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Indirect Electrochemical oxidation process of synthetic toxic azo dyes with in situ electro –generated active chlorine for textile dyeing industry waste water treatment

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Abstract : The removal of reactive dyes from effluents by electro coagulation has become an attractive method in recent years. This paper deals with the removal of the reactive textile dyes Samarone yellow, Fast sulphon black F, Acid Orange from an aqueous medium by the electro coagulation method using platinised titanium, mild steel, aluminium, Copper and stainless steel electrodes. The effects of electrolyte concentration, initial pH, current density, electrode area, inter electrode distance, dye concentration, and treatment time on the decolourization efficiency have been investigated. The optical density of the dye solution was measured before and after electrolysis, and hence the decolourization efficiency (DE) was calculated. UV spectroscopy has been used to investigate the nature of dye before and after decolourization.

Key words: Electrocoagulation, wastewater treatment, textile dyes, Samarone yellow, Fast sulphonblack F, Acid Orange, decolourisation efficiency

1. Introduction

In general, the wastewater generated from textile industries is found to contain high degree of pollutants with high total dissolved solids and suspended solids. The wastewater is highly colored and viscous due to dyestuff and suspended solids respectively. The textile industry is estimated to consume as much as two-third of the total annual production of dyes¹. Azo dyes are the largest and most versatile class of dyes and are commonly used to dye various materials such as textiles leathers, plastics, cosmetics and food². They are the major group of dyes used in the textile industry and contribute between 50-65% of the colours in textile dyes^{1,3}. The inefficiencies in the dyeing process result in dyestuff losses between 2-50% to the waste water with the lower limit for basic dyes and the upper for azo dyes. Ultimately these dyes find their way to the environment and end up contaminating rivers and groundwater in the location of the industries³. Colours in water bodies reduce light penetration, alter the pH, increase the Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) and thereby make aquatic life difficult⁴. Dye house effluents are therefore of serious environmental concern. Several treatments of textile effluents to achieve decolourisation have been reported. These include physicochemical methods such as filtration, specific coagulation, use of activated carbon and chemical flocculation. Some of these methods are effective but quite expensive^{5,6}. Although, biotreatment offers a cheaper and environmentally friendlier alternative for colour removal in textile effluents, it has its own demerits. Anaerobic decolourisation of azo dyes produces aromatic amines which are toxic to aquatic life³ mutagenic to humans and cannot be degraded further under anaerobic conditions^{7,8}. It has been reported that the only safe biodegradation method for azo dyes is combined aerobic treatment⁹. However, there are very few reports of aerobic bacteria that can grow with azo compounds². Electrochemical methods can also be used to decolourise dyes. Recently electrochemical methods¹⁰⁻¹³ and chemical methods^{14,15} have been used to decolourize various dye solutions. The present work is undertaken to decolourise an aqueous solution of

Samarone yellow, Fast sulphonon black F and Acid Orangedye by electrochemical methods using platinised titanium, mild steel, aluminium, copper and stainless steel as anodes and graphite as cathode

2. Methodology

Dye solution : 50 ppm of Samarone yellow, Fast sulphon black F , Acid Orange dyes solution was used.

2.1. Decolourisation Process

The optical density of the dyes solution before and after decolourisation was measured by the instrument Photoelectric Colorimeter -112. Graphite was used as cathode. Platinised titanium /Mild steel / Copper/Aluminium /SS were used as anode. The electrolysis was carried out in an undivided cell with a stirring bar (**Fig- 1**). UV-Visible spectra were recorded in a Lamda 35 model.

| | | |
|--------------------------|---|--|
| Cathode | : | Graphite |
| Current Density | : | 0.005 A/cm ² |
| Volt | : | 2 and 4 Volts |
| Duration of Electrolysis | : | 5 mts |
| Initial OD | : | 0.10 (Samaron yellow) 0.05 (Fast Sulphon Black F) 1.29 (Acid Orange) |
| Electrolyte | : | 3.75 gm and 7.5 gm of NaCl dissolved in 100 ml of dye solution |
| Dye Solution | : | 0.05 gm in 100 ml Samaron yellow, Fast Sulphon Black F and Acid Orange |

