**Original Research Article**

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ELECTROCOAGULATION TREATMENT FOR REMOVAL OF REACTIVE BLUE 19 FROM AQUEOUS SOLUTION USING IRON ELECTRODEJayanthi K ¹, Rathinam R ^{2*}, Pattabhi S ¹

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ABSTRACT: In this present study, electrocoagulation was conducted to evaluate the removal capacity of Reactive Blue 19 (RB 19) dye from aqueous solution by using Iron electrode in batch reactor. The effects of operating parameters such as electrolyte concentration, pH, dye concentration and current density on colour removal have been investigated. The results reveal that Electrocoagulation (EC) is very effective and able to achieve 98.72% colour removal at pH 7, stirrer speed 250 rpm, dye concentration 100ppm and current density 3.7mA/cm² with supporting electrolyte concentration of 0.075M in the time duration of 60 minutes. The absorbance of treated and untreated samples were characterized by UV-Visible spectroscopy to assess the disappearance of colour and the functional groups of dye were identified using FT-IR to confirm the structural changes in decolourization process. The morphological characterization of the sludge obtained from the process was analyzed by SEM.

KEYWORDS: Electrocoagulation, Reactive Blue 19, Iron electrode, Decolourization, Wastewater treatment

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1. INTRODUCTION

The widespread disposal of industrial wastewater containing organic dyes onto land and water bodies has led to serious contamination in many countries worldwide because of their toxicity and threat for human life and the environment [1]. Textile manufacturing involves wide range of chemical usage, which is known for their hazardous nature as well as potential to contaminate the

environment. Wastewater generated by textile dyeing and finishing activities is known to contain considerable amount of pollutants, which are biologically difficult to degrade. So far, several biochemical, chemical and physical treatment methods were applied to treat textile industry wastewater, however with limited success [2-4]. Dye bath effluents, in particular are not only aesthetic pollutants by nature of their colour, but may interfere with light penetration in the receiving bodies of water and thereby disturbing biological processes. Furthermore, dye effluent may contain chemicals which are toxic, carcinogenic, mutagenic and teratogenic to microbes and fish species [5]. The pollution induced by dyestuff losses and discharge during dyeing and finishing processes in the textile industry has been a serious environmental problem for years [6]. The treatment of wastewater for reuse in the textile industry by means of other advanced technologies including Ozonation, electroflocculation and advanced oxidation was also studied in several works [7-10]. Reactive dyes are extensively used in textile industry, fundamentally due to the ability of their reactive groups to bind textile fibers by covalent bond formation [11]. To detect any adverse effects of textile dyes, tests for mutagenicity [12], genotoxicity [13], carcinogenicity [14] and teratogenicity [15] have been conducted. Conventionally textile industry wastewater is treated through biological, physical and chemical methods [16,17]. Biological treatment processes are often ineffective in removing dyes which are highly structured polymers with low bio-degradability [18]. However, various physico-chemical techniques, such as chemical coagulation, adsorption on activated carbon, reverse osmosis and ultrafiltration [16,17] are also available for the treatment of aqueous streams to eliminate dyes. But those later were limited by the low concentration ranges that can be treated coupled with the high concentrations in reject streams. Further, the main drawbacks of chemical coagulation are the addition of further chemicals. In recent years, Ozonation [18,19] and photo oxidation [20,21] have been proposed as alternatives because they are qualified to be very effective. But the high cost of these methods leads to further consideration. Indeed, electrochemical method has been successfully tested [16, 22] to deal with dyeing wastewater. But as for some dyes, which have good water solubility and the size of the small molecule, traditional electrochemical ways are found to be ineffective. Electrocoagulation (EC) is an alternative technology for wastewater treatment and recovery of valuable chemicals from wastewater [22]. This method involves a sacrificial anode, usually aluminum or iron, where the coagulating metal cations are released in-situ as long as an electrical current is applied [23]. The EC process is highly dependents on the chemistry of the wastewater especially its conductivity. In addition, other characteristics such as pH, particle size and chemical constituent influence the process. The mechanism of removal of pollutants by EC process with iron electrodes in an electrolytic system produces iron hydroxide, $Fe(OH)_n$ where $n = 2$ or 3 which in turn react with dye active groups [24]. Electrocoagulation is a process consisting metallic hydroxide flocs within the wastewater by electro dissolution of soluble anodes, usually constituted by iron or aluminium. This method has been practiced for most of the twentieth century with limited

