

(RESEARCH ARTICLE)



## Electrochemical degradation of reactive industrial textile dye using graphite as potential catalytic electrode

Vidyasagar C. C <sup>1,\*</sup>, Prakash. K <sup>2</sup> and Manjunatha N. K <sup>3</sup>

<sup>1</sup> Department of Studies and Research in Chemistry, Rani Channamma University, Belagavi-591156 Karnataka, India.

<sup>2</sup> Department of Environmental Science, Gulbarga University, Kalaburagi-585106, India.

<sup>3</sup> Department of PG Studies and Research in Geography, Rani Channamma University, Belagavi-591156 Karnataka, India.

Global Journal of Engineering and Technology Advances, 2023, 17(02), 131–140

Publication history: Received on 03 July 2023; revised on 19 November 2023; accepted on 22 November 2021

Article DOI: <https://doi.org/10.30574/gjeta.2023.17.2.0127>

### Abstract

In recent years, the indirect electrochemical degradation of industrial effluents has gained popularity. This study examines the electrochemical aqueous solution degradation of reactive azo dyes employing graphite carbon electrodes as a possible catalyst. The findings suggested that the degradation of dyes was significantly influenced by the starting pH and the supporting electrolytes. Studies on chemical oxygen demand (COD) and UV-Vis were used to assess the effectiveness of the degrading process. Reactive dye may be used to obtain maximum colour removal efficiencies of 99% and chemical oxygen demand (COD) removal efficiencies of 88%. The LC-MS investigation indicated the breakdown of reactive dye and verified that the azo groups and aromatic rings were eliminated.

**Keywords:** Carbon electrodes; Graphite electrode; Electrochemical degradation; Reactive azo; LC-MS

### 1. Introduction

Numerous things, including the huge increase in industrial waste, marine dumping, air deposition, etc., contribute to the environmental disaster on a worldwide scale and result in water contamination. Industries are the main cause of pollution in soil and water. Natural impurities removed from cotton fibre, as well as processing chemicals and dyes, contribute a significant amount of pollutants to the effluent of the dyeing industry, which produces harmful colourants, chemicals, and heavy metals that harm the aquatic environment. Nearly 2 million tonnes of untreated industrial and agricultural waste are released into the environment every day [1-6]. This trash has an unpleasant colour and lowers the quality of recipient water bodies, necessitating the addition of oxygen in order for the dye pollutants to be digested. In aquatic animals, dyes frequently combine with metal ions and cause toxicity. Aquatic life requires the presence of dissolved oxygen (DO) in the water. Increases in organic content may have an impact on the chemical oxygen demand (COD) and biological oxygen demand (BOD) of water bodies (BOD) [6-9]. Organic and inorganic components may both be present in wastewater, depending on the source. BOD and COD both reduce DO, rendering the water unsuitable for consumption. By 2050, 65% of the world's population would lack access to safe drinking water, according to current estimates. Water-based resources health issues for the general public are brought on by decreased water quality [10-14]. All perennial aquatic resources could no longer be suitable for their intended usage due to the fast growing population and the resulting wastewater output. Wastewater produced in metropolitan areas will not be fully treated in the coming years. In order to determine the state of wastewater generation and treatment in class I cities (population greater than 100,000) and class II towns, the Central Pollution Control Board conducted research. According to the most recent study, India's 921 Class I and Class II municipalities produce roughly 26254 million gallons of wastewater every day [15-19].

\* Corresponding author: Dr. VIDYASAGAR. C. C

The demand for produced items will rise along with the population. As a result, it is anticipated that the amount of industrial trash would increase more quickly than that of municipal wastes. Industrial wastewater management has changed significantly in recent years. Industries are understanding the necessity and advantages of utilizing water for a variety of uses in declining order of necessary purity before ultimate treatment and release to the environment as a result of legal regulations and technical improvement [20, 21]. The biggest environmental negative consequences from diverse businesses' wastewater production cause biosystem imbalance. The demand for produced items will rise along with the population. As a result, it is anticipated that the amount of industrial trash would increase more quickly than that of municipal wastes. Industrial wastewater management has changed significantly in recent years. Industries understand the necessity and advantages of utilizing water for a variety of uses in declining order of necessary purity before ultimate treatment and release to the environment as a result of legal regulations and technical improvement. The biggest environmental negative consequences from diverse businesses' wastewater production cause biosystem imbalance [22-24].

### **1.1. Operations for dyeing textiles**

The textile industry is made up of a wide and dispersed set of companies that manufacture and/or process textile-related materials (fibre, yarn, and fabric) for use in manufacturing industrial, household, and fashion goods. Companies involved in the textile industry acquire and prepare fibres, turn them into yarn, thread, or webbing, turn the yarn into fabric or items connected to it, and colour and finish these materials at various stages of manufacturing. The majority of textile mills specialise in the dyeing process since it is a sophisticated procedure to turn raw fibres into completed clothing and non-apparel textile goods. In the process of creating synthetic cotton and wool textiles, there is little distinction between knitting and weaving (Hashem et al. 2005).

