Degradation of Organic Cibacron Navy FN-B Dye by Photocatalysis Process Using ZnS

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Abstract The photocatalysis process was studied in this research. UV irradiation as the illumination source was investigated to remove the Cibacron Navy FN-B organic dye from simulated wastewater using Zinc Sulfide treated with Hydrogen Peroxide as the catalyst. Four sets of experiments were conducted throughout the work; the effect of pH (4, 6, 8, and 10), ZnS dosage (0.5, 1.0, 1.5, and 2.0 gm), the initial concentration of dye (25, 50, 75, and 100 mg/L), and the concentration of H2O2 (0, 50, 100, 150, and 200 mg/L) on the photocatalysis process was examined. The effect of contact time was studied implicitly within the sets (0, 15, 30, 45, 60, 75, and 90 min). The optimum conditions for the best decolorization of dye were found to be as: pH=6.2 (the normal pH of the dye solution), ZnS=1.5gm, Co=25mg/L and H2O2=200mg/L, the decolorization of Navy dye increased with increasing the contact time with the ZnS. The addition of H2O2 enhanced the decolorization rate by 8%. A mechanism of the Navy dye degradation in the UV photocatalysis system was proposed. The Pseudo first order reaction rate was found to be applicable on the process and the first order reaction rate constant (k) was found to be 0.033 min⁻¹ with a correlation coefficient of 97.3%.

Key words Cibacron Navy FN-B dye, H2O2, organic dye, photocatalysis, ZnS

1. Introduction

Polluted surface water is one of the foremost problems facing mankind in the world. Due to the increased industries and lack of sense of responsibility, the surface water represented mostly by rivers and lakes is used as receiving water bodies of different types of wastes [1]. Industrial development led to an increase in the bright and colorful products. The rapid growing population of the world enlarged the demands for such products. To meet these demands, dye consuming industries including textile, paper, leather, printing, plastic and carpet, are expanding. As a result, the usage of dyes is increasing dramatically [2]. During the dyeing operation a significant amount of dyes remain unfixed on the fabric [3] and hence, a high concentration of dyes occurs in the textile wastewater. The majority of dyes are non-hazardous themselves, but they easily form toxic complexes when mixed with water [4]. Many treatment techniques for textile wastewater were implemented such as coagulation, adsorption, and membrane separation [5], nevertheless these techniques tend to change the wastes from one phase to another (liquid to solid) [6], for that the need for new processes has appeared. Advanced Oxidation Processes (AOPs) have been proposed by a lot of researchers as a method of eliminating pollutants.
having the photocatalysis as one of these processes. Heterogeneous semiconductor photocatalysis has appeared during the last decades as one of the best techniques used in protecting the environment from hazardous pollutants [7,8]. This technique offers complete mineralization, no waste disposal problems, works in normal pressure and temperature conditions, and it is low cost [9,10]. An excellent semiconductor photocatalyst should have all or most of the following points: it should be (1) active to light (photoactive), with an ability to make use of visible and near UV light (2) inert both chemically and biologically (3) stable toward photo deterioration (4) nontoxic and (5) economical [9]. An effective photocatalyst is a semiconductor with a direct band gap that has the ability to absorb photons with greater or equal energy to the catalyst band gap and rapidly generate the electron-hole pairs, which in turn creates radicals in the system (•OH). These radicals are effective oxidizers that can decompose the organic materials presented in the system [11]. Zinc sulfide (ZnS) has been focused on as a semiconductor in the photocatalysis process owing to its non toxicity, high chemical stability, and to its safe environmental nature [12,13]. ZnS is an II-VI commercially significant semiconductor with a large exciton binding energy of about 40 eV and a band gap of 3.67 eV [11]. A lot of researchers have studied the effect of using ZnS as a catalyst in removing different dyes by photocatalysis process [14-17], while other researchers studied using other catalysts to remove different types of organic pollutants, ZnO was studied by [18-21], TiO₂ [22-24], V₂O₅ [25], Ag₂CrO₄-GO [26], while [27] studied the effect of supporting the catalysts by graphene on the degradation of organic dye. The objective of this research was to study the use of ZnS as a photocatalyst to remove the Cibacron Navy FN-B organic dye from a synthetic wastewater, enhanced by Hydrogen Peroxide (H₂O₂) under UV light irradiation, considering the effect of pH, initial concentration of dye, catalyst dosage, H₂O₂ concentration, and contact time on the removal efficiency.

