PHOTOCATALYTIC DEGRADATION OF DIRECT VIOLET 4-AZODYE IN AQUEOUS SOLUTION USING A-FE$_2$O$_3$THIN FILMS

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Abstract

This study involves the preparation of α-Fe$_2$O$_3$ thin films coated on microscopic glass slides by thermal spray followed by thermally- induced decomposition of Prussian Blue(PB), Fe$_4$[Fe(CN)$_6$]$_3$, in air at 250°C. XRD and SEM were used to characterize the synthesized thin films for surface morphology texturing. Photocatalytic activity of α-Fe$_2$O$_3$ thin films was investigated using direct violet 4-azodye, employing heterogeneous photocatalytic process. Two different types of light have been used in this study, one using UV light and the other using visible light using a 100-watt tungsten lamp. α-Fe$_2$O$_3$ thin film does not give any significant effect upon using UV light while visible light caused more than 69.5% degradation of direct violet 4-azodye in the presence of 90.66 mg/L of H$_2$O$_2$. We studied the effect of different parameters on photocatalytic degradation process including changes in H$_2$O$_2$ concentration and pH of the medium, were studied.

Keywords: α-Fe$_2$O$_3$thin film; direct violet 4 azo dye; photodegradation.

1. Introduction

Great efforts were made to search for new oxides with smaller bandgaps to enhance visible light absorption. The band gap of Fe$_2$O$_3$ is nearly ideal 2.2 (eV) which makes it stands out with its high photochemical stability in aqueous solutions. The suitability of Fe$_2$O$_3$ as a photocatalyst was examined by studying the kinetics and mechanisms of the photocatalytic oxidation of sulfur dioxide in aqueous colloidal suspensions of 3–25(nm) Fe$_2$O$_3$ [1]. The results showed that the small hematite crystals possessed photocatalytic activity for the oxidation of sulfite [S(IV)],which readily depleted when the colloidal solutions containing 1(mM)S(IV), and 0.1(mM) of the nano- Fe$_2$O$_3$ particles were illuminated with light of 320 (nm) in the presence of air. Also, the ability of Fe$_2$O$_3$ (3–20nm) in size was examined as a photocatalyst [2]. The photocatalytic activity of hematite was compared with the activities of suspensions of ZnO and TiO$_2$.While ZnO and TiO$_2$ were found to be quite active photoxidation catalysts in the degradation of chlorinated hydrocarbons, only negligible photocatalytic activity was found for Fe$_2$O$_3$. Several tests have been carried out to compare the efficiencies of several semiconductors as photocatalysts [3].

Environmental cleanup and water splitting applications have been one of the most active areas in heterogeneous photocatalysis. An ideal photocatalyst should be

stable, inexpensive, non-toxic and of course, highly photoactive [4]. Another primary criteria for the degradation of organic compounds is that the redox potential of the $H_2O/^{\cdot}OH$ couple $(OH^{-} = {}^{\cdot}OH + e^{-}; E° = -2.8V)$ lies within the band gap of the semiconductor [5]. Several semiconductors have band gap energies sufficient for catalyzing a wide range of chemical reactions. Thus, understanding the fundamental nature of Fe_2O_3 for photochemical properties is necessary.

Much amounts of toxic colored dye effluents are produced by textile industries. These effluents induce many problems to the environment. Many chemical and physical methods such as adsorption, precipitation, air stripping, reverse osmosis, ultrafiltration and flocculation are used for removal of these contaminants in wastewaters. Heterogeneous photocatalysis is a promising technique for photodegradation of various toxic chemicals that are encountered in waste waters [6]. Heterogeneous photocatalytic oxidation is an effective method to remove low concentrations of organic contaminants [7-12].

The major advantage of this technique is that it can degrade various complex organic chemicals, which has not been affected by some other methods. The general classes of compounds that have been degraded by heterogeneous photocatalysis include; alkenes, aromatics, haloalkanes, carboxylic acids, aliphatic alcohols, alkanes, halo aromatics, surfactants, polymers, pesticides, herbicides and dyes.

In the application of waste treatment by photocatalyst it would be more suitable if the catalyst was immobilized, so the material would not have to be separated from a solution. Thin films are one of the most important materials due to technological applications [13].

