Int. J. Electrochem. Sci., 11 **(2016)** 1883 - 1897

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Decolourization of Reactive Blue 19 Dye Effluents by Electrocoagulation in a Batch Recycle New Electrochemical Reactor

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Received: 22 October 2015 / *Accepted:* 19 December 2015 / *Published:* 1 February 2016

The efficiency of electrocoagulation to treat reactive blue 19 dye effluent was investigated, using a recycle batch reactor with aluminium electrodes. A new cell arrangement was suggested where the anode consisted of an array of horizontal aluminium cylinders embedded between an upper and a lower aluminium screen cathode. An advantage offered by the horizontal tubes used as anode is the possibility of using the inner side of these tubes as a heat exchanger to control the reaction temperature if needed. Different operating parameters, affecting the efficiency of color and COD removal, such as current density, flow rate, initial dye concentration, electrolyte concentration and pH were studied. Increasing the current density and the electrolyte concentration increased the color and COD removal. Inversely, a higher flow rate and a higher initial dye concentration decreased the removal rate. The pH of the waste needed to be neutral or nearly neutral to accomplish a high efficiency. A color removal of 97.4% and COD removal of 93% were achieved under optimum operating conditions. Electrical energy consmption ranged from 1.08 to 33.4 kWh/kg dye removed depending on the operating conditions.

Keywords: Reactive blue dye 19, electrocoagulation, wastewater treatment, batch recycle reactor.

1. INTRODUCTION

In view of the increasingly stringent environmental policy adopted by industrialized countries, a greater care has been directed to treating waste water. Significant amounts of water are consumed during processing in many industries using dyes as textile, paper, plastic, leather, food and cosmetics industries. 1-15% of the dye is estimated to be lost in dyeing and finishing processes and are released into waste waters. About 10,000 dyes and pigments are used in the textile industry, most of them are toxic substances to humans and aquatic life; 50,000 tones of dyes are estimated to be discharged from dyeing and coloration industries. One of the main sources of environmental contamination is the dye pollutants from these industries, the disposal of these colored waste waters is a threat to the environment [1-5].

Color bath effluents throw shading to the recieving streams. Shading interfers with entrance of daylight into waters, impedes photosynthesis, hinders the development of oceanic biota and interfers with gas solubility in water bodies. Besides, the waste may contain chemicals which are dangerous, cancer-causing, mutagenic, or teratogenic in different microbilogic, fish species [6].

Numerous methods to remove dyes from colored effluents are available: adsorption, precipitation, chemical degradation, photodegradation, biodegradation, chemical coagulation and electrocoagulation. The efficiency of adsorption and precipitation is limited, though they are time-consuming and costy; activated carbon is the most widely used adsorbent for the decolorization of colored effluents but it is too expensive. Chemical degradation using oxidants such as chlorine and ozone is the most effective but it produces very toxic products as the organochlorine compounds in case of chlorine; and in case of ozone a large dose is required which is economically infeasible. Photooxidation using UV/H2O2 or UV/TiO2 causes secondry pollution through the chemicals it uses. The least effective is the biodegradation due to the toxic effect of dyes on the bacterial development. Chemical coagulation is not highly recommended since it causes extra pollution due to side reactions and large amounts of sludge [3,7-11].

Developing more efficient and lower cost techniques for wastewater treatment became vital day after day; these techniques need to be of reduced chemical and energy consumptions, as well as of reduced installation space when high land price is taken into account. Among the developing technologies, electrocoagulation is one that received attention from the scientific community during last years [12-14]. It was proved as an effective method for the treatment of wastewater. It was tested successfully for the treatment of municipal wastewater, textile wastewater, poultry manure wastewater, landfill leachate, rose processing wastewater, chemical mechanical polishing wastewater, oily bilgewater, heavy metal contaminated groundwater, restaurant wastewater, dyeing wastewater, olive oil mill wastewater, and paper-recycling wastewater [15].

The electrocoagulation procedure is broadly acknowledged to deliver less sludge than the traditional coagulation process. From the perspective of reasonable advancement, electrocoagulation is ecologically friendly in light of the fact it does not create additional toxins in the water, for example, sulfate or chloride particles [4]. Also, the energy source for the process can be a solar photovoltaic panel that converts solar energy into direct electric current [16]. Furthermore, the energy consumption of the electrocoagulation cell can be reduced by collecting the hydrogen produced during the treatment [17].

The aim of the present work is to examine the performance of a new electrocoagulation cell design in treating the harmful coloured wastes. The cell uses an anode made of an array of horizontal tubes placed between two horizontal screen cathode to ensure uniform current distribution on the anode. The suggested new cell design has numerous advantages: i) the tubes can be used as a heat exchanger, as a cooling fluid can be passed inside to absorb heat in case of exothermic reactions, ii) H_2 gas bubbles evolve at the lower screen cathode which improves the mixing conditions and hence the mass transfer, iii) the turbulence generated downstream the lower cathode screen yields better mixing conditions. The effect of different operating parameters, namely: current density, flow rate, initial dye concentration, pH and sodium chloride concentration on reactive blue19 dye removal and on the COD reduction was studied.

Reactive blue 19 (RB 19) textile dye is easily available and commonly used. Researchers are concerned with mutagenic properties of RB 19 due to the presence of electrophilic vinyl sulfone groups [18]. Fig (1) shows the chemical structure of the dye and table 1. illustrates the general properties of the dye.

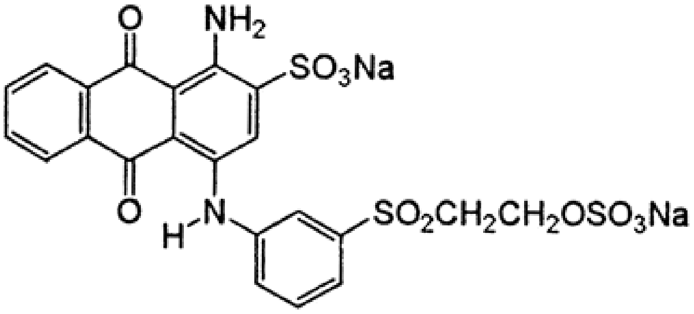

Figure 1. Chemical structure of Reactive blue 19 dye.

Table 1. General properties of reactive blue 19

Property	Value
Commercial Name	Ariazol Brill, Blue R-SP
C. I. number	61,200
Chemical Formula	$C_{22}H_{16}N_2Na_2 O_{11}S_3$
λ_{max} (nm)	594
Molecular Weight (g/mol)	626.54

2. EXPERIMENTAL PART

Fig 2. shows the electrocoagulation unit used in the experiments. The electrocoagulation unit consisted of a plexiglass square tank, 12 cm x 12 cm with 15 cm height. The anode consisted of 4 cylindrical aluminium rods of diameter 1.6 cm and length 12 cm; the aluminium cylinders were located between two aluminium screens (mesh number 10) working as cathode. The distance between each Al screen and the Al rods was fixed at 0.5 cm; the distance between rods was 1.4 cm; the distance from the rods center to the bottom of the cell was 7.5 cm.

