COMPARATIVE STUDY OF ADVANCE DEGRADATION OF INDIGO CARAMINE: A SYNTHETIC DYE

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Abstract - Organic pollutants have detrimental effects on ecology. These pollutants have adverse effects on human and aquatic life. Environmental safety communities always focused on the treatment of effluents from industries. Effluents cannot be treated effectively by conventional technologies. Those technologies for treatment are continuously rationalized for better results. Thus the new modern technologies come in phase to deal with the pollutants. Advanced Oxidation Process is been studied for the degradation of such pollutants. Indigo Caramine is broadly used dye in textile, medical, food preservative and pharmaceutical field. The degradation of the dye was observed by mainly combination of UV/H2O2 Fenton and Fenton like techniques. The decolourization and degradation of dye was determined by the absorbance and the organic matter in it was determined by Chemical oxygen demand. The comparative study between photo Fenton and Fenton like process is reported

Keywords - Organic Pollutant, Advance Oxidation Process, Degradation, Chemical Oxygen Demand.

I. INTRODUCTION

20th century is on the edge of advanced technologies, with such innovations and advances world end up in ignorance of its parallel side effects on ecosystem. The numerous effects are encountered. Nowadays we utilized synthetic products, Indigo Caramine is one of them.

It is the most primarily used synthetic dye. In commercial production and manufacturing processes 15% of this dye is lost [1]. The dye enters the water bodies in ecosystem and harms the aquatic and marine life which results in disturbing the life cycle.

Such results had significant role in water treatment process.

The Conventional methods include adsorption, chemical precipitation, ion exchange, coagulation–flocculation, membrane filtration, electrochemical treatments but they were unsuccessful in degrading the organic pollutants present in the water, Indigo Caramine is one of them. [2] The conventional process retains the pollutant concentration by either changing their phase or no degrading it. Advanced Oxidation Process is an effective process which results in degrading stable and complex organic structure.

It completely decomposes the pollutant. The AOP's include different process in which mainly focus on producing strongly oxidising hydroxyl radicals (•OH). This can be in homogenous or heterogeneous phase. The different combinations of AOP's which came into practise are (UV) Ultraviolet rays, ozonolysis, Fenton process (Fe+2 and Fe+3), photo catalytic oxidation (UV/TiO2), Photo Fenton and Fenton likesystems, Ozone-hydrolysis peroxide UV radiation (O3/H2O2/UV), Hydrogen Peroxide H2O2-UV radiations (H2O2/UV), Ozone –UV. Radiations (O3/UV), ozone and catalyst, ozone and hydrogen peroxide (H2O2/ O3) – Peroxane. [3] AOP's remove 60% of COD and degrade the colour of the effluent.

II. PROPERTIES OF DYE

Table no.1 Properties of Indigo Caramine [4]

Chemical formula	$C_{16}H_8N_2Na_2O_8S_2$
IUPAC name	3,3'-dioxo-2,2'-bisindolyden-5,5'-disulfonic acid disodium salt
Molecular mass	466.35 g/mol
Max absorption	608 nm
CAS Number	860-22-0

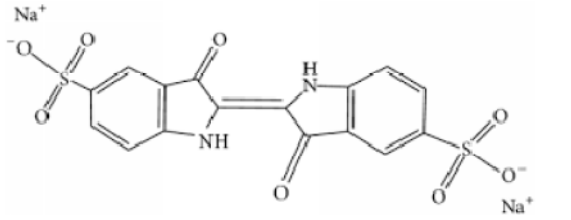


Figure .1 Structure of Indigo Caramine [4]

III. ADVANCE OXIDATION PROCESS

The process in which the strong oxidizing hydroxyl radicals (•OH) are generated which oxidizes the organic compounds into carbon dioxide and water. The generation of hydroxyl radicals (•OH) can be amplified by several techniques which results in effective oxidization of organic matter. The techniques are ozonolysis , UV light, TiO2 , electronic beams or γ-beams , photolysis , ultrasound and high voltage discharge. Among this, mainly UV/H2O2 Fenton and Fenton like techniques were studied and compared.

IV. CHEMICAL OXYGEN DEMAND

It is defined as a "measure of the oxygen equivalent of the organic matter content existing in the

compound that is susceptible for to oxidation by a strong chemical oxidant". It is an indirect method to calculate the organic matter content of the sample. COD is found to be more scientific and time saver than BOD because COD calculated the total biochemical and non-biochemical oxygen requirement. COD is always more than BOD. In determination of COD, we are able to calculate the available organic matter from which we conclude the degradation of synthetic pollutant.

V. METHODOLOGY

5.1 Reagents and Materials

All the experiment was performed by AR grate chemicals from Merck, SRL and sd-FINE. The solutions were prepared using distilled water. The stock solution of 10-3 M Indigo Caramine as synthetic pollute was prepared.

