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Textile Waste Water Treatment by Advanced Oxidation Process

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Abstract: *The color produced by dyes in water makes it aesthetically unpleasant & can acute or chronic effects on exposed organisms which depend on the concentration of the dye and the exposed time. Many dyes are considered to be toxic and even carcinogenic. Textile industries processes are most industrial that release colored wastewater containing dye that become major environmental concern. EF is the effective process to be used for removal of acidic, basic and color dyes from Wastewater. EF process is the one of the types of APOs are most widely used for waste water treatment of various types of industrial wastewater and efficient wastewater treatment since photocatalyst is environmentally friendly process and considerable advantages such as ability to destroy pollutants without exertion of potentially hazardous oxidants. Electro Fenton is the popular AOPs and constitutes an indirect electrochemical way to generate OH in aqueous solutions and was developed and extensively applied by Brillas' and Outram's groups which developed in order to implementation of a new and powerful advanced oxidation method. In this process Fenton's reagent is electrochemically generated in situ avoiding the use of high quantities of H_2O_2 and iron (II) salt.*

Keywords: Waste Water Treatment, AOPs, Textile Dyes, Electro Fenton, Color and Dyes Removal, etc.

I. Introduction

A dye is a colored substance that has an affinity to the substrate to which it is being applied. Even a small quantity of dye does cause high visibility and undesirability. The color produced by dyes in water makes it aesthetically unpleasant. They can have acute or chronic effects on exposed organisms which depend on the concentration of the dye and the exposed time. In addition to that many dyes are considered to be toxic. Textile industries processes are among the most industrial that release colored wastewater containing dye that become major environmental concern. Without treatment disposal of dye wastewater cause harm for aquatic species and environment. AOPs adopted for the treatment of industrial effluent. AOPs are the energy efficient process has been identified for the high color, dyes, toxic compounds, organic matter and COD removal of the effluent as comparing to other processes. AOPs are tertiary treatment process use for different types of industrial waste water treatments with high removal rate with low cost. Textile industrial wastewater contains large amount of organic matter, dyes, COD and color which can easily removal by using AOPs.

Application of AOPs

1. Chemical Industry
2. Pharmaceutical Industry
3. Pulp and Paper Industry
4. Textile Industry
5. Food Industry
6. Landfill Leachates
7. Dye-Process Industrial Waste
8. Pre-treatment to wastewater
9. Organic pollutant destruction
10. Toxicity reduction
11. Biodegradability improvement
12. Odor and color removal

Types of AOPs for Textile Wastewater Treatment

1. Fenton (Fe^{2+} or Fe^{3+}/H_2O_2)
2. Electro Fenton
3. Photo-Fenton (Fe^{2+} or $Fe^{3+}/H_2O_2/UV$)
4. Photocatalytic Oxidation with ZnO/UV, TiO_2/UV, TiO_2/H_2O_2/ UV

The Factors Due to This AOPs Becomes Popular are Follows

1. Low cost.
2. Easy in operation.
3. Low sludge production.
4. Low operational and maintenance cost.
5. High efficiency.
6. Low chemical consumption.
7. Low time consumption.

Classification of Textile Dyes

1. **Based on Application**
   Based on its application characteristics such as acid, basic, mordant, reactive, direct, disperse, Sulphur dye, pigment, vat, azo insoluble.
2. **Based on Chemical Structure**
   Based on its chemical structure such as nitro, azo, carotenoid, , acridine, quinoline, indamine, diphenyl methane, xanthene Sulphur, anthraquinone, indigoid, amino- and hydroxy ketone, phthalocyanine, inorganic pigment, etc.
3. **Anionic, Non-ionic and Cationic**
   Dyes on the basis of the general structure. The major anionic dyes are the direct, acid and reactive dyes.

