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Electrochemical Oxidation of Dye by using Graphite and Titanium Based Electrodes

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ABSTRACT

The treatment of synthetic textile dye using electrochemical oxidation is found to be a very effective method for the degradation of non-biodegradable pollutants by decreasing the organic load and color. Hence the present investigation concerns with the study of various parameters such as NaCl Concentration, Electrolysis Time, Current Density, pH, Dye Concentration. These parameters influence the performance of the electrochemical oxidation process of synthetic textile dye to remove the color and COD by using Graphite and Titanium based electrodes. The result indicate that the removal of color and COD using Graphite electrode is 95.44% and 37.10% ,by using Titanium based electrode is 96.30% and 37.87% based on optimum conditions. The removal of color and COD increased by varying NaCl Concentration, Electrolysis Time, Current Density, pH, Dye Concentration. Due to effectiveness and ease in operation, this technique can be applied for a large volume and industrial scale of textile polluted water.

KEYWORDS: Electro-oxidation, COD, Color, Remazol Red RB 133**,** Graphite electrode, Titanium based electrode.

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1. INTRODUCTION

Dyes pollutants from the textile industry are an important source of environmental contamination. They pose serious problems because of their strong color, high COD and low biodegradability. These effluents usually contain dyes such as Remazol Red RB 133, a well known non biodegradable dye, Therefore, most of traditional methods of wastewater treatment are becoming inadequate. Electrochemical technology and its application on wastewater treatment have become increasingly interesting, because of its advantages especially for color removal. Electrolytic effect could be influenced by pH, electrolyte concentration, current density etc. Consequently, it is imperative to study these factors and to find how to operate electrochemical oxidation more effectively. In the present study, investigation of the decolorization and mineralization of aqueous solution of textile dye Remazol Red RB 133 by electrochemical oxidation and effect of experimental parameters on color removal and chemical oxygen removal.

1:1 ELECTROCHEMICAL TREATMENT

Electrochemical treatment has been developed as alternative of conventional water and wastewater treatment. Electrochemical treatment mainly consisted of cathode, anode and power supply.

The mechanism of electrochemical oxidation of wastewater is a complex phenomenon involving coupling of electron transfer reaction with a dissociate chemisorptions step. Basically two different processes occur at the anode; on anode having high electro-catalytic activity, oxidation occurs at the electrode surface (direct electrolysis); on metal oxide electrode, oxidation occurs via surface mediator on the anodic surface [indirect electrolysis]. In direct electrolysis, the rate of oxidation is depending on electrode activity, pollutants diffusion rate and current density. In indirect electro-oxidation, chloride salts of sodium or potassium are added to the wastewater for better conductivity and generation of chlorine/hypochlorite ions. The reactions of anodic oxidation of chloride ions to form chlorine is given as

$2Cl^- \longrightarrow Cl_2 + 2e^-$

The liberated chlorine form hypochlorous acid

$Cl_2 + H_2O \longrightarrow H^+ + HOCl$

And further dissociated to give hypochlorite ion

$HOCl \; H^+ + OCl^-$

The generated hypochlorite ions act as main oxidizing agent in the pollutant degradation. The direct electro- oxidation rate of organic pollutants depends on the catalytic activity of the anode, on the diffusion rate of the organic compounds in the active points of anode and applied current density.

In the electrochemical oxidation process, the organic and toxic pollutants present in wastewater such as dye usually destroyed by either the direct or indirect oxidation process.

2: MATERIALS AND METHODOLOGY

2.1: MATERIALS

Ramezol Red RB133 is a reactive group of azo dye. Reactive dyes are a chromoshore with amine functional group and it is also a group of Vinyl Sulfone dyes, also known as Reactive Red 198. Vinyl sulfones can be used as true reactive dyes on cotton, silk, and wool. Reactive Dyes are capable of forming chemical covalent bonds with the Hydroxyl groups of cellulose fibre. These dyes are very dangerous because it causes toxicity and potentially dangerous to both humans and environment.

The molecular structure of Remazol Red RB 133 is shown in the figure 1. The characteristics of Remazol Red RB 133 are summarized in Table 1.