The electrical circuit consisted of 20V dc. power supply with a voltage regulator, a multirange ammeter, all connected in series with the cell, a voltmeter was connected in parallel with the cell to measure its voltage.

The reactive blue dye 19 (RB19) was supplied by Sigma-Aldrich, the synthetic wastewater was prepared by dissolving RB19 in distilled water. The dye concentration was determined by using UV/Vis spectrophotometer (UNICO®1200) at 592 nm.

The HCl and NaOH used to adjust the pH were of AR grade; pH measurements were carried out using HANNA digital pH meter (3015pH meter).

COD was measured using COD reactor (HI839800, 2008 series) and multiparameter bench photometer for laboratories (HI83099).

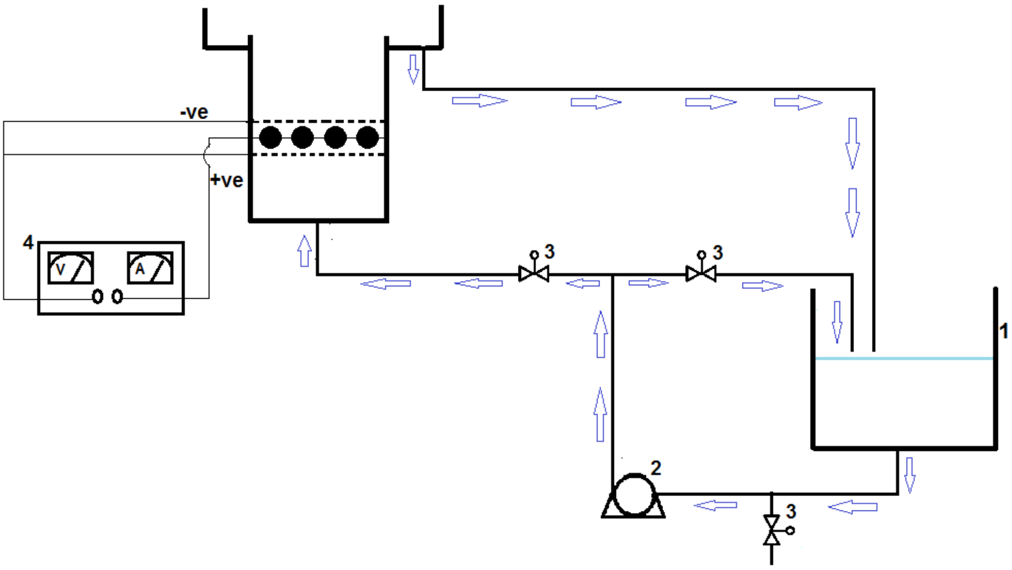

Figure 2. Electrocoagulation unit 1. Storage tank 2. Centrifugal pump 3.Valve 4. D.C power supply 5. An aluminium screen cathode 6. An array of aluminium cylinders (anode)

3. RESULTS AND DISCUSSION

Electrocoagulation (EC) involves many chemical and physical steps that use sacrificial electrodes to supply ions into the wastewater. In an EC process the coagulant is produced ‘in situ’ and it involves three successive stages: (i) formation of coagulants by electrolytic oxidation of the electrode, (ii) destabilization of the contaminants, particulate suspension, and breaking of emulsions and (iii) aggregation of the destabilized phases to form flocs [19].

The most widely used electrode materials in EC process are aluminium and iron.

In the case of aluminium, main reactions are

Anode : $Al \rightarrow Al^{3+}+3e$ (1)

Cathode : $3H_2O+3e^- \rightarrow 3/2\ H_2 +3OH^-$ (2)

Ions generated by electrode reactions (1) and (2) react to form various monomeric species such as $Al(OH)^{2+,}$ $Al(OH)_2^+$, $Al\ _2(OH)_2^+$, $Al(OH)_4$, and polymeric species such as $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$,

$Al_8(OH)_{20}^{4+}$, $Al_{13}O_4(OH)_{24}^{7+}$, $Al_{13}(OH)_{34}^{5+}$, which transform finally into $Al(OH)_3(s)$ according to complex precipitation kinetics. Freshly formed amorphous $Al(OH)_3(s)$ have large surface areas which is beneficial for a rapid adsorption of soluble organic compounds and trapping of colloidal particles. Finally, these flocs are removed easily from aqueous medium by sedimentation or H_2.

The perfromance of the suggested cell was evaluated for the removal of blue reactive dye and the studied parameters were namely: the current density, the solution flow rate, the initial dye concentration, the electrolyte concentration and the pH.

3.1. Effect of current density

Current density is a dominat parameter in electrocoagulation since it determines the coagulant production rate and controls the rate of gas bubbles formation and their size thereby controlling the flocs growth [2]. To sudy the effect of current density on the color removal efficiency, four different values of current density were used; best color removal was met with the highest current densiy used as depicted in fig (3).

