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Decolourization of Nigrosine WS (AB2) Dye by Solar Photo-Fenton Process

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Abstract:
Number of physical and chemical treatment methods has been reported for the treatment of dye effluents. Among themone of the widely used and effective chemical treatment methods are AOPs for the removal of recalcitrant organic constituents from textile industrial and municipal wastewater.On the basis of solubility of dye in water, highly soluble Nigrosine WS (Acid Black 2) dye was studied which is widely used in dying of leather, wood and textile.The homogenous Photo-Fenton process was investigated for the decolourization of Nigrosine WS (Acid Black 2) dye under solar irradiation in aqueous solution. A detailed investigation of decolourization of dye was carried out using H_2O_2 and $FeSO_4.7H_2O$ as catalyst. The combination of these reagents generates $HO^{\bullet}$ radical, a strong oxidizing agent which is responsible for decolourization of dye. Results show that decolourization of dye depends on concentration of dye, H_2O_2, $FeSO_4.7H_2O$ and pH of the aqueous solution. The optimum condition for the decolourization of dye was determined. This method gave complete dye removal in just 2 hour of time period.

Key words*: Acid Black 2, Advance Oxidation Process, decolourization, Photo-Fenton, recalcitrant organic constituents*

1. Introduction

The industrial water demand is on a rise and will account for 8.5% and 10.1% of the total freshwater abstraction in 2025 and 2050 respectively. India is also projected to move into the category of water stressed nation by 2020 [1]. So the recycling or treatment of waste water is not only important but also necessary to meet the fresh water demand of future generation. Over 7,00,000 tons of approximately 10,000 types of dyes and pigments are produced annually worldwide. From this amount, about 20% is discharged as industrial effluents during the textile dyeing and finishing processes without previous treatment [2]. The colour and toxicity of dyes not only influences the quality of life, but also influences the efficiency of conventional wastewater treatment methods. Many dyes are difficult to remove due to their complex structure and synthetic origin and the limitations have attached to the conventional treatment methods to treat such waste water, especially for decolourization. So to overcome the inconvenience of conventional treatment methods various chemical oxidation techniques have emerged in the last few decades, particularly for the treatment of industrial wastewater. Among these techniques, the advanced oxidation processes (AOPs), are considered to be a potential treatment method for the removal of colour which are characterized by the production of the hydroxyl radical ($HO^{\bullet}$) as a primary oxidant. Among the various AOPs, the use of Fenton reagent (H_2O_2/Fe^{2+}) with UV or solar irradiation is one of the most effective methods for colour removal from wastewater.

Kaiqun W. et al., (1998) have studied the photo degradation of Malachite Green (MG) under visible light irradiation in the presence of Fe^{+3} / H_2O_2 or Fe^{+2} / H_2O_2 and compared with the dark reaction. It was found that visible light irradiation can accelerate significantly the rate of MG degradation, comparing to that in the dark.Mariana N. et al., (2003) have reported the study of degradation of two azo dyes, Reactive Yellow 84 (RY84) and Reactive Red 120 (RR120) by Photo-Fenton and Fenton-like oxidation. The results reveal that Photo-Fenton process is more effective for degradation of azo dyes.Ashok et al., (2013) have investigated the degradation of Acid Violet 54 (AV54) by Photo-Fenton under irradiation of visible light in aqueous solution. The experimental data demonstrated that Photo-Fenton process is effective technique for the degradation of AV54 dye in aqueous solution because AV54 get 100% mineralized in 55 minutes. Sunil Kumar et al., (2013) have investigated the photocatalytic bleaching of Nigrosine WS (Acid Black 2) dye by ZnO in aqueous solution. The experimental data demonstrate that photocatalytic process is effective technique for the degradation of Nigrosin WS dye by ZnO from aqueous solution which gave 67% mineralization of the dye in 240 minutes.

Till now no research has been done to evaluate the efficiency of Photo-Fenton process for decolourization of Nigrosine WS (Acid Black 2) dye. From the above literature review it can assume that the Photo-Fenton process could be the efficient method for decolourization of Nigrosine WS (Acid Black 2) dye with the advantage of less chemical requirement and short treatment period.

2. Objectives

- To decolourize the Nigrosine WS (Acid Black 2) dye by using Homogeneous Solar Photo-Fenton Process.
- To evaluate the optimum condition for decolourization of Nigrosine WS (Acid Black 2) dye by Homogeneous Solar Photo-Fenton Process.