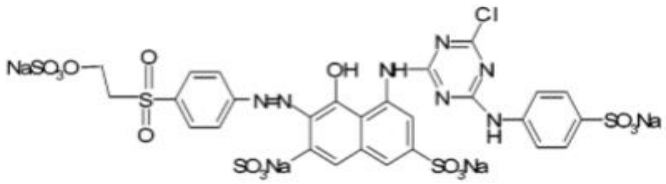

Fig 1: Molecular Structures Of Remazol Red RB 133

Table 1: Characterization of the Remazol Red RB 133

Sl. No.	Parameters	value
1.	Color Index	Ractive Red RB133
2.	Chromophore	Azo
3.	Reactive Anchor Systems	MCT and VS[a]
4.	Molar Mass (Nonhydrolyzed Dye)	984.2
5.	Percentage Of Pure Dye	63%
6.	Water Solubility at 293 K (g/L)	70
7.	Acute Oral Totoxicity LD_{50} (mg/kg)	2000

8.	Fish Toxicity LC_0 (mg/L)	>500
9.	pH value(at 10 g/L water)	7
10.	COD value (mg/g)	540
11.	BOD_5 value (mg/g)	<10
12.	DOC value (mg/g)	120

Monochlorotriazine (MCT) and vinylsulfone (VS).

Molecular Formula: $C_{27}H_{18}ClN_7Na_4O_{16}S_5$

Molecular Weight: 984.21g/mol

The choice of electrode material is of great importance as it affects the selectivity and the efficiency of the process. The use of electrode materials that are inexpensive, high physical and chemical stability and durable must be favoured. In the present study, Graphite and Titanium based electrode are selected as anode and cathode materials

2.2 METHODOLOGY

The electrochemical cell consists of an undivided reactor made of borosil glass with two parallel electrodes having an inter-electrode gap of 2cm. The electrochemical cell has a volume of 400ml in a 500ml capacity of beaker. Both anode and cathode are placed vertical and parallel to each other with batch operation. Ramezol Red RB 133 is prepared by using distilled water to the desired concentration. Prepared synthetic dye is transferred into electro chemical cell.

The electrodes are connected to the respective anode and cathode lead of the DC rectifier. The electrolytic cell is equipped with a magnetic stirrer in order to keep the electrolyte well mixed. During the experiment, samples are collected at different time intervals and analyzed for various parameters according to the APHA methods. The schematic diagram of the experimental setup is shown in the figure 2.

A (+) = Anode.

C (-) = Cathode.

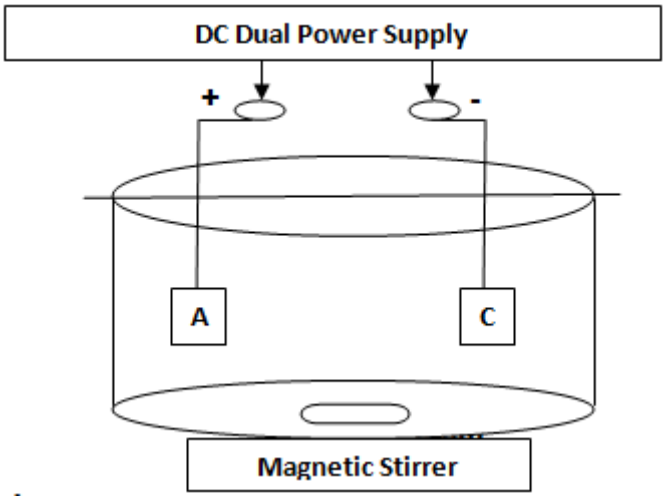

Fig 2: The Schematic Diagram Of The Experimental Setup.

The percentage of color removal under different parameters is determined by varying of NaCl Concentrations, Time, Current Density, pH and Dye Concentration.

The chemical oxidation demand of the effluent sample is determined by closed reflux method, using COD digestion apparatus model ET 108,Lovibond.The absorption of the sample is recorded to measure color on Elico Scanning mini Spectrophotometer(SL 177),recording the spectra over 340nm to 1000nm range. The pH is determined by pH meter. The percentage of color and COD removal calculation as follows:

$$\text{Color removal (\%)} = \frac{(Abs_{(508)(i)} - Abs_{(508)(t)})}{Abs_{(508)(i)}} X100$$

Where,

$Abs_{(508)(i)}$=Initial absorbance of the raw sample at a wavelength of 508nm.

