Photo-Electrochemical Treatment of Disperse Blue1 Dyes in simulated textile Effluent: Parameter Optimization Method

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ABSTRACT

In this present study, a hybrid technique consisting of Electrochemical and UV irradiation is applied simultaneously to degrade simulated dyeing wastewater containing Disperse blue 1 dye. Several operational parameters such as the effects of pH, current intensity, temperature, initial concentration, and kinetic of the dye concentration on treatment efficiency were studied.

The experimental results show that the decolourization rate of the wastewater is highest at low dye concentration consequent on the fact that it gave a percentage decolourization of 82.1 at a dye concentration of 25mg/L in a short time interval of 180 minutes. The influence of pH was also evaluated and the result showed higher efficiency of decolourization at alkaline PH. Similar evaluations were done for current and temperature. Finally, a comparative study was carried out to compare the efficiency of decolourization for a single electrochemical treatment, and the hybrid technique applied here. The result showed a relatively better efficiency of 89.1% for the photoelectrochemical technique compared to an88.7% for the electrochemical method.

Keywords: Graphite electrodes; Disperse blue1 dye; Photoelectrochemical degradation; UV-Vis Spectrophotometer

1. Background

Textile industries demand and consume large volumes of water and generate large quantities of coloured dye effluents as a result of processes that include pretreatment, dyeing, printing, and finishing [1–3]. Factually, most of the textile effluents are highly toxic and potentially carcinogenic and as a result, are considered a very serious threat to environmental safety and human survival. The treatment of wastewater contaminated with dye using various types of electrodes electrochemically or photo-electrochemically has been investigated and reviewed by many scientific research groups such as [4].

Disperse blue 1 which is the main focus of this paper is a dye derivative that finds application extensively used in the textile industry, cosmetics, leather dyeing, photography, and as a biological stain. The excessive applications that this dye derivative finds in the textile industries have informed and inspired our decision to study how it can be degraded photo-electrochemically to determine the optimal degradation condition, which is essential for any application process; to drastically reduce its environmental impact on man and plants.

The techniques for the removal of colour from wastewater contaminated with dye can be categorized into four: *Biological techniques*: decolourization by enzymatic processes, *Membranes*: reverse osmosis, Nanofiltration, etc., *Oxidationtechniques:* electrochemical oxidation, photo-electrochemical oxidation, ozone, etc., and *Physicochemical techniques*: ion exchange, coagulation/flocculation, etc [5]. The Traditional wastewater treatment technologies commonly used have proven to be markedly ineffective for handling wastewater of synthetic textile dyes because of the chemical stability of these pollutants [6].

The photo-electrochemical degradation of dye in wastewater can be considered a hybrid process because it combines the efficiency of ultraviolet radiation and the electrochemical process. Although there are many research reports on the electrochemical degradation of textile dyes in wastewater [7, 8], the photo-electrochemical treatment of wastewater contaminated with textile dye is still a novel methodology or treatment process [10].

The photo-electrochemical process is very efficient because it combines both the energy generated from the ultraviolet (UV) radiation and the electrodes to properly degrade the textile dye in the wastewater [5]. The efficiency of this process is dependent on consistent energy supply; this is the major drawback of this technique because its dependence on energy increases its cost. Above the inherent

drawback of this process stated above, it is still a preferable process because it does not generate pollutants and as a result is environmentally compatible [9, 10].

The mechanism of the photo-electrochemical process is based on oxidation which can either be direct oxidation that has to do with the reaction that takes place at the surface of the electrode immersed in the wastewater containing dye or the indirect oxidation that happens as a result of the actions of the molecules formed at the anode [11]. The mechanism of this process further elucidates its compatibility with the environment.

The hybridized treatment process which we refer to as photo-electrochemical process can easily be automated as reported by other authors [12], and very easy to comprehend because the energy generated by the electrodes in the wastewater containing dye, actually initiates the degradation of the dye. The UV radiation plays the role of degrading the halogenated organic compounds generated by the radicals formed as a result of the electrode surface reactions in the dye wastewater solution. This can also be considered as a setback of the electrochemical process since it doesn't incorporate UV radiation that further degraded the halogenated compound it forms.