In the present communication, we report the photodegradation of direct violet 4-azodye using Fe_2O_3 films immobilized on glass substrates where filtration is not required for reuse and there is no leaching of Fe_2O_3 during the degradation reaction. Other advantages of Fe_2O_3 are its low cost and non-toxicity.
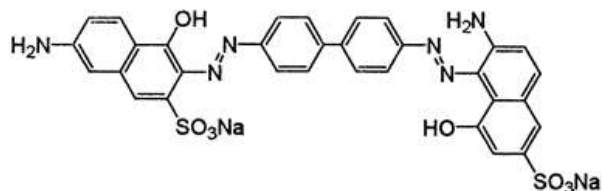
Chemical structure of direct violet 4-azodye [14]

Experimental
2.1. Chemical

All chemicals were of high-grade quality and were used as received. Potassium ferrocyanide $K_4[Fe(CN)_6].3H_2O$, ferric chloride $(FeCl_3)$, hydrochloric acid, NaOH and H_2O_2 (30%) were purchased from Merck. Direct violet 4-azodye (molecular formula $C_{32}H_{22}N_6Na_2O_8S_2$: λ_{max} = 515 nm) was purchased from Asma dye. The substrate was clear microscope glass slides.

2. 2. Catalyst preparation

2.2.1. Thermal spray technique

Thermal spraying is a group of processes in which a feedstock material is heated and propelled as individual particles or droplets onto a surface. The thermal spray gun generates the necessary heat by using combustible gases or an electric arc. As the material is heated, it changes to a plastic or molten state and then confined and accelerated by a compressed gas stream to the substrate. The particles strike the
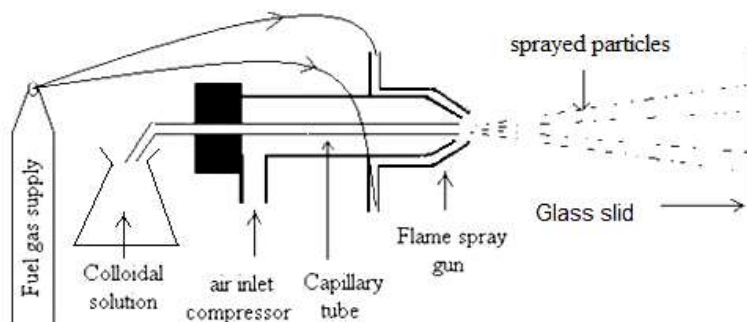

Fig. 1: Thermal spray system

substrate, flatten, and form thin platelets (splats) that conform and adhere to the irregularities of the prepared substrate and to each other. As the sprayed particles impinge upon the surface, they are cooled and build up, splat by splat into a laminar structure forming the thermal spray coating. Figure (1) illustrates a typical coating cross section of the laminar structure of oxides and inclusions used in the present study. The coating that has been formed is not homogeneous and typically contains a certain degree of porosity, and, in the case of sprayed metals, the coating will contain oxides of the metal. The properties of the applied coating are dependent on the feedstock material, the thermal spray process and application parameters, and post treatment of the applied coating [15].

2.2.2. Preparation of thin films

An aqueous solution of Potassium ferrocyanide, $K_4[Fe(CN)_6] \cdot 3H_2O$, (0.1 molar) was prepared in 100 ml water. An aqueous solution of anhydrous ferric chloride, $FeCl_3$, (0.2 molar) was prepared in 100 ml water. These two solutions were mixed slowly by using a magnetic stirrer. The mixture was left to be stirred for 30 minutes vigorously.

$$Fe^{+3} + [Fe(CN)_6]^{4-} \longrightarrow Fe[Fe(CN)_6]^-$$
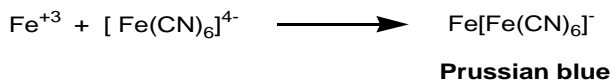
Prussian blue

The colloidal solution of Prussian blue formed was sprayed onto a glass slide by thermal spray technique. The glass slide was washed with methanol, isopropanol and consequently by deionized water then dried by the flame before spraying. The

spraying process took about 30 seconds. The formed thin film was then calcenide at 250 C° for 1 hour.

2. 3. Catalyst characterization

XRD: The X-ray diffractograms of various Fe_2O_3 samples were measured by using a Brukeraxs, D8 advance diffractometer (Billerica, USA). The patterns were run with Ni-filtered copper radiation ($\lambda = 1.54$ Å) at 30 kV and 10m A with a scanning speed of $2\theta = 2.5\circ$ min^{-1}.

SEM: A cross section of polymeric beads was captured using JEOL JSM-6360A with an operating voltage in the range of 0.5-30 kV.

2.4. Dye solution

A dye solution of 20 mg/L prepared from stock solution of 1000 mg/L .Fresh solutions of the dyes were always prepared just before use and diluted according to the requirements of the experiments. In all experiments 3 slides coated with Fe_2O_3 are used.

