

Effect of Process Parameters on the Electro coagulation of Azo-Dye Wastewater in a Kenyan Textile Factory

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Abstract: Textile industries release large volumes of dye wastewater that contain different dyes. Azo dyes contain strong N=N bond which are not easily broken by conventional methods. The discharge of this type of wastewater to natural watercourse can pose serious environmental impacts to aquatic life and man. A study was carried out to investigate the effects of process parameters on the electrochemical treatment of textile dye wastewater from a Kenyan Textile Factory using stainless steel as anode material. Two model dyes namely C.I. Reactive Red 76 (RR) and C.I. Disperse Blue 79 (DB) obtained from Rift Valley Textile Factory (RIVATEX) in Kenya were used for the study. The process parameters investigated were: surface area to volume ratio, supporting electrolytes, inter-electrode distance and pH. Specific energy and pollutant removal of the electrochemical process was used in coming up with optimal conditions as; surface area to volume ratio of 16 m²/m³ in RR and 20 m²/m³ in DB, NaCl supporting electrolyte 4g/l and 6g/l in RR and DB respectively, inter-electrode distance of 12 mm and a pH of 6.5 for both dyes. Sodium chloride was found to be a better supporting electrolyte than sodium sulphate in the electrocoagulation of both dyes. A pH of 6.5 was found optimum for efficient dye removal due to formation of Fe (III) as a coagulant in "situ".

Key words: Azo dyes, wastewater, electrocoagulation.

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I. Introduction

There are more than 100,000 types of commercially available dyes with over 7x10⁵ tons of dyes produced yearly. Direct, reactive, acid, disperse, pre-metalized, vat and basic dyes account for about 85% of the total dyes used in the industry. The total dye consumption of the textile industries alone is in excess of 10⁷ kg/year and estimated 90 % of this total end-up on fabric [1]. Consequently, approximately 10⁶ kg/year of dyes are discharged into the waste streams by textile industries. Dyeing industry effluents constitute one of the most problematic wastewaters to be treated not only for their high chemical and biological oxygen demands, suspended solid and content of toxic compounds but also for colour. Moreover, the human eye can detect concentration of 0.005 mg/L of dye in water and therefore, presence of dye exceeding this limit would not be permitted on aesthetic grounds and may also be toxic to the aquatic environment [2].

The electrochemical process (EC) has been known to be highly dependent on the chemistry of the wastewater, especially its conductivity. In addition, other characteristics such as pH, particle size, and chemical constituent influence the process [3]. Electrocoagulation has been applied in textile dye wastewaters [4, 3], restaurant wastewater [5], semiconductor wastewater [6], distillery alcohol wastewater [7], tannery wastewater [8], dairy wastewater [9], pulp and paper mill effluent [10], tea wastewater [11] among others. Catalysts have also been introduced to make electrocoagulation more efficient in the treatment of dye wastewater [12]. Electrochemical treatment combined with wood ash leachate (ELCAS) was effective in Kraft and paper mill colour reduction in Kenya. However, over electrical polarization within electrodes, which causes excess voltage remains the biggest impediment in this method [13].

II. Materials and methods

2.1 Electrochemical cell

A sample of 250 mL wastewater was placed in a 300 mL glass beaker. Stainless steel (SS) electrodes were suspended into the solution and kept apart using an insulator and were connected in series with a Digital Multimeter. The reaction was carried out to complete colour removal while recording current and the time taken to form flocks. Absorbance measurements were taken at an interval during the process to monitor colour removal. Specific energy was calculated using equation 1.

$$P = \frac{VIt}{v} * 1000 \dots \dots \dots \text{Equation 1}$$

Where;

P=specific energy in kWh/m³

V= cell potential in Volts

I= current in Amperes

t= time taken to form flocs in hours

v= sample volume (cm³) used in the reaction

Fouling on SS electrodes was removed by rinsing in 8% sulphuric acid.

2.2 Materials and Analytical techniques

Two azo dyes; Reactive Red 29 (C₂₆H₁₃ClN₇Na₅O₁₅S₄) and Disperse Blue 79 (C₂₄H₂₇BrN₆O₁₀) were provided by REAL and their structures are shown in Fig 1a and b respectively. Optical density was determined by UV-VIS spectrometry at 525nm for RR and 515nm for DB dye. Electrical conductivity and pH were determined using procedures in standard methods for the examination of water and wastewater [14].