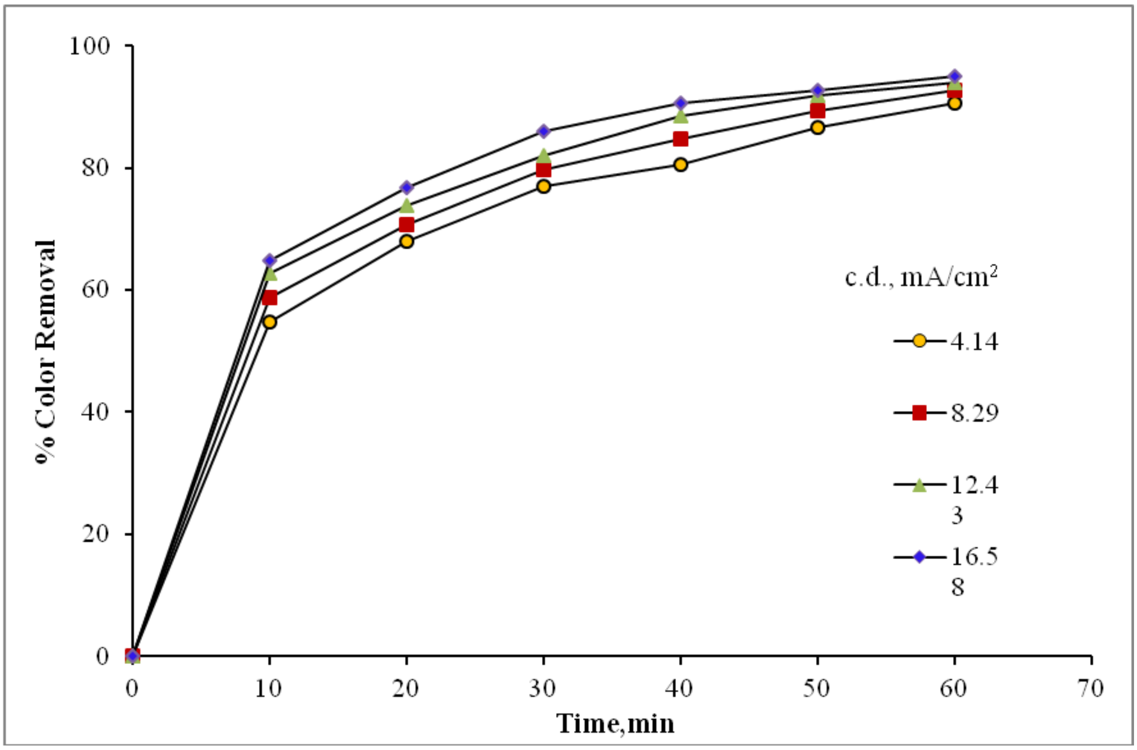

Figure 3. The effect of current density on the color removal efficiency (C_o=50 mg/L; pH=7.75; NaCl Conc.=1g/L; flow rate=1146 mL/min, T=25±2°C)

This result may be explained through the following facts: (i) According to Faraday's law, increasing the value of the current increases the concentration of Al3+ .

$$m=QM/FZ \tag{11}$$

where: m is the mass of the substance liberated at an electrode in grams; Q is the total electric charge passed through the substance; F = 96485 C mol−1 is the Faraday constant; M is the molar mass of the substance; z is the valency number of ions of the substance (electrons transferred per ion).

(ii) The number of small sized H2 bubbles is increased with a consequent increase oftheir floating ability of the electrocoagulated dye to the solution surface [20–23] (iii) The small sized rising H2 bubbles may enhance the rate of mass transfer of Al3+ from the anode surface to the solution bulk; this tends also to eliminate anode passivity [20] which decreases the efficiency of the process.

The same positive behavior of increasing the current density was observed when measuring the %COD removal as shown by Figure 4.

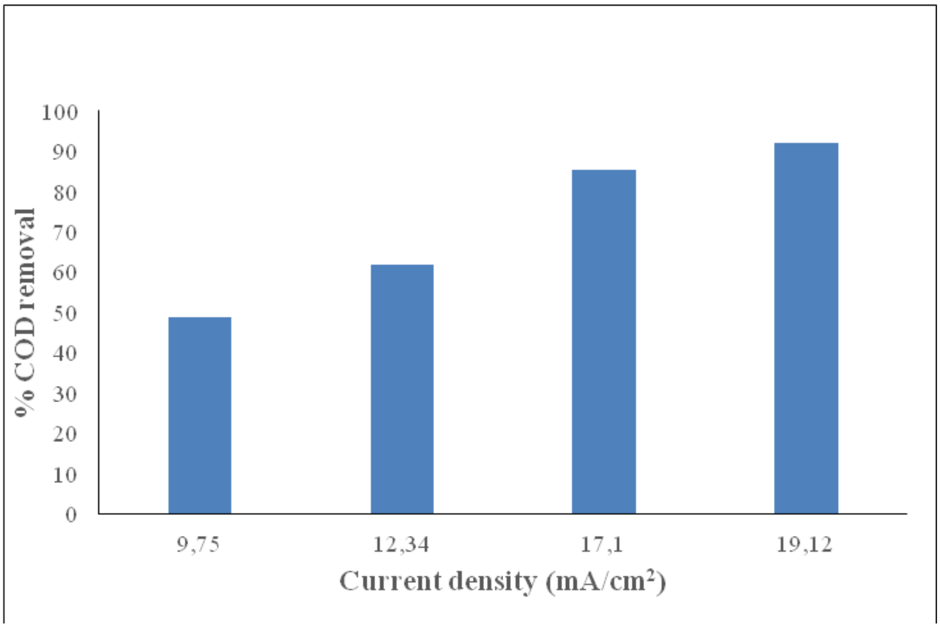

Figure 4. The effect of current density on the % COD removal (C_o=50 mg/L; pH=7.75; NaCl Conc.=1g/L; flow rate=1146 mL/min, T=25±2°C)

However, adverse effects like heat generation or excessive oxygen evolution at the anode may arise in case of high current so it is advisable to limit the current density to the present value [21].

3.2. Effect of solution flow rate

The effect of flow rates on the rate of the dye removal was studied in order to examine the performance of the present cell in case of continuous operation.

The experiments were carried out at 390, 540, 870 and 1239 mL/min with 50 mg/L dye concentration to investigate the effect of the solution flow rate. A constant current density of 16.58 mA/cm^2 was applied in each case; the initial pH was maitained at 7.75 and NaCl concentration was 1 g/L. The removal efficiency as function of flow rate is shown in Figure 5. It was noted that the removal efficiency decreased from 95.1% at 390 mL/min to 90% at 1239 mL/min.

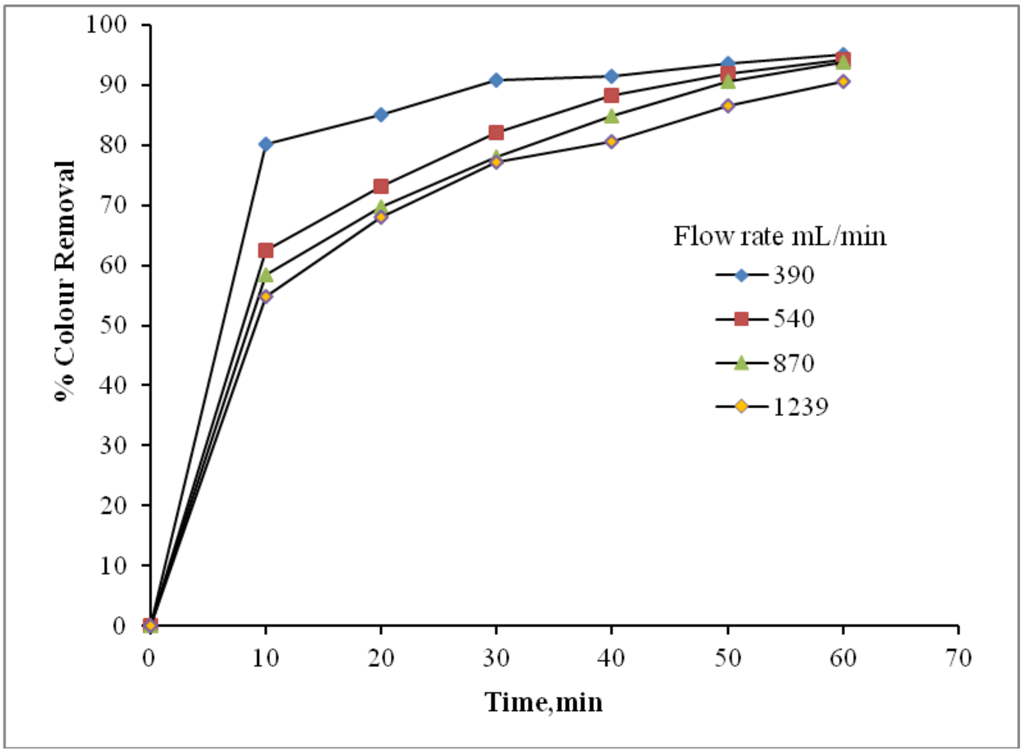

Figure 5. Effect of flow rate on the % color removal (c.d = 16.58 mA/cm^2; Co=50 mg/L; pH=7.75; NaCl Conc.=1g/L;, T=25±2^{o}C)