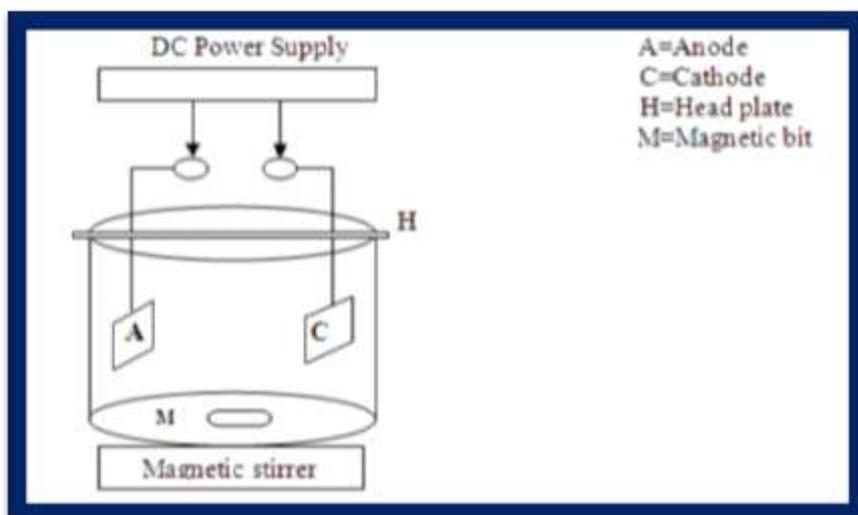


Figure: 1 Schematic diagram of experimental setup

3. Results and Discussion

Decolourisation process was carried out in an undivided glass cell, provided with a stirring bar. 100 ml of the dye solution was taken (50 ppm of Samarone yellow, Fast sulphon black F and Acid Orange). Graphite was used as cathode. One of the metal specimens (platinised titanium / Mild steel /Aluminium etc) was used as anode. 3.75 gm of sodium chloride was added. Current was passed for 5 minutes (4 volts; current density = 0.005 A/cm²). The pH of the dye solution, before and after decolourisation was measured. The optical density was measured before and after decolourisation. The decolourisation efficiency (DE) was calculated using the relation

$$\text{Percentage decolourization} = [\text{Initial O.D} - \text{Final O.D} / \text{Initial O.D}] \times 100$$

$$\text{DE} = [\text{OD}_1 - \text{OD}_2 / \text{OD}_1] \times 100$$

Where

OD₁ = Optical Density before decolourisation

OD₂ = Optical Density after decolourisation

DE = Decolourization efficiency

The results are summarized in **Table 1, 2 and 3**. It is observed that platinised titanium offers the maximum DE of 90%, 80%, 83.72%

Table: 1 Decolourization efficiency of Samaron yellow solution

| S. NO | Anode | NaCl 3.75 g | | | | NaCl 7.5g | | | |
|-------|-----------------|-----------------------|-----|-----------------------|-----|-----------------------|-----|-----------------------|-----|
| | | 2 volt | | 4 volt | | 2 volt | | 4 volt | |
| | | OD After electrolysis | DE |
| 1 | Pt/Ti | 0.02 | 80% | 0.01 | 90% | 0.01 | 90% | 0.01 | 90% |
| 2 | Cu | 0.06 | 40% | 0.04 | 60% | 0.02 | 80% | 0.03 | 70% |
| 3 | Mild Steel | 0.04 | 60% | 0.05 | 50% | 0.05 | 50% | 0.04 | 60% |
| 4 | Stainless Steel | 0.03 | 70% | 0.03 | 70% | 0.03 | 70% | 0.03 | 70% |
| 5 | Al | 0.05 | 50% | 0.04 | 60% | 0.04 | 60% | 0.04 | 60% |