II. Literature Reviews

Advanced oxidation processes (AOPs) have led the way treatment of aqueous waste and rapidly becoming the chosen technology for many applications. COD reduction of textile industry wastewater by electro-Fenton (EF) oxidation at batch experimental conditions. The wastewater samples with a COD of 590 mg /l in average taken from outlet of an equalization tank of a textile industry. Wastewater samples treated in a batch reactor equipped with two iron electrodes. [2] The EF tests were conducted at different H_2O_2 doses such as 313, 626, 940 and 1253 mg /l and constant electrical power of 24 W and pH of 3. For each EF test electricity consumption was determined based on per unit of COD mass removed (kW/kg). The COD removal increased with decreasing H_2O_2 dose. The highest treatment efficiency was attained at 313 mg/l of H_2O_2 by which more than 85% of COD removed within 10 min of reaction time. EF process as alternative method for textile wastewater treatment. [2]

The optimization and reduction of the toxicity level of the textile industry wastewater using electrochemical oxidation. The effect of current density and pH and found that the maximum removal of COD and color at the current density of 0.28A/cm2 and at a pH of 5. The performance of graphite electrode for COD removal was also reached within 120th minute at 2.5 M of NaCl concentration. [3]

The biodegradability improved because ratio of BOD_5 /COD was increased by 94.46% from 0.015 to 0.271 and the toxicity level successfully reduced from 1.195% to 0.129%. The removal of oil and grease up to 82.02%. The graphite electrode effective for textile wastewater. As for the COD removal the highest percentage of sodium chloride shows the low percentage of COD removal which is the 3.0M of NaCl concentration.

The optimum concentration of NaCl 2.5 M where the color and COD removal both showed as 79.67% and 75.12%. [3] The optimum pH in the study was identified as pH 5 and the highest percentage of colour and COD removal 92.02% and 86.67%. The optimum current density is 0.28 A/cm^2 which gives 93.89% of colour removal and 85.38% for COD removal. The optimum current density is 0.28A/cm^2 due to the decrease in percentage colour and COD removal at the current density of 0.51A/cm^2. To determine the effect in the distance between the electrodes due to the decolorization process, different distance between the electrodes such as 1, 3, 5 and 7 cm placed in order to run the electrochemical oxidation process. The distance of 3cm is optimized to be the best distance between the electrodes in the process of color and COD removal. At 3 cm distances between electrodes 76.03% and 75.76% color and COD removal. [3]

The effect of TiO_2/UV on acid blue 9 has shown the degradation efficiency to be 97%. The degradation found to be of zeroth order with the initial concentration of dye and catalyst affecting the kinetics and the order of reaction. The optimal values of hydrogen peroxide and ferrous ion concentrations found to be 3 and 0.3 M which resulted in a COD reduction of 56.4% with temperature having a mild effect. More than 95% of color was removed with Fenton's oxidation process for RB5, RB13 and AO7 azo dyes. 100% color removal and more than 90% decrease in COD with the Fenton process conducted at pH 3, Fe^{2+} dose = 400 mg/L and H_2O_2= 550 mg/L on industrial waste water. [4]

Advanced Oxidation Processes (AOPs) like ozonation, hydrogen peroxide, UV radiation and their combination for comparison of treatment efficiencies for remediation of textile wastewater. The treatment efficiencies of various options depend on the characteristics of the wastewater to be treated. Advanced oxidation processes are better treatment options than the conventional treatment methods commonly adopted in wastewater treatment plants. These methods provide complete removal of refractory organics like dyes and reduce the toxicity of the effluent discharged into the streams and rivers. Various combinations of AOP processes like ozone, UV, H_2O_2, EF etc. efficient treatment of textile wastewater depending on characteristics of wastewater. [4]

UV-H_2O_2 process is able to destroy totally the chromophoric structure of dyes with the varying reaction rates for different dyes. Dose of H_2O_2 also plays a vital role in discoloration process. Removal efficiency increases as the doses of H_2O_2 is increased up to a certain critical value after which the efficiency starts to decrease. the decolorization efficiency decreased from 90.69% to 82.3% when the dose was increased from 10 cm^3 to 12 cm^3. When initial dye concentration in increased the production of hydroxyl radicals decreases and thus the removal efficiency decreases. [4]