success. Recently, there has been renewed interest in the use of electrocoagulation owing to the increase in environmental restrictions on effluent wastewater. Indeed, electrocoagulation has been tested successfully to treat urban wastewater [25], restaurant wastewater [26,27] and oil–water emulsion [26–28]. It has also been used to remove clay suspension [29,30] and heavy metal [31–33]. The major objective of this study is focused on removal of colour by an efficient method to determine the optimal operational conditions for the reuse of effluents generated by dyeing process.

2. MATERIALS AND METHODS

In this study, Reactive Blue 19 (CAS No.2580-78-1) stock solution was prepared by dissolving Reactive Blue 19 in double distilled water. Chemical structure of RB 19 is shown in Fig. 1. The concentration of working solution was varied from 50 to 400 mg/L and appropriate amount of supporting electrolyte concentrations were added. Chemicals used in the experiments are of analytical grade obtained from Himedia laboratories Pvt Ltd. The solution pH was adjusted by 0.1N of H₂SO₄/NaOH.

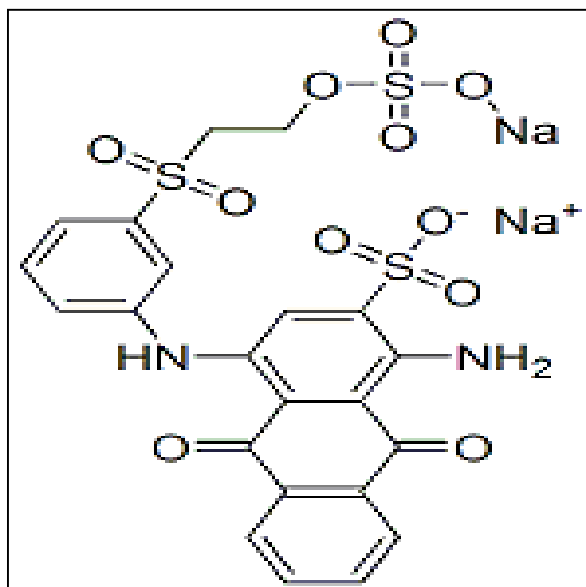


Fig.1. Reactive Blue 19

Electro coagulation cell

The electrochemical cell (Fig. 2.) was separated into two compartments with commercially available iron electrodes as anode and cathode, placed vertically and parallel to each other. The dimension of the electrode was 4cm × 8cm. The thickness of the iron electrode was 0.8cm. The distance between two electrodes was maintained as 5cm to minimize the ohmic losses. The solution was constantly stirred using a magnetic stirrer in order to get homogenous sample. The anode and cathode compartments were connected separately by a regulated DC power supply.

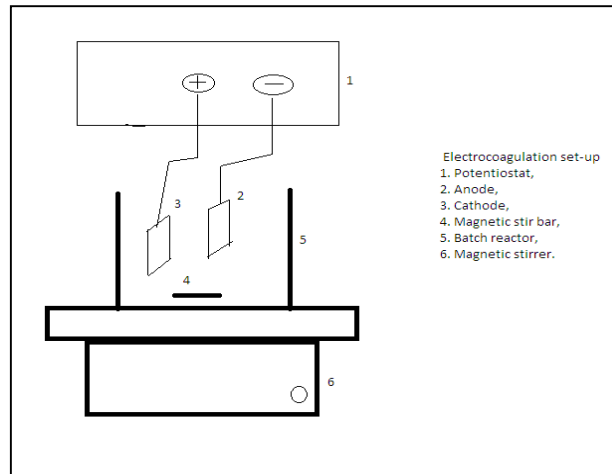


Fig.2. Electro coagulation set up for the treatment of Reactive Blue 19

Experimental Procedure

Experiments were carried out at a laboratory scale, in cell equipped with two iron electrodes (both anode and cathode). A potentiostat is used to apply the desired potential (Fig 2). At each experiment, 500 ml of synthetic waste water having known concentration of Reactive Blue 19 was supplied. The samples were kept in agitation using a magnetic paddle. The cathode and anode were connected to the respective terminals of the DC rectifier and electric power was supplied by a stabilized power source equipped with digital ammeter and voltmeter. After completion of the process, the power was switched off and the electrodes were disconnected. The treated dye sample was centrifuged at 5000rpm for 15minutes and the supernatant liquid was taken for the analysis. The colour removal is measured using spectrophotometer. Apparent colour of samples is determined by measuring the absorbance at 594nm.