3. Materials and Methods

3.1. Chemicals

- Nigrosine WS (Acid Black 2): The solid Nigrosine WS was used throughout the investigation without any further purification. The Nigorsine WS (C.I. No. 50420) was purchased from High Purity Laboratory Chemicals (HPLC), Mumbai.
- $FeSO_4.7H_2O$: 98% pure crystalline $FeSO_4.7H_2O$ (M.W. = 278.02) was bought from Qualigens fine chemicals, Mumbai.
- H_2O_2 (30% w/v): Used directly without any dilution and bought from MercSpecialities Private Limited.
- 0.1 N H_2SO_4: 2.77 ml of conc. H_2SO_4 (96%) was diluted in 1000 ml of deionised water.
- 0.1 N NaOH: 4.0 gm ofNaOH dissolved in 1000 ml of deionised water.

All laboratory reagents were used of analytical grade without any further purification. The deionised water is used for dilution throughout the investigation.

3.2. Apparatus

- pH meter: to check the pH of aqueous dye solution.
- Spectrophotometer: to measure the absorbance of dye solution for determining colour intensity.
- Magnetic stirrer: to provide continues stirring throughout the investigation.
- Centrifuge machine: to settle down the iron and dye particles.
- Weighing machine: to weigh the Nigrosine WS dye for different dye concentration.
- Lux meter:to measure the solar irradiation throughout the investigation.

3.3. Preparation of Solutions

3.3.1. Preparation of dye solution

There were six different concentrations of Nigrosine WS dye was prepared such as 5, 10, 25, 50, 75 and 100 ppm using de-ionized water for dilution. For each concentration of Nigrosine WS dye, 200 ml of freshly prepared dye solution was used throughout the investigation for decolourization.

3.3.2. Preparation of $FeSO_4.7H_2O$

There were six different concentration of $FeSO_4.7H_2O$ (M.W. = 278.02)was prepared such as 0.1, 0.01, 0.001, 0.2, 0.02, 0.002 M as catalyst.

3.3.3. Preparation of H_2O_2 (30% w/v)

The different dose of H_2O_2 (30% w/v) was applied directly without any dilution such as 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2 ml for each 200 ml of Nigrosine WS dye concentration.

3.4. Determination of maximum absorbance wavelength

Two dye concentration that is 50 and 100 ppm of Nigosine WS was used to determine the maximum absorbance wavelength. The absorbance was measured at each 25 nm of interval, between 400 – 700 nm that is visible wavelength range. Then the graph of wavelength and absorbance was plotted.

3.5. Experimental setup

The experimentation was carried out in Bharati Vidyapeeth Institute of Environment Education and Research (BVIEER) campus, Bharati Vidyapeeth University, Pune, India. The investigation was done using solar light in the month of December 2013, mostly between 11:00 am to 4:00 pm.

To investigate the decolourization of Nigrosine WS dye, 200 ml of dye solution of six different concentrations such as 5, 10, 25, 50, 75 and 100 ppm were taken in 500 ml capacity of borosilicate glass beaker (Figure 1). The initial absorbance of dye solution was measured at 570 nm by spectrophotometer after the calibration. The initial pH of dye solution was measured and adjusted.

Figure 1: Experimental setup

To find out the optimum condition for decolourization of Nigrosine WS dye six different concentration of $FeSO_4.7H_2O$ and H_2O_2 (30% w/v) was applied.After addition of $FeSO_4.7H_2O$ and H_2O_2 (30% w/v) in 200 ml of dye solution, the glass beaker was stirred at 2000 rpm for 3 hours with the magnetic stirrer. The absorbance of solution was checked at each half an hour by spectrophotometer at 570 nm. For that 5 ml of sample had been taken out each time and 0.1 N NaOH was added to raise the pH above 7 in order to stop further $HO^{\bullet}$ radical formation. The sample was centrifuged at 3000 rpm for 3 minutes to settle down the iron sludge particles before measuring the absorbance of the solution. The solar irradiation was noted down at each half an hour by digital Lux meter in Lux unit and then an average was calculated.

4. Observations and Results

4.1. Maximum absorbance wavelength for Nigrosine WS dye

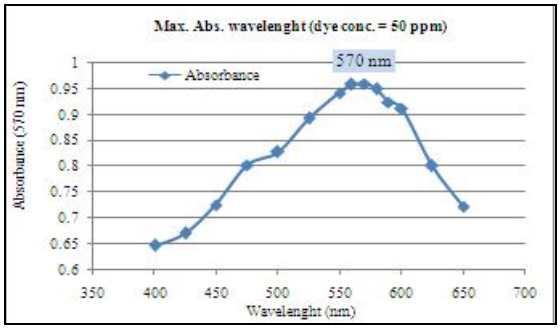

Figure 2

A single peak was observed at 570 nm which was used as the maximum absorbance wavelength and at which decolourization of Nigrosine WS dye was determined by measuring absorbance at each half an hour.