Disperse Blue 1 is a blue to black [13] coloured amino-anthraquinone dye. Its IUPAC name is 1,4,5,8-tetraaminoanthracene-9,10-dione and the molecular Formula is ($C_{14}H_{12}N_4O_2$). The disperse blue 1 dye is based on anthraquinone ($C_6H_4(CO)_2C_6H_4$) [14] and the reason for its deep colour is because of conjugation. It has a lambda max(Wavelength of maximum absorption) of 615 nm [15] and a melting point of 331 °C [16]. Its structure is as shown below.
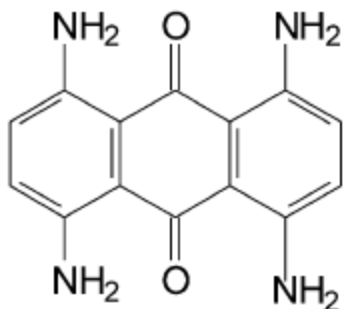

Fig. 1:   **Structure of disperse blue 1 dye**

Apart from the greater degradation efficiency that is obtainable in photo-electrochemical treatment, there is also a reduction in energy cost because both the photochemical and electrochemical process was done simultaneously thereby driving the cost of energy down and the extra labour of setting up another experiment to investigate photochemical efficiency on a dye using ultraviolet (UV) radiation.

This study concerns itself with the optimization of the photo-electrochemical process in the degradation of simulated disperse blue 1 dye (in a simultaneous process), as well as comparing its efficiency with that of the electrochemical process.

2. Materials and Method

All the chemicals used in the study were of analytic reagent (AR) grade. The Disperse blue 1 dye used in this study was obtained from Aldrich Chemical Company Ltd (USA).

2.1. Experimental Setup for PEO Process

The schematic diagram of the experimental setup is shown in Figure 2. The dye bath comprised of a 500 ml capacity glass beaker which served as the reservoirfor the prepared dye. A 30v/5A DC power supply was used. The main component of the experimental setup is the electrochemical reactor. It consists of two flat graphite electrodes of dimensions (7 cm x 3 cm x 0.2 cm) which were both used as theanode and cathode; both kept at4 cm apart. Holes of the sizes of the electrode are bored on a PVC lid to hold the electrodes rigidly in a fixed vertical position. Morealso, a sizable spherical hole is drilled on the lid to allow for the penetration of UV light irradiation and periodic collection of samplesduring the process. A magnetic stirrerwas used for stirring the solution, and the experiment was conducted in a UV chamber to minimize energy loss.
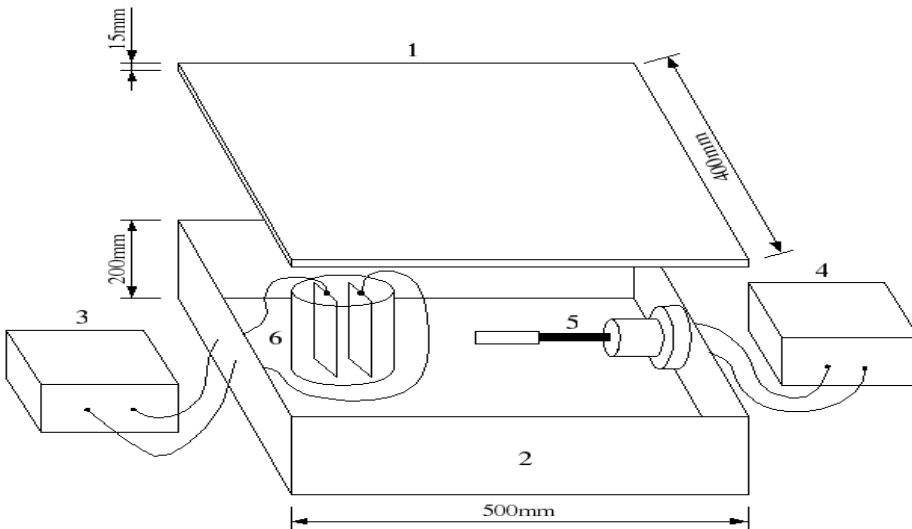
Fig. 2: Schematic photochemical and photoelectrochemical system: 1,2– box, 3 potentiostat, 4 – lamp reactor, 5 - ultraviolet lamp (125 W), and 6 - quartz cell with or without DSA electrodes.

