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Comparative study of photo-degradation of dye Acid Orange -8 by Fenton reagent and Titanium Oxide- A review

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ABSTRACT

The present work is focused on the homogeneous and heterogeneous photocatalytic degradation of dye Acid Orange 8(AO8), a non biodegradable dye from dye manufacturing industries. Aqueous solutions of azo dye Acid Orange 8 were treated with Fenton reagent and titanium Dioxide. The degradation of dye was determined by visible spectrophotometer .Results indicate that dye degradation is dependent on concentration of dye ,photocatalysts (Fenton reagent and titanium Dioxide) ,Hydrogen peroxide(H_2O_2) and ph of the experimental solutions . The kinetics of degradation of the dye in the dilute aqueous solutions follows first order kinetics. The results indicated that the treatment of the dye by Fenton reagent was more efficient than Titanium dioxide at optimum conditions.

Keywords: Acid Orange 8, Titanium Dioxide, Fenton reagent and photocatalysis.

INTRODUCTION

Today protection of environment has become a major and crucial factor. As we know that the increase in the number of industries and factories due to industrial revolution raises the issue of protection of the environment. The release of textile industry wastewater in natural environment is very problematic to aquatic life and mutagenic to human.

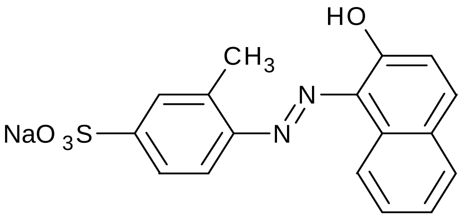
Textile effluent are complex mixtures containing a wide variety of dyes, natural impurities extracted from fibers and other pollutants such as dispersants, leveling agents, herbicides, acids, alkalies, salts and sometimes heavy metals. These effluents are notoriously known to have a strong color, large amount of suspended and dissolved solids, broadly fluctuating pH, high chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD) and presence of metal ions[1]. The environmental concern of these potentially carcinogenic pollutants in contaminated water has drawn the attention of many research workers [2].

Azo dyes are versatile class of colored organic compounds, which are characterized by the presence of one or more azo bonds (-N=N-). These dyes do not decompose rapidly through natural processes and are resistant to aerobic degradation. . Many physical and chemical methods including adsorption, coagulation, membrane process, oxidation, ozonolysis and biological treatment have been used for the treatment of various effluents and dyes. Wastewater originating from dyes production and application industries pose a major threat to surrounding ecosystems, because of their toxicity and potentially carcinogenic nature [3]·

Advanced Oxidation Processes (AOPs) have provided innovative, cost effective catalyzed chemical oxidation for treating pollutants in low or high concentration from contaminated soil, sludge and water. AOPs are based on the generation of hydroxyl radical ($^\bullet$OH) which has high oxidation potential (2.8V) that completely converts organic contaminant into CO_2, H_2O and inorganic ions or biodegradable compounds [4]. Common AOPs which are widely used are H_2O_2/UV, TiO_2/UV/H_2O_2, H_2O_2/ O_3, O_3/UV, Photo Fenton reagent, Sonolysis etc. Fenton reagent is a mixture of iron (II) ions & hydrogen peroxide. It has exceptionally strong oxidizing ability in comparison to other oxidizing agents. It was first identifying by H.J.H Fenton in1894 [5].

MATERIALS AND METHODS

Acid Orange 8



Mol. Formula = $C_{17}H_{13}N_2NaO_4S$, Mol. Wt. =364.36

Acid Orange 8 is mono azo group containing acid dye. It is dark orange powder, which is soluble in water. Acid dyes are the best choice for dyeing the silk fiber. It is toxic and carcinogenic in nature.

1. For Fenton Process

A) Materials: Monoazo dye Acid Orange 8 (95% dye content) was used.