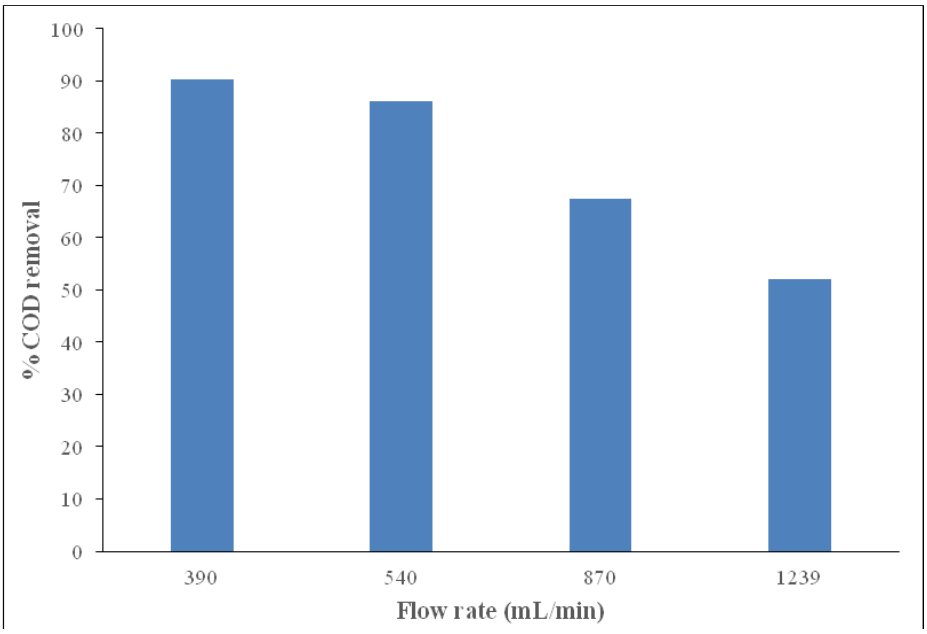

Figure 6. Effect of flow rate on the % COD removal (c.d = 16.58 mA/cm^2; Co=50 mg/L; pH=7.75; NaCl Conc.=1g/L;, T=25±2^{o}C)

Increasing the flow rate decreases the residence time and hence the formed coagulant can not achieve a high removal degree. Longer holding time, corresponding to lower flow rate, means that the untreated dye solution remains in the electrocoagulation cell for a longer time period, which in turns provides more time for the reaction. The decrease in the % dye removal rate with increasing solution flow rate is also attributed to the fact that high flow rates tend to disperse the electrocoagulated dye. Accordingly low flow rates are recommended in the continuous operation of the present cell in order to increase the residence time and hence the % of dye removal and to avoid the adverse effect of dispersing the electrocoagulated dye which takes place at high flow rates. The same fact applies to the COD removal which makes a longer residence time much more beneficial and then the lowest flow rate yields the highest COD removal as shown in figure 6 [24].

3.3 Effect of initial dye concentration

50, 75,100 and 125 mg/L were used as initial dye concentration to investigate the effect of the dye concentration on the color removal and COD decrease. Figure 7 shows that the lowest initial concnetration yielded the highest color removal. This is most probably due to insufficient amount of aluminium hydroxide complexes produced, i.e., according to Faraday's law (equation 11) constant number of Al^{3+} is formed at a constant electric current, for all dye concnetrations, thereby, the amount of flocs formed in case of high dye concntrations is insufficient to adsorb the increased number of dye molecules [4,21]. A plot of % COD removal vs the initial dye concentration follows the same behavior and the highest % COD removal was achieved at the lowest initial dye concentration (Figure 8) since at higher concentrations the dye removal decreased.

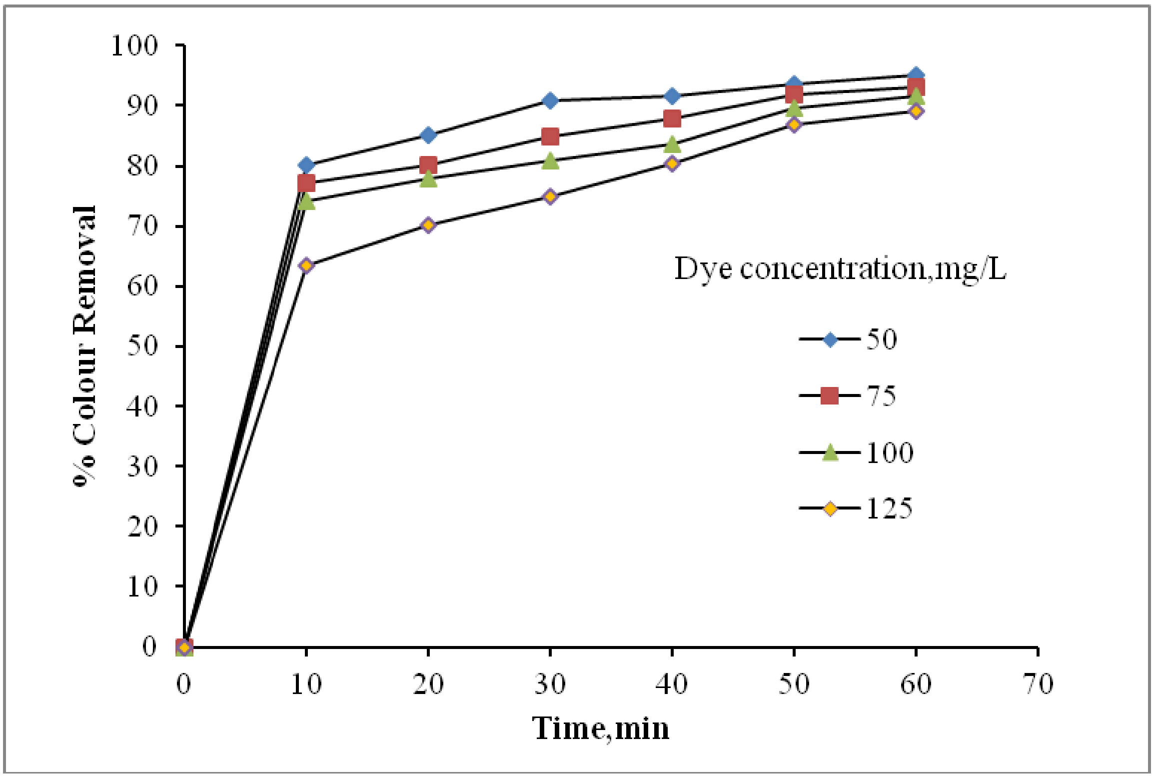

Figure 7. Effect of the initial dye concentration on the % color removal (c.d =16.58mA/cm^2; pH=7.75; NaCl Conc.=1g/L; flow rate=390 mL/min, T=25±2°C)