H2O2 Of 30% W/V was used. FeSO4 and FeCl3 solution were prepared of 10-2 M. Absorbance measurement was made on UV –VIS spectrophotometer 118 from Systronics. Monochromatic UV light of 8 watt and 245 nm, Digital pH meter and magnetic stirrer from Remi Equipment's were used.

Potassium dichromate of 0.25 N, FAS (Ferrous Ammonium Sulphate) of 0.1 N were prepared and utilized. Silver sulphate reagent and mercury sulphate were used. Ferroin indicator in titration was utilized. The heating mental, round bottom flask, water-condensers were used in set up as shown in figure 4.

5.2 Experimental set up



Figure 2 The 800 ml photo-reactor and 245 nm UV light on magnetic



Figure 3 UV –VIS spectrophotometer 118





Figure 4 Heating mental with water cooled condenser for determination

5.3 Mechanism

In Photo Fenton process, H2O2 in presence of Ferrous sulphate and UV light gives strong oxidising agent as shown in the eq(1)

$$Fe^{2+} + H_2O_2 + UV \longrightarrow \bullet OH + Fe^{+3} + OH^- \qquad eq(1)$$

In Photo Fenton like process, H2O2 in presence of Ferric chloride and UV light gives strong •OH radicals as shown in the eq(2).

$$Fe^{+3} + H_2O_2 + UV \longrightarrow \bullet OH + Fe^{2+} + H^+ \qquad eq(2)\ [5]$$

5.4 Chemical Oxygen Demand

Closed reflux method is used to determine the Chemical oxygen demand. This procedure is more economical and generates less amount of hazardous waste.

To generate operative results, the sample must be homogenous with suspended solids. Most of the organic matter is oxidized by boiling mixture. In this method, the reflux or digestion is being carried out for standard 2 hours in round bottom flask and water cool condensers. Potassium dichromate is found to be most suitable oxidant which has ability to oxidized wide range of organic pollutant. Concentrated sulphuric acid act as a primary catalyst and silver sulphate is the secondary catalyst for digestion. The eq (2) chemical reaction shows the change in state of

Chromium, it accepts the electrons which are released by the organic matter. [6]

Chemical reactions

Organic matter + oxidant $\longrightarrow$ $CO_2 + H_2O$ eq(1)

Oxidation reaction

$Cr_2O_7^{2-} + 14H^+ + 6e^- = 2Cr^{3+} + 7H_2O$ eq(2)

5.5 Experimental Procedure

5.5.1 Calibration and maximum absorption (λmax)

The calibration curve was observed and it obeyed Beer and Lambert's law. The maximum absorption of Indigo Caramine was observed in VIS range of spectra and it was found out to be 608 nm. The concentration and absorbance graph was plotted to calculate the concentration of solution at particular time and to note its percentage degradation.

5.5.2 Photo Fenton and Fenton like

The synthetic pollute was prepared of concentration of 10-3M by adding 466.36mg of Indigo Caramine in 1 L of distilled water. Different solution were prepared by keeping the concentration of pollute constant and varying the concentration of FeCl3, FeSO4 and H2O2. The 100 ml of dye, different concentration of FeCl3, FeSO4 and H2O2 are added with water to make up the volume of 800 ml. The solution pH was maintained to 3.5 by 1 N HNO3 and 1 N NaOH. The solution is transferred into 800 ml photo reactor and it was exposed to the 245 nm UV radiations. The certain conditions were achieved at room temperature and the percentage degradation was obtained for that particular time interval.

5.5.3 Chemical Oxygen Demand (COD)

FAS solution was of concentration 0.1 N was prepared by dissolving 39 g in 20 ml of H2SO4 to dodge the hydrolysis process , then it is diluted to 1 L distilled water. Potassium dichromate of concentration 0.25 N was solution was prepared by dissolving 12.259 g in 1 L distilled water. Sulphuric acid -Silver sulphate reagent is prepared by dissolving 5.5 g of Ag2SO4 in 543.47 ml of H2SO4. FAS is standardized by potassium dichromate with Ferroin indicator.

0.1 g of HgSO4 is sprinkled into the round bottom or reflux flask and beads are added to avoid the bumping of liquid due heating. The 10 ml of water, 5ml of K2Cr2O7 and 15 ml of H2SO4 - Ag2SO4 reagent is added into round bottom flak and is settled in the heating digester.

When the photo reactor is exposed to the UV light, at particular time interval the sample is collected. The 1 ml of sample was diluted up to 10 times. This 10 ml of sample was added with 5ml of K2Cr2O7, 15 ml of H2SO4 - Ag2SO4 reagent in the round bottom flask in which the 0.1 g HgSO4 is already sprinkled in it.