- Photo catalyst $FeSO_4$ (Merck, 99% purity)
- H_2O_2 (Merck, 6% purity)
- Stock solution of dye Acid Orange 8 was prepared in double distilled water and diluted as required.
- The concentration of different ingredients in the reaction mixture was
  [Dye] =$3x10^{-5}$ M, [$FeSO_4$] =$3x10^{-5}$ M, [H_2O_2] =$2.91x10^{-2}$ M

B) Procedure and Analysis

- To carry out the photo bleaching, the reaction mixture was irradiated under light source (2 x 200 W Tungsten lamps).
- A water filter was used to cut off thermal radiation.
- The pH of the solution was measured by pH meter (Systronics, 106).
- The progress of the reaction was observed at definite time intervals by measuring absorbance using spectrophotometer (Schimadzu, UV- 1700) at 490 nm.
- The rate of decrease of absorbance with time was continuously monitored.

2. For Titanium Oxide

A) Materials

- For photo catalytic degradation 0.001M (0.0364 g / 100 mL) stock solution of dye Acid Orange 8 was prepared in double distilled water.
- Aqueous solutions of desired concentrations were prepared from the stock solution.
- The desired pH of the solution was adjusted by the addition of previously standardized sulphuric acid and sodium hydroxide solutions. All laboratory reagents were of analytical grade.

B) Procedure and Analysis

- To carry out the photochemical reaction, 100 ml of dye solution of desired concentration (3x 10^{-5}M) was taken in 250 ml round bottom flask and appropriate amount of solid TiO_2 catalyst (0.30 g) was added to it.
- Solution was then irradiated with visible light source of tungsten lamp (2X200 w, Sylvania) to provide energy to excite TiO_2 loading.
- A water filter was used to avoid thermal reaction.
- Air was continuously bubbled in the reaction mixture by aerator for continuous stirring of reaction mixture and continuous supply of oxygen to the reaction mixture.
- The pH was measured with pH meter (systronic). About 3 ml aliquot of the dye solution was withdrawn after a specific time interval and its absorbance was measured using spectrophotometer (Schimadzu, UV- 1700 pharmaspec) at 490 nm, after filtration through a G-3 sintered glass crucible. The rate of decrease of color with time was continuously monitored.

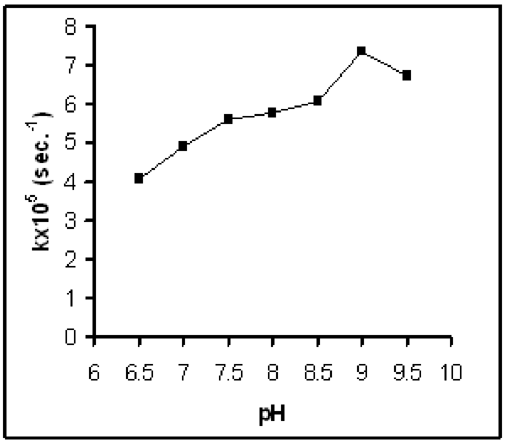
- ***VARIATION IN REACTION PARAMETERS***
  - *pH*
  - *Concentration of $FeSO_4$*
  - *Concentration of the dye*
  - *Concentration of H_2O_2*

Effect of Variation in pH

[Acid Orange 8] = 3×10^{-5} M

TiO_2 = 0.30 g **λ_{max} = 490nm**

Irradiation time =180 min



Observation:-The rate of photo catalytic bleaching increases with an increase in pH up to 9.0 there after there is an adverse effect on the rate of reaction on increasing pH further.

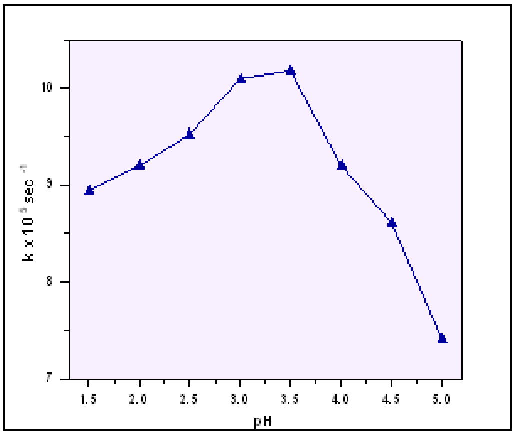
Explanation:
Increase in the pH increases the number of OH^- ions. These OH- ions will generate more •OH radicals by combining with the hole of the semiconductor.

[Acid Orange 8] = 3×10^{-5} M

[$FeSO_4$] = 3×10^{-5} M λ_{max}= 490 nm

[H_2O_2] = 2.91×10^{-2}

Irradiation time =180 min



Observation:
The rate of photo catalytic bleaching increases with an increase in pH up to 3.5. There after there is an adverse effect on the rate of reaction on increasing pH further.