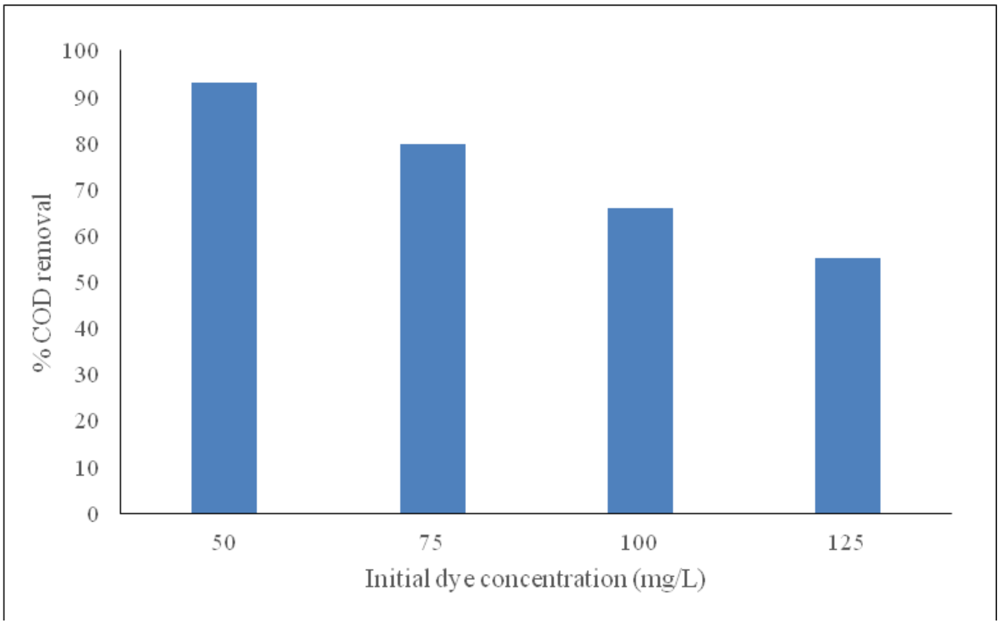

Figure 8. Effect of the initial dye concentration on the % COD removal (c.d=16.58mA/cm^2; pH=7.75; NaCl Conc.=1g/L; flow rate=390 mL/min, T=25±2^{o}C)

3.4 Effect of pH

The values of pH were varied between 4 and 10 by adding 0.1M NaOH and 0.1M HCl solutions to evaluate the effect of pH of the dye solution.

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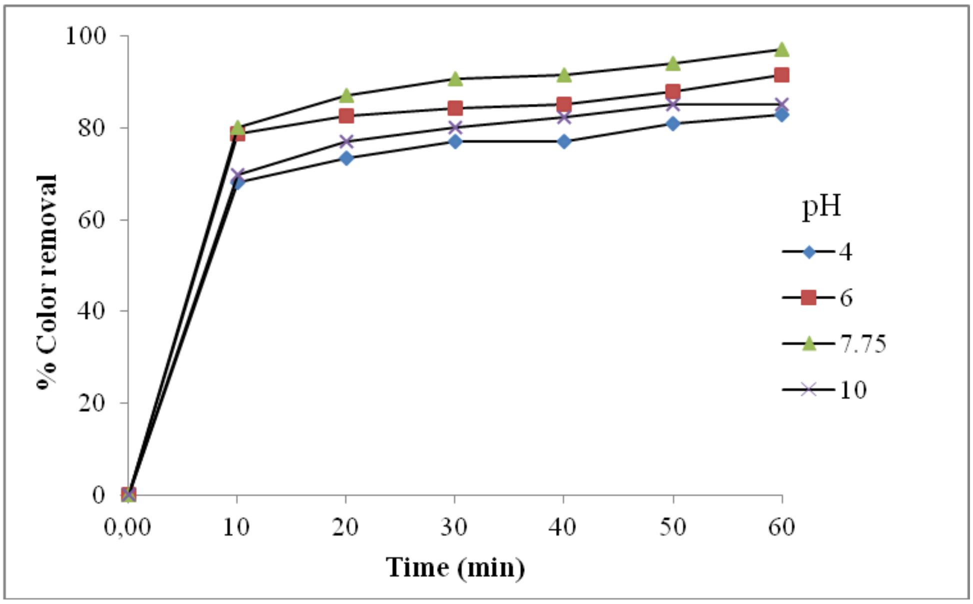


Figure 9. Effect of pH on the color removal efficiency (c.d=16.58mA/cm^2; C_o=50 mg/L; NaCl Conc.=1g/L; flow rate=390 ml/min, T=25±2^{o}C)