$Abs_{(508)(t)}$= Absorbance of the treated sample at time intervals, t in min.

$$\text{Color removal(\%)} = \frac{(COD_{(i)} - COD_{(t)})}{COD_{(i)}} X100$$

Where

$COD_{(i)}$ = Initial COD concentration in mg/L.

$COD_{(t)}$ = Initial COD concentration removal in mg/L. at time intervals, t in min.

3. RESULTS AND DISCUSSION

The electrochemical oxidation of textile dye using Graphite and Titanium based electrode as anode and cathode for determining the percentage of color removal by varying NaCl Concentrations, Time, Current Density, pH and Dye Concentration.

3.1 Effect of NaCl Concentration:

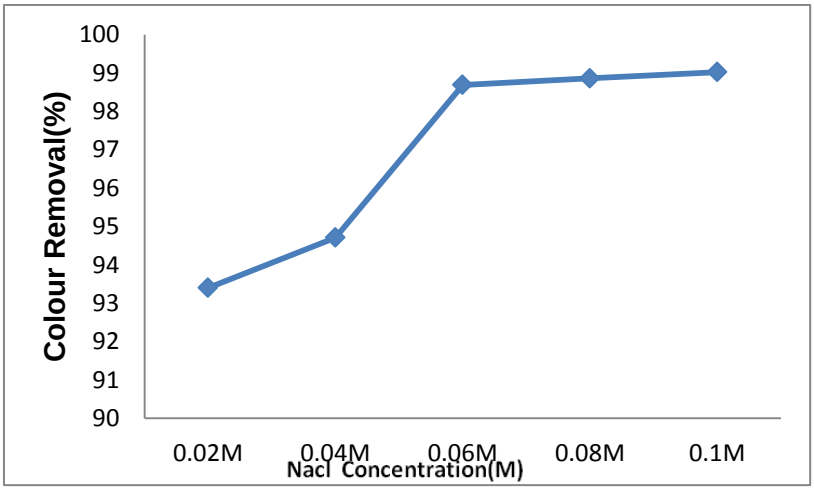

Fig 3: The Effect of NaCl Concentration On Color Removal Efficiency by using graphite electrode.

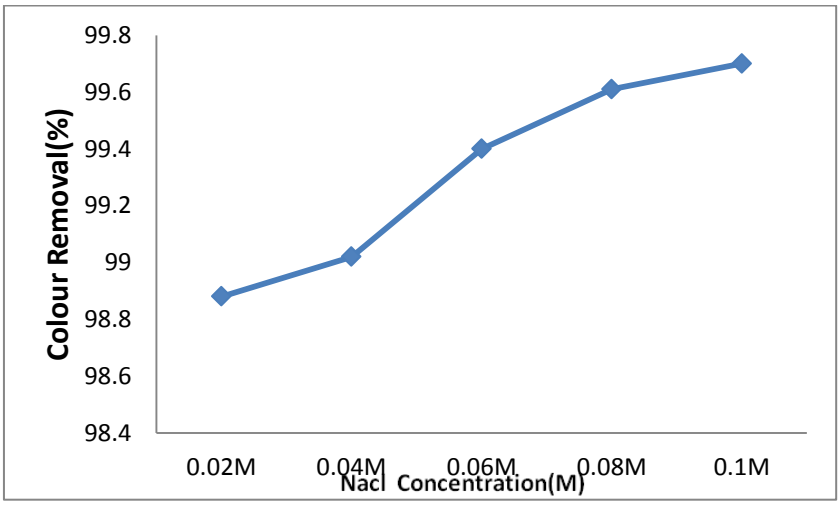

Fig 4: The Effect Of NaCl Concentration On Color Removal Efficiency by using Titanium based electrode

In case of Graphite electrode(fig 3), the increase in NaCl concentrations of 0.02M, 0.04M, 0.06M, 0.08M and 0.1M, increases the percentage of color removal efficiency from 93.04% to 99.02%. In case of Titanium based electrode(fig 4),

the increase in NaCl concentrations of 0.02M, 0.04M, 0.06M, 0.08M and 0.1M, increases the percentage of color removal efficiency from 98.88% to 99.70%.