The standard two hours reflux is given at constant temperature. After heating uninterruptedly for two hours the heater is turned off and left to cool down. The colours of the sample before and after sample are shown in the figure. After the uniform heating the condensers are allowed to cool down. With addition of Ferroin indicator the sample in the round bottom flask is titrated with the FAS solution. The colour change was witnessed and depicted in the figure 5. The required FAS is calculated for both blank and sample. [6]

The COD is calculated by the given formula

$$\text{COD as oxygen mg/lit} = \frac{(A-B)\times 8000\times M\times N}{\textit{sample volume in ml}}$$

Where, A = ml FAS is used for blank
B = ml FAS is used for sample
M = molarity of FAS
N = dilution factor

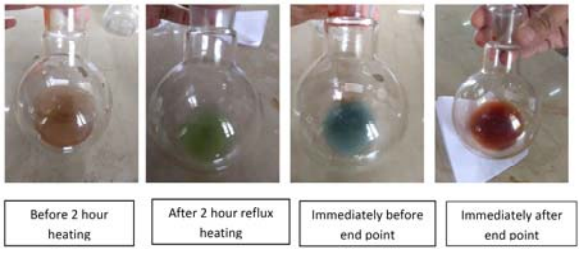
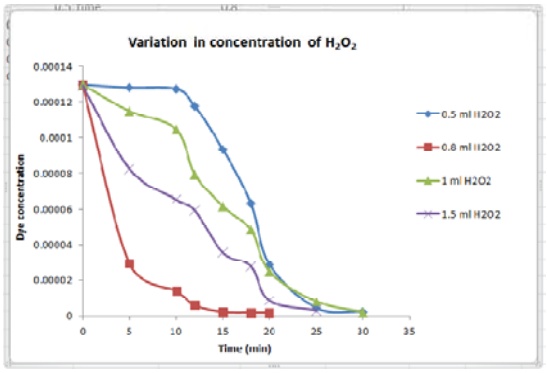


Figure 5

VI. RESULTS AND DISCUSSION

The degradation of colour and organic matter was calculated for the different combination of FeCl3, FeSO4 and H2O2 while keeping the dye concentration constant. The percentage degradation was calculated and the decrease in COD was observed. It was found that percentage degradation of dye and kinetics primarily depends on the concentration of Fenton reagent and catalyst.

For Fenton process, the concentration of H2O2 is varied and FeSO4 is kept constant. Afterwards the concentration of FeSO4 is varied when H2O2 is optimized. The following graph shows the degradation in variation of combination in concentration of H2O2 and FeSO4.



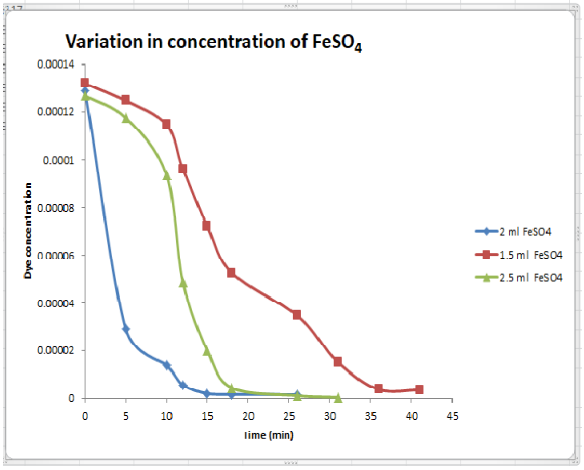


Figure. 6 Optimization of H2O2 and FeSO4 for Photo Fenton process

Similarly for Photo Fenton like process, initially the concentration of H2O2 is varied while FeCl3 was kept constant. Subsequently the concentration of FeCl3 is varied when H2O2 is optimized. The succeeding graphs display the variation in rate of decrease in concentration of dye.