### **1.2. Dyeing**

Dyeing is the application of chemical pigments to fibre or cloth in order to provide colour. According to product utilization and raw fabric ingredients, the technique is broadly separated into reactive, indanthren, dispersion, sulphur, vat, and naphthol dyeing. The dyes' chromophore and auxochrome groups, which also contribute to pollution, are what give the colour. Water is used in the dyeing process to transfer colours and to heat the treatment baths in the form of steam. The most extensively used fibre in the world, cotton, is a substrate that requires a lot of water to process. For instance, 0.6–0.8 kg of NaCl, 30–60 g of dyestuff, and 70–150 l of water are needed to dye 1 kg of cotton with reactive dyes.

### **1.3. Environmental concern of reactive dyes**

The most problematic substances in textile dye effluents are reactive dyes (Carliell et al. 1994 and 1996). Due to their complicated structure and synthetic origin, they are distinguished by their great water solubility as well as their high stability and persistence. They provide a significant resistance against chemical and photolytic deterioration since they are purposefully made to resist degradation. Additionally, under normal aerobic conditions encountered in standard biological treatment systems, reactive dyes, including many textile colours, typically do not biodegrade (Brown and Hamburger, 1987). The reactive dyes family is one of them that is of particular interest. Although they are often non-toxic, they can produce aromatic amines, which are potentially carcinogenic, mutagenic, and toxic breakdown products, in anaerobic settings (such as aerobic sediments and intestinal habitats). The fact that cotton is one of the most widely produced textile fibres in the world, with annual production exceeding 25 million tonnes, provides insight into the extensive use of reactive dyes, their large-scale production, and the environmental damage caused by the wastewater they produce. Additionally, the high degree of hydrolysis of reactive dyes in alkaline baths further increases the potential environmental harm of their effluents.

---

## **2. Material and methods**

### **2.1. Experimental setup**

#### *2.1.1. Chemical Treatment*

Experimental setup used for laboratory scale chemical treatment is shown in Figure 1. The AR grade chemical reagents such as Sodium hypochlorite (NaOCl), Calcium hypochlorite ( $\text{Ca}(\text{OCl})_2$ ), Ferrous sulphate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) and Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) were used for the experiments.

### 2.1.2. Experimental setup for electrochemical treatment

The unit includes two components: The dyestuff bath and the Power system. The dyestuff bath is setup with Borosil beaker and its capacity is of 250 ml. It includes two electrodes (a cathode and an anode). Two types of electrodes, Graphite carbon and Stainless Steel, in any single experiment; both the electrodes used were of same material. Spacing between the two electrodes was 2 cm.

### 2.2. pH

Measurement of *pH* is one of the most important and frequently used tests in water chemistry. Practically every phase of water supply and wastewater treatment, e.g. acid–base neutralization, water softening, precipitation, coagulation, disinfection and corrosion control is *pH*–dependent. At a given temperature the intensity of the acidic or basic character of a solution is indicated by *pH* or hydrogen ion activity. Alkalinity and acidity are the acid– and base–neutralizing capacities of water and usually are expressed as milligrams of  $\text{CaCO}_3$  per liter. In this study *pH* was measured by a water analyser– Systronics, Model–371 (Figure 3) after calibrating the *pH* meter with buffer solutions of *pH* 4.0, 7.0, and 9.2 (APHA 1999, Method no. 4500–B of Standard Method).

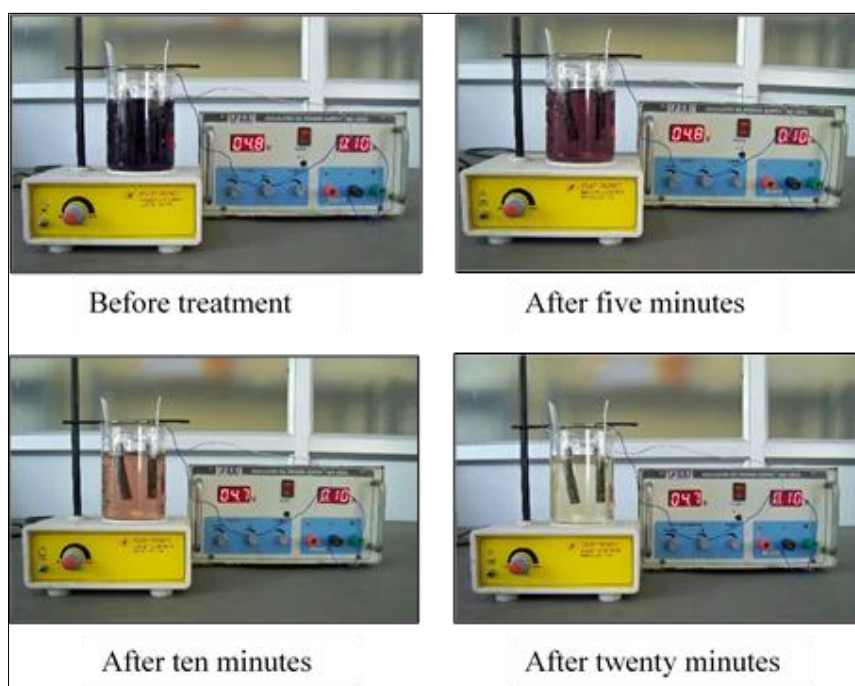
### 2.3. Chemical oxygen demand (COD)