2. 5. Photocatalytic degradation reactor

Photo reactors were: **(1)** white light reactor: a tungsten lamp of 100 or 40 watt of an elliptical bulb was used. The tungsten lamp was in direct contact with the solution of the dye and catalyst during photodegradation. The reaction vessel was a beaker of 250 ml. **(2)** UV light reactor: a UV low pressure mercury lamp of 25 cm length was used. A 20 cm of UV lamp has been immersed in dye /catalyst solution in a cylindrical- shape reactor. The reactor was fixed on a magnetic stirrer of low or moderate speed. The two reactors are represented schematically in Figure 2.
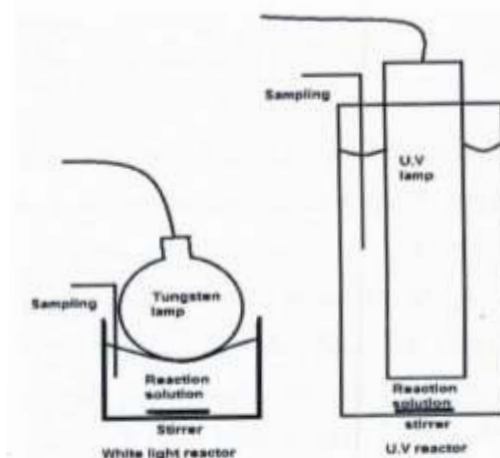

Fig. 2: White light and U.V photo reactors

2.6. U.V-Visible recording spectrophotometer

The Shimadzu 160A UV/Vis double beam recording spectrophotometer was used to record the changes in the absorbance of the dye during the reaction.

2.7. Experimental Procedure

The photodegradation cell was fed with 150 mL of the reaction mixture under stirring. Before irradiation, each sample was kept in the dark for 30 min. During irradiation, continuous stirring was maintained to keep homogeneity. Samples (ca. 3 mL) were withdrawn at specific times for analysis. The concentration of the dye in each sample was evaluated spectrophotometrically using UV-Visible absorption at the maximum absorption wavelength of the dye (Direct violet 4-azodye λ_{max} = 515 nm) and compared with the dye concentration calibration curve.

3. Results and discussion

3. 1. Characterization of Fe_2O_3 thin film

3. 1. 1. SEM

Figure 3 shows a scanning electron microscopy (SEM) image of Fe_2O_3 thin film prepared by flame spray of precursor followed by thermal induced oxidative decomposition at 250˚C. Those images explain the morphology of Fe_2O_3 thin film surface.
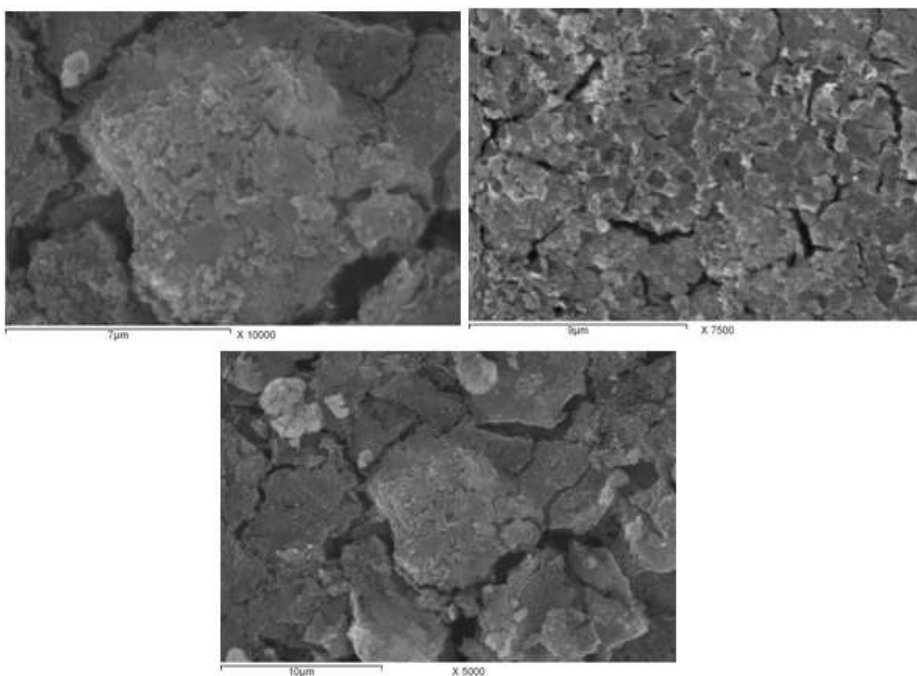

Fig. 3: SEM image of α- Fe_2O_3 thin film.

In this method, the precursor is the same one like used in Zboril et al. 2004 [16] and has been used in preparing thin film by spraying Prussian blue (PB, the precursor prepared) on glass slide by flame spray technique. Thermal induced oxidative decomposition has been done in separated step at 250 ˚C. All that steps affect directly the morphology of Fe_2O_3 thin film. The effect of flame spraying is obvious by caves and cavity what characterize this way. The particles of Fe_2O_3 are condensed and stick with each other because there is no mobility on the surface of microscopic glass slide, which make particles in bulk view what does not happen in Zboril et al. method, which give α- Fe_2O_3 in 4 nm particles size.