Table: 2 Decolourization efficiency of Fast sulphon Black F solution

| S. NO | Anode | NaCl 3.75 g | | | | NaCl 7.5g | | | |
|-------|-----------------|-----------------------|-----|-----------------------|-----|-----------------------|-----|-----------------------|-----|
| | | 2 volt | | 4 volt | | 2 volt | | 4 volt | |
| | | OD After electrolysis | DE |
| 1 | Pt/Ti | 0.02 | 60% | 0.01 | 80% | 0.01 | 80% | 0.01 | 80% |
| 2 | Cu | 0.02 | 60% | 0.02 | 60% | 0.02 | 60% | 0.02 | 60% |
| 3 | Mild Steel | 0.03 | 40% | 0.02 | 60% | 0.03 | 40% | 0.02 | 60% |
| 4 | Stainless Steel | 0.04 | 20% | 0.03 | 40% | 0.03 | 40% | 0.03 | 40% |
| 5 | Al | 0.04 | 20% | 0.03 | 40% | 0.03 | 40% | 0.02 | 60% |

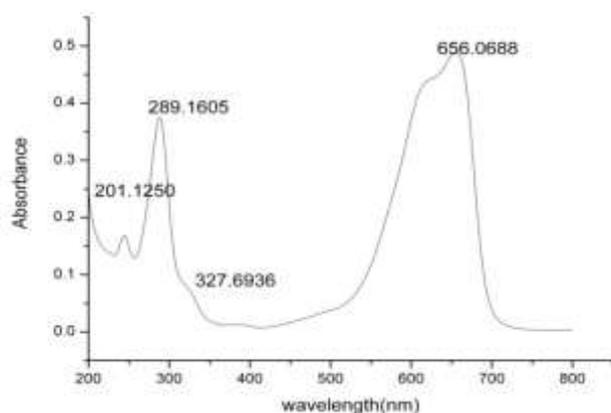
Table: 3Decolourization efficiency of Acid Orange solution

| S. NO | Anode | NaCl 3.75 g | | | | NaCl 7.5g | | | |
|-------|-----------------|-----------------------|--------|-----------------------|--------|-----------------------|--------|-----------------------|--------|
| | | 2 volt | | 4 volt | | 2 volt | | 4 volt | |
| | | OD After electrolysis | DE |
| 1 | Pt/Ti | 0.24 | 81.39% | 0.22 | 82.95% | 0.22 | 82.95% | 0.21 | 83.72% |
| 2 | Cu | 0.50 | 61.24% | 0.47 | 63.56% | 0.49 | 62.01% | 0.43 | 67.54% |
| 3 | Mild Steel | 0.60 | 53.49% | 0.57 | 55.81% | 0.53 | 58.91% | 0.48 | 62.79% |
| 4 | Stainless Steel | 0.62 | 51.93% | 0.59 | 54.26% | 0.55 | 57.36% | 0.50 | 61.24% |
| 5 | Al | 0.61 | 52.71% | 0.56 | 56.59% | 0.56 | 56.59% | 0.51 | 60.47% |

3.1 UV-Visible absorption spectra

Typical UV-Visible spectra for untreated (before electrolysis) and treated (after electrolysis) dye solutions have been done and changes in absorbance of dye solutions were investigated in an undivided electrolytic cell for the purpose of evaluating the dye solution decolourization during the electrolytic process.

In the case of **Samaron yellow** dye (before decolourization) the three peaks were appeared at 269 nm, 295 nm, 422 nm(**Fig.2a**). After decolourization, only one peak was appeared at 205 nm(**Fig.2b**). It is revealed that the losing absorbing bands over the decolourisation process. This showed that decolourization of dye had taken place more effectively. The maximum efficiency of decolourization process is about 90%.

**Fig.2a.** UV-Visible spectrum of Samaron Yellow (before decolorization)

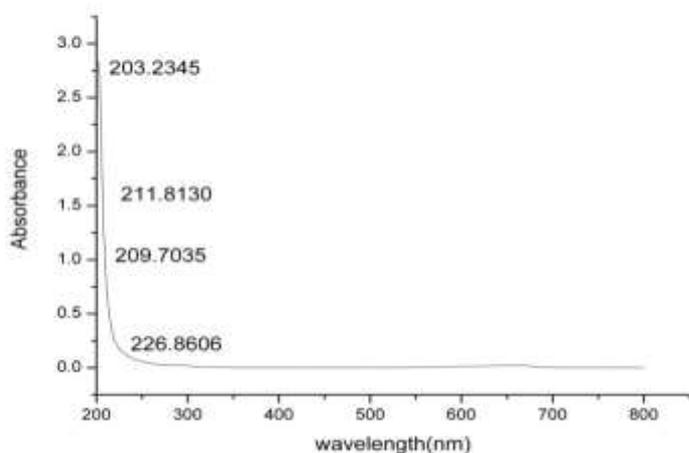


Fig.2b. UV-Visible spectrum of Samaron yellow (After decolourization)