Experiment shows that the electrolysis of Remazol Red RB 133 with NaCl, results in an indirect electrochemical oxidation effect with the generation of chlorine/hypochlorite which is the main pathway for removal of pollutants. Therefore, results indicate that the color removal increases with increase in the chloride concentrations.

3.2 Effect of Time:

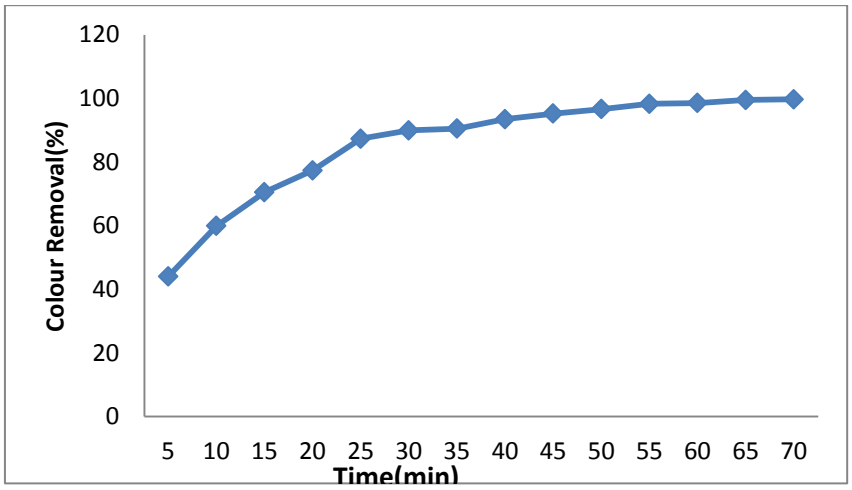

Fig 5: The Effect of Time on Color Removal Efficiency by using graphite electrode.

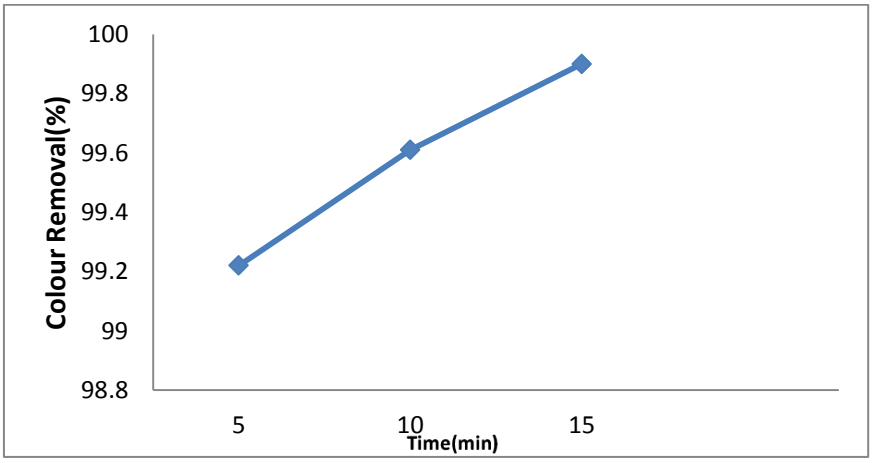

Fig 6: The Effect Of Time On Color Removal Efficiency by using Titanium based electrode.

In case of graphite electrode (fig 5), the increase in the time of electrolysis from 5 minutes to 70minutes yields an increase in the color removal efficiency from 44.04% to 99.71%.In case of Titanium based electrode (fig 6), the increase in the time of electrolysis from 5 minutes to 15 minutes yields an increase in the color removal efficiency from 99.22% to 99.90%. During electrolysis, the positive electrode undergoes anodic reaction while cathodic reaction occurs on the negative electrode. The released ions oxidises the dye molecule. The color removal efficiency depends directly on the concentration of ions produced by the electrodes. When the electrolysis period increases, the color removal efficiency also increases.