As stated previously, a simulateddyebath effluent was prepared in the laboratory in distilled water at 1000 mgL^{-1}of the dyestuff. From this effluent various concentrations25, 75,120 mg/l of the same dye, were subsequently generated using the appropriate dilution technique. To enhance the conductivity of the effluent, 10 ml of 0.05 mol L^{-1}NaCl was prepared and added as a supporting electrolyte to simulate the conductivity of industrial effluent. The mixture was allowed to equilibrate and degas for 10 min, with the use of the magnetic stirrer. With the aid of a DC supply, the current passed through the mixture was regulated while a voltage of 5.0V was maintained. The pH of theeffluent was adjusted to pH 4, 7, and 9 by using either of 1 M HCl or 1 M NaOH respectively, and it was measuredby using pH meter.

2.3. Analytical measurements

UV–Vis analysis: UV-Vis experiments were carried out using Varian UV-Vis-NIR-500 spectrophotometer. Untreated and treated effluents were analyzed by the UV – Vis spectrophotometer. The spectrophotometer was used together with a cell with a 1 cm optical path length to measure the UV spectra.

Decolourization measurements

 The absorbance was measured at the visible maximum dye absorption wavelength (615 nm for Disperse blue 1 dye). The selection of maximum wavelength in the spectrum was made during the course of preparing the calibration curve for the dye

samples. Samples were collected each 30min during the combined photoelectrochemical treatment, and the decolourization was reported in percentage.

Colour removal was calculated by using the following formula (1) [22]:

$$\text{Color Removal (\%)} = \frac{Abs_i\text{-}Abs_f}{Abs_i} \times 100 \qquad (1)$$

where Abs is the average of absorbance values as it is maximumabsorbency visible wavelength. Abs_{i} $_{the}$ value before electrolysis, Absf the value after electrolysis.Figures 5, 6, and 7 show the percentage ofcolour removal with respect to time.

2.4 Kinetic Evolution

In accordance with previous studies, the degradation of the dye with the photoelectrochemical treatment follows a first-order reaction.The plot**ln [Abso/Abst]** versus **time** for Disperse blue 1 dye was linear assuming that the degradation reaction approximately follows the first-order kinetics. It is to be noted that $K_d$is an implicit value. The decolourization rate constants (K_d) were calculated from the slope of semilogarithmic absorbance values rate *versus* exposition time (t) or charge (Q), following the kinetic Equations (2):

$$\text{In } \frac{Abs_i}{Abs_f} = k_d \times t \qquad (2)$$

3. Results and Discussion

3.1 Effect of initial Dye concentration

Figure 3 shows the trend of decolourization of the Disperse blue 1 dye at different initial concentrations over time. The voltage and current intensity of this experiment were maintained at 5.0V and 1A respectively. It was found that the lower the initial concentration, the higher the decolourization rate was. The 25

mgL dye sample experienced the highest decolourization than the 75 mgL and 120 mgL samples. This is because, as the amount of dye material increases, the amount of unit electrode treatment increases. However, more organic molecules cover the anode surface and are not conducive to the production of ·OH, so the degradation efficiency will be reduced [17].