Fig 1a: Structure of Reactive Red 29 dye

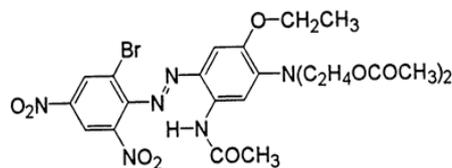


Figure 1b: Structure of Disperse Blue 79

III. Results and discussion

3.1 Effect of surface area to volume ratio

The results of surface area to volume ratio (S/V) in m²/ m³ are illustrated in Figure 2. There was a reduction in specific energy as the S/V ratio decreased from 28.0 m²/ m³ to 16.6 m²/ m³ and an increase in specific energy when the S/V decreased from 16.0 m²/ m³ to 8.0 m²/ m³. The lowest specific energy was recorded at S/V ratio of 16 m²/ m³ in RR dye and 20 A/m³ in DB dye. The current in RR and DB was constant at 0.10 A which translated to current densities of 25.0 A/m² and 20 A/m² respectively. These current densities are in agreement with the recommended range of between 20- 25 A/m² for long life of electrodes [15]. Optimum S/V ratios vary depending on the nature of wastewater such as tea wastewater with an optimum of 18.1 m²/ m³ [16]. It was found that electrode surface area influences; current density, position and rate of cation dosing and bubble production (Table 1).

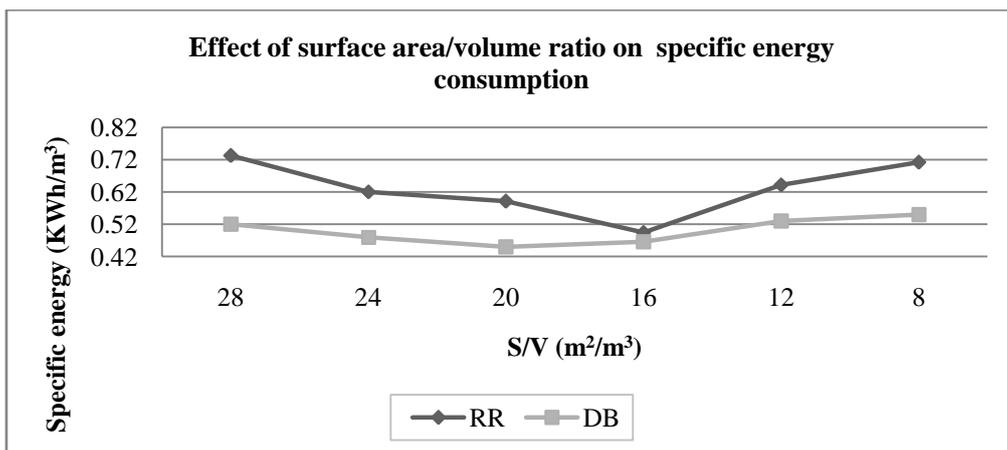


Figure 2: Effect of surface area/ volume ratio on specific energy at 10 V, 10 mm inter-electrode spacing and 1% NaCl supporting electrolyte for RR and DB dyes

Table 1: Effect of S/V on current density for RR and DB dyes

S/V , m ² /m ³	Current density, A/m ²	
	DB	RR
28.0	15.7	15.7
24.0	16.7	18.3
20.0	20.0	22.0
16.0	22.5	25.0
12.0	33.0	26.7
8.0	40.0	35.0

As the S/V ratio increased, current density decreased (Table 1) which agreed with results by Holt and Mitchel[17]. As the surface area increases, the current reduces since it is distributed on a larger surface and this reduces the ratio of current/surface area thus lowering the rate of release of Fe (III) hence reduced electrocoagulation.

3.2 Effect of supporting electrolytes

The effect of the type of supporting electrolyte and concentration was investigated on specific energy and time for decolourization of the dye wastewater. The results are shown in Figures 3a and 3b.