3.3 Effect of Current Density:

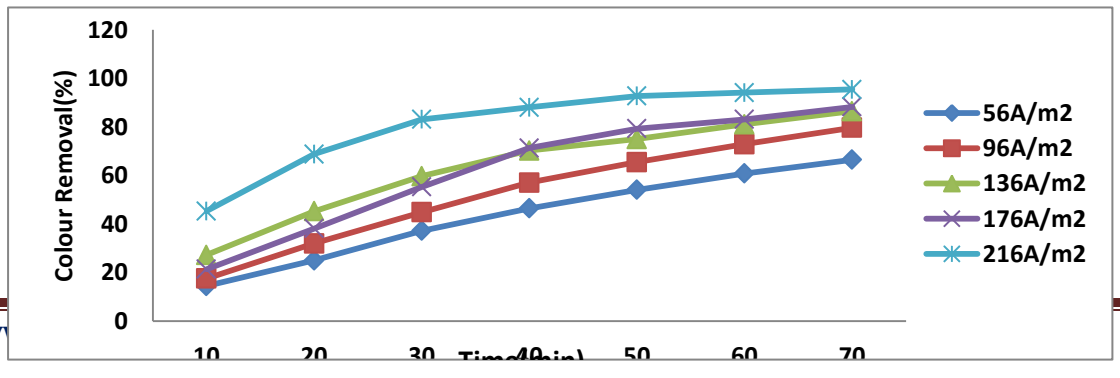

Fig 7: The Effect of Current Density on Color Removal Efficiency by using graphite electrode

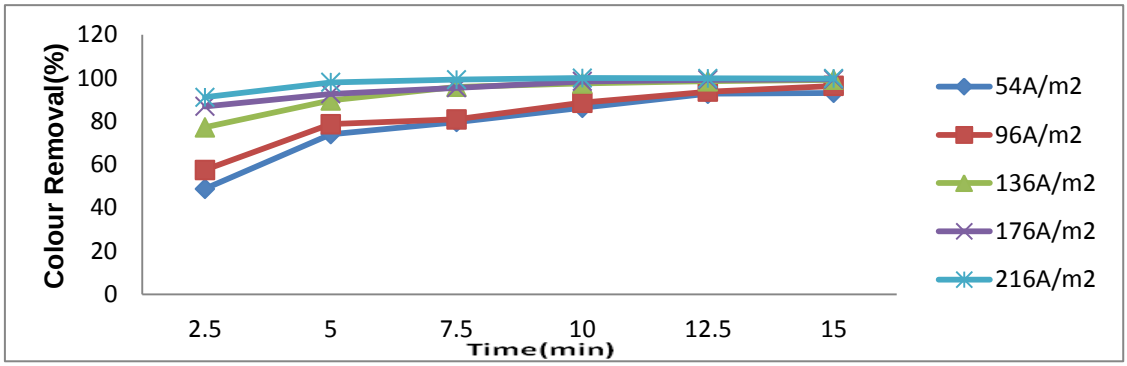

Fig 8: The Effect of Current Density on Color Removal Efficiency by using Titanium based electrode

In case of Graphite electrode (fig7),the increase in current density of 56A/m^2, 96 A/m^2, 136 A/m^2, 176A/m^2 and 216 A/m^2 increase in the color removal efficiency from 66.53% to 95.44%. In case of Titanium based electrode(fig 8), the increase in current density of 56A/m^2, 96 A/m^2,136 A/m^2,176A/m^2 and 216 A/m^2 increase in the color removal efficiency from 93.07% to 99.70% .Increase in current density increases the rate of color removal due to the increase in generation of chlorine/hypochlorite ions produced by the electrodes at the higher current density. These ions oxidize the dye molecules. So, decolorization increases with increase in current density.