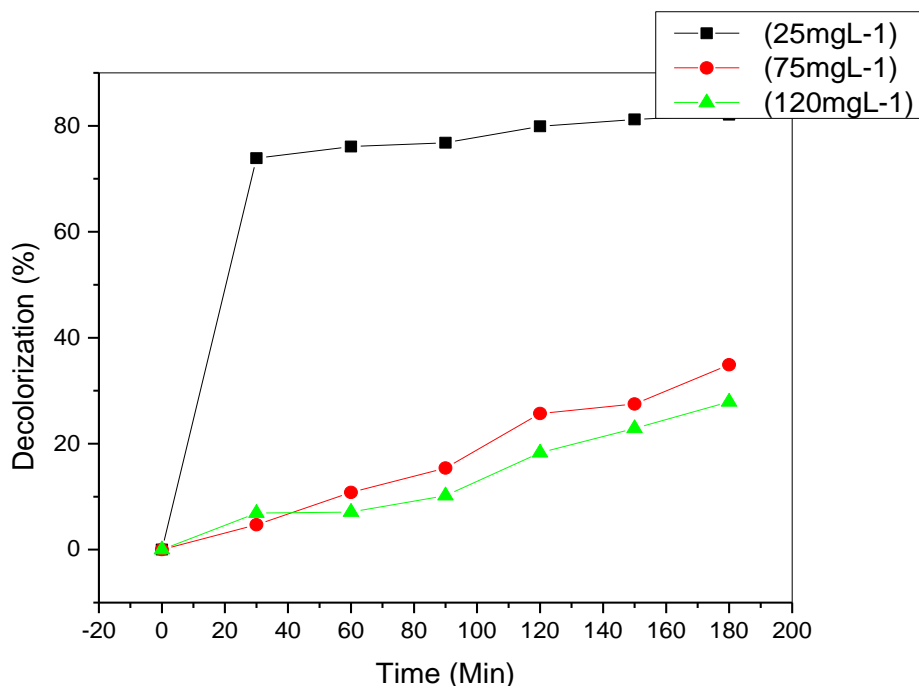**Fig 3:** Comparison of % decolorization for three initial concentrations (25, 75 and 120 mgL^{-1}

3.2 Effect of pH value

Figure 4 shows the decolourization rate of the Disperse blue 1 dye effluent at 3 different pH conditions (4, 7, 9). Although they all appear to show a low rate of decolourization because of the low current intensity and the stable nature of the

dye structure, it can be seen from the figure below that the variation of the pH did have a significant effect on the colour removal process. In addition to the relatively higher percentage, decolourization at pH 9 compared to pH 7 and 4; we also notice a higher decolourization rate for alkaline condition, than in the acidic and neutral conditions. The reason may be that the stronger the alkalinity condition is, the stronger the hydroxyl radical is,the higher the oxygen evolution potential is, More also, the presence of a large amount of OH- in alkaline conditionsfavours the formation of hydroxyl radicals, which are the major oxidants in charge of degrading the dye.
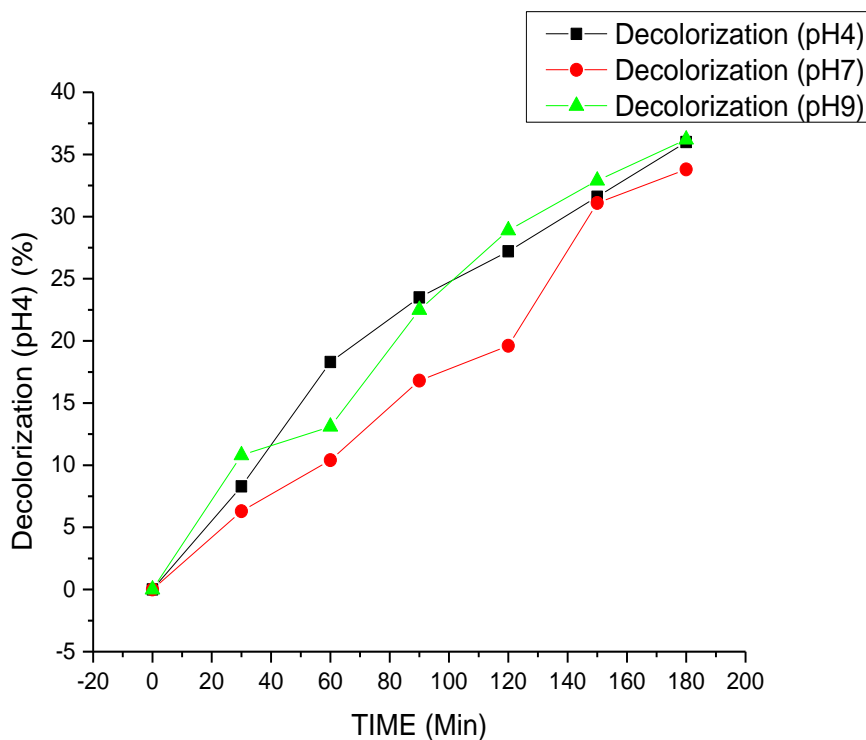