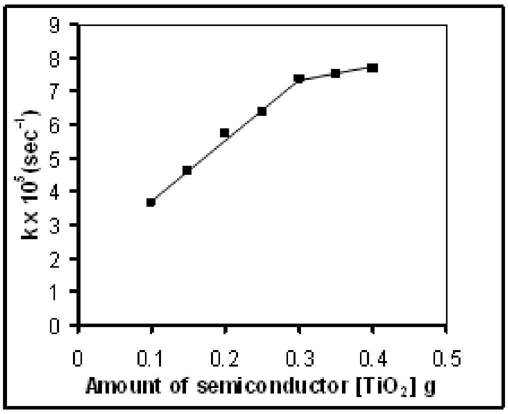
Explanation:
It was observed that at high pH (pH > 3.5), the generation of $^{\bullet}OH$ gets slower because of the formation of the ferric hydroxo complexes. On the other hand, at very low pH (< 2.0), hydrogen ions acts as $^{\bullet}OH$ radical scavengers.

Effect of Amount of TiO_2

[Acid Orange 8] = 3 x 10^{-5} M

pH=9.0 Irradiation time = 180 min

λ_{max} = 490 nm



Observation: The rate of dye decolourization increases with increasing catalyst level up to 0.30g and beyond this, the rate of reaction becomes almost constant. (TiO_2 varying from 0.10 to 0.40g.)

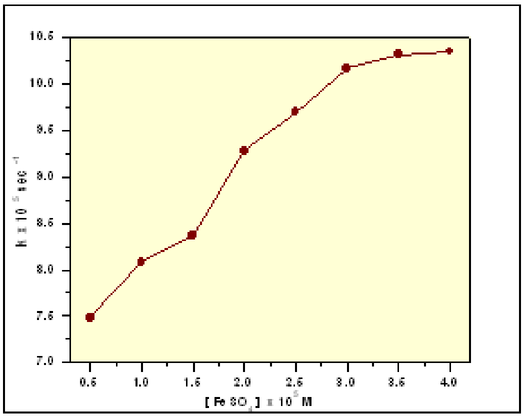
Explanation:
Initially the increase in the amount of catalyst increases the number of active sites on the TiO_2 surface that in turn increases the number of $^{\bullet}OH$ and $O_2^{\bullet}$radicals.

Effect of variation in concentration of $FeSO_4$

[Acid Orange 8] = 3 x 10^{-5} M

pH = 3.5 Irradiation time = 180 min

λ_{max} = 490 nm [H_2O_2] = 2.91 x 10^{-2} M



Observation:
The rate of photo bleaching increases with an increase in the concentration of catalyst $FeSO_4$ up to 3 x 10^{-5} M.

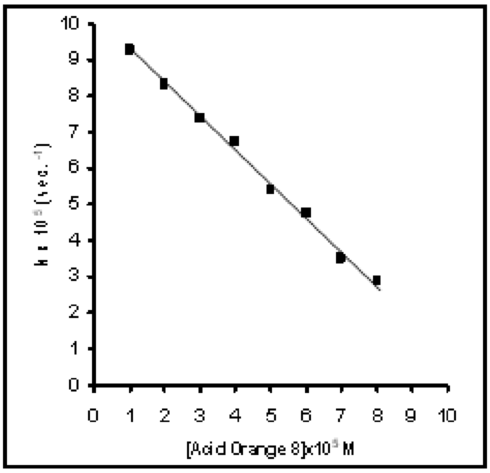
Explanation:
Increasing the rate of photodegradation. After the optimal Fe^{2+} addition, the higher dose of Fe^{2+} resulted in a brown turbidity that causes the recombination of $^{\bullet}OH$ radicals and Fe^{2+} reacts with $^{\bullet}OH$ as a scavenger. Therefore, on further increase, the rate becomes almost constant.