Chemical oxygen demand (COD) is defined as the amount of a specified oxidant that reacts with the sample under controlled conditions. The quantity of oxidant consumed is expressed in terms of its oxygen equivalence. Because of its unique chemical properties, the dichromate ion ( $\text{Cr}_2\text{O}_7^{2-}$ ) is the specified oxidant; it is reduced to the chromic ion ( $\text{Cr}^{3+}$ ) in this test. Both organic and inorganic components of the sample are subject to oxidation, but in most cases the organic component predominates and is of the greater interest.

In this study COD was determined by Open Reflux (titrimetric) method (APHA 1999, Method no. 5220–B of Standard Methods). For COD analysis 20 mL of sample was taken in COD digestion flask (250 mL) and to this flask 10 mL of 0.01 M standard  $\text{K}_2\text{Cr}_2\text{O}_7$  solution and 1 g of  $\text{HgSO}_4$ , and added 30 mL of concentrated sulfuric acid (98%, Added 5.5 g  $\text{Ag}_2\text{SO}_4/\text{Kg H}_2\text{SO}_4$ ) were added slowly with stirring and refluxed for two hours at 423 K. Blank considered of double distilled water was also prepared. Then the sample and blank solutions were cooled to room temperature and COD value was determined by titrating with 0.01 M standard  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  solution using ferroin indicator.

## 3. Results and discussion

### 3.1. Electrochemical degradation studies

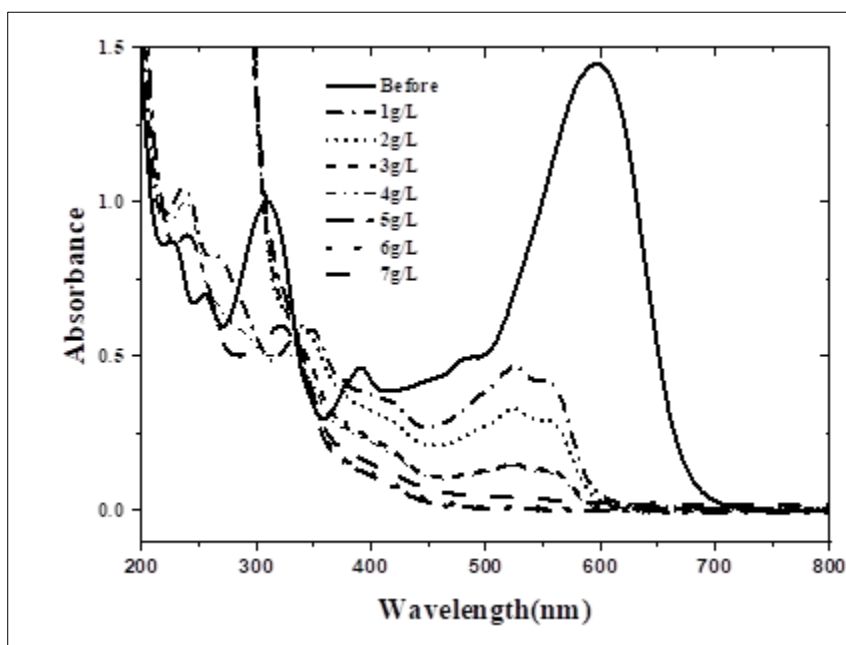


**Figure 1** Electrochemical decolorization process of reactive dye: 50 ppm (w/v); *pH*: 3;  $\text{NaCl}$ : 5 g  $\text{L}^{-1}$ ; time: 20 min

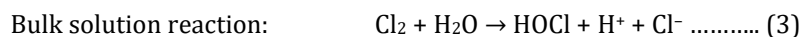
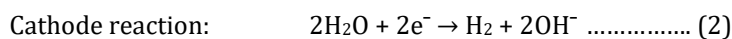
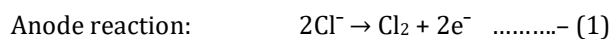
Under ideal electrolyte conditions, the dye was quickly and nearly completely decolorized by the electrochemical breakdown (Figure 1). The proportion of reactive dye decolorization after electrochemical treatment was determined to be 99.93% in 20 minutes. Through UV-Vis absorbance measurements, the level of decolorization was tracked.