Fig. 4 Effect of pH on the % removal of Colour (decolorization) of 25mgL^{-1}disperse blue dye (1 A, 5 V, Conc. NaCl; 0.05molL$^{-1)}$.

3.3 Effect of current intensity

Figure 5 shows the change tendency of the decolourization rate of disperse blue 1 at varied current intensity (1A and 3A). it can be seen from the figure that contrary to the decrease in colour removàl observed in the photoassisted electrochemical batch process, there is a conversely increase in colour removal with high current intensity. This is so because the overpotential of the electrode increases with increased current intensity thereby generating more chlorine/hypochlorite that effects the decolourization. More also, there is little or no formation of organic halogenated compounds in the effluent as a result of simultaneous UV irradiation and electrochemical treatment.
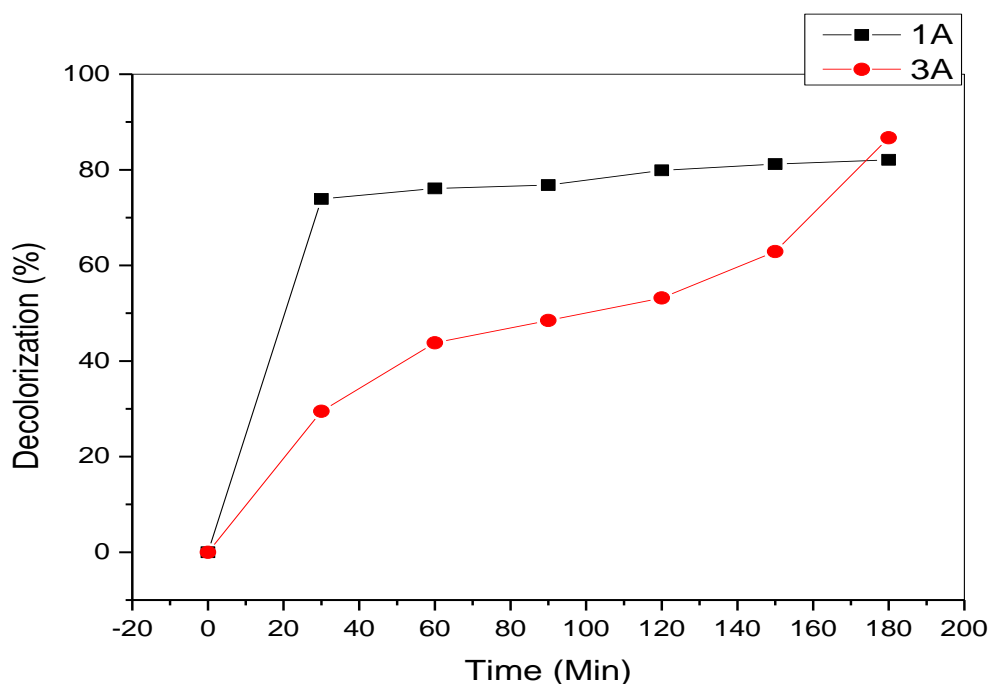