Analytical procedure

The UV-Vis spectra of Reactive Blue and its removal during electrocoagulation were recorded using UV-Visible spectrophotometer (UV-1700 Pharma Spec, Shimadzu, Japan). The characteristics peak of dye was observed at 592nm. FT-IR and SEM studies were also made.

Calculations

$$\text{Removal Efficiency (\%)} = \frac{C_0 - C_e}{C_0} \times 100$$

Where,

C_0 - Initial concentration of dye before electro coagulation (mg/L)

C_e - Present concentration of dye after electro coagulation (mg/L)

$$\text{Energy consumption } E = \frac{U \times I \times t \times 1000}{V}$$

Where,

E - Energy Consumption (kWh/ml)

U - Cell voltage (v)

I - Current (A)

T - Time (h)

V - Volume of wastewater (ml)

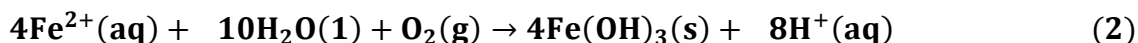
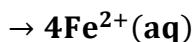
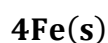
3. RESULTS AND DISCUSSION

3.1 Electro coagulation

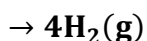
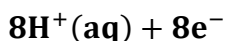
Iron electrodes were able to transfer high numbers of Fe⁺ ions into solution and they produced higher amount of sludge. The cost of iron electrode is also much low, when compared with other electrodes so it is economically important. The removal efficiency of RB 19 was high by electrocoagulation using iron electrode pairs.

Two mechanisms have been proposed for the Production of Fe (OH)_n

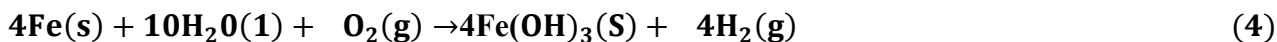
• Anode:



• Cathode:



• Overall:



The insoluble metal hydroxides of iron can remove pollutants by surface complexation or electrostatic attraction. The prehydrolysis of Fe³⁺cations also leads to the formation of reactive clusters for wastewater treatment [24]. The role of the iron matrix generated during electrolysis is to destabilize the colloidal suspension by reducing the attractive forces, thereby lowering the energy barrier and enabling particles to aggregate.

3.2 Effect of supporting electrolyte concentration

The effect of supporting electrolyte concentration is essential parameter on colour removal of Reactive Blue 19. Where, there are four different electrolyte concentrations were considered such as 0.025, 0.05, 0.075 and 0.1M at the applied current density of 3.75 mA / cm² and at initial pH 7, RB 19 concentration was 100mg/L at the stirring speed of 250 rpm. As in Fig.3, increasing the supporting electrolyte concentration resulted in increasing colour removal efficiency and reduction of cell voltage that caused a decrease in electrical energy consumption. After 30 minutes of electrolysis, when the concentration of supporting electrolyte is increased from 0.025 to 0.1M NaCl, the removal efficiency improved significantly from 93.5, 94.81, 96.41 and 98.72% respectively. This was due to Cl⁻ anions destroying the passivation layer and catalyzing the dissolution of electrode material via pitting corrosion phenomena, which is a type of localized corrosion formed by high

chloride concentration in the solution [36]. Increase in NaCl concentration leads to an increase in pollutant removal efficiency. Another benefit of increasing electrolyte concentration is increasing the electrical conductivity of the solution which allows more current passing through the circuit. Therefore the colour removal was high in 0.075M shows 96.41% removal among the four different concentrations. This concentration was taken as optimal condition for further steps have been carried out.