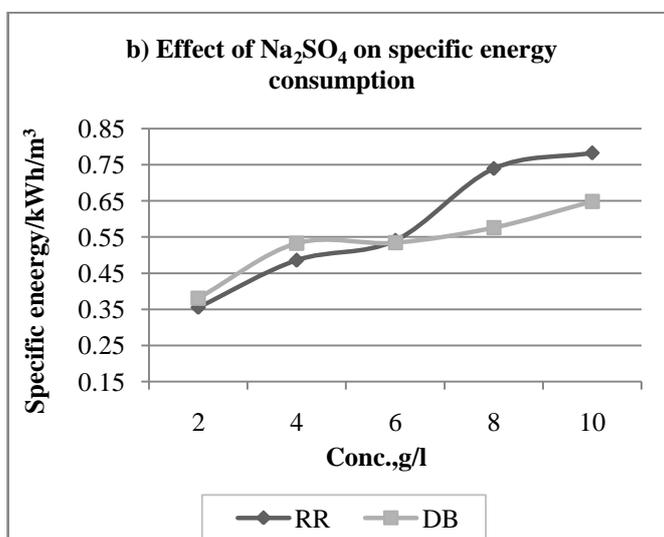
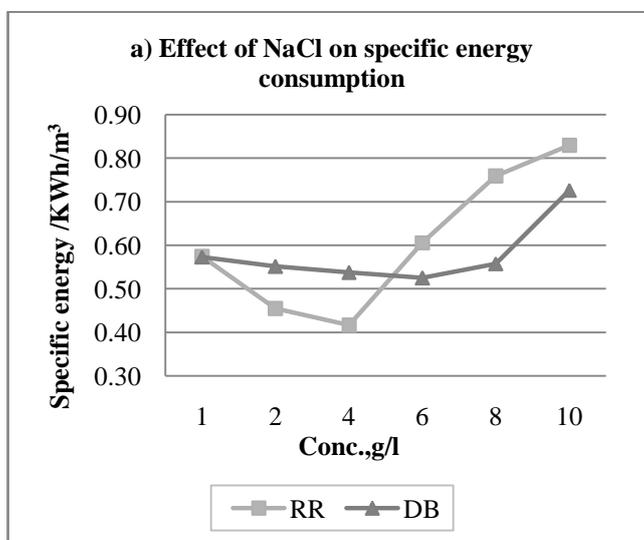


Figure 3: Effect of supporting electrolytes on specific energy using 10 mg/L dyes a) NaCl b) Na₂SO₄ on RR and DB dyes.

There was a decrease in specific energy as the concentration of NaCl increased from 1-4g/l in RR and 1-6g/l in DB. The optimum concentration in RR was 4 g/L and 6g/L for DB with current density of 23 A/m² and 37 A/m² respectively. The optimum NaCl concentrations differs in different dyes and concentration as found out with C.I. acid yellow 36 that gave an optimum of 8 g/l with a dye concentration of 50 mg/L [18]. Sodium sulphate had a higher specific energy requirement than sodium chloride for decolourization; however coagulation time reduced with increasing concentration in both electrolytes.

The presence of sodium chloride in solution causes formation of hypochlorite ion at the anode as shown in Eqns. 2-4.