Fig.5 Effect of current intensity on the % decolorization for the same concentration of dye (25 mgL^{-1}, 5 V, NaCl conc. 0.05M)

3.4 Effect of Temperature

As shown in figure 6, the colour removal efficiencies at different temperatures were studied. The maximum colour removal efficiency at 25^0C and 50^0C after 180 minutes was obtained to be 43.6% and 46.7% respectively. It was clearly observed that the percentage decolourization gradually increased with increasing simulated effluent temperature. From the results, it can be deduced that, apart from pH, current intensity, kinetics, and initial concentration popularly reported by many authors such as [18, 19, 20,], the temperature of the reaction also contributes to the percentage decolourization of the disperse blue 1 dye effluent. This increase in the percentage decolourization observed can be ascribed to the effect of the UV light in the hybrid process that acts to prevent the formation of halogenated intermediates in the treated effluent during the degradation process.
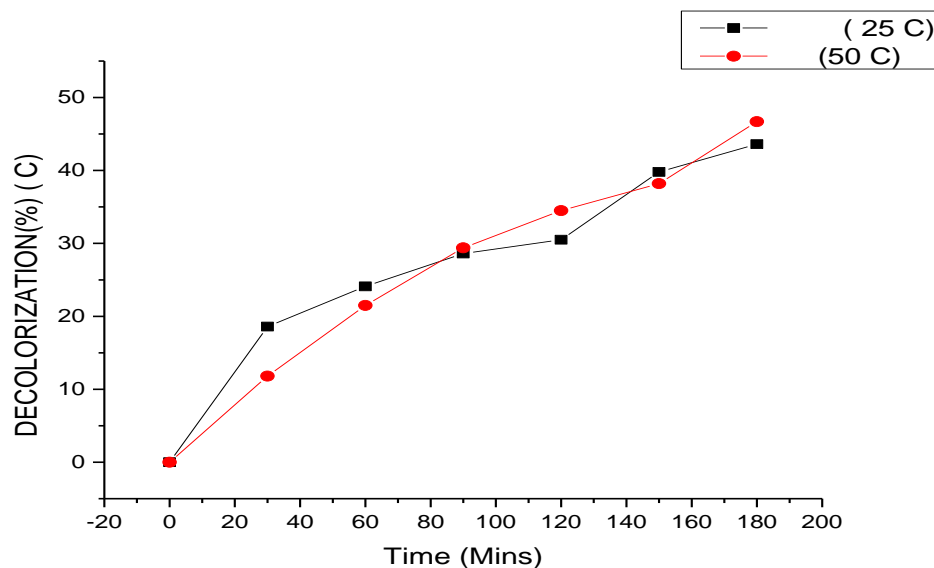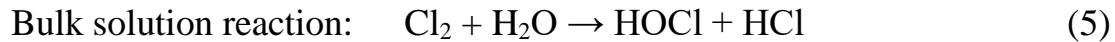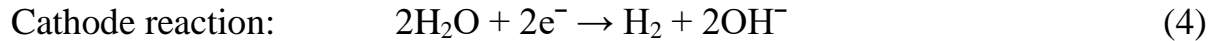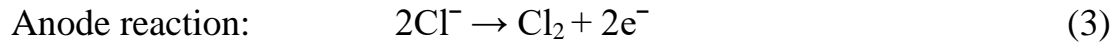

Fig. 6: Effect of temperature on the % removal of Colour (decolorization) for the same concentration of dye (25mgL^{-1} ,1A , 5V, NaCl conc. 0.05M)

3.5 Comparative study of electrochemical and photochemical technique

Fig 7 compares two investigated experimental degradation processes- the electrochemical and the photoelectrochemical process, all carried out under the same experimental conditions. The former which occurs in the absence of UVlight irradiation shows only 88.7% colour removal after 3 hours of mineralization. The photoelectrochemical process, on the other hand, shows a higher efficiency of colour removal of 89.1%. The lower efficiency of the electrochemical process stems from the relatively smaller amount of oxidizing agents present in the degradation process. Electrochemical oxidation takes place with the help of various oxidants such as nascent oxygen, ozone, hydrogen peroxide, free chlorine, and free radicals such as OH_, ClO, and Cl.