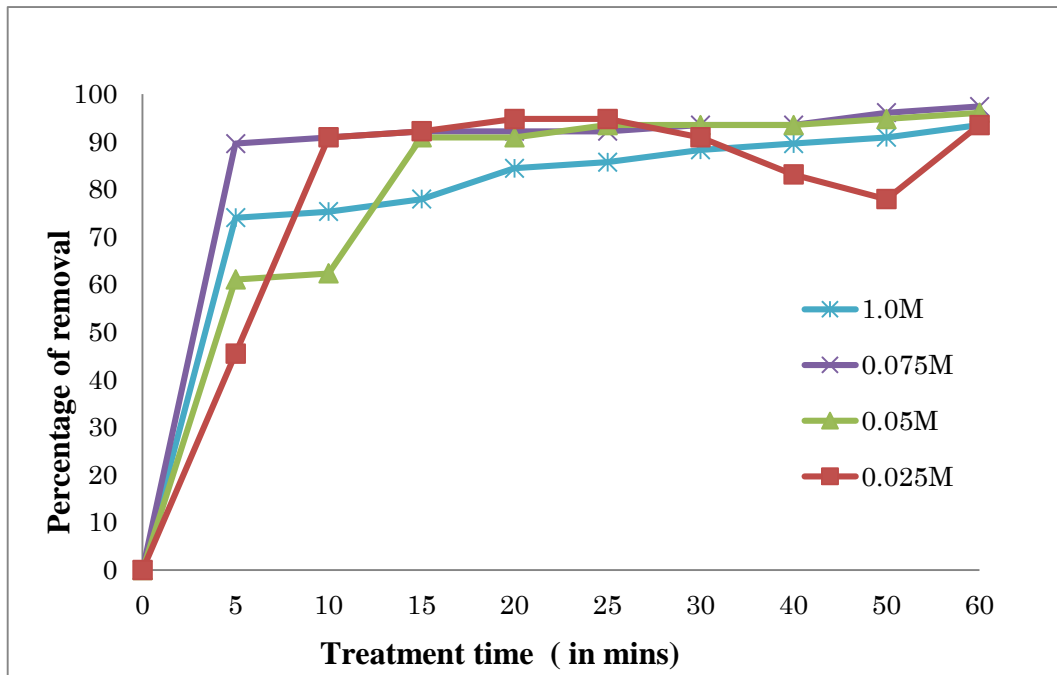


Fig.3. Effect of supporting electrolyte concentration on colour removal

3.3 Effect of applied current density

Another experimental study was carried out to determine the effects of applied current density on colour removal. The current density plays a major role in the activation of electrocoagulation processes and it was demonstrated. In this study 5, 10, 15, 20 and 25V potentials were applied corresponding to 0.9, 1.87, 2.81, 3.75, 4.68mA/cm² at initial pH of 7, supporting electrolyte concentration of 0.075M and initial dye concentration was 100mg/L at the stirring speed of 250rpm. The treatment efficiency was increased with increasing current density. The results are shown in Fig.4. The removal efficiency increased from 89.6 to 97.41%. The highest removal efficiency was reached at 3.7mA/cm². Therefore, it is considered as an optimal current density for this study.