4.2. Effect of aqueous pH

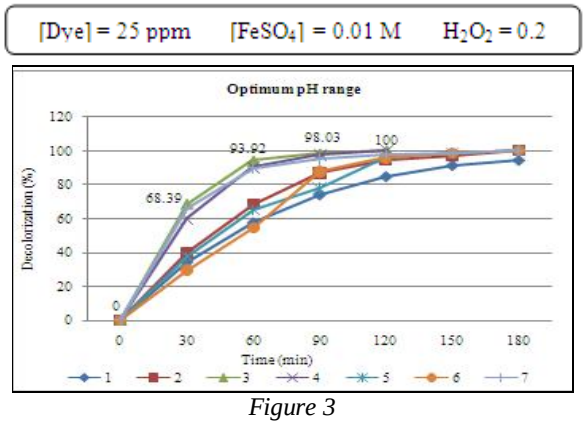

Figure 3

The pH range of 3-4 is more efficient for decolourization and as the pH increases the rate of decolourization decreases. At low pH, 1 and 2 dye solution was taking more time to decolourize and same for the increasing pH i.e. 5 to 7. However, pH 3 was used as the optimum pH because decolourization of AB2 was more in first hour than the pH=4. At lower pH 1 and 2, dye removal was less because reaction between hydrogen peroxide and iron was significantly affected resulting reduction in the hydroxylradical

production. At lower and higher pH, dye removal was less also because of hydroxyl radicals scavenging of H^+ ions (Spinks J.W.T. and Woods R.J., 1990).

4.3. Effect of concentration of $FeSO_4.7H_2O$

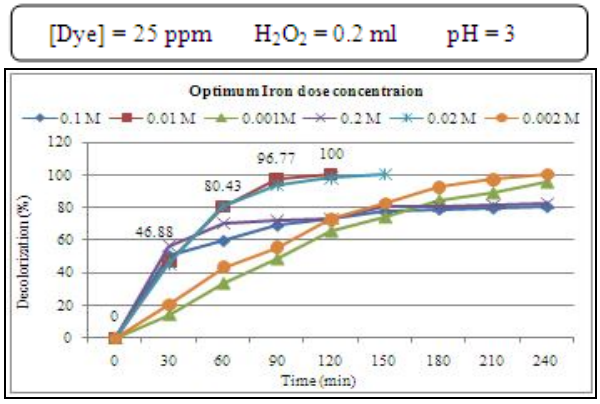

Figure 4

The maximum efficiency of decolourization of 100% was achieved by 0.01 M and 0.02 M iron concentration in shortest time period of 2 hours, but 0.01 M was taken as optimum iron concentration because of less time taken for 100% of decolourization. The less decolourization observed at small iron dosage may be because of less production of $HO^{\bullet}$ for the oxidation process i.e. 0.001 M and 0.002 M. The large concentration of $FeSO_4.7H_2O$ has negative effect on decolourization process. An increase of $FeSO_4.7H_2O$ concentration did not improve the decolourization process i.e. 0.1 M and 0.2 M (Malik P.K. and Saha S.K., 2003).

4.4. Effect of concentration of H_2O_2 (30% w/v)

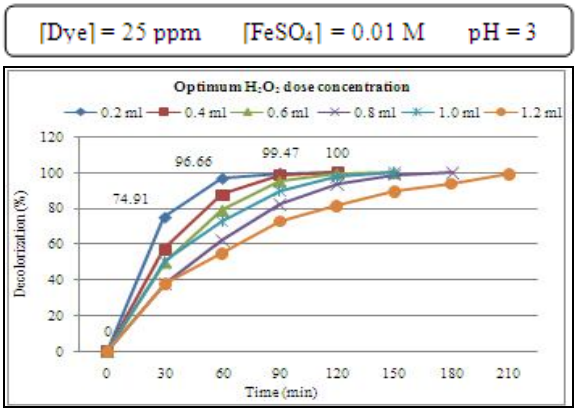

Figure 5

The result shows that the small amount of H_2O_2 has taken the shortest time for decolourization. The optimum dose range of H_2O_2 was found as 0.2 – 0.6 ml, from which more than 99 % colour removal can be achieved just within 2 hours. However, 0.2 ml of dose was taken as the optimum dose due to more decolourization just within first one hour. The increased amount of H_2O_2 did not give improved decolourization i.e. 0.8 -1.2 ml. This may be due to the recombination of hydroxyl radicals and also hydroxyl radical's reaction with H_2O_2 contributing to the hydroxyl radical scavenging capacity (Modirshala et al., 2006).