The final TOC of a dye containing initial TOC concentration of 62 mg/dm^3 and undergoing 100 % decolorization to be 4.34 mg/dm^3 (93% removal efficiency). Under optimal conditions, the removal efficiency increased from 90.69% to 100% by increasing the UV power from 18 to 54 W. This increase in decolorization is due to the increased production of hydroxyl radical. [4]

TiO_2 is preferred over other due to its stability under various conditions also its high potential to produce radicals and its easy availability and low price. Effect of TiO2/UV on acid blue 9 has shown the degradation efficiency to be 97%. The kinetics of the degradation was found to be of zeroth order with the initial concentration of dye and catalyst affecting the kinetics and the order of reaction. More than 95% of color was removed with Fenton's oxidation process for RB5, RB13, and AO7 azo dyes. 100% color removal and more than 90% decrease in COD with the Fenton process conducted at pH 3, Fe^{2+} dose = 400 mg/L and H_2O= 550 mg/L on industrial waste water.[4]

Degradation of C.I. Acid Orange 7 using boron-doped diamond electrode and reported that more than 90% of COD removal. 94% dye removal using a pilot plant electrochemical reactor for textile wastewater treatment. The current density increased from 1 to 5 A/dm^2 and becomes insignificant beyond 3 A/dm^2. The influence of electrolyte pH on pollutant degradation with under acid, alkaline and neutral conditions. [5]

Electrooxidation (EO) treatment using activated carbon cloth (ACC) electrodes on textile dye bath wastewater. ACC electrode pairs were used as anode/cathode for EO experiments. The effect of current density (50–150 A/m2), operating time (0–90 minutes) and solution pH (6-11) were tested for removal of chemical oxygen demand (COD), color and chloride as well as the changes in conductivity. 95.5% COD and color removal efficiencies were obtained at current density (CD) of 100 A/m^2 at solution pH of 10 for 90 minutes. The chloride concentration decreased from 4254 to 35.5 mg/L and solution conductivity decreased from 160 to 131 mS/cm at same conditions. [6]

The removal of COD from real dye wastewater by the electro-Fenton process in which hydrogen peroxide was generated by polyacrylonitrile-based activated carbon fiber cloth cathode. COD removal efficiency was over 70% for 240 minutes of treatment. Four electrode combinations (SS-SS, Iron-Iron, Aluminium-Aluminiumn and Iron-Aluminum) use for removal of color and COD. Iron electrodes enhanced efficient treatment and 98.8% color removal efficiency at 12V and 15 minutes treatment time with a sludge generation rate of 22.7 g/L. 80.3% COD removal efficiency was obtained at 5.8V and 5.7 minutes treatment time with a sludge generation rate of 5.7 g/L.

Textile dye wastewater was treated with electrochemical oxidation in a batch reactor. A maximum COD removal efficiency of 97.17% obtained at a reactor volume of 300 mL, electrolysis time of 6 hours and current density of 4.0 A/dm^2. [7] Electro-Fenton (EF) process used for Degradation of a monoazo dye, Reactive Red 195 (RR-195). Hydrogen peroxide electro-generated by reduction of dissolved oxygen in acidic solution. EF process allows production of active intermediates react with organic compounds leading to their mineralization. Electrochemical cell carbon paper (CP) used as cathode and a Pt sheet used as anode. At room temperature in an open, undivided and cylindrical glass cell of 500 mL capacity. H_2O_2 continuously generated from two-electron reduction of O_2 at cathode electrode while Fe^{3+} added to solution. Effect of applied current, initial pH and reaction time studied in an attempt to reach higher dye removal efficiency. Degradation of RR195 followed by total organic carbon (TOC). electro-Fenton with carbon paper allowed 75% TOC degradation after 240 min of electrolysis. [15]

