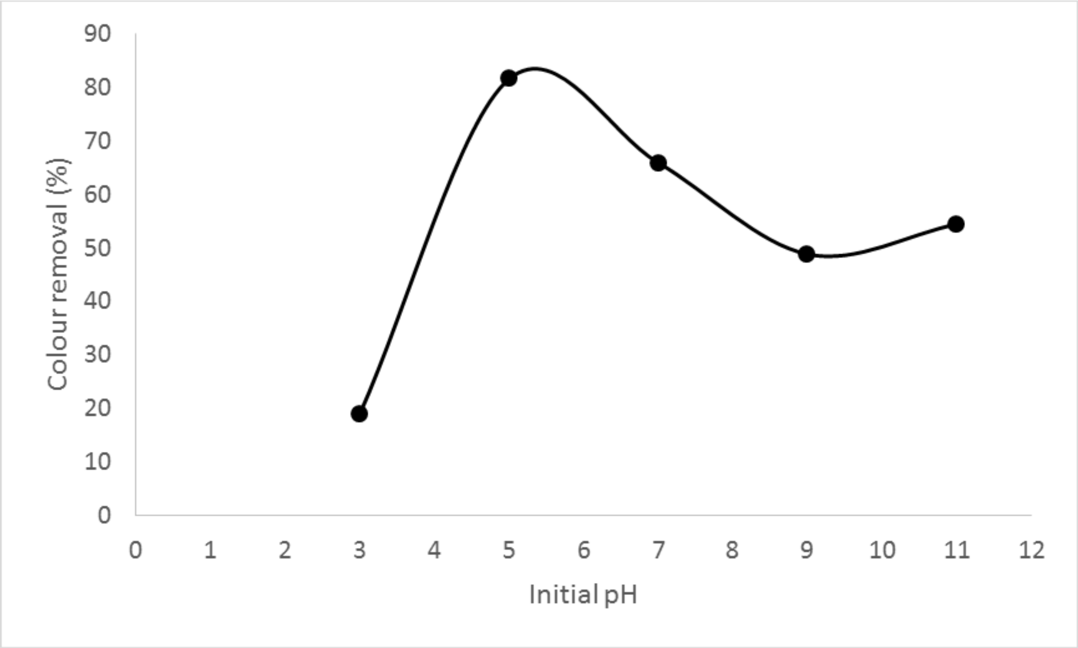
Fig. 4. *Effect of initial dye concentration on color removal efficiency.*

3.3. Effect of pH

The pH of the dye solution was adjusted using 0.1 M HCl and 0.1 M NaOH. In order to ensure complete solubility of the dye, instead of aqueous solution, 50 % (v/v) of aqueous ethanol was used. The dye concentration chosen was 0.1 % (w/v) and the electrocoagulation was studied between pH 3-11. Fig. 5a-5b shows the efficiency of colour removal at various initial pH. It is obvious that electrocoagulation was not effective at pH of 3 (19 % decolourization efficiency) while pH of 5 had the highest colour removal efficiency of 81 %, followed by pH of 7 with decolourization efficiency of 66 %. It can be seen from Fig. 5(b) that the optimum pH for the decolourization is 5.5. This is consistent with literature which showed that, the optimum pH for electrocoagulation with aluminum electrode is within the range of 5-6 [41]. The decolourization efficiency of dye depends on pH according to the order: 5 > 7 > 11 > 9 > 3.



5(a)



5(b)

Fig. 5. *Effect of initial pH on the colour removal efficiency of dye (a) plotted as a function of electrocoagulation time (b) plotted as a function of pH.*

The effective colour removal % (EC_R) was also evaluated for the decolorization of dye based on initial pH variation (Fig. 6). The results also confirm that the decolourization rate of dye is not constant throughout the period of electrocoagulation as indicated by the varying amount of colour removed per the same time interval. This could be explained considering the actual electrocoagulation process. The coagulant, $Al(OH)_3$ is formed as the reactants are generated, and new coagulants replace the existing ones after exhaustion or inactivation due to adsorption processes. These are time dependent processes that occur at variable rates. Hence, electrocoagulation rate is not constant and varying amount of dye colour is removed per time.