2. Experimental

2.1 Materials
The materials used in this study are represented by the following:
- Cibacron Navy FN-B organic dye: obtained from AL-Kut textile factory south of Baghdad, Iraq (Department of Dying and Printing), used to simulate the synthetic wastewater.
- Simulated wastewater solutions were prepared by dissolving a defined quantity of the dye in the required volume of distilled water.
- Base and acid of 0.1 M (NaOH and H₂SO₄): used to adjust the solution pH to the required value.
- Zinc Sulphide (ZnS): used as a catalyst.
- Hydrogen Peroxide (H₂O₂) (50%w/w) with a molecular weight of 34.01g/mole supplied by HOPKIN & WILLIAMS: used to enhance the oxidation in the photocatalysis process.

2.2 UV/ZnS irradiation process and apparatus
The UV light irradiation was obtained from the UV lamp water sterilizer, TUV 215 MM T5 6W, Made in China.

The experimental reactor used for the photocataytic degradation of navy dye was consisted of a batch photoreactor of 1000ml cylindrical beaker with working volume of 500ml equipped with the UV lamp as the illumination source. The solution in the reactor was constantly stirred via a magnetic stirrer.

In order to limit the effect of visible light (solar radiation) and to eliminate the dangerous effect of the UV lamp, the setup was wrapped with aluminum paper during operation.

2.3 Characterizations
2.3.1 The Standard curve of Cibacron Navy FN-B dye. The UV-visible spectra of different concentrations of Cibacron Navy FN-B dye was measured (figure 1). The absorption-concentration at 600 nm was plotted and it showed linear relation (figure2). This curve was used during the experimental
work to measure the unknown concentration of the dye in the withdrawn samples.

The spectrum of Cibacron Navy FN-B dye showed $\lambda_{\text{Max}}$ at 600 nm (Figure 1), this wavelength was used to measure the Navy dye absorption in the UV–Vis spectrophotometer, since it corresponds to the maximum absorption of the dye. While Figure 2 shows a linear relation between the absorption and the concentration represented by equation (1) with a value of $R^2=0.996$.

$$Y = 0.0213X$$

Where $Y$ represents the absorbance of the spectrophotometer for the samples of Cibacron Navy FN-B, and $X$ refers to the concentration of dye in the sample, in mg/L.

### 2.4 Photocatalytic activity

The photocatalytic activity of ZnS was evaluated by observing the photo degradation of Cibacron Navy FN-B dye in aqueous solution. In a typical photocatalytic run, 500 mL of the aqueous solution containing the desired concentration of dye in the range (25–100) mg/L and (0.5-2) gm of ZnS were loaded in the beaker. The solution was magnetically stirred for about 30 min in order to reach an equilibrium adsorption-desorption between the catalyst and dye [11]. For the experiments where the effect of $\text{H}_2\text{O}_2$ on the photocatalysis process was studied, the required amount of $\text{H}_2\text{O}_2$ range (50-200mg/L) was added before irradiation. The irradiation of the mixed solution was achieved using the UV lamp. At a defined time interval (each 15 minutes), about 10 mL of the solution was withdrawn from the suspension and filtered by using membrane filter. The clarified samples were analyzed photometrically at 600 nm wavelength. Concentration of navy dye in solutions was measured by using the obtained standard curve.

After determining of navy dye concentration versus time, the percentage removal of dye was calculated through equation (2):

$$\text{Removal of Dye} \% = \frac{C_0 - C_t}{C_0} \times 100$$

Where: $C_0$ and $C_t$ are concentration of the dye initially and at time $t$, respectively.