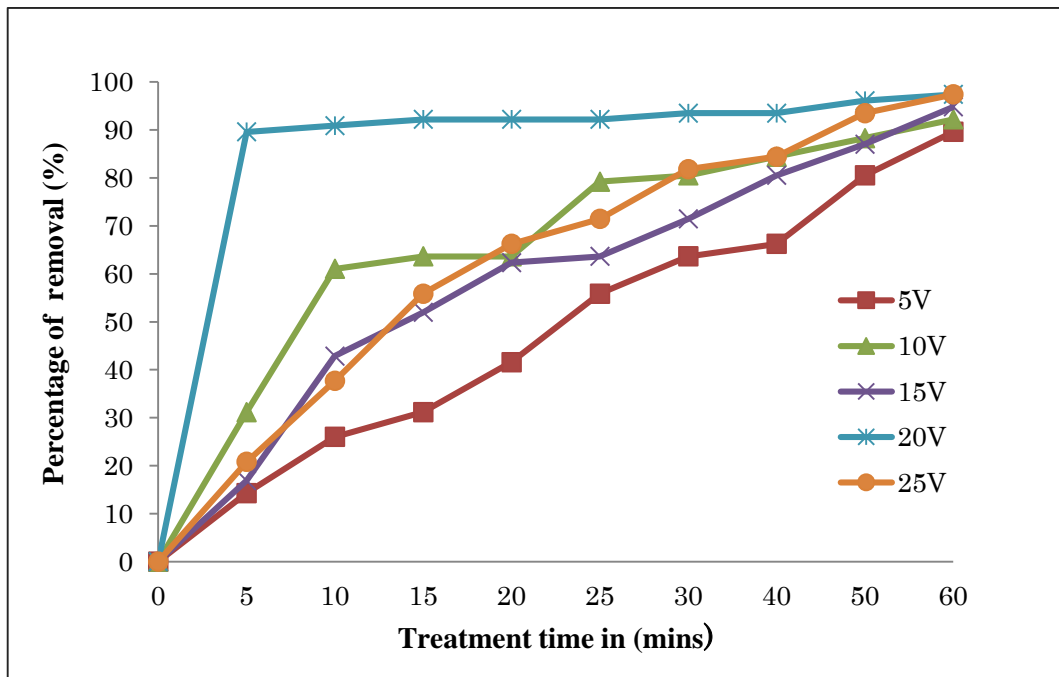


Fig.4 Effect of applied current density on colour removal

3.4 Effect of initial Reactive Blue dye concentration

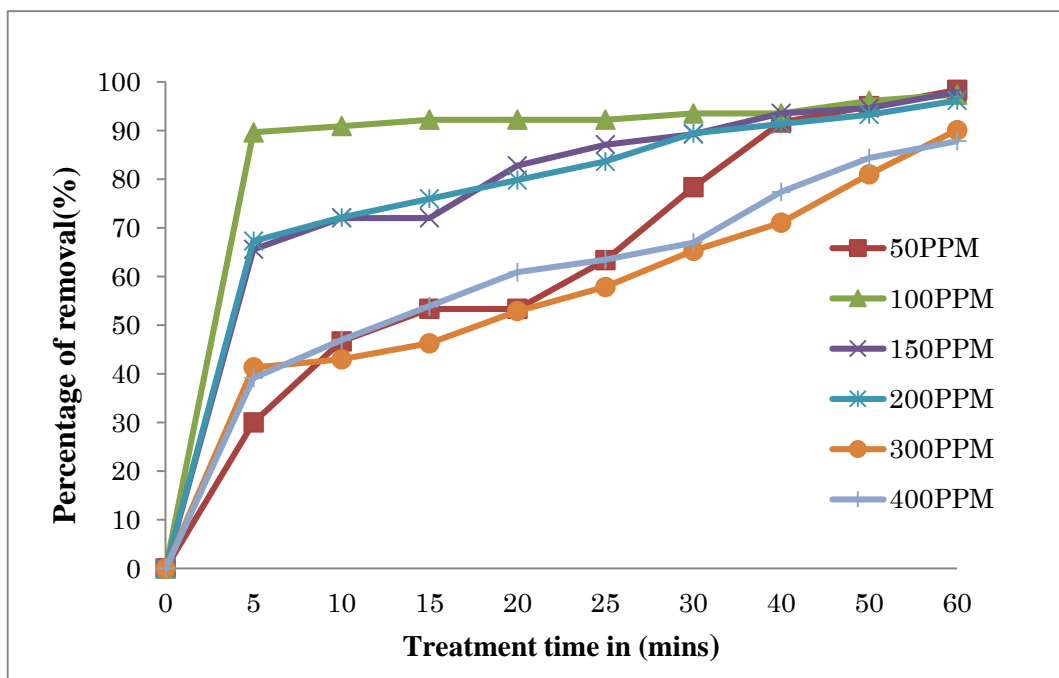


Fig.5. Effect of dye concentration on colour removal

Investigation of the dye concentration was conducted under certain conditions (pH, stirring speed, current density and electrolyte concentration). From this condition, the rate of removal of colour was compared with raw solution, after 30 minutes of electrocoagulation process the removal efficiency was 86, 96.25, 84.34, 86.24, 74 and 47.98% at the initial concentration of 50, 100, 150, 200, 300 and 400mg/L respectively at following optimized parameters such as constant current density of 3.75 mA/cm², pH 7 and the supporting electrolyte concentration 0.075M of NaCl with the stirring speed of 250 rpm. The results are shown in Fig.5.