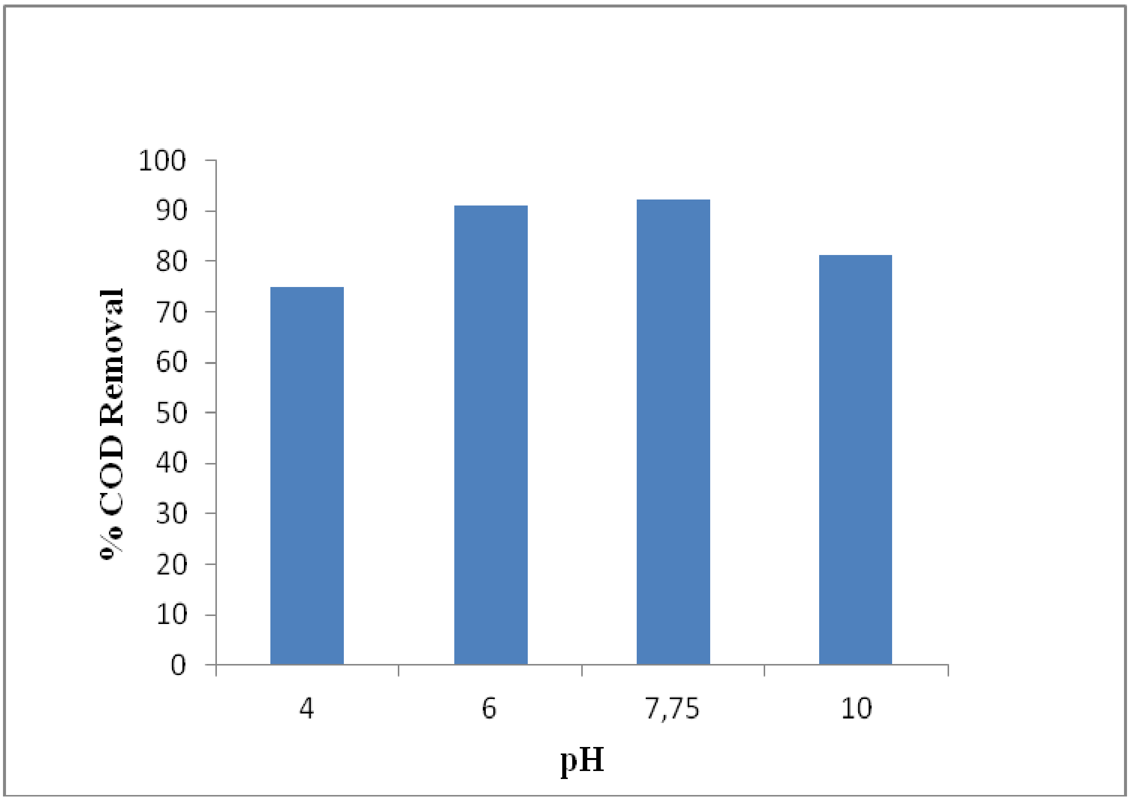


Figure 10. Effect of pH on % COD removal (c.d=16.58mA/cm^2; C_o=50 mg/L; NaCl Conc.=1g/L; flow rate=390 ml/min, T=25±2°C).

Fig. 9 shows that the best performance was at the nearly neutral medium, same result was found by former researchers [2, 21, 22]. In the pH range of 2 to 5, Al^{3+} is converted into soluble monomeric species such as $Al(OH)_2^+$ and $Al(OH)^{2+}$. At pH between 5 and 8 these monomeric cations can evolve to polymeric species such a $Al_2(OH)_2^{4+}$, $Al_6(OH)_{15}^{3+}$; soluble monomers and polymeric cations are converted into insoluble $Al(OH)_3$ flocs [23]. Due to amphorism, aluminium hydroxide dissolves at high pH and has the lowest solubility between 5 and 8.

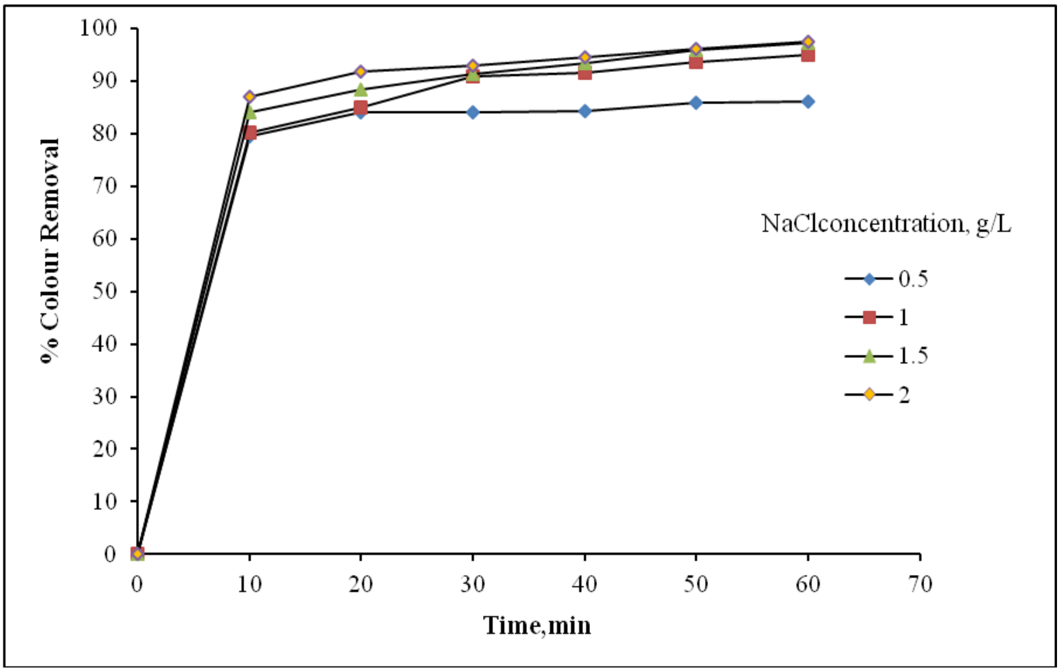
When pH reaches 10 the formation of soluble $Al(OH)^{4-}$ is predominant; this soluble complex is useless for the waste treatment [4, 20].

3.5 Effect of electrolyte concentration

To have a better understanding of the effect of the electrolyte concentration in the waste, four concentrations of NaCl were used: 0.5, 1, 1.5 and 2 g/L.

In fig.11, the concentrations 1, 1.5 and 2 g/L have a very close behavior achieving higher color removal than the lowest concentration of 0.5 g/L keeping the highest concentration with the maximum removal efficiency. This maybe attributed to the fact that the antipassive Cl^- ions destroy the passive oxide layer (Al_2O_3) that covers the aluminium anode and prevents the dissolution of Al to Al^{3+} and hence diminshes the amount of flocs that can interact with the dye.

Fig. 12, shows that the COD removal efficiency increases with increasing NaCl concentration.



Fgure 11. Effect of NaCl concentration on the color removal efficiency (c.d=16.58mA/cm^2; C$_o$=50 mg/L; pH = 7.75; flow rate=390 ml/min, T=25±2^{o}C).