### 3.2. Effect of supporting electrolytes

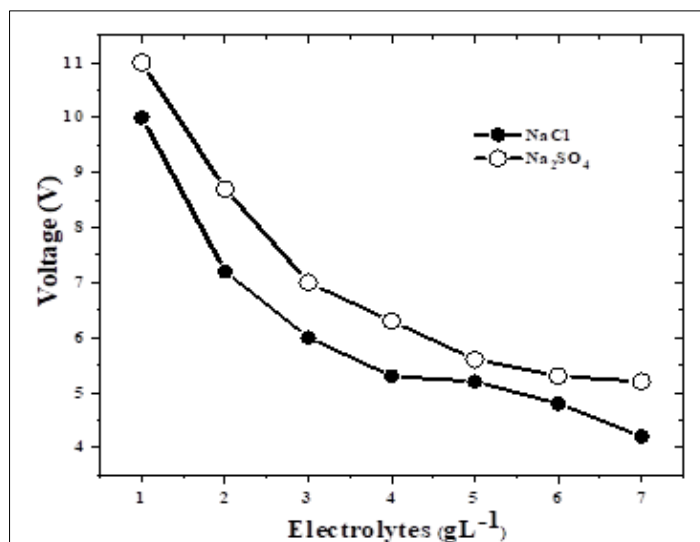
UV-Vis spectra (Figure 2) show that the decolorization effectiveness of reactive dye rises when NaCl is added to the dye solution during electrolysis. This discovery led to the conclusion that the use of NaCl as an electrolyte can increase the degradation efficiency and reduce the time required for electrolysis, which may be explained by the interaction between the dye molecule and the electrogenerated chlorine/hypochlorite. The following figure outlines a potential process for electrochemical deterioration in the presence of NaCl.



**Figure 2** Absorption spectra for reactive dye solution before and after electrolysis for different concentration of NaCl. Electrolysis condition: concentration of the dye solution: 50 ppm (w/v); pH: 3; current density  $170 \text{ A m}^{-2}$ ; time: 20 min

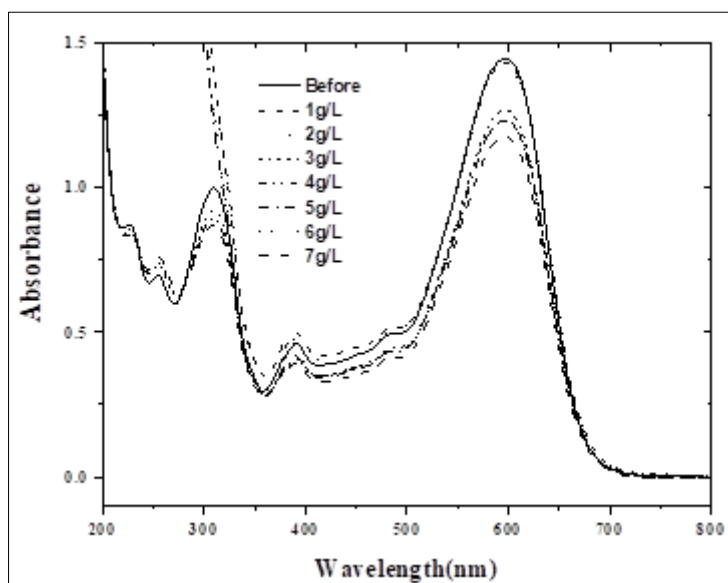


The above mechanism was classified as indirect electro-oxidation of pollutant. Increase in the concentration of NaCl upto  $5 \text{ g L}^{-1}$  accelerated the degradation rate, enabling the decolorization efficiency of reactive dye.



**Figure 3** Influence of different supporting electrolytes concentration on applied voltage during electrolysis of dye solution. Electrolysis condition: concentration of the dye solution: 50 ppm (w/v); pH: 3; current density 170 A m<sup>-2</sup>

The ideal concentration of NaCl in the sequential degradation study was set at 5 g L<sup>-1</sup> since subsequent increases in NaCl concentration (> 5 g L<sup>-1</sup>) resulted in a minor improvement in decolorization efficiency. Additionally, the working voltage at the specified current density decreases as the NaCl content rises (Figure 3).



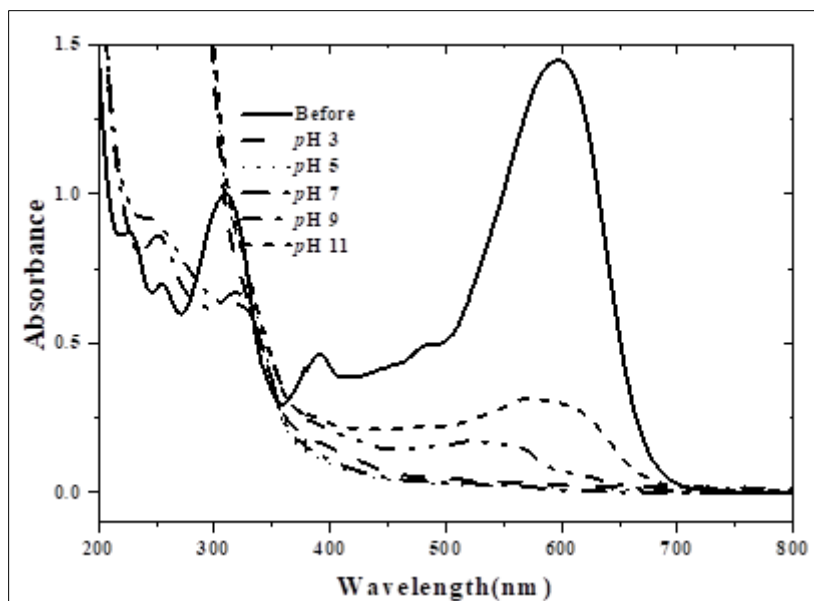
**Figure 4** Absorption spectra for reactive dye solution before and after electrolysis for different concentration of Na<sub>2</sub>SO<sub>4</sub>. Electrolysis condition: concentration of the dye solution: 50 ppm (w/v); pH: 3; current density 170 A m<sup>-2</sup>; time: 20 min