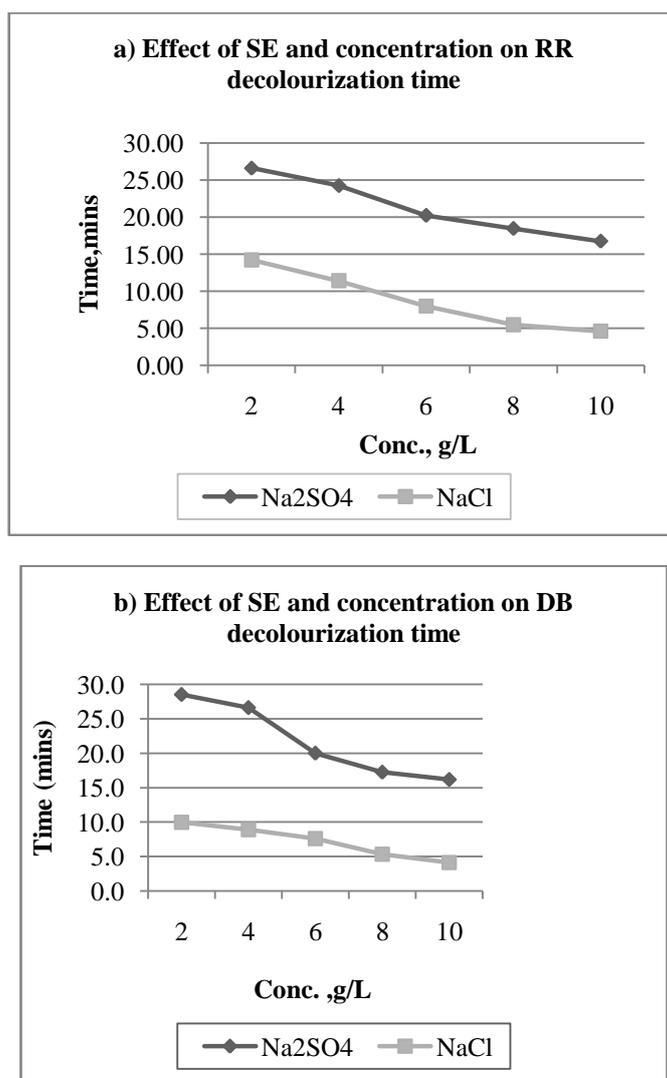
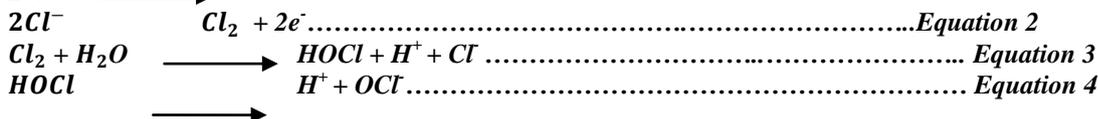
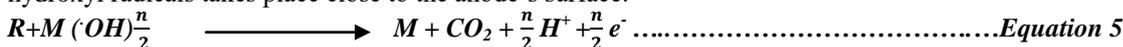


Figure 4: Effect of supporting electrolytes and concentration on decolourization of a) RR and b) DB dyes

The hypochlorite ion leads to increased dye removal by oxidation of the dye molecules [15] as shown in equations 5 and 6. The electrochemical oxygen transfer reaction between an organic compound R and the hydroxyl radicals takes place close to the anode's surface:





Sulphate ions have also been found to produce peroxodisulphates during oxidation using BDD electrodes (equation 7) which are very specific powerful oxidants that oxidize organic matter hence increasing COD and colour removal rate [19].



Results indicated that sodium chloride was more efficient in the reduction of coagulation time than sodium sulphate in both dyes (Fig. 4a and 4b). Comminellis and Chen[15] reported that addition of anions will also slow down the electrode passivation with a positive effect following the order:



Therefore addition of a certain amount of Cl⁻ into the aqueous solution will inhibit the electrode passivation process largely as well as reduce the specific energy for electrocoagulation giving another advantage over the SO₄²⁻ which has a lesser effect.

3.3 Effect of Inter-electrode distance

The effect of inter-electrode distance between the anode and cathode was investigated by varying the electrode gap at 5, 7, 9, 10, 12, 14 and 16 mm using an insulator as shown in Figure 5. Specific energy was high at an inter-electrode distance of 7 and 10 mm than at 12 -16 mm. However, the lowest specific energy was obtained at 12 mm inter-electrode spacing which had a corresponding current density of 25 A/m² in RR and 30 A/m² in DB.