3.4 Effect of pH:

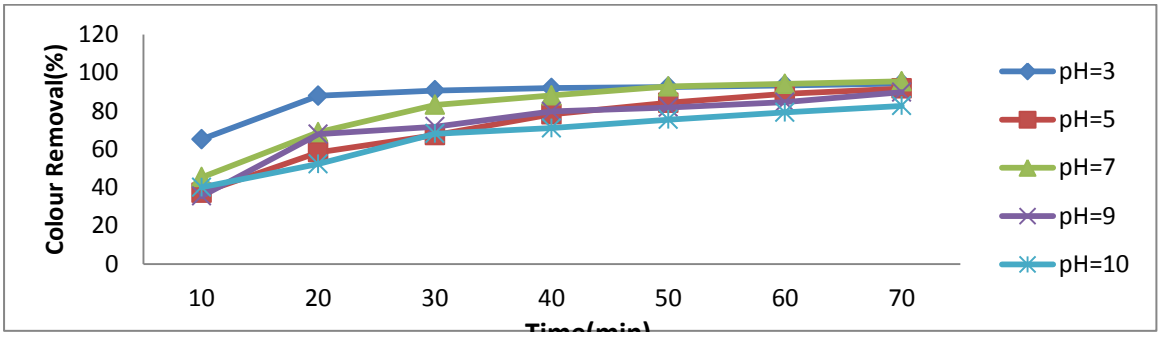

Fig 9: The Effect Of pH on Color Removal Efficiency by using graphite electrode

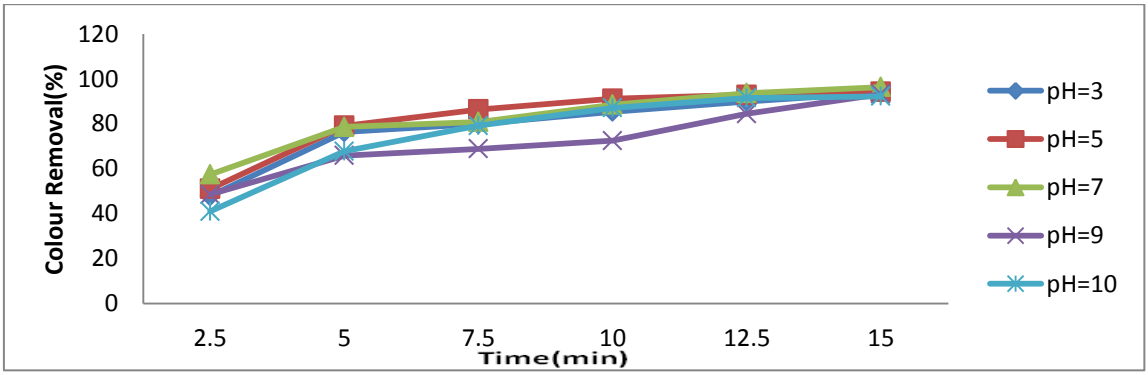

Fig 10: The Effect of pH on Color Removal Efficiency by using Titanium based electrode

In case of Graphite electrode (fig 9), the increase of 3,5,7,9 and 10 decrease in the color removal efficiency from 95.44% to 82.66%. In case of Titanium based electrode (fig 10) an increase pH of 3,5,7,9 and 10 decrease in the color removal efficiency from 96.3% to 92.16%. Increase in the pH decreases the rate of color removal .The maximum efficiency of color removal is observed at pH in the range of 5-9. At low pH, chlorides are reduced during the electrolysis process producing free chlorine, while at high pH the chlorides are reduced producing chlorates. Only in moderate acidic, alkaline and neutral conditions chlorides remain stable with the continuous production of free radicals.

3.5 Effect of Dye Concentration:

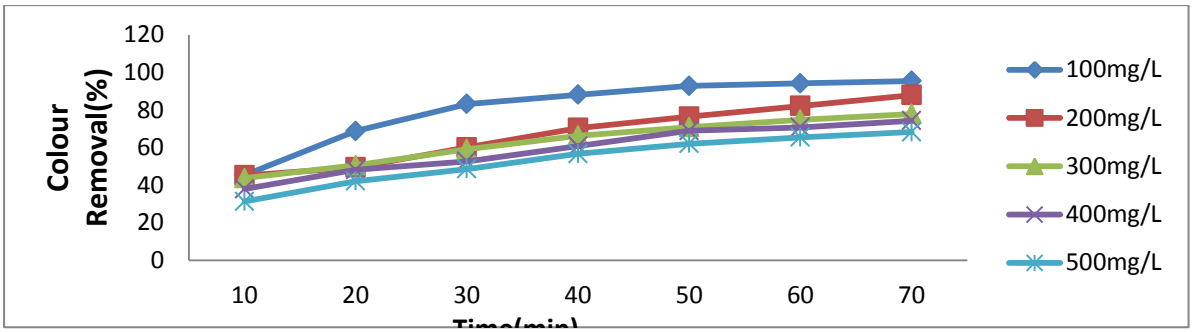

Fig 11: The Effect of Initial Dye Concentration on Color Removal Efficiency by using graphite electrode.