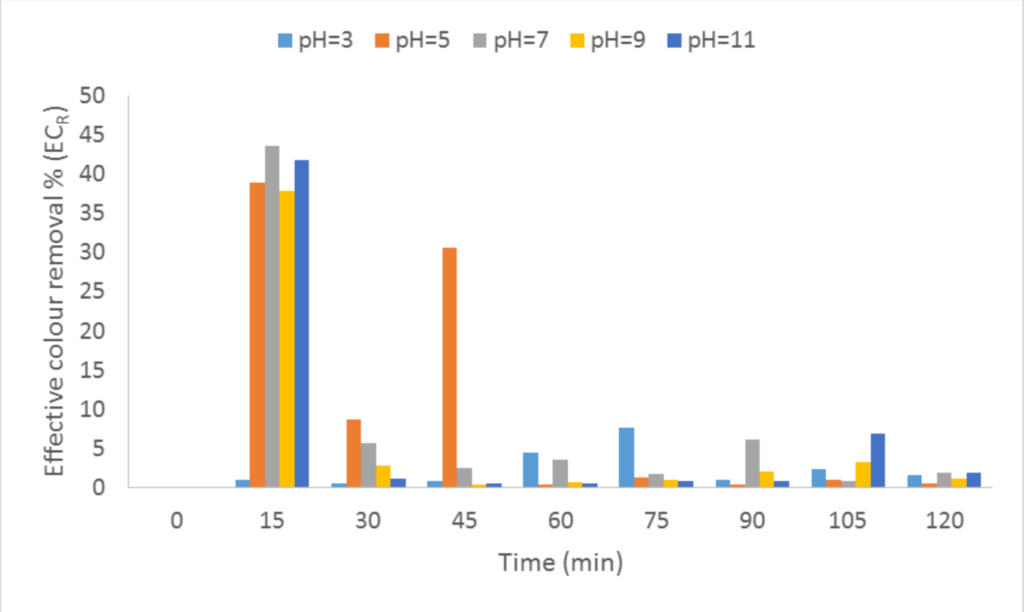


Fig. 6. *Effective colour removal % (EC_R) of dye per 15 min interval at different initial pH.*

3.4. Kinetic Modeling of Dye Colour Removal

The different integral kinetic models were employed to investigate the kinetics of dye colour removal. The kinetic mechanism for dye removal using electrocoagulation process is quite complicated. The first-order (Eq. 4), second-order (Eq. 5) and zero-order (Eq. 6) kinetic models were investigated.

$$ln(A_t/A_o)= - kt \tag{4}$$

$$(1/A_t-1/A_o)= kt \tag{5}$$

$$(A_t- A_o)= - kt \tag{6}$$

Where A_t is the absorbance at a time, t during electrocoagulation and A_o is the initial absorbance before electrocoagulation. k is the rate constant. The results of the plots (not shown) of $\ln(A_t/A_o)$ vs t, for Eq (4), $1/A_t-1/A_o$ vs t for Eq (5) and A_t - A_o vs t for Eq (6) did not yield a straight line graph from the origin. This shows that electrocoagulation process did not follow any of the linearized kinetic models presented above. Arslan et al [41] had similar results of non-validity of conventional kinetic model on a kinetic evaluation undertaken for color and COD abatement rates during electrocoagulation of simulated acid dyebath effluent using aluminum electrodes. Electrocoagulation process is more complicated to be described by a simple linearized equation. Other possibilities for non-validity of simple linearized kinetic models in describing electrocoagulation process maybe due to the fact that electrocoagulation curve can be divided into two possible linear portions: before coagulation point and after coagulation point (Fig. 1). The first-order kinetic model may be valid, as reported by other researchers [36, 42] for data taken before coagulation point. Once, the coagulation point is reached, simple kinetic models do not hold any longer. Therefore effective modelling of the kinetics of electrocoagulation should terminate at coagulation point. Beyond coagulation point, a different mechanism may occur. From this study, rapid electrocoagulation occurred which reached coagulation point within 15 min. The real kinetics of the dye removal can only be evaluated within the first 15 min. Attempt to model the whole electrocoagulation curve by single linearized form can only lead to error or oversimplification of the kinetic model.

4. Conclusion

Decolourization of a dye solution of azo-2-naphthol using aluminium electrodes was investigated in ethanol. The removal efficiency was greatly affected by the operating time, initial pH and initial dye concentration. Electrocoagulation was rapid, reaching coagulation point within 15 minutes. Decolourization efficiency up to 77 % was achieved. With the adjustment of initial pH, decolourization efficiency of 81 % in 50 % aqueous ethanol was achieved at pH 5 - 5.5. Increase in initial concentration of dye also increased the removal efficiency. The effective dye colour removal % (EC_R) was evaluated and this parameter indicates that the amount of dye removed per unit time was not constant. The electrocoagulation data could not be described by simple integral linearized kinetic models.

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