The optimization of electrochemical oxidation technique for textile wastewater treatment and analysis of the degradation product. Reactive Blue 109, platinum plate electrode (10 mm x 10 mm) and stainless steel (10 mm x 10 mm) chosen as best anode and cathode. Effects of operational parameters such as supporting electrolyte (sodium chloride) concentration, current density, initial pH and electrolysis time on pH changes and percentage of color, chemical oxidation demand (COD), biochemical oxidation demand (BOD), total organic carbon (TOC) and surfactant removal were determined. Optimum range for each of these operating variables. The percentage of color, COD, BOD, TOC and surfactant removal in the aqueous phase removed effectively. Optimum operating conditions, sodium chloride concentration of 0.1 M, current density of 20.0 mA/cm2, initial pH of 4 and electrolysis time of 75 minutes, the percentage of color and COD removals efficiency reached 96%. [16]

Electro-Fenton Process

Advanced oxidation process used in wastewater treatment technology which is Electro Fenton process. This process is modification of conventional Fenton process. It consists of electrolysis cell that regenerates Fenton reagent by electrochemical reaction between anode and cathode. In this electrochemical reaction which is combination of two reaction Fenton reaction and electrochemical oxidation (EO) and the reaction works in single reaction chamber. EO is electrochemical reaction as Fenton is a chemical reaction who oxidizes the pollutant by electrochemical process.

Various Parts of Electro Fenton Process

1. Electrolysis cell
2. DC power supply
3. Magnetic stirrer if required
4. Electrodes

Development of effective methods for the degradation of such organic pollutants to less harmful compounds or more desirable to their complete decolorization. There is need of automation, high efficiency and environmental compatibility. Growing interest in the use of effective direct or indirect electrochemical degradation of organic pollutants in waters. Ferrous ions and in acidic aqueous medium the oxidation power will be enhanced due to the production of a very reactive one-electron oxidizing agent hydroxyl radical (•OH) from the Fenton reaction. •OH, generate by the simultaneous electrochemical reduction of O_2 in the presence of catalytic amounts of ferrous ions.

Anode Reaction : $Fe^{+3} + e^- = Fe^{+2}$

Cathode Reaction : $O2 + 2H^+ + 2e^- = H_2O_2$

Electro-Fenton Method is Used for

1. To removal of many kinds of recalcitrant pollutants.
2. To treatment of landfill leachate.
3. Phenol degradation.
4. Reduction of Turbidity, BOD, COD and Color from various types of wastewaters.
5. Treatment of various types of industrial waste water.

III. Material and Methodology

Raw Materials

1. Hydrogen Peroxide (H_2O_2) - This is the strong oxidant and its application in the treatment of various inorganic and organic pollutants is well established. H_2O_2 consist of two hydrogen molecules and two oxygen molecules.
2. Fenton's Reagents (Fe salt/ $FeSO_4$ Solution) - Metal salts (e.g., iron salts) which are strong oxidants that is the Fenton's process. Fe^{+3} and Fe^{+2} is used to oxidation of H_2O_2 which decompose or cause of degradation of waste water. The amount of this Fenton reagent is based on the amount used of H_2O_2.
3. Acid or Alkali - H_2SO_4 acid or NaOH alkali to be used for pH maintain of waste water. The optimum Value of pH necessary for the Fenton process.
4. Electrodes - Iron or Aluminum electrode are used for the electro Fenton process

Preparation of Acid Orange-II Dye Solution for Color Adsorption

1. 5 mg (5 ppm) of Acid Orange II dye (Yellow Powder) add in 1 L distilled water.
2. Stirring the solution for complete mixing of dye.
3. Similarly, we can make synthetic water of various concentrations solution.
4. After addition acid orange II dye color of solution becomes yellow.
5. Measure pH of solution should be maintained between 5-7 using 0.1 N NaOH or 0.1 N H_2SO_4 for maximum adsorption.