### 3. Results and Discussion

#### 3.1 Decolorization efficiency of UV process

Four sets of experiments were conducted. The first set studied the effect of pH on the photo-degradation, while the further sets of experiments considered the initial concentration of dye, the catalyst dosage, and the effect of $\text{H}_2\text{O}_2$. The effect of the contact time was studied implicitly within the sets.

#### 3.1.1 The effect of pH

The first set of tests examined the effect of pH on the removal of dye
concentration, as shown in figure 3. The initial concentration of dye was fixed to 25 mg/L, the catalyst dosage was fixed to 0.5 gm, and no hydrogen peroxide was added, while the pH ranged from 4 to 10.

The original pH of the solution was found to be 6.2. The pH was adjusted by adding base or acid (NaOH and H₂SO₄) reaching the required pH level. Figure 3 showed that the highest removal was at pH = 4 (83%), the second best removal was at the normal pH of the solution without adjusting (pH=6.2 and R=79%).

The effect of pH on the removal of dye can be explained in terms of point of zero charge (pH_{pzc}). The surface charge of the catalyst is negative for pH values greater than its pH_{pzc}, positive for pH values less than its pH_{pzc}, and neutral for pH value equal to its pH_{pzc} [28]. The Cibacron Navy FN-B dye molecule has a negative charge, which leads to electrostatic interaction between ZnS surface and the dye molecule, eventually resulting in higher removal efficiency of dye at pH levels less than the pH_{pzc} of ZnS. The pH_{pzc} for ZnS was found to be 4.2 [29], from that it was concluded that at pH = 4, the ZnS has its highest removal.

Since this work is concerned in enhancing the ZnS catalyst with H₂O₂, therefore, the pH_{pzc} should be taken for the ZnS treated with H₂O₂, which was found to be equal to 6.5 [30]. Therefore, the optimum pH taken in this study was the normal pH of the solution (6.2). The dye removal at the chosen pH (79%) slightly differs from that at pH=4, in addition to the reduction in time and cost of adjusting the pH level.

3.1.2. The effect of catalyst dosage. The optimum catalysts dose is obtained by measuring the oxidation of the same dye concentration using different catalysts dose. Four ZnS dosages (0.5, 1, 1.5, and 2 gm) were tested keeping all other conditions constant (pH=6.2, initial concentration of dye C₀=25 mg/L). The highest removal rate was obtained at dose 1.5 gm. Table 1 illustrates the relation between the ZnS dosage and the percentage removal of dye.

| C₀, mg/L | pH  | ZnS, gm | % Removal |
|----------|-----|---------|-----------|
| 25       | 6.2 | 0.5     | 79        |
|          |     | 1       | 84        |
|          |     | 1.5     | 88        |
|          |     | 2       | 37        |

Table 1 illustrated that increasing the ZnS dosage increased the dye removal reaching its peak (88%) at the 1.5 gm dosage of ZnS, and then it was reduced dramatically to 37% for the 2 gm dosage.
be explained as follows; increasing the ZnS dose should lead to an increase in the active sites that creates radicals (•OH) by photocatalyst process and eventually increasing the number of degraded dye molecules. However, when increasing the catalyst dose beyond the optimum amount, the opacity of the suspension is increased leading to light scattering, which eventually hampers the photons penetration and by that less catalyst particles could be activated [31].

3.1.3. The effect of initial concentration of dye. Four experiments (Table 2) were carried out at different initial concentrations (C₀) of Cibacron Navy FN-B dye.

| pH  | ZnS, gm | C₀, mg/L | % Removal |
|-----|---------|----------|-----------|
| 6.2 | 1.5     | 25       | 88        |
|     |         | 50       | 69        |
|     |         | 75       | 52        |
|     |         | 100      | 47        |

It becomes clear from this table that the removal efficiency of Cibacron Navy FN-B dye from aqueous solution by using UV Lamp irradiation decreases with the increase of initial dye concentration. This can be attributed to the fact that for the same catalyst dosage the same number of oxidizing radicals (•OH) are created, increasing the dye concentration will lead to increasing the molecules absorbed on the catalyst surface and decreasing the active sites that generate these radicals [32], moreover, increasing the dye concentration leads to increasing the absorbed light by the dye molecules and reducing the photons reaching the catalyst surface [33].