The impact of Na<sub>2</sub>SO<sub>4</sub> on the deterioration of dyes is shown in Figure 4. It was discovered that the decolorization efficiency was lower than NaCl's. The production of stronger oxidizing agents like Cl<sub>2</sub>, HOCl, and OCl<sup>-</sup> is thought to be the cause of the increased decolorization effectiveness in the presence of NaCl. The formation of persulphate ions, which may oxidize organic dyes, is thought to be the cause of the decolorization in the presence of Na<sub>2</sub>SO<sub>4</sub>.

### 3.3. Effect of initial pH

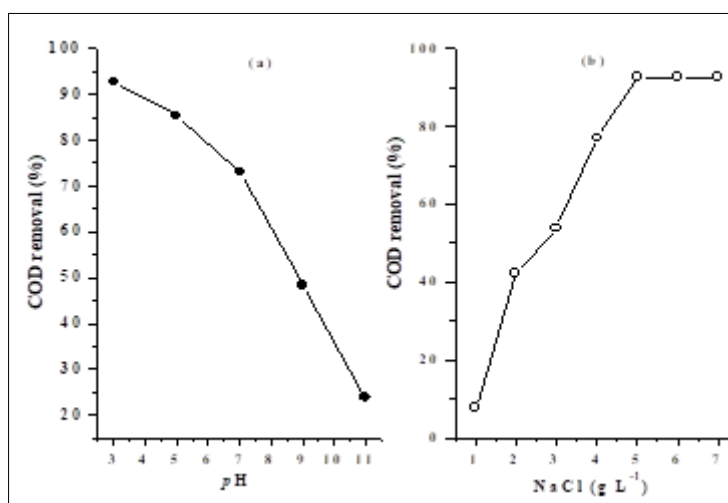
One of the key elements that affect how well an electrochemical process works is the pH of the solution. As a result, tests were done to determine how pH affected how quickly reactive degraded. When the concentration of NaCl was at 5 g L<sup>-1</sup>, there was a noticeable variation in the degree of decolorization. Using 1M H<sub>2</sub>SO<sub>4</sub> or NaOH, the original pH of the

solution (3-11) was changed. The electrolysis was done at room temperature for 20 minutes with a current density of  $170 \text{ A m}^{-2}$  and a dye concentration of 50 ppm (w/v) (300 K). It was evident from the UV-Vis spectra that the presence of chromophores is what causes the absorption in the visible range (azo groups).



**Figure 5** Absorption spectra for reactive dye solution before and after electrolysis at different pH. Electrolysis condition: concentration of the dye solution: 50 ppm (w/v); NaCl:  $5 \text{ g L}^{-1}$ ; current density  $170 \text{ A m}^{-2}$ ; time: 20 min