3.5 Effect of initial pH

In this study, the effect of pH on colour removal was investigated at pH 3.0, 5.0, 7.0, and 9.0 under the optimized conditions. The maximum removal efficiency was obtained at 98.72% at pH 7.0, the effect of pH on colour removal illustrated in Fig. 6. In this condition pH of the solution does not change during all stages, because the electrocoagulation exhibits some pH buffering capacity, especially in alkaline medium [37]. According to the results, with increase in the dye concentration, percentage of colour removal also decreases. When the pH is less than 6, Fe (OH)₃ is in soluble form and when the pH is greater than 9 Fe (OH)₃ is in soluble form. Hence it proves that Fe (OH)₃ has the major role in the removal of colour. Therefore the pH was maintained between 6 and 8 for an efficient colour removal.

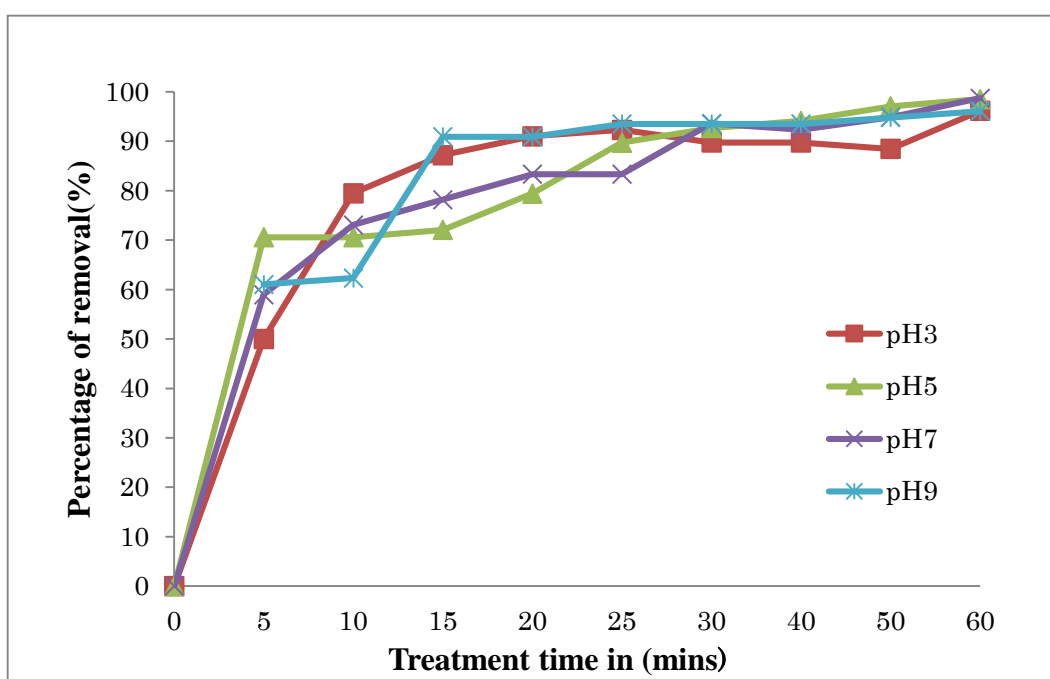


Fig.6. Effect of pH on colour removal

3.6 UV -Visible absorbance changes in the degradation of Reactive Blue 19

The UV- Visible absorbance of initial and final electrolysis is presented in Fig.7. In visible region absorbance peak at 594nm was due to Reactive Blue 19. It represented that the peak disappears gradually during electrocoagulation process with increasing treatment time and high removal efficiency was achieved at 60mins of electrolysis at 3.7mA/cm² of applied current density. It can be concluded that when electrochemical treatment was applied, Reactive Blue 19 degraded completely by decrease in the absorbance peak of pure dye.