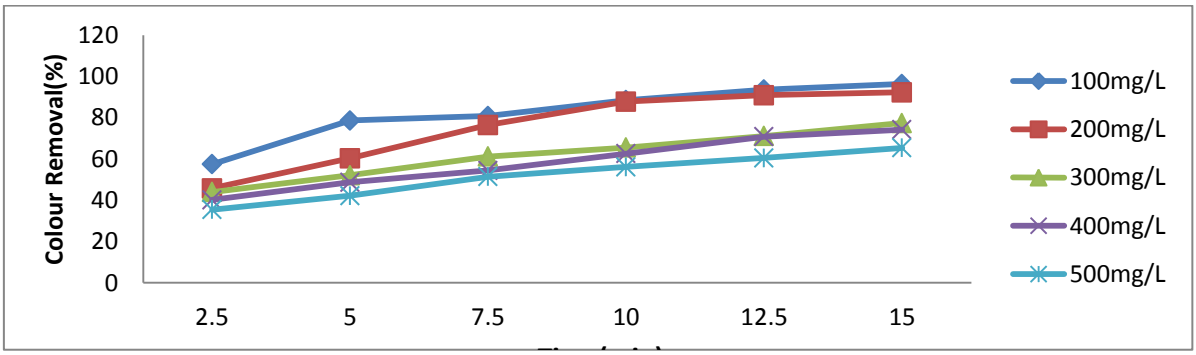

Fig 12: The Effect of Initial Dye Concentration on Color Removal Efficiency by using Titanium based electrode

In this case of Graphite electrode(fig 11), an increase in initial dye concentration of 100mg/L ,200mg/L ,300mg/L, 400mg/L and 500mg/L decreases the color removal efficiency from 95.44% to 68.31%. In case of Titanium based electrode(fig 12), an increase in initial dye concentration of 100mg/L ,200mg/L ,300mg/L, 400mg/L and 500mg/L decreases the color removal efficiency from 96.3% to 65.35%.The rate of color removal decreases with increase in initial concentration. This is explained by the fact that dye molecules tend to associate with increase in dye concentration to clusters of low diffusivity; this lowers the rate of dye diffusion to the anode surface with a consequent decrease in the rate of dye oxidation. or using lower NaCl concentration which discharge the lower potential Cl_2 , So lower NaCl concentration is not sufficient to oxidize the higher dye concentration

3.6 Effect of Dye Concentration on COD Removal:

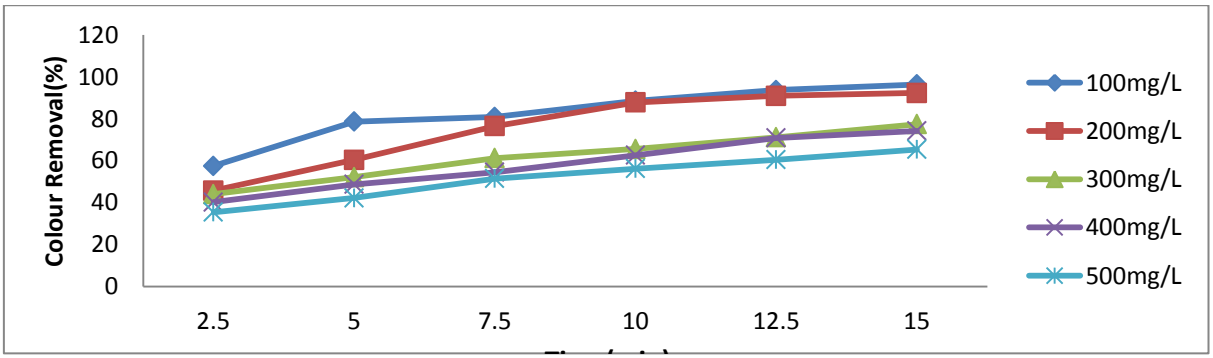

Fig 13: The Effect of Initial Dye Concentration On Color Removal Efficiency by using graphite electrode.