### 3.4. Analysis of COD

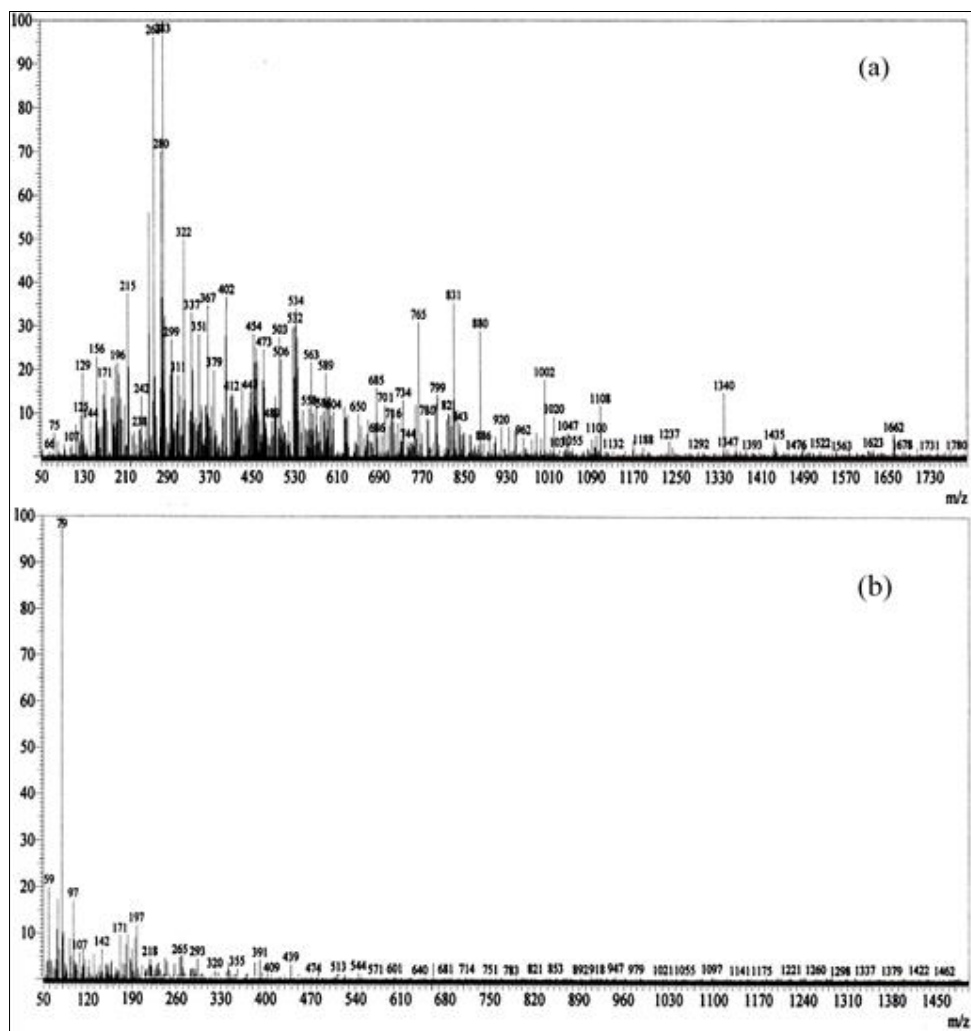


**Figure 6** Effect of pH and NaCl concentrations on COD removal of reactive dye. Electrolysis condition: concentration of the dye solution: 50 ppm (w/v); current density  $170 \text{ A m}^{-2}$ ; time: 20 min

The standard COD measurement is known to be affected by a number of inorganic substances (Lenor *et al.* 1999). Of these, chloride may have the significant effect on the test which is due to its reaction with potassium dichromate (Chatzisyneon *et al.* 2006). The COD was measured by adopting open reflux titrimetric method. In the present study, it can be seen that the degradation of NNWB from their aqueous solutions may proceed by indirect electrochemical oxidation rather than direct electrochemical process. The electrolysis was carried out at a current density of  $170 \text{ A m}^{-2}$ . At this current density,  $\text{Cl}_2$  generated in the solution drives the oxidation process. In the absence of chloride containing electrolytes, the COD removal and dye degradation efficiencies were very low (Abu and Abdel, 2005). The maximum COD removal efficiency (92.63 %) was observed at pH 3 (Figure 12a). The percent removal efficiency of COD increased with increase in the concentration of NaCl (Figure 12b). This confirmed that the electrogenerated chlorine/hypochlorite will play an important role in the electrochemical degradation process of the dyestuffs.

### 3.5. LC-MS studies

LC-MS technique was employed to monitor the extent of degradation of dye molecule before and after electrolysis. Since, this technique is specifically useful to study the cleavage of azo groups, formation of intermediates and hence the extent of mineralization occurs during electrolysis. The dye solution (50 ppm, w/v) was subjected to electrolysis at a current density of  $170 \text{ A m}^{-2}$  and at pH 3 keeping NaCl concentration at  $5 \text{ g L}^{-1}$ . MS spectrum recorded before electrolysis shows a greater number of peaks at higher  $m/z$  values due to the presence intact dye of high molecular weight and other impurities (Figure 13a).

