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USE OF ELECTRO FENTON PROCESS FOR REAL EFFLUENT OF DYES AND DYE INTERMEDIATES

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ABSTRACT: In this experiment, use of electro fenton process for removal of COD (chemical oxygen demand) from real effluent of dyes and dye intermediates was studied. Purpose of this study is to determine the optimum value of current, optimum value of Ph, optimum time period & the optimum dosage of hydrogen peroxide and ferrous ion for removal of COD (chemical oxygen demand) from real effluent of dyes and dye intermediates. From the results, it is suggested that Electro Fenton (EF) method can efficiently used to degrade COD (chemical oxygen demand). The best COD removal efficiency obtained was 85.33 %, when current value is 400 A, treatment time is 300 min and pH value is between 2-3.5. The optimum dose of hydrogen peroxide (H_2O_2) is 1.5 ml/min. The optimum dose of ferrous ion (Fe^{2+}) is 11000mg/L.

KEYWORDS: Electro Fenton, dyes and dye intermediate, COD (chemical oxygen demand), Removal efficiency.

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1.INTRODUCTION

A large volume of waste waters is produced by the Dyes and dye intermediate industry as they consumes large amount of water in different steps in the dyeing process. Waste water from dyeing units requires proper treatment before releasing into the stream as is often rich in color, containing residues of reactive dyes and chemicals. The effluents generated from different steps in the dyeing process are heavily colored; contain high concentrations of salts, and exhibits high COD (chemical oxygen demand) ,BOD(biological oxygen demand) values so Dyes are unfavorable from an ecological point of view. Due to their intensive color, high content of surfactants and other organic and inorganic compounds, a significant toxicity and poor biological recovery This wastewater is difficult to treat with the use of old physicochemical and biological methods. Alternative technology has been developed to help solving the problem. The development of new treatment methods that are called advanced oxidation processes (AOPs), which are characterized by production of the hydroxyl radical (OH•) as a primary oxidant. The EF is one of the most effective methods of organic pollutant oxidation among various AOPs. Therefore, the Electro Fenton has been applied to treat a real waste water of dye and dye intermediate industry. There are two types of electro-Fenton (EF) processes. In the first one the Fenton's reagents (Fe (II) and H_2O_2) are added to the reactor externally. In the second one, H_2O_2 is added externally and Fe (II) is produced from sacrificial cast iron anodes.

Mechanism Of Electro-Fenton Process

Fenton reagent, mixture of hydrogen peroxide and iron (II) salt is discovered by Henry J.H. Fenton in 1890s that is used to destroy organic compounds. The oxidation power of hydrogen peroxide on certain organic molecules is He described by him, in which under the addition of Fe (II) as a catalyst OH^- radicals are produced from hydrogen peroxide. This system is considered as the most promising treatment among AOPs for remediation of highly contaminated water.

Oxidation of organic compound is faster in solution which contains H_2O_2 and Iron (II) salts that form hydroxyl radicals in reaction:

$$H_2O_2+Fe^{2+} \rightarrow Fe^{3+} +OH^-+HO\cdot$$

This reaction is used for waste water treatment and it is most efficient at pH ranging from 2-5, Molar H_2O_2 to Fe^{2+} about 1:1.

Recently, the Fenton's reagent has been produced in situ electrochemically (electro-Fenton) in two ways:

(a) by addition of a catalytic amount of Fe^{2+} ions, reduction of oxygen and regeneration of Fe^{2+} on a suitable cathode in acidic media:

$$O_2+2H^++2e \rightarrow H_2O_2 \quad E_o = 0.67 \text{ V}$$

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$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad E_o = 0.771 \text{ V}$$

(b) by addition of H_2O_2 and electrochemical production of Fe^{2+} ions with a sacrificial Fe anode according to the anodic reaction:

$$Fe \rightarrow Fe^{2+} + 2e^-$$

In this case, a part of Fe^{3+} ions is produced from Fenton's reaction (3) between supplied H_2O_2 and electro regenerated Fe^{2+} which precipitates as $Fe(OH)_3$.

Therefore, the organic pollutants can be removed by oxidation with OH* radicals and simultaneously by electro coagulation with the Fe $(OH)_3$ precipitate.

2. MATERIALS AND METHODS

Preparation of Sample:

The Experiment was conducted on real dye and dye intermediate effluent contained from Mahavir synthesis pvt. Ltd, (Surat). Sample has been taken and stored in accordance to the Standard Methods for the Examination of Water and Wastewater.

The initial characteristics of sample were determined.