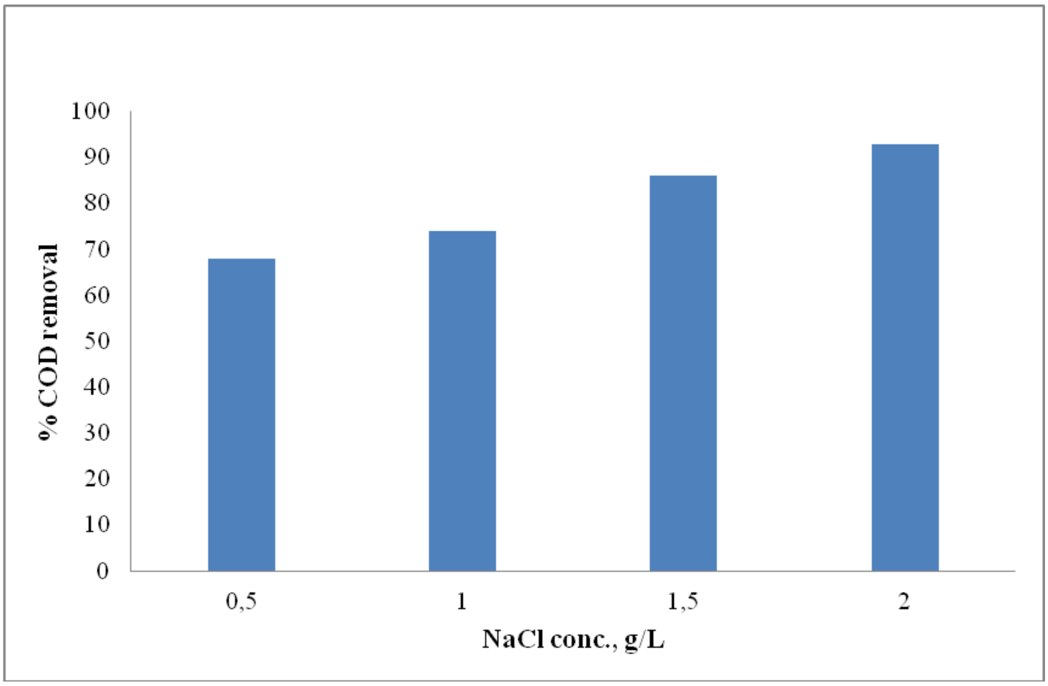


Figure 12. Effect of sodium chloride concentration on the % COD removal (c.d=16.58mA/cm^2; C$_o$=50 mg/L; pH = 7.75; flow rate=390 ml/min, T=25±2^{o}C).

3.6. Calculation of energy consumption

To assist in evaluating the economic feasibility of the electrocoagulation process in treating colored effluents the electrical power consumption was calculated as follows:

$$\text{Energy consumption (kWh/kg dye removed)} = \frac{VIt*10^{3}}{60(C_o-C_t)*trated\ volume\ (L)} \qquad (12)$$

Where:

V=the cell voltage (V), I=the electric current (A), t=the electrolysis time (min), C_o=the initial dye concentration (mg/L), C_t= the concentration at any time t (mg/L).

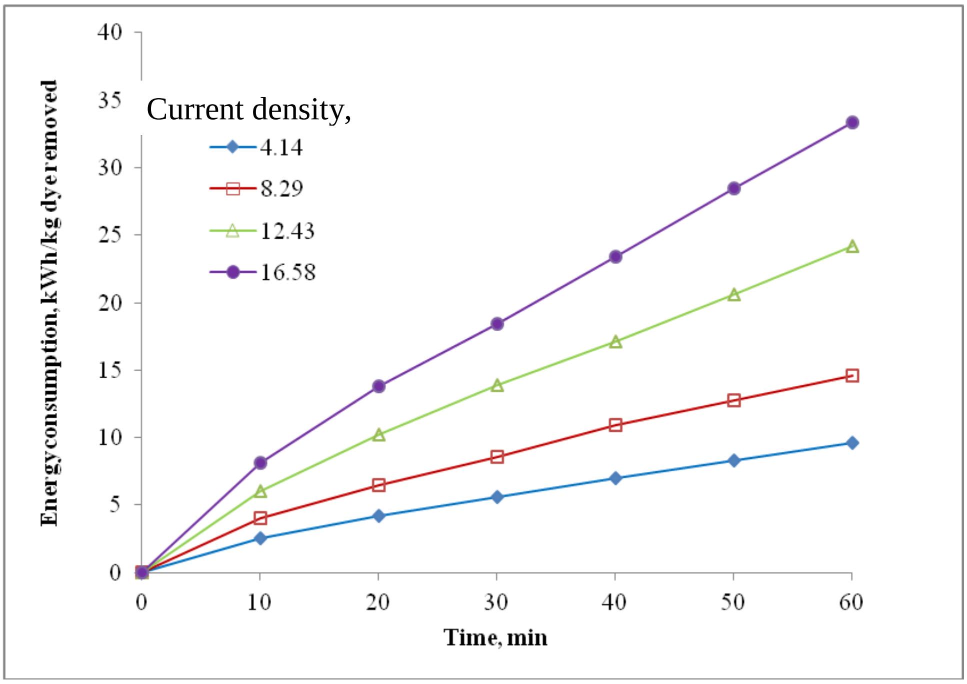


Figure 13. Effect of current density on the energy consumption (flow rate=390 mL/min; C_o=50mg/L; pH=7.75; Nacl conc. =1g/L).

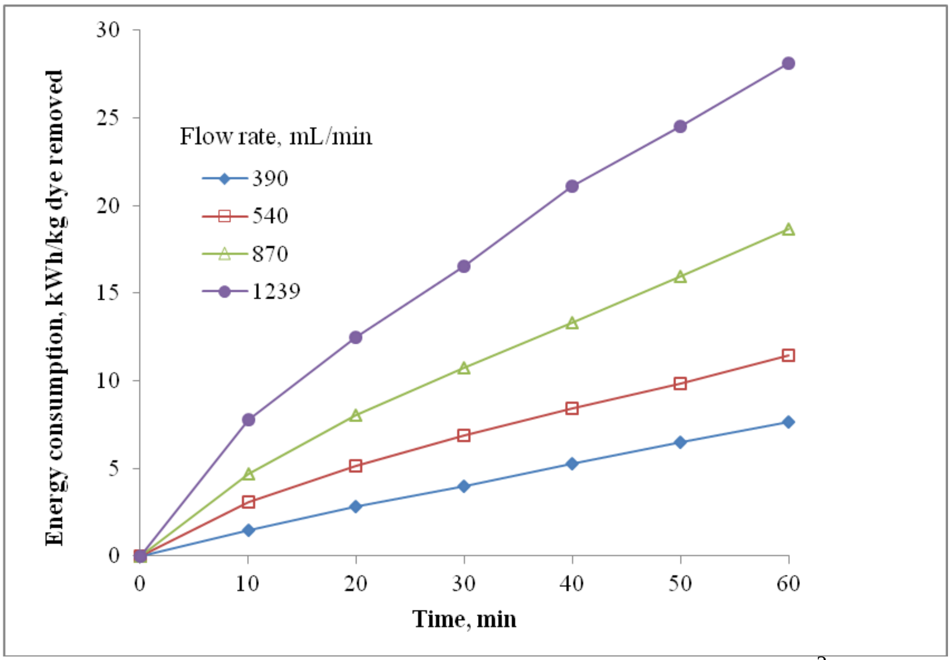


Figure 14. Effect of flow rate on the energy consumption (c.d.= 4.14 mA/cm^2; C_o=50mg/L; pH=7.75; NaCl conc.=1g/L)