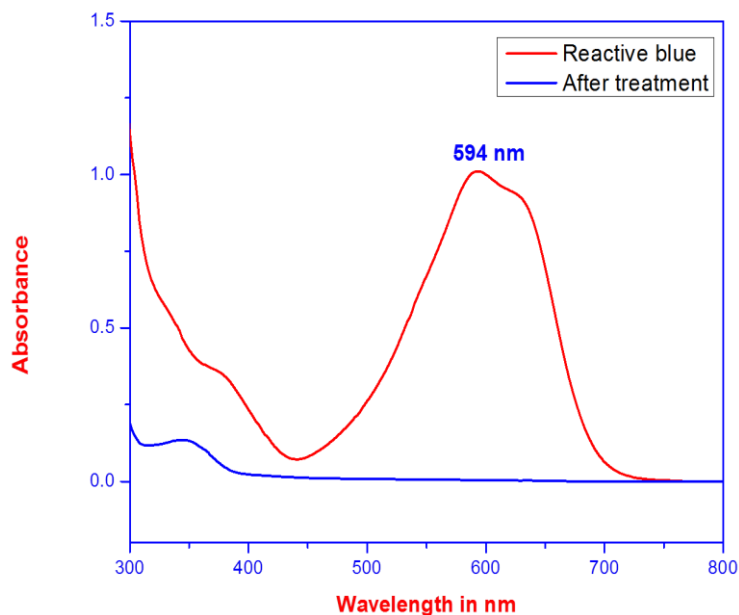


Fig.7. UV-Visible spectrum of Reactive Blue 19 before and after electrocoagulation process

3.7 FT- IR studies

The result of IR spectra shows that some structural changes might have occurred during electrocoagulation process. Fig.8 illustrates that the FT-IR spectra of Reactive Blue 19 before and after electrolysis shows several bands distinguished in the spectra.

a) FTIR spectrum (Fig.8) before treatment process is corresponding to the dye IR spectrum, although the observed bands at 1629.07 cm^{-1} shows that aliphatic amines [34] and then the peak at 2362 cm^{-1} typical of $\text{C}=\text{O}$, 1141 cm^{-1} peak might be due to symmetric vibrations of sulfonate groups. b) The peak at 3437 cm^{-1} ($3000\text{-}3500\text{ cm}^{-1}$) in after treatment process, O-H stretching and bendings respectively indicating metal phosphate is hydrated [35]. The peak at 1631.55 cm^{-1} is due to the stretching of $\text{C}=\text{O}$ in carboxylic groups. The band at 1007 cm^{-1} can be assigned to P-O stretching and bending vibrations shows in Fig.8. The peaks at 1629 cm^{-1} , 2362 cm^{-1} and 1141 cm^{-1} were absent and hence, it shows the clear difference between the relative intensities. From this IR spectrum it could be understood that the main chromophore groups of dye was decolorized by this efficient process.

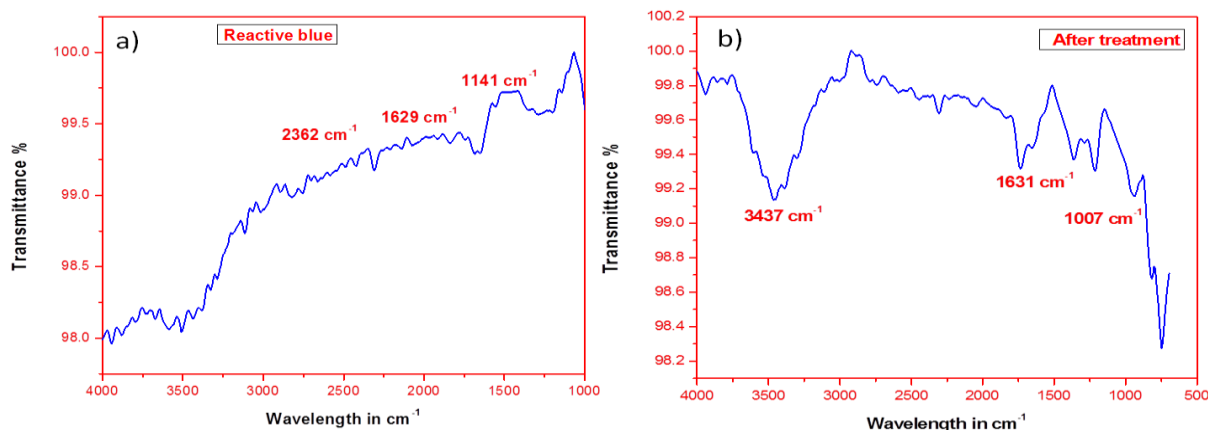


Fig 8. FTIR spectrum of Reactive Blue 19 before and after electro coagulation process