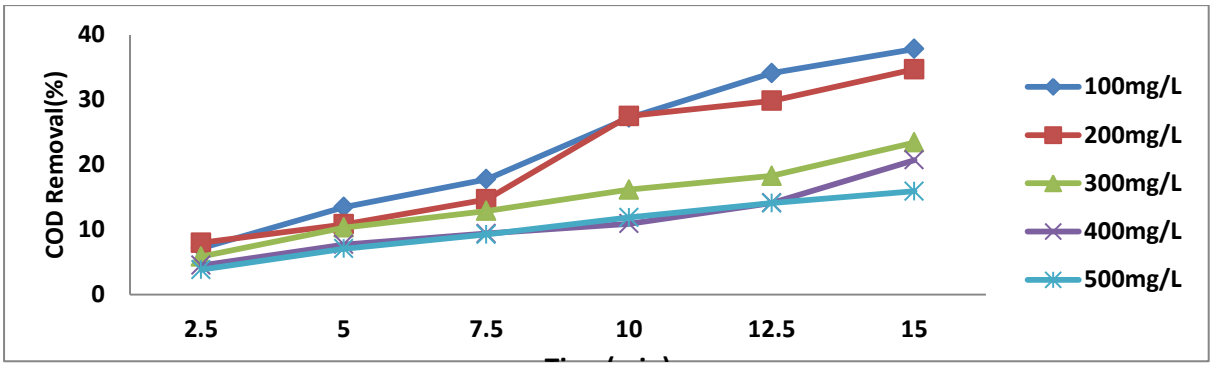

Fig 14: The Effect of Initial Dye Concentration On COD Removal by using Titanium based electrode

Fig 13 shows effect of initial dye concentration on the color removal efficiency. In this case an increase in initial dye concentration of 100mg/L ,200mg/L ,300mg/L, 400mg/L and 500mg/L decreases the color removal efficiency from 96.3% to 65.35%. Fig 14 shows effect of initial dye concentration on the COD removal. In this case decrease the percentage of COD is from 37.82% to 15.89%. The percentage of COD removal gradually decreases with respect to increase in initial dye concentration. This may due to the generation of hypochlorite and free chlorine is less. These less amount of ions is not sufficient for oxidize the higher dye concentration.

Table 2: Performance of Electrodes at Optimum Conditions.

Sl. No	Parameters		Graphite Electrode	Titanium Based Electrode
1	Difference in weight of electrodes(g)	Anode	0.35	0.05
		Cathode	-	-
2	Color Removal (%)		95.44	96.30
3	COD Removal (%)		37.10	37.82
4	Current density taken(A/m^2)		216	96
5	Energy consumption(KWh/Kg COD removal)		167.22	9.295
6	COD Removal Rate(Kg of COD/hr/A/m^2)		0.086	0.88

From the results, it is observed that for higher current density, rate of COD removal decreases and increases the energy consumed per kg of COD removal. This may be due to the electrolysis reaction that becomes dominant at higher current densities.

4. CONCLUSIONS

The following conclusions are drawn from the results of the present study:

- The percentage of color removal for Graphite and Titanium based electrodes is found to be 93.40% and 98.88% at an optimum NaCl concentration of 0.02M respectively.
- The percentage of color removal for Graphite and Titanium based electrodes is found to be 99.71% at an optimum time of 70minutes and 99.90% at an optimum time of 15minutes respectively.
- The percentage of color removal for Graphite and Titanium based electrodes is found to be 95.44% at an optimum current density of $216A/m^2$ and 96.30% at an optimum current density of $96A/m^2$ respectively.

- The percentage of color removal for Graphite and Titanium based electrodes is found to be 95.44% and 96.30% at an optimum pH of 7 respectively.
- The percentage of color and COD removal for Graphite and Titanium based electrodes is found to be 95.44% and 37.20% at an optimum dye concentration of 100mg/L and 96.30% and 37.82% at an optimum dye concentration of 100mg/L respectively.
- The COD removal rates are 0.086 Kg of COD/hr/A/m^2 for Graphite electrode and 0.88 Kg of COD/hr/A/m^2 for Titanium Based electrode at the optimum conditions.
- The energy consumptions are 167.22 KWh/Kg COD removal for Graphite electrode and 9.295KWh/Kg COD removal for Titanium based electrode at the optimum conditions.
- From the results obtained, Titanium based electrode is found to be more effective and efficient in terms of color removal, COD removal, energy consumption and COD removal rate when compared to Graphite electrode.

The overall experimental results indicate that the electrochemical oxidation method can be used effectively to treat the textile dye.

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