In the case of **Fast Sulphon Black F** (before decolourization) the four peaks were appeared at 218 nm, 293nm,480 nm,604nm(**Fig.3a**). After decolourization, only one peak was appeared at 205.34 nm(**Fig.3b**). It is revealed that the losing absorbing bands over the decolourisation process. This showed that decolourization of dye had taken place more effectively. The maximum efficiency of decolourization process is about **80%**.

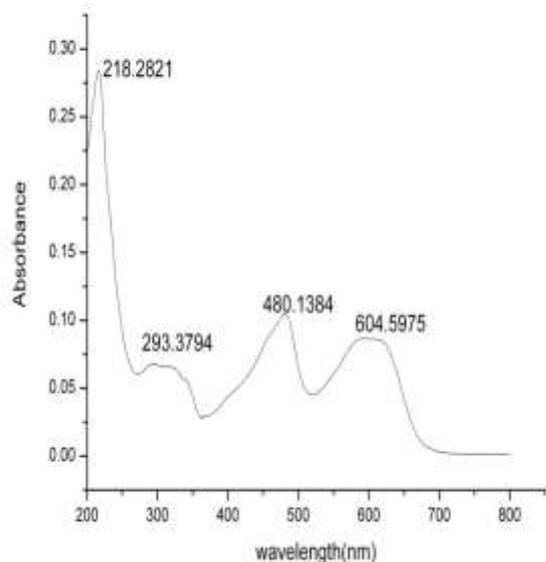


Fig.3a. UV-Visible spectrum of Fast Sulphon Black F (before decolorization)

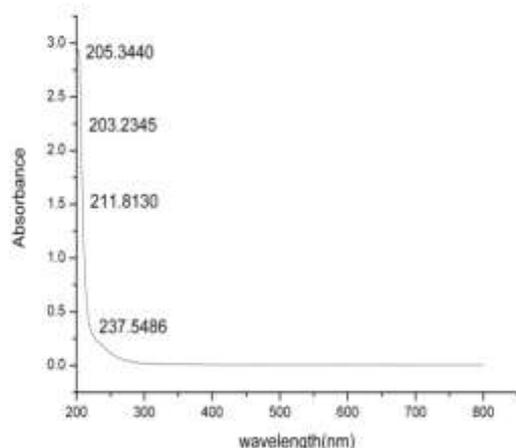


Fig.3b. UV-Visible spectrum of Fast Sulphon Black F(After decolourization)

As in the case of **Acid Orange** (before decolourization) the four peaks were appeared at 201nm, 289nm, 327nm, 656nm (**Fig.4a**). After decolourization, only one peak was appeared at 203 nm (**Fig.4b**). It is revealed that the losing absorbing bands over the decolourisation process. This showed that decolourization of dye had taken place more effectively. The efficiency of decolourization process is about **83.72%**.

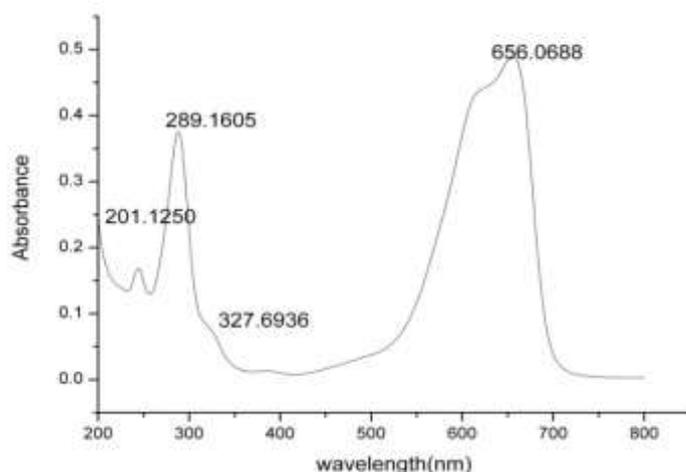


Fig.4a. UV-Visible spectrum of Acid Orange (before decolorization)