3.8 SEM analysis

SEM analysis provides information about morphology of the sludge generated by electro coagulation process using iron electrodes. From Fig.9, SEM shows that the Fe sludge floccule composed primarily of Fe compounds with Reactive blue 19. It clearly indicates that the sludge was micro sized particles (10 μ m) that are mostly amorphous in nature.

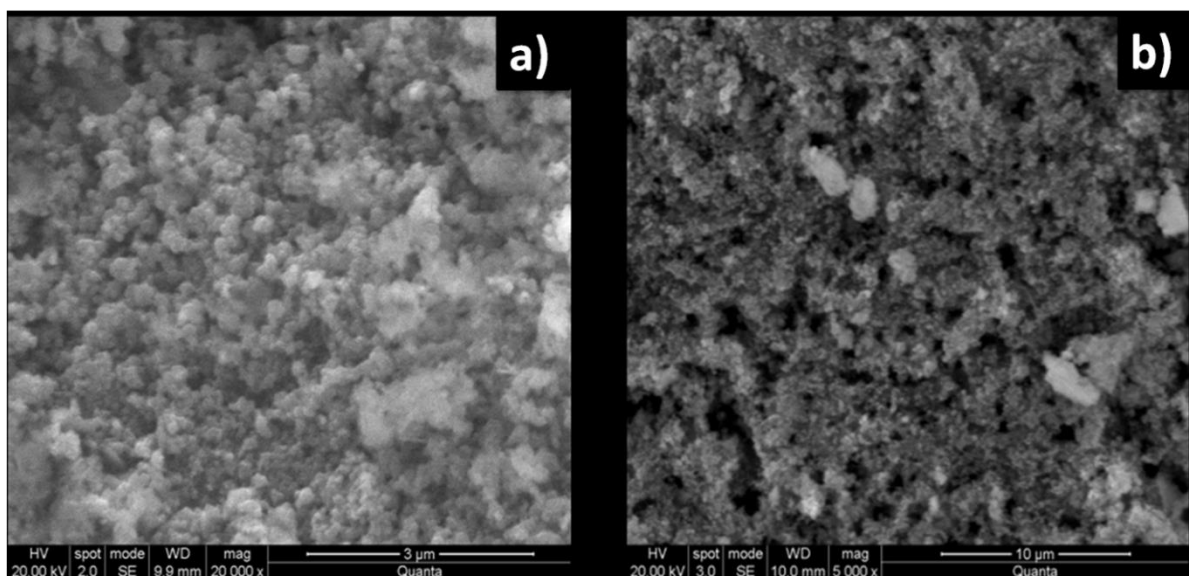


Fig.9. SEM images of a) Reactive Blue 19 and b) Sludge obtained from electro coagulation of Reactive Blue 19

4. CONCLUSION

The results shows that the electrocoagulation process using Iron electrode is very effective treatment for Reactive Blue 19 and it is also found to be cost effective. The colour degradation of concentrated Reactive Blue 19 is completely occurred through the electrocoagulation process at different parameters. The maximum colour removal was achieved in the presence of 0.075M NaCl which increased the efficiency of electrocoagulation process. It can be concluded that maximum 98.72 % colour removal was reached under the optimized conditions of initial pH 7.0, current density of 3.75 mA/cm² and treatment time of 60 minutes. Energy consumption was decreased when increasing the supporting electrolyte concentration from 0.025M to 0.1M NaCl, while it increases with increasing current density from 0.9 mA/cm² to 4.68 mA/cm². The UV-Vis spectrum confirms the removal of Reactive Blue 19 from aqueous solution. The SEM study confirms the amorphous nature of the dye and the morphological changes. The literature reveals that, all the essential operating parameters influencing the EC process includes pH, current density and type of electrode etc. Iron electrode is more effective for Reactive Blue 19 degradation by electrocoagulation process than other techniques due to its simple complex formation reactions and cost effectiveness.

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