The possible mechanism of electrochemical degradation is given below:

Anode reaction:	$2Cl^- \rightarrow Cl_2 + 2e^-$	(3)
Cathode reaction:	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	(4)
Bulk solution reaction:	$Cl_2 + H_2O \rightarrow HOCl + HCl$	(5)
	$HOCl \rightarrow H^+ + OCl^-$	(6)

The presence of salt in the dye effluent results in the formation of hypochlorite. Moreover, HOCl and hypochlorite ions also combine to form chlorate. This reaction decreases the efficiency of colour removal in an electrochemical oxidation process.

However, with the photoelectrochemical process, the UV treatment achieves the decomposition of the small amount of halogenated compounds generated during the electrochemical treatment.
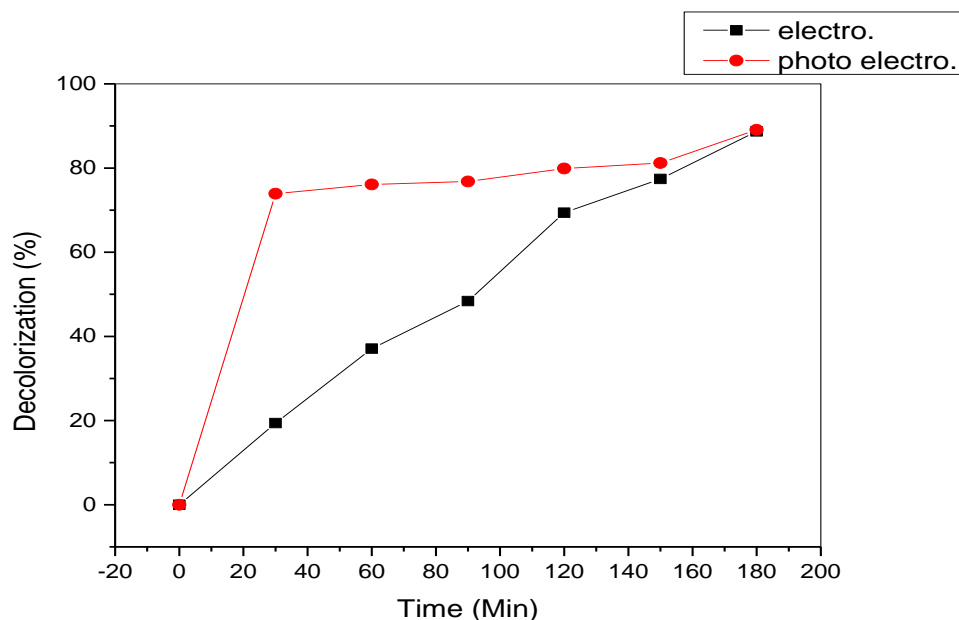
Fig. 7: comparison between electrochemical and photoelectrochemical technique for25 mgL^{-1} disperse blue dye under the same experimental conditions (1 A, 5 V, Conc. NaCl; 0.05molL^{-1}).