4.5. Effect of initial dye concentration

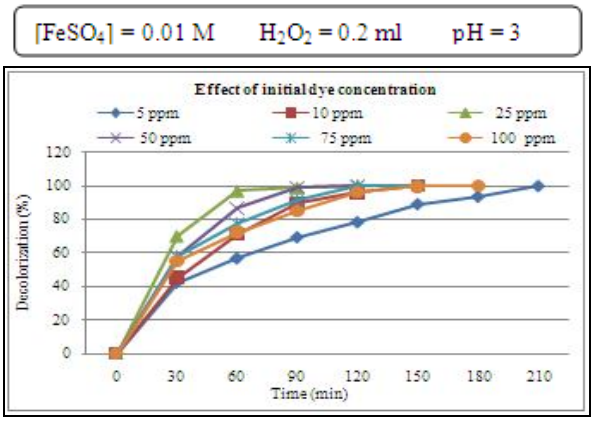

Figure 6

Result shows that optimum dye concentration range for optimum iron and H_2O_2 dose is 25-75 ppm. But the decolourization rate decreases with the increasing dye concentration. The 100% decolourization can be achieved with increased dye concentration but more time is required i.e. 75 ppm and 100 ppm. It may be attributed to the fact that as the concentration of AB2 increases, it starts acting like a filter for the incident light, where its large concentration permits the desired light intensity to react with the dye molecule in the bulk of the solution. Thus, increasing reaction time results in the decrease of decolourization rate ofAB2 (Ashok et al., 2013).The decolourization rate also decreases as the dye concentration decreases i.e. 5 ppm and 10 ppm. It may be due to unconsumed Fe^{+2} ions present into the solution.

4.6. Effect of stirring

To study the effect of stirring on the rate of decolourization, the investigation was done in the absence of stirring and 10 % of the initial stirring, i.e. 200 rpm at optimum iron and H_2O_2 dose at fixed pH 3 for the duration of 3 hours for six different dye concentrations.

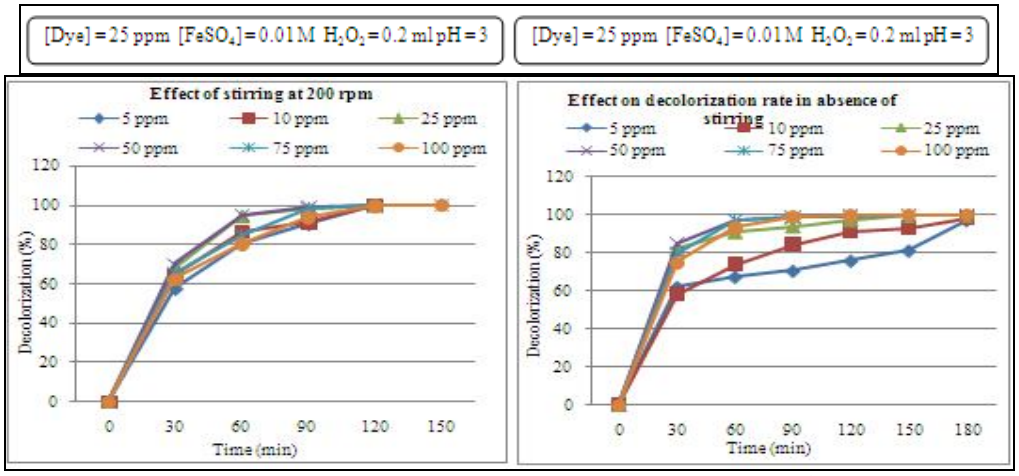

Figure 7 *Figure 8*

Result proves the effect of stirring on the decolourization rate. The 100% of decolourization can be achieved within 2 hours up to 50 ppm, while more half an hour is required to 75 and 100 ppm solution for 100% decolourization. In case of absence of stirring, 100% decolourization cannot be achieved but 99% of decolourization can be achieved within 3 hours of time duration. Absence of stirring also gives rise to the Fe^{+2} sludge formation.

5. Discussion

The use of solar light instead of UV light reduces the operating cost of treatment method. Results of this study prove that decolourization rate of AB2 dye depends upon the several factors such as initial dye conc., aqueous pH, and conc. of iron, H_2O_2 and on stirring. The 10% of initial stirring gives improved and fast decolourization but the absence of stirring increases the decolourization time as well as gives iron sludge which is unconsumed after the reaction. So stirring below 200 rpm is must require to avoid iron sludge production for the decolourization of AB2.

6. Conclusion

The optimum condition of Photo-Fenton process gives 100% decolourization of AB2 dye in 2 hour of time period. The optimum dose of $FeSO_4.7H_2O$ is 0.01 M, (30% w/v) H_2O_2 is 0.2 ml, and optimum pH range is 3-4 which gives complete decolourizationin the presence of direct sunlight. The results of this study are sufficient to conclude that Homogenous Photo-Fenton method is prominent and cost effective method for complete removal of Nigrosine WS (C.I. Acid Black 2) dye with major advantage of simple handling without any specific technical equipment. The treatment method requires less investment and energy demand.The only criteria required throughout the reaction for efficient result is continuous and large solar irradiation exposure. So this method is efficient and cost effective treatment method in tropical region where sun light is abundant.

7. Acknowlesgement

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