The best percentage removal was found in the initial dye concentration of 25 mg/L.

3.1.4. The effect of Hydrogen peroxide. The effect of ZnS treated with H₂O₂ on the photo-degradation process was investigated by measuring the oxidation of different H₂O₂ concentrations, keeping all other conditions constant at the obtained optimum values (pH=6.2, ZnS=1.5gm, and C₀ = 25mg/L). H₂O₂ dosages ranging from 0, 50, 100, 150, and 200 mg/L were tested (figure 4).

![Figure 4](image)

**Figure 4.** The effect of H₂O₂ on the decolorization ratio

From this figure it can be seen that increasing the concentration of H₂O₂ enhanced the ZnS performance in removing the dye. This can be credited to the fact that H₂O₂ is an oxidizing agent, which would increase the created radicals responsible for dye degradation.

Figure 4 showed that the highest removal rate (96%) was obtained at the H₂O₂ dosage 200 mg/L.
Therefore, it was chosen as the optimum condition for this set.

3.1.5. The effect of contact time. The variations in the decolorization percent of Cibacron Navy FN-B dye with time was tested during each experiment performed.

Figure 5 elucidates the UV-Vis absorption spectra of Cibacron Navy FN-B dye using ZnS treated with H$_2$O$_2$ photocatalyst as a function of wavelength during different UV irradiation time intervals (0, 15, 30, 45, 60, 75, and 90 min).

![Figure 5. UV-Vis absorption spectra of dye with regard to UV irradiation time using ZnS treated with H$_2$O$_2$ photocatalyst](image)

The effect of time variation on dye absorption was clearly demonstrated in Figure 5, especially within the visible wavelength (400-800 nm), where the sample taken after 90 min had the lowest absorption value.

Figure 6 depicts the decolorization rate of dye with respect to time for different concentrations of H$_2$O$_2$ treated ZnS taken the other variables as the optimum values found during this work.

![Figure 6. The effect of time on decolorization rate of dye](image)

This figure showed that the decolorization rate of dye increased gradually with time reaching its highest levels at the end of the 90 min time interval. Increasing the contact time leads to the oxidization
of greater number of dye molecules by the oxidizing radicals (•OH) in the suspension and by that increasing the decolorization rate of the solution.

3.2 Proposed degradation mechanism of Navy dye in the UV photocatalyst system

The heterogeneous photocatalysis reaction was found to follow these steps [34]: the reactant is diffused to the surface, the reactant is adsorbed onto the surface, reaction is conducted on the surface, the product is desorbed from the surface, and finally the product is diffused from the surface.

When ZnS is introduced to the solution of Cibacron Navy FN-B dye, the dye is adsorbed on the surface of ZnS. The solution is exposed to UV irradiation leading to the production of electron hole (e’ h”) pairs in the ZnS. The electrons generated in the conduction band (CB) of the catalyst (ZnS) react with the adsorbed oxygen molecules to create superoxide anion radicals (•O”). On the other hand, the holes generated on the valence band (VB) of the ZnS interacts with the surface hydroxyl group creating the extremely reactive hydroxyl radicals (•OH). Water molecules can be dissociated in the aqueous solution throughout the photogenerated holes creating radicals. The produced radicals (anion and hydroxyl) react with the Cibacron Navy FN-B adsorbed on the ZnS leading to the degradation of dye.