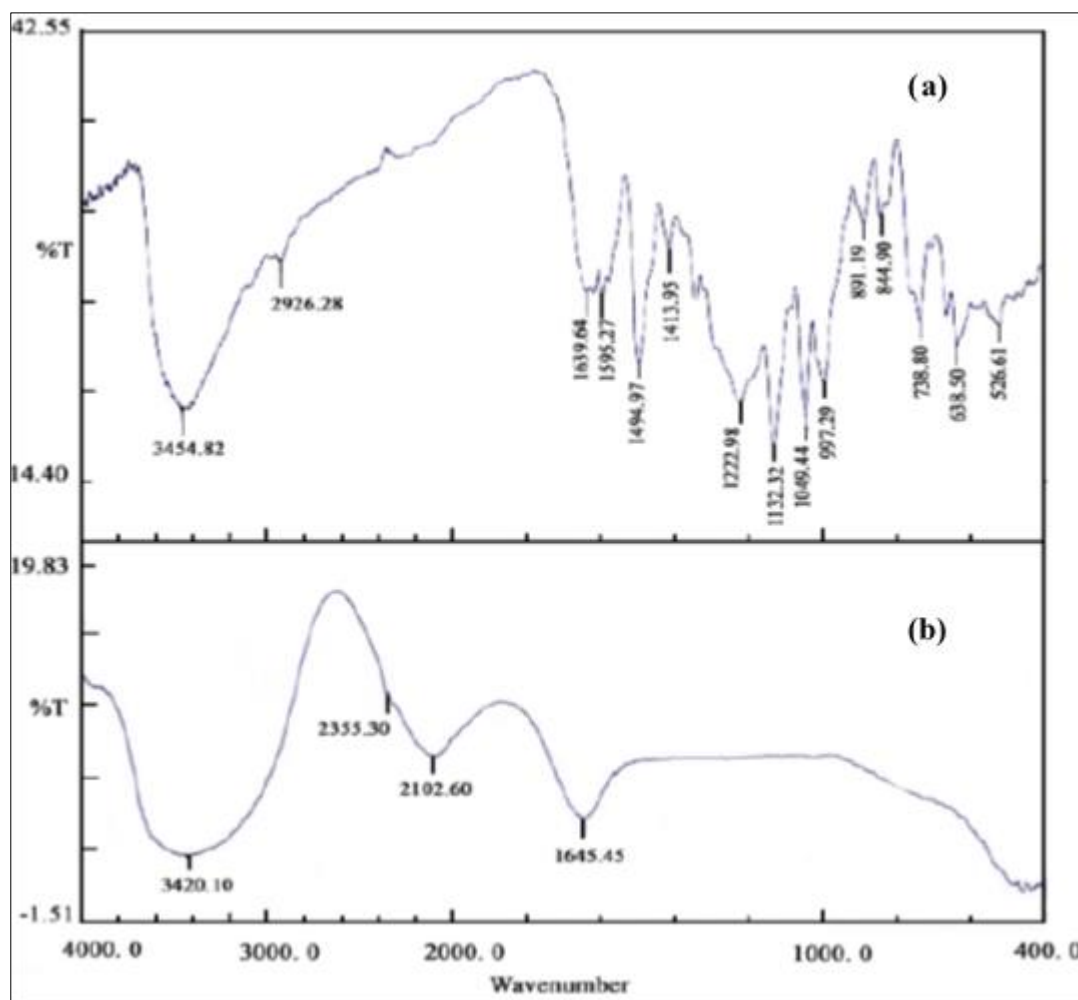


**Figure 7** Mass spectrum of NNWB (70–80%) (a) before electrolysis and (b) after electrolysis. Electrolysis condition: concentration of the dye solution: 50 ppm (w/v); pH: 3; NaCl:  $5 \text{ g L}^{-1}$ ; current density  $170 \text{ A m}^{-2}$ ; time: 20 min

The MS spectrum of the electrolyzed dye solution shows, the absence of majority of the earlier peaks. This indicated the decomposition of the dye molecules in to colorless low molecular weight fragments (Figure 13b). The remaining peaks in the mass spectrum may be due to the presence of substituted aromatic compounds, particularly different substituted benzene like moieties.

### 3.6. FT-IR

The FT-IR spectrum of dye NNWB obtained before electrochemical treatment showed several bands at fingerprint region. After the electrochemical degradation a significant reduction in the number of bands were observed in fingerprint region (Figure 14). This further concludes the disappearance of many functional groups of the dye molecule.



**Figure 8** FT-IR spectrum of NNWB (70–80%) (a) before electrolysis (b) after electrolysis. Electrolysis condition: concentration of the dye solution: 50 ppm (w/v); pH: 3; NaCl: 5 g L<sup>-1</sup>; current density 170 A m<sup>-2</sup>; time: 20 min

#### 4. Conclusion

In the present study the degradation of textile dyes (Reactive dye) and wastewater has been undertaken through chemical and electrochemical methods. For chemical treatment NaOCl, Ca(OCl)<sub>2</sub> and Fenton's reagent were used as oxidizing agents to degrade textile dyes and wastewater. From the results it is concluded that, the chemical method of treatment is not an efficient way for the effective degradation of dyes and wastewater. Chemical treatment causes additional pollution due to the undesired reactions and large amount of sludge formation. Moreover, these methods are highly expensive and require longer times for the degradation. From the proposed electrochemical degradation methods, the experimental results were obtained nearly 100 % decolorization and COD removal of the textile dyes and wastewater with less time consuming and low power consumption. The developed electrochemical methods can be used for the effective degradation of textile dyes and wastewater on commercial scale. Also, this method does not pose disposal problem after the treatment.

#### Compliance with ethical standards

##### *Acknowledgments*

The authors are grateful to Rani Channamma University, Belgaum for laboratory facilities, the authors are also thanking Science and Engineering Research Board, Department of Science and Technology Govt of India and Vision group on Science and Technology, govt. of Karnataka for the financial assistance in terms of project grants.



*Disclosure of conflict of interest*

There are no conflicts to declare.