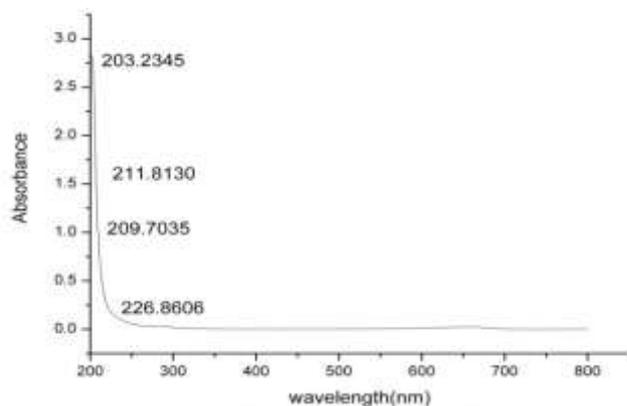


Fig.4b. UV-Visible spectrum of Acid Orange (After decolourization)

The spectrum recorded before decolourisation of selected dyes showed that the wavelength of the maximum absorbance (λ_{max}) were 422 nm(**Fig.2a**), 604 nm(**Fig.3a**) and 656 nm(**Fig.4a**) in the visible region and corresponds to chromophore group. In addition the aromatic structure absorbance was observed between 200 to 300 nm(**Fig.2a,3a&4a**), in the UV region. This corresponds $\pi - \pi^*$ electron transition. The spectrum recorded after electrolysis for 5 mts, when the decolourisation efficiency were 90%,82%,83.72% for platinised titanium anode. the maximum absorbance due to chromophore has completely disappeared. The chromophore has been completely destroyed. The lonely peak in the region of 200-300 nm(**Fig.2b,3b &4b**) indicates that the aromatic structure is still there but the concentration is negligibly small. The destruction of the aromatic ring is not complete. That is why the decolourisation efficiency is not 100%

4. Mechanism of decolourisation

When sodium chloride solution is electrolysed, negative chloride is (Cl^-) is produced. It transfers the electrons to the metal surface and hence Cl^+ is produced^{16,17}. It is highly reactive. It decolorizes the coloured material into colourless product.

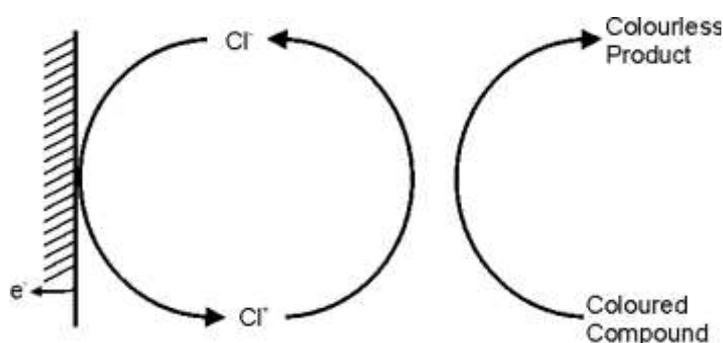


Figure:5 Electrochemically regenerated Cl^+

5. Conclusion

The removal of the reactive textile dyes Samaron yellow, Fast sulphon black F , Acid Orange from an aqueous medium by the Electrochemical method using platinised titanium, mild steel, aluminium, Copper and stainless steel electrodes have been investigated. It is observed that platinised titanium offers the maximum DE of 90%, 80% and 83.72%.The maximum DE of platinised titanium 90%; Cu 80 %; SS 70%; Mild steel offers 62.79 % and 60.47 %. The decolourisation efficiency is in the decreasing order. Pt/Ti>Cu>SS>Mild Steel>Al.In the case of platinised titanium, the DE is very high. This is attributed to the fact, that this metal readily accepts the electron released by Cl^- . Hence Cl^+ is produced readily, easily and abundantly. This Cl^+ converts the coloured compounds in to colourless products. The decrease in DE of other metals (mild steel, aluminium, Copper and stainless steel) is attributed to the fact that these metals accept the electron from Cl^- less readily and produced Cl^+ species less readily and slowly. Electrochemical decolorization of dye solution takes less time than any other decolorization methods

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