Chemical Oxygen Demand(COD)	1666mg/L
Ammonia Nitrogen(NH3-N)	128mg/l
Color	1400 hazan
PH	7.8
Total Solids(TS)	464mg/l

Experiment Set ups:

The electro-Fenton experiments were carried out on pilot scale using plastic tank of 300L as reactors with the diameter of 30cm by vertically positioned 20 iron electrodes spaced by 5 cm,dimension of each electrode was 50 mm 1500 mm 1mm. The electrodes are connected to a digital direct current (DC) power supply. Initial pH of effluent was adjusted with concentrated sulphuric acid to the desired values between 2-3.5 before adding Fenton reagents. Before turning on the electrical current,a pre-decided amount of ferrous and hydrogen peroxide (H_2O_2) were added into samples in each batch to activate electro-Fenton reactions. Experiments were conducted at the 400 A current supply. The sample was mixed with recycling. DC power supply was turned off at an appropriate time intervals and the reactions was terminated. samples were taken out for analysis at fixed time interval of 45 minutes. The samples were allowed to stand 30 minutes settling time at the end of each run. COD was measured using a procedure as per standard methods.

Apparatus:

Reactor (plastic tank): 300 liter plastic tank is used as the reactor tank in the experimental studies.

Electrodes: Iron electrodes are used as the anodes and cathodes with the dimension of 1500 mm high. 50 mm wide. 1 mm thick.

pH: pH meter is used to determine the pH of the samples. To obtain the optimum pH value, the pH of samples was adjusted by adding sulphuric acid (H_2SO_4).

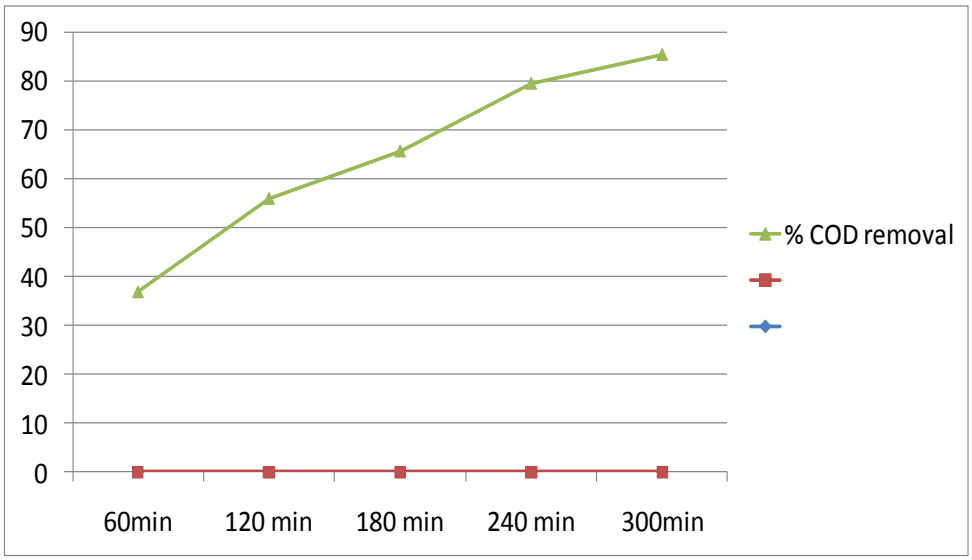
Chemical Oxygen Demand analysis: COD analyses are performed according to the standard methods

IMAGE: PILOT SCALE ELECTRO FENTON

3. RESULTS AND DISCUSSION

(1) Optimum Treatment Time

Sr.no	Time(min)	%COD removed
1	60	36.97
2	120	56.00
3	180	65.66
4	240	79.46
5	300	85.33



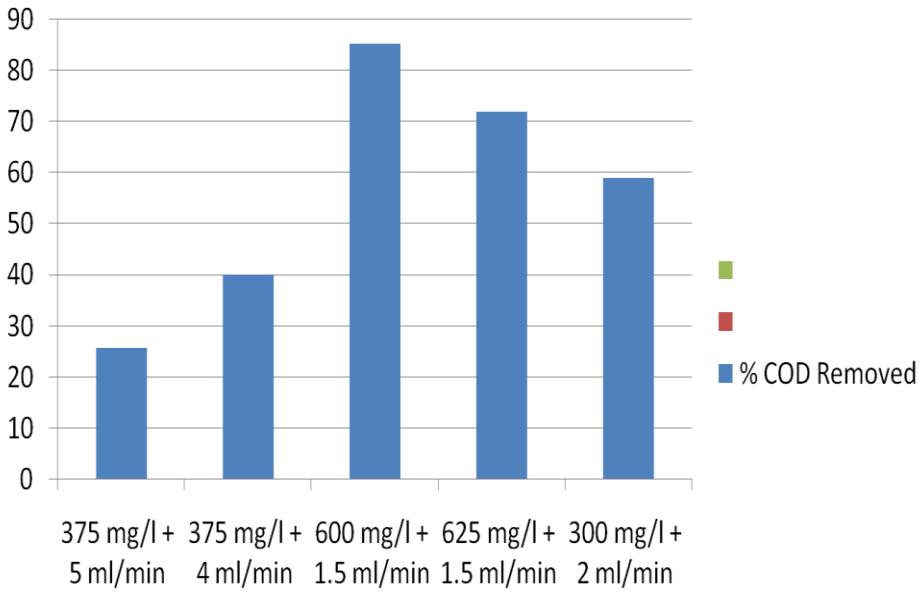
Effects of treatment time on COD removal efficiency at current 400 A, pH 3, H2O2 1.5ml/min+Fe^{2+} 600 mg/L.and settling time of 30 minutes