Effect of variation in Acid Orange 8 concentrations

[Acid Orange 8] =3 x 10^{-5} M

pH = 9.0 λ_{max} = 490 nm

Irradiation time =180 min



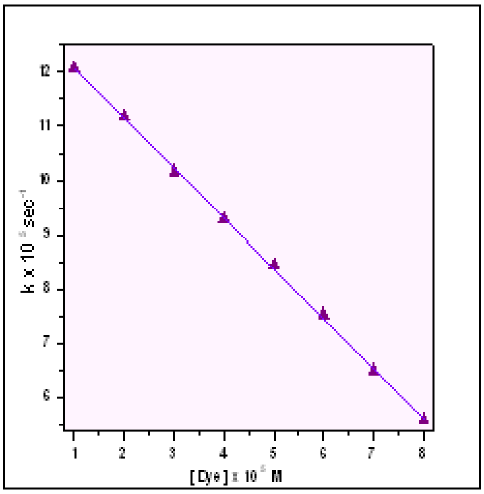
Observation:
It has been observed that the rate of photo catalytic degradation decreases with increase in the concentration of Acid Orange 8.

Explanation:
The increase in initial concentration of the dye, while the irradiation period and catalyst dose are kept constant, the concentration of unabsorbed dye in solution increases, leading to lesser penetration of light through the solution on to the surface of TiO_2.

[Acid Orange 8] =3 x 10^{-5} M

pH = 3.5 λ_{max} = 490 nm

Irradiation time =180 min

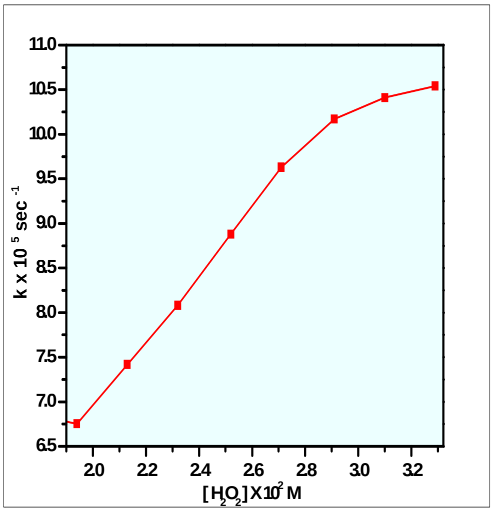


Observation:
The results reveal that the rate of photo bleaching of dye decreases with the increase in the concentration of the dye.

Explanation:
This can be explained on the basis that the increase in the initial concentration of the dye lies in consistency of the hydroxyl radicals concentrations for all the dye molecules and therefore the rate of decolorization decreases.

Effect of variation in hydrogen peroxide concentration

[Acid Orange 8] = 3 x 10^{-5} M *[$FeSO_4$] = 3 x 10^{-5} M* *pH = 3.5*
λ_{max}= 490 nm *Irradiation time = 180 min*

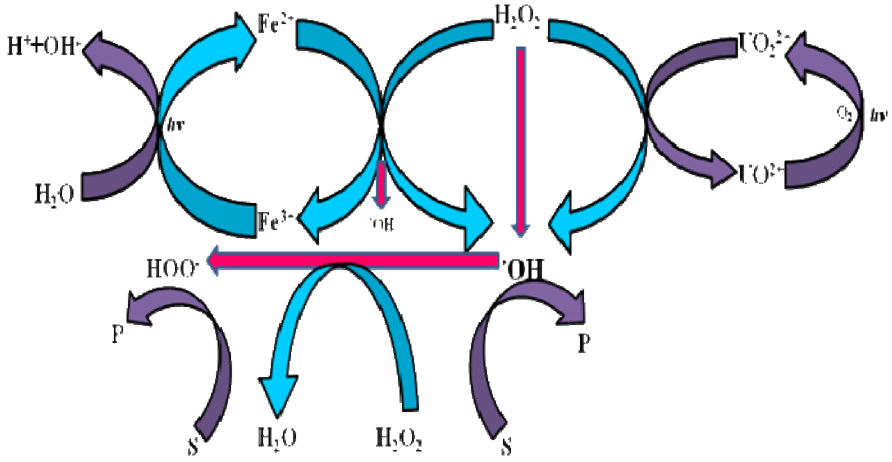


Observation:
The result reveals that the rate of photo bleaching of dye increases with the increase in the concentration of H_2O_2 up to 2.91 x10^{-2} M.