Preparation of BR-46(Basic Red) Dye Solution for Dye Adsorption

1. 5 mg (5 ppm) of BR46 dye (Crystal Violet) add in 1 L distilled water.
2. Stirring the solution for complete mixing of dye.
3. Similarly, we can make synthetic water of various concentrations solution.
4. Measure pH of solution should be maintained between 5-7**.**

Electro Fenton Treatment Procedures

1. Take 1-2 L synthetic waste water sample and measure concentration unit by spectrophotometer.
2. Transfer sample in reaction vessel and stirred for mixing.
3. The scheduled Fe^{2+} or Fe^{3+} dosage was achieved by adding the necessary amount and Fenton Agent add 1:1 proportion of H_2O_2.
4. A known 200-900 mg/l volume of 35% H_2O_2 solution was added in single step.
5. Start DC current supply. (Readings can take at different DC supply 12-30 V)
6. Take sample each 30 min time of intervals up to 120 min reaction time.
7. Settlement was achieved for 10 minutes and then withal each sample.
8. Measurement of concentration unit for each sample.
9. At time of reaction continuous stirring process will require.
10. Finally, by comparing the initial and experimental values calculate % reduction of color and dyes from synthetic wastewater.

Effects of Various Parameters

1. **The Effect of Current Density on Removal Efficiencies -** The electrochemical reactor was operated under different current density (50, 75, 100, 150 A/m2) conditions. COD and color removal efficiencies as well as variations of the chloride concentration and solution conductivity were affected when the current density was increased. The COD and color removal efficiencies decreased when the applied current density reached up to 150 A/m^2. The pollutant removal rate increased initially with increase of current density. The optimum current density is 0.28A/cm^2 for color removal and COD removal. The optimum current density is 0.28 A/cm^2. Due to the decrease in percentage color and COD removal at the current density of 0.51A/cm^2.

2. **The Effect of Solution pH on Removal Efficiencies -** The electrochemical reactor was operated under different pH (6, 8, 10, and 11) conditions. COD and color removal efficiencies as well as variations of the chloride concentration and solution conductivity affected by changing the solution pH. The COD and color removal

efficiencies increased for solution pH. The optimum pH in the study was identified as pH 5-6 and the highest percentage of color and COD removal.

3. **Energy Consumption and Cost Analysis -** The operating cost is one of most important parameters for wastewater treatment plants. The cheapest and most effective processes are preferred for wastewater treatment plants. The formula of energy consumption is given by Eq.

   $E = I * V * t / V_R$
   E (kWh/m^3) is electrical energy consumption,
   V = voltage (V), I = current (A),
   t = time (h) and V_R = wastewater volume (m^3)

4. **Effect of Distance between Electrodes (cm) -** The distance between electrodes from 1cm, 3cm, 5cm and 7cm is taken into consideration to determine the optimum electrode distance. The distance of 3 -3.5 cm is optimized to be the best distance between the electrodes in the process of color and COD removal. The highest percentage obtained in 3-3.5 cm distances between electrodes.

5. **Effect of Contact Time -** The duration of electrochemical oxidation from 10 min, 30 min, 50 min, 80 min, 120 min and 170 min is taken into consideration. To determine the optimum time due to the decolorization process, different parameters of time were used to run the electrochemical oxidation process. The effects of time showed that 120 minutes was the optimum time in this process.

IV. CONCLUSION

We study the various treatment methods for dyes wastewater and also study various photocatalytic oxidation processes for dyes wastewater. As per literature we analyse of various parameters effect on EF process and selection of best one AOPs process for dyes wastewater treatment. The effect of parameters like pH, Voltage, distance between two Electrodes, Concentration of dyes, Contact Time and catalyst loading in which maximum reduction of dyes and colors occurs from textile wastewater. EF process are effective processes to be used for removal of acidic, basic and color dyes from Wastewater. This process is the one of the types of APOs are most widely used for waste water treatment of various types of industrial wastewater and efficient wastewater treatment since photocatalyst is environmentally friendly process and considerable advantages such as ability to destroy pollutants without exertion of potentially hazardous oxidants. This process can be conducted under room conditions and organic pollutants can be completely decomposed into CO_2 and H_2O.

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