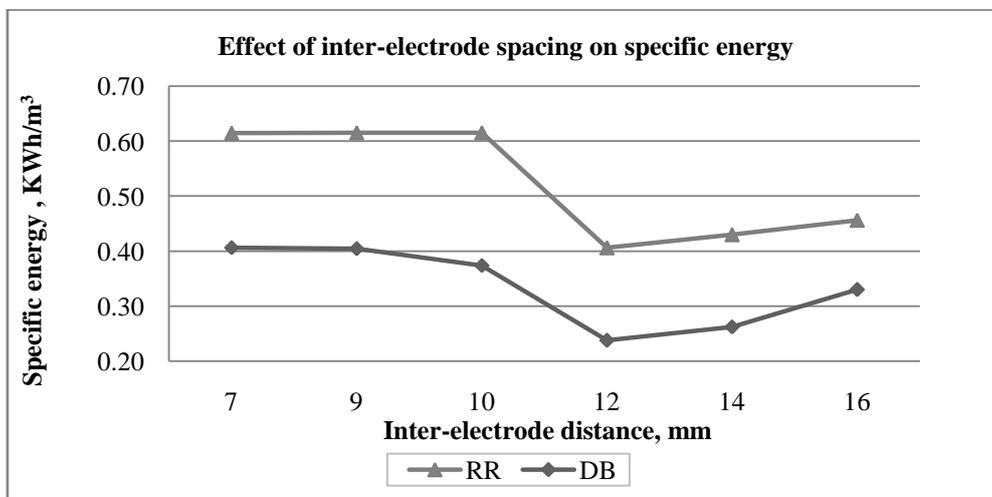


Figure 5: Effect of inter-electrode spacing on specific energy using 10 V and 1% NaCl for RR and DB dyes

At 7 and 10 mm electrode gap, the current density was 30 and 40 A/m², respectively and could have led to high over potential hence slowed the activity of the production of Fe (III). This could be attributed to a high rate of release of Fe (II) ions initially which were not all immediately oxidized to Fe (III) coagulant but remained in the Fe (II) state.

When the electrode gap was increased from 12 to 16 mm, specific energy increased. This could be attributed to less interaction of the dye with the metal hydroxyl decreasing electrostatic attraction thus reducing the efficiency of dye removal. The results are in agreement with those of Dalvand *et al* [20], who discovered that dye removal efficiency reduced from 98.6% to 90.4% when the inter-electrode distance was varied from 10 to 30 mm while using sacrificial electrodes.

The increase in inter-electrode distance leads to an increase in cell potential (V) which also increases the resistance and adversely affects the wastewater treatment. According to Ohm's law, the amount of electric current through a metal conductor in a circuit is directly proportional to the voltage impressed across it, for any given temperature as shown in Eqn. 8.

$$V = IR \dots\dots\dots \text{Equation 8}$$

Ohmic potential drop (IR drop) is the potential drop due to solution resistance and hence the difference in potential required to move ions through the solution. IR drop has a significant influence on electrochemical parameters and its variation is governed by Eqn. 9.

$$IR = I \cdot \frac{d}{A \cdot K} \dots\dots\dots \text{Equation 9}$$

Where:

I = current (A)

d = distance between cathode and anode (m)

A = active anode surface area (m^2)

κ = specific conductivity ($10^3 mS/m$)

Eqn.9 implies that, IR drop will increase by increasing the distance between electrodes. During the reaction, the current suddenly drops after some time; hence applied voltage must be increased in order to maintain a constant current. This situation occurs due to the rising of Ohmic loss (IR drop) which leads to reduction in the rate of anodic oxidation. Therefore, increasing the inter-electrode distance leads to increase in IR drop hence reduces the efficiency of electrocoagulation process [21].

3.4 Effect of pH

The effect of pH on colour removal was investigated by adjusting the pH of the wastewater to 4.0, 6.0, 6.5, 7.0 and 8.0 using either NaOH to increase the pH or HCl to reduce the pH. The results obtained are shown in Fig.6.