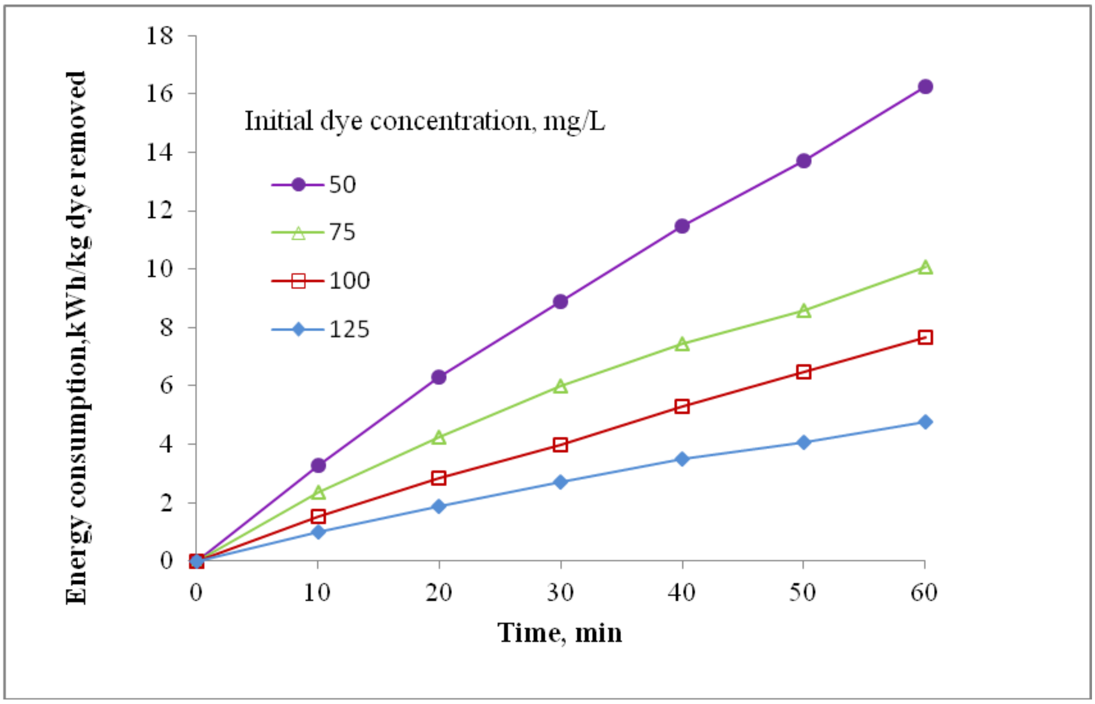


Figure 15. Effectof initial dye concentration on the energy consumption (c.d. = 4.14 mA/cm^2; flow rate=390 mL/min, pH=7.75; NaCl conc.=1g/L)

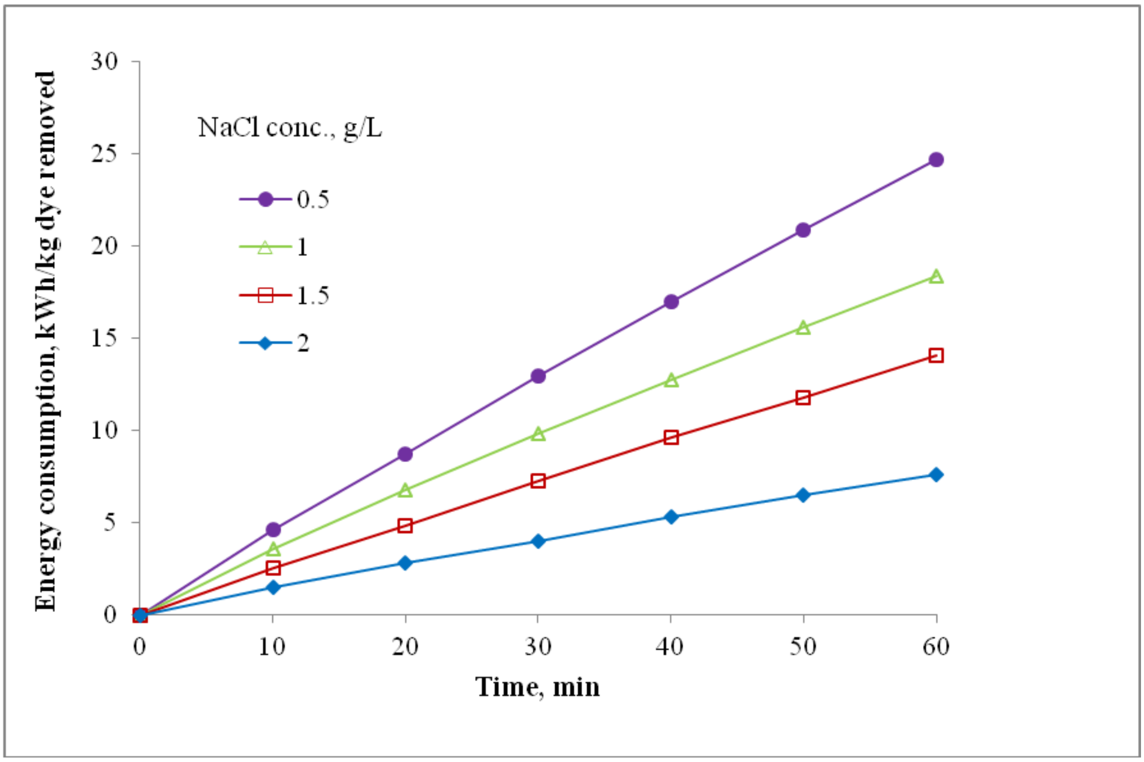


Figure 16. Effect of electrolye concentration on the energy consumption (c.d. = 4.14 mA/cm^2; flow rate=390 mL/min, C_o=50 mg/L; pH=7.75)

Figs (13-16) show the energy consumption at different operating parameters. Inceasing the sodium chloride concentration and the initial dye concentration had a positive effect and decreased the energy consumption while greater current density values and greater flow rates increased the energy consumption. These results are in agreement with previous researches [25-27].

The values of energy consumption ranged from 1.08 to 33.4 kWh/kg dye depending on the operating conditions.

4. CONCLUSION

Decolorization of reactive blue 19 dye effluents using electrocoagulation was investigated in a batch recycle reactor using aluminum electrodes. Electrocoagulation proved capable to achieve high color removal efficiency that reached 97.38%. Also, the % COD removal was tracked and found to achieve 93% under optimum operating conditions. The operating conditions studied were the current density, the flow rate, the initial dye concentration, pH and the sodium chloride concentration. Increasing the current density and the sodium chloride concentration had a positive effect on the removal percentage. Inversely, a higher flow rate and initial dye concentration diminished the rate of color and COD removal.

The pH value that accomplished the highest efficiency was found to be 7.75. The energy consmption was also calculated, to assess the economic feasiblity of the process, and found to range between 1.08 and 33.4 kWh/kg dye removed depending on the different parameters.

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