3.6 Decolorization kinetics evolution

In the dye decolourization process, it is the cleavage or breakage of the anthraquinone group that eliminates the colour present in the dye. The primary cause of the colour of a dye in the presence of conjugation. From the effect of concentrations of 25, 75, and 120mgL^{-1} on the treatment process; the 25mgL^{-1} had the highest absorbency which implied that it had the highest decolourization. The plot of the kinetic constants (k_d) against time (t) for 25mgL^{-1} led to the observation that the photo-electrochemical treatment of the Disperse blue 1 dye follows a pseudo-first-order reaction which implies the first-order law with respect to the dye concentration. This is in affirmation with the work of other authors (s). The kinetic constant of the decolourization was calculated at a varied reaction time interval to determine the efficiency of the photo-electrochemical treatment technique on the dye.
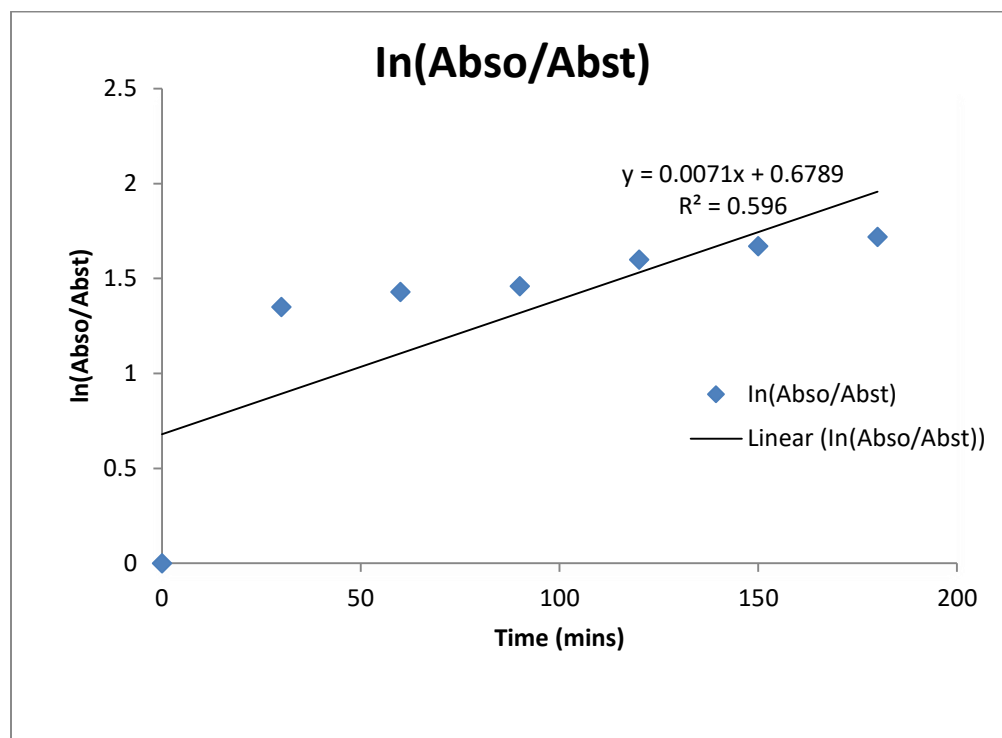
Fig. 8: The representation of ln (Ao/At) *vs.* time (Figure 1a) showed that in the studied case, the dye degradation follows first-order reaction kinetics.

4. Conclusion

Photo-electrochemical degradation of Disperse Blue 1 dye was investigated using graphite electrodes and sodium chloride as a supporting electrolyte. The operating parameters such as pH, temperature, current intensities, and initial dye concentration were studied in a goal to optimize these parameters efficient degradation of the aforementioned simulated dye effluent.

With a reaction condition involving a very small amount of dye concentration, supporting electrolyte, current intensity, applied voltage, and long reaction time duration; the decolourization kinetic constants values (k_d) increased with time, evidenced that the treatment process is a first-order reaction and decolourization percentage of 82.1 was achieved at 25mg/L. This informs that the lower the dye concentration the higher the percentage decolourization.

The consistent stirring of the effluent promotes the degradation rate by moving the dye molecules to the electrode surface so that the hydroxyl radicals generated at the electrode interface can reactively interact more randomly and efficiently with the dye in the wastewater.

It is evident that the hybridized photo-electrochemical process which involves using UV irradiation and electrochemical treatment simultaneously is a better technique for the removal of reactive blue 1 dye in wastewater from textile industries because it is both economical, eco-friendly and efficient.

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