Enhancing the ZnS photodegradation process with Hydrogen peroxide (H2O2) leads to the extra production of radicals. H2O2 can be used as a reducing agent in alkaline solutions and as a powerful oxidizer in an acidic solution. Through the catalysis process the H2O2 is converted into highly reactive hydroxyl radicals (•OH), adding more sites responsible of dye degradation to the solution.

The degradation mechanism of Navy dye by ZnS treated with H2O2 can be suggested to be as follows (equations 3-9):

\[
\text{ZnS} + \text{UV light energy} \rightarrow e^- + h^+ \quad (3)
\]

\[
e^- + O_2 \rightarrow \cdot O_2^- \quad (4)
\]

\[
h^+ + OH^- \rightarrow \cdot OH \quad (5)
\]

\[
2H_2O_2 \rightarrow 2H_2O + O_2 \quad (6)
\]

\[
h^+ + H_2O \rightarrow \cdot OH + H \quad (7)
\]

\[
\text{Navy Dye} + \cdot OH \rightarrow \text{Oxidation Process} \quad (8)
\]

\[
\text{Navy Dye} + \cdot Q^- \rightarrow \text{Reduction Process} \quad (9)
\]

Both oxidation and reduction processes lead to degradation of dye into simple products such as H2O and CO2.

Figure 7 illustrates a schematic diagram of the proposed degradation mechanism of Navy dye under UV irradiation using ZnS catalyst treated with H2O2.
Figure 7. proposed degradation mechanism of Navy dye under UV irradiation using ZnS catalyst treated with H$_2$O$_2$

Other researchers [35] suggested that the pseudo first order kinetics rate is applied on the photocatalytic oxidation of different pollutants irradiated through ZnS (equations 10 or 11).

$$\ln(C_0/C_t)=kt$$  \hspace{1cm} (10)

or

$$C_t = C_0e^{-kt}$$  \hspace{1cm} (11)

Where $k$ represents the first order reaction rate constant ($\text{time}^{-1}$).

Figure 8 depicts a plot of $\ln(C_0/C_t)$ versus irradiation time, in which a straight line was introduced with a slope representing $k$.

Figure 8. Pseudo first order kinetics rate relation

The first order reaction rate constant was found to be equal to 0.033 (Figure 8) with a correlation coefficient of data fitting ($R^2$) equal to 97.3%. The results of Pseudo first order reaction rate were compared to results of previous studies showing similarity and were summarized in Table 3.

| Catalyst                  | Dye                     | $k$, min$^{-1}$ | $R^2$ | Reference |
|---------------------------|-------------------------|-----------------|-------|-----------|
| Pure ZnS                  | Methylene Blue          | 0.010           | 0.961 | [11]      |
| Ni-ZnS                    | Methylene Blue          | 0.013           | 0.906 | [11]      |
| ZnS treated with H$_2$O$_2$ | Cibacron Navy FN-B     | 0.033           | 0.973 | Present study |
4. Conclusions
The effect of ZnS catalyst in removing the Cibacron Navy FN-B dye through the photocatalysis process was studied. UV light irradiation was used as the illumination source and ZnS performance was enhanced by H\textsubscript{2}O\textsubscript{2}. The effect of pH, ZnS dosage, initial concentration of dye, H\textsubscript{2}O\textsubscript{2} concentration, and contact time were investigated. The optimum conditions were found to be as: pH=6.2 (the normal pH of the dye solution), ZnS=1.5gm, Co=25mg/L, and H\textsubscript{2}O\textsubscript{2}=200mg/L, the decolorization of Navy dye increased with increasing the contact time with the ZnS. The addition of H\textsubscript{2}O\textsubscript{2} enhanced the decolorization rate of dye by about 8% leading to increasing the radicals (anion and hydroxyl) responsible for the dye degradation. The final removal of dye (using the optimum conditions) was 96%. The mechanism of the Navy dye degradation in the UV photocatalysis system was proposed. Finally, the Pseudo first order reaction rate was applied and the first order constant (k) was found to be 0.033 min\textsuperscript{-1}.

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