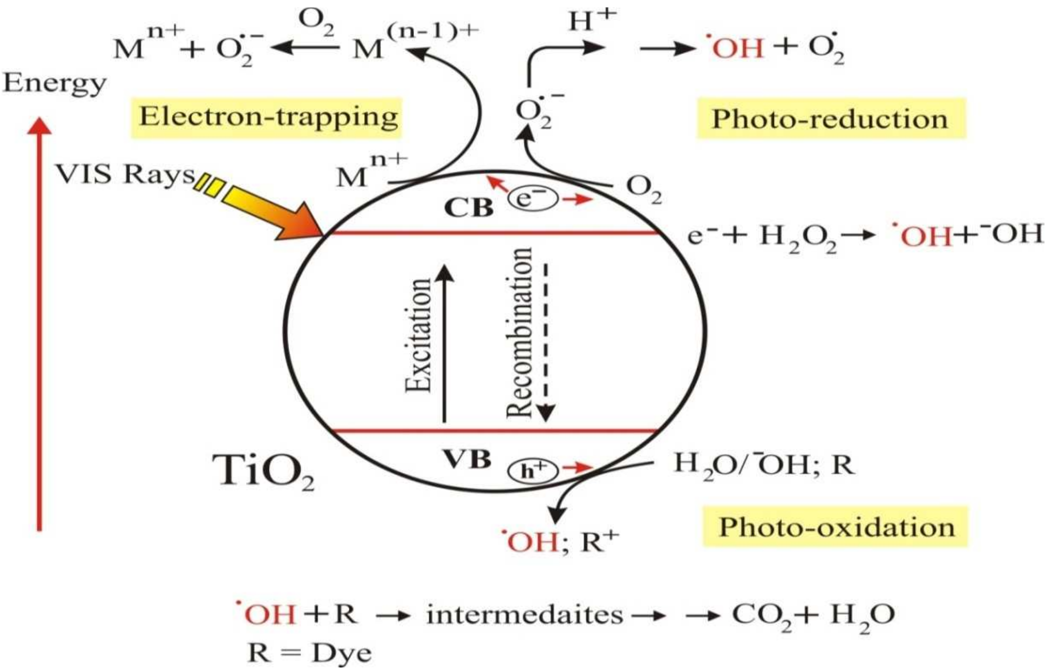
Explanation:
This can be explained on the basis that at higher concentration of H_2O_2, more hydroxyl radicals are produced which degrade more dye molecules.

Further increase in [H_2O_2] has negligible effect due to the recombination of •OH radicals and also hydroxyl radicals reaction with H_2O_2 contributing to the •OH scavenging capacity.

FENTON MECHANISM



Where S = Acid Dye Acid Orange 8
Fig- Schematic representation of Photo-Fenton Chemistry



TiO_2-semiconductor photocatalytic processes.

CONCLUSION

Coagulation, sedimentation, filtration before the application of AOPs could remove solids that interfere with these processes. However, the use of pretreatment step which is followed by biological treatment processes, could achieve lower cost and sufficient organic compounds removal.

The degradation of Dye Acid Orange-8 was investigated with homogeneous (Photo –Fenton Process) and Heterogeneous (visible –TiO_2) AOPs. The influence of pH, dosage of nano catalyst, H_2O_2 concentration and constant time on the rater of degradation more studied.

The experimental results reveal that:

1. The maximum degradation was achieved at pH=3.5. At pH=3.5 the percentage degradation is achieved maximum when compared with heterogeneous process of maximum achieved at pH=9.0.
2. The optimum H_2O_2 concentration is **2.91 x 10^{-2}** at which maximum removal of the dye Acid Orange -8 is achieved with Homogeneous AOPs.
3. The maximum removal achieved with 0.30g/L of TiO_2 dose in Heterogeneous processes where as in Photo-Fenton process maximum removal achieved with **3 x 10^{-5}** M of Fe^{2+} concentration.
4. The degradation process only visible exposure and H_2O_2 are not enough for complete degradation. However addition of catalyst makes faster the reaction and achieved the maximum percentage removal of compound concentration as in short reaction time.

5. The Homogeneous photo-catalysis is a prominent method for degradation of dyes and dye intermediates contained industrial wastewaters, in aqueous system under simple handling with no specific technical equipments is necessary and also in–expensive with less investment less energy demand and produce harmless byproducts.

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