---

**References**

- [1] Robert, L., Chiu, H. M., Shiau, S. C., Yen, R. Y. L., Hung, Y. T. Degradation and sludge production of textile dyes by Fenton and Photo-Fenton processes, *Dyes and Pigments*. 2007; 73: 1–6.
- [2] Robinson, T., McMullan, G., Marchant, R., Nigam, P. Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative, *Bioresour., Technol.* 2001; 77: 247–55
- [3] Rodrigues, E., Pickard, M. A., Vazquez-Duhlt, R. Industrial dye decolourisation by laccases from ligninolytic fungi, *Curr. Microbiol.* 1999; 38: 27–32.
- [4] Sakalis, A., Ansorgova, D., Apek, M. H., Jandera, P., Voulgaropoulos, A. Analysis of sulphonated azodyes and their degradation products in aqueous solutions treated with a new electrochemical method. *Intern. J. Environ. Anal. Chem.* 2004; 84: 875–888.
- [5] Sakalis, A., Mpoulmpasakos, K., Nickel, U., Fytianos, K., Voulgaropoulos, A. Evaluation of a novel electrochemical pilot plant process for azo dyes removal from textile wastewater, *Chem. Eng. J.* 2005; 111: 63–70.
- [6] Sanroman, M. A., Pazos M., Ricart M. T., Cameselle C. Electrochemical decolourisation of structurally different dyes, *Chemosphere*. 2004; 57(3): 233–239.
- [7] Sanroman, M. A., Pazos, M., Ricart, M. T., Cameselle, C. Decolourisation of textile indigo dye by DC electric current, *Engineering Geology*. 2005; 77: 253–261.
- [8] Scott, J. P., Ollis, D. Integrated chemical and biological oxidation processes for water treatment, review and recommendations, *Environ. Prog.* 1995; 14: 88–103.
- [9] Shaw, C. B., Carliell, C. M., Weatly, A. D. Anaerobic/treatment of coloured textile effluents using sequencing batch reactor, *Water Research* 2002; 36: 1993–2001.
- [10] Sheng, H. L., Chi, F. P. Treatment of textile wastewater by electrochemical method, *Water Research*. 1994; 28: 277–282.
- [11] Singh, M. M., Szafran, Z., Ibanez, J.G. Laboratory experiments on the electrochemical remediation of environment. Part 4: Colour removal of simulated wastewater by Electrocoagulation–Electroflotation, *J. Chem. Educ.* 1998; 75: 1040–1041.
- [12] Slokar, Y. M., Le Marechal, A. M. Methods of decoloration of textile wastewaters, *Dyes and Pigments*. 1998; 37: 335–356.
- [13] Somasiri, W., Ruan, W., Xiufen, L., Jian, C. Decolourization of textile wastewater containing acid dyes in UASB reactor system under mixed anaerobic granular sludge, *Electron. J. Environ. Agric. Food Chem.* 2006; 5(1): 1224–1234.
- [14] Subrahmanyam, M., Subba Rao, K. V. Photocatalytic degradation of textile dyes using TiO<sub>2</sub> based catalyst, *Indian Journal Environmental Protection*. 1997; 18: 266–272.
- [15] Szpyrkowicz, L., Juzzolino, C., Kaul, S. N., Dniele, S., De Faveri, M. D. Electrochemical oxidation of dyeing baths bearing disperse dyes, *Ind. Eng. Chem. Res.* 2000; 39: 3241–3248.
- [16] Szpyrkowicz, L., Naumczyk, J., Zilio-Grndi, F. Electrochemical treatment of tannery wastewater using Ti/Pt and Ti/Pt/Ir electrodes, *Water Research*. 1995; 29: 517–524.
- [17] Szpyrkowicz, L., Radaelli, M., Daniele, S. Electrocatalysis of chlorine evolution on different materials and its influence on the performance of an electrochemical reactor for indirect oxidation of pollutants, *Catal. Today*. 2005; 100: 425–429.
- [18] Tanaka, K., Padermpole, K., Hisanaga, T. Photocatalytic degradation of commercial azo dyes, *Water Research* 2000; 34(1): 327–333.
- [19] Thomos, O., Burgess, C. UV-Visible Spectrophotometry of water and wastewater, Elsevier publications, The Netherlands; 2007.

- [20] Vandevivere, P. C., Bianchi R., Verstraete W. Treatment and reuse of wastewater from the textile wet-processing industry: review of emerging technologies. *J. Chem. Technol. Bio.* 1998; 72: 289-302.
- [21] Venceslau, M. C., Tom, S., Simon, J. J. Characterization of textile wastewaters- a review, *Environmental Technology.* 1994; 15: 917- 929.
- [22] Sanakousar. F. M, Vidyasagar C C, Victor Jimenez perez. K. Mounesh. Thermal decomposition synthesis of cylindrical rod-like  $\text{MoO}_3$  and irregular sphere-like  $\text{Ag}_2\text{MoO}_4$  nanocrystals for accelerating photocatalytic degradation of industrial reactive dyes and biosensing application. *J. Envi. Chem. Eng.* 2023; 11: 109371.
- [23] Sanakousar. F. M, Vidyasagar C C, Victor Jimenez perez. K. Mounesh. Mechanistic insight into the photodegradation of organic pollutant and electrochemical behaviour of MWCNTs/Cu-Co $3\text{O}_4$  nanocomposite. *Reaction Chem. & Eng.* 2023; 7: 1540.
- [24] Sanakousar F. M, Vidyasagar. C. C, Victor Jimenez perez. K. Prakash. Recent progress on visible-light-driven metal and non-metal doped zinc oxide nanostructures for photocatalytic degradation of organic pollutants. *Mater. Sci. Semi. Processing.* 2022; 140: 106390.