Figure shows the optimum treatment time for the removal efficiency of COD .The best removal efficiencies were obtained when treatment time is 300 minutes. COD removal was achieved 84%. The results shows that when treatment time exceeds 300 minutes the removal efficiency of COD has decreased. Hydrogen peroxide is added in a single step and in a continuous mode with feeding time. This result in the increase of initial COD removal with the decrease in feeding time and it reach highest when hydrogen peroxide was applied all at once. Also that, the decrease of feeding time, the concentration of hydrogen peroxide during the initial period would increase. This phenomenon will be more hydroxyl radicals would be generated resulting from the chain reaction between hydrogen peroxide and ferrous ion. the treatment time is to complete the oxidation reaction largely due to the dosage of H_2O_2. In general, the time to terminate the electro-Fenton can vary significantly with the

increases amount of H_2O_2. Besides that the process of electro-Fenton very fast in the first 250- 300 minutes and then slowed down till it was complete in 330 minutes.

(2) Effect of H_2O_2 Dosage + Fe^{2+} Dosage

Fe2+ (mg/l)+ H2O2 (ml/min) dosage	Initial COD (mg/l)	FINAL COD (mg/l)	%COD REMOVAL
375 mg/l + 5 ml/min	1666	1249.5	25.69
300 mg/l + 2 ml/min	1666	682.22	59.05
375 mg/l + 4 ml/min	1666	998.76	40.05
600 mg/l + 1.5 ml/min	1666	244.40	85.33
625 mg/l + 1.5 ml/min	1666	466.31	72



GRAPH OF % COD REMOVAL Vs. Fe $^{2+}$+H_2O_2 Dosage

The H2O2 Dosage + Fe^{2+} Dosage are an important factor in the electro-Fenton process. The results showed that the best removal efficiency of COD is obtained at 1.5ml/min dosage of H_2O_2 + 600mg/l dosage of $Fe2^{+}$ .Which is of 84% of COD removal. The increased of H_2O_2 concentration ability to remove more pollutants in wastewater. Addition of $H_2O_{2\ results}$ in the increase in hydroxyl radical. As Fenton's reagent dosage increases the efficiency of hydrogen peroxide for degrading organic pollutants in the sample decreases. At the high dosage of H_2O_2, the decrease in removal efficiency was due to the hydroxyl radical scavenging effects of H_2O_2 and the recombination of the hydroxyl radical. efficiency. It is seen that, the removal efficiency were increased when the dosage has been increased. However, a higher oxidant doses higher than optimum dose cannot provide adequate results. In electro-Fenton process, ferrous ion concentration is requirement to generate this process. The optimum Fe^{2+} concentration is 600 mg/L for 84% of COD removal respectively. Usually, the efficiency of electro-Fenton process increases with Fe^{2+} concentration because the concentration hydroxy radical. The main oxidizing agent (H_2O_2) in the electro-Fenton process increases with the increase in Fe^{2+} concentration. The excess of ferrous ion use in the electrolyte solution can consume the hydroxyl radicals and affect the extent of degradation. After the electro-Fenton process the excess amount of Fe^{2+} / Fe^{3+} will be contamination for soil and groundwater because the excess amount of $Fe2^{+}$ / Fe^{3+} produces extra amount of sludge and increase total dissolved solids and electrical conductivity.

4. CONCLUSION

Use of electro fenton process for real effluent of dyes and dye intermediates was studied in this Experiment. Optimum conditions for electro-Fenton process were found at current 400 A, treatment time 300 minutes, pH 3, H_2O_2 dosage 1.5ml/min and Fe^{2+} dosage 125gm. Hence, electro-Fenton is recommended as a powerful technique for the removal of COD in effluent of dye & dye intermediate industry.

CONFLICT OF INTEREST

The authors declare that no competing financial interests exist.

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