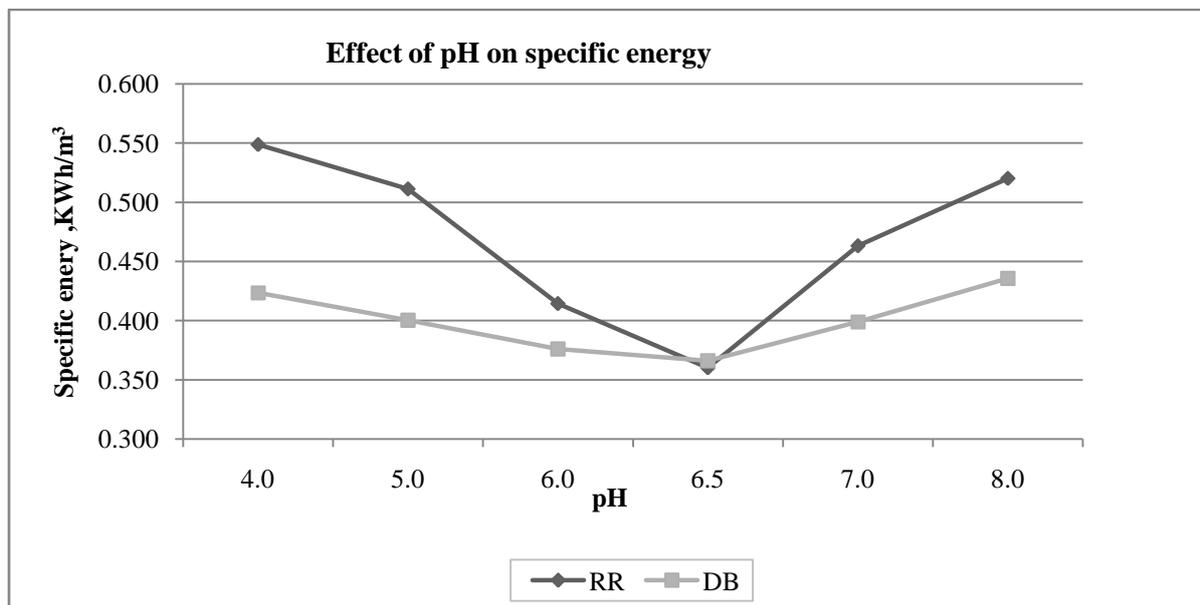


Figure 6: Effect of wastewater pH on specific energy at 10 mm electrode spacing, 1% NaCl and 10 V for RR and DB dyes

Solution pH determines the speciation of metal ions and also influences the state of other species in solution and the solubility of products formed. Hence solution pH influences the overall efficiency and effectiveness of electrocoagulation [22]. Specific energy for complete colour removal was high at pH 4 and reduced gradually until pH 6.5 then increased as the pH increased. In both RR and DB, the lowest specific energy consumption for decolourization was at a pH of 6.5 which is in agreement with the optimal pH range of 6.5 – 7.5 suggested to be optimal for a given pollutant in electrocoagulation using iron electrodes [22]. At low pH, speciation of iron is mainly Fe^{2+} which is very stable in acidic media; however, at pH 6.0 – 6.5, $Fe(OH)_3$ complex is the most stable hydroxide of iron [20]. The most stable complex must have a lower crystal field stabilization energy (CFSE) hence the stability of Fe (II) is due to it having lower CFSE as opposed to Fe (III) with higher energy. This arises because Fe (II) is a d^6 system while Fe (III) is a d^5 system. Since Fe (III) is a coagulant, stable complex was formed at pH 6.5 that required less specific energy than at all pH values.

IV. Conclusion

This study investigated an electrochemical treatment method for textile azo-dye wastewater using stainless steel anode. Two model dyes; a reactive dye (C.I. Reactive Red 76, RR) and a disperse dye; (C.I. Disperse Blue 79, DB) obtained from a Kenyan Textile Factory, RIVATEX were used in this study. The results gave optimum conditions as; S/V ratio of $16 m^2/m^3$ in RR and $20 m^2/m^3$ in DB, NaCl supporting electrolyte 4g/l and 6g/l in RR and DB respectively, inter-electrode distance of 12 mm and a pH of 6.5 for both RR and DB dyes. The pH of the treated wastewater increased by 1.74 % in DB and 1.24 % in RR as a result of discharge of hydrogen ions at the cathode. DB had a lower energy demand than RR at optimized conditions. Removal of dye in wastewater by electrocoagulation was achieved when Fe(III) (Brownish red) was formed in “situ” hence oxidation of Fe had to go through Fe(II) (green) then Fe (III) before flocks could form. Dye molecules formed flocs which were adsorbed on the surface of the coagulant and pushed on the surface by the electro-generated

hydrogen gas from cathode. Formation of dye flocs could have been possibly due to the compression of the electrical double layer by Fe (111).

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