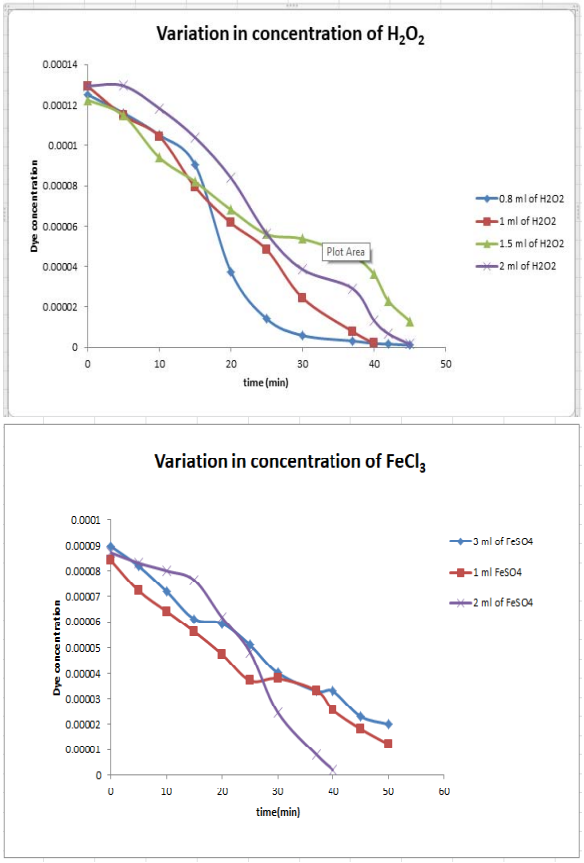


Figure 7 Optimization of H2O2 and FeCl3 for Photo Fenton like process

For the optimized parameter, COD is calculated for both the cases and the decrease in the COD was observed. The graph was plotted between COD removal and time. The comparison between two processes is depicted from the graph.

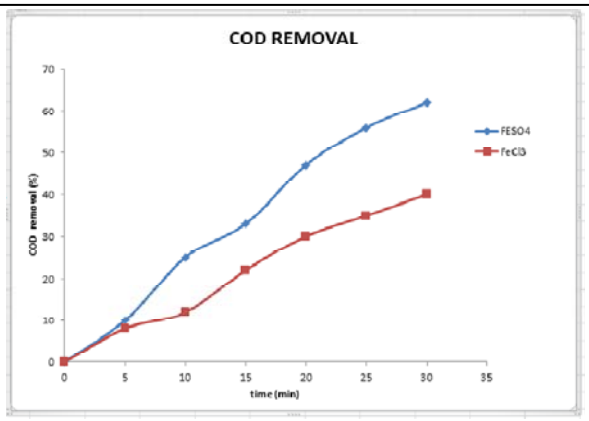


Figure 8 Comparison between COD removal of FeSO4 and FeCl3

CONCLUSIONS

For the concentration of 1.25 × 10-4 M, the optimized parameters were obtained. For Photo Fenton process the optimized parameter was 2 ml of FeSO4 and 0.8 ml of H2O2 with 98.16% degradation. The COD removed in this process was 62%.

For Photo Fenton like process, the optimized parameter was 2 ml of FeCl3 and 1 ml of H2O2 with 98.04% degradation. The COD removed in Fenton like process was 40%.

From COD result we conclude that the organic pollutant was degraded more in Fenton process as compared to Fenton like process and the kinetics was fast in Fenton process. The acidic medium is the major requirement and drawback of the Fenton processes. Thus after the treatment of AOP's on effluent water, it should be neutralized before dumping it into the water bodies in the society. The oxidants effectively decolorized the dyes however do not remove COD entirely. Thus even after the removal of colour, the solution should be exposed to UV light to remove the available organic matter in it.

AOP's technologies are extensively upgraded for more effective and efficient results in degradation of organic hazardous pollutants. AOP's are establishing its roots in solar technologies where utilization of nanoparticles such as TiO2 is relevant for cost effective processes. Due to which it can work for the wide range of pH.

REFERENCES

[1] UV Photolytic Decolorization Study of Synthetic Waste Water Containing Indigo Carmine Dye in Presence of H2O2 FARTODE A. P.1, PARWATE D.V.2 Deprtment of Chemistry K.D.K.College of Engineering, Nagpur-440009. 2Deprtment of Chemistry, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur-440033. Corresponding author E-mail:fartodeanup@rediff.com

[2] TREATMENT OF TEXTILE WASTEWATER BY ADVANCED OXIDATION PROCESSES – A REVIEW ADEL AL-KDASI1 Department of Chemical AZNI IDRIS1 & Environmental Engineering KATAYON SAED2* 2Department of Civil Engineering CHUAH TEONG GUAN1 Faculty of Engineering, University Putra Malaysia 43400 UPM Serdang, Selangor, Malaysia

[3] Indian Institute of Technology Delhi Department of Civil Engineering CEL212 Environmental Engineering (Second Semester 2013-14)

[4] UV Photolytic Decolorization Study of Synthetic Waste Water Containing Indigo Carmine Dye in Presence of H2O2 FARTODE A. P.1, PARWATE D.V.2 Deprtment of Chemistry K.D.K.College of Engineering, Nagpur-440009. 2Deprtment of Chemistry, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur-440033. Corresponding author E-mail:fartodeanup@rediff.com

[5] Decolourisation of Reactive Orange 4 by Fenton and photo-Fenton oxidation technology M. Muruganandham, M. Swaminathan) Department of Chemistry, Annamalai University, Annamalai Nagar 608002, India Received 23 October 2003; received in revised form 12 January 2004; accepted 7 March 2004

[6] ENVIRONMENT AGENCY The determination of chemical oxygen demand in waters and effluents (2007)

[7] Practical methods for water and air Pollution Monitoring S.K.BHARGAVA

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