3. 1. 2. XRD

XRD measurements of Fe_2O_3 thin film which suggest amorphous phase without any crystalline phases. This is similar to amorphous Fe_2O_3 powders, prepared by thermal induced oxidative decomposition at 250˚C of the same precursor [16].
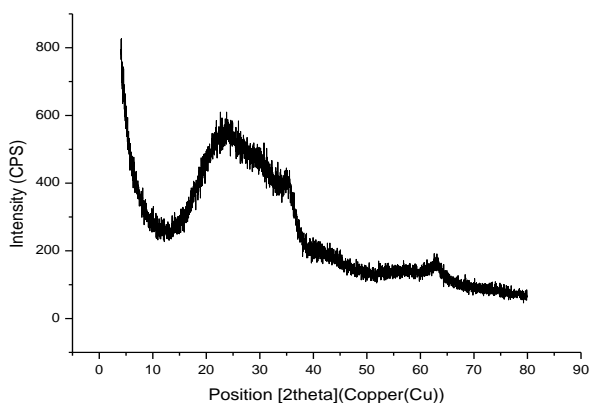

Fig. 4: XRD of α- Fe_2O_3 thin film prepared by flame spray of precursor followed by thermal- induced oxidative decomposition at 250˚C of precursor thin film on glass slide.

3.2. Photo degradation of direct violet 4-azodye by Fe_2O_3 thin film

In present study we have taken an azo dye, direct violet 4-azodye, (λ_{max} =515 nm) and examined the various parameters for the optimal removal of that dye from solution.

3. 2. 1. Photolysis of direct violet 4-azodye
3. 2. 1. A. Using UV irradiation

The dye under investigation has been subjected to UV irradiation without any additives to get an idea about its stability towards UV light. The data obtained indicate that the exposure of 150 mL, 20 mg/L dye to UV light exhibits a degradation behavior with a constancy rate as shown in Fig. 5. The data also indicate that the degradation process consumes about 70 % of the dye used within 60 min.

The addition of hydrogen peroxide as oxidant to the degradation medium strongly accelerated the rate of degradation. The data depicted in Fig. 6 indicate that the absorbance of the used dye completely disappeared within 16 min time range upon using 22.66 mg/L hydrogen peroxide.
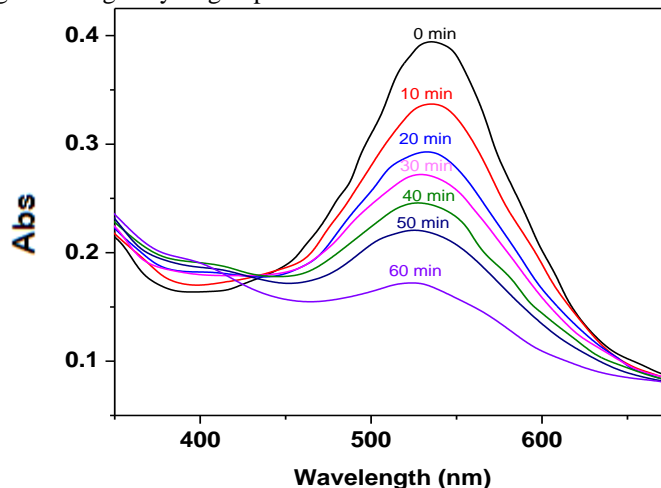

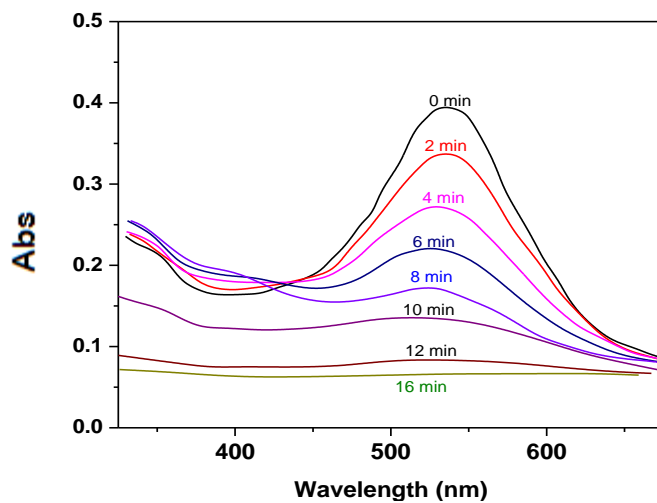**Fig. 5: The effect of UV light on direct violet 4-azodye (20 mg/L) without additives.**

Fig. 6: The effect of UV light on direct violet 4-azodye (20 mg/L) in the presence of 22.66 mg/L of H_2O_2.

Furthermore, the photodegradation process was monitored using UV light in presence of both H_2O_2 and iron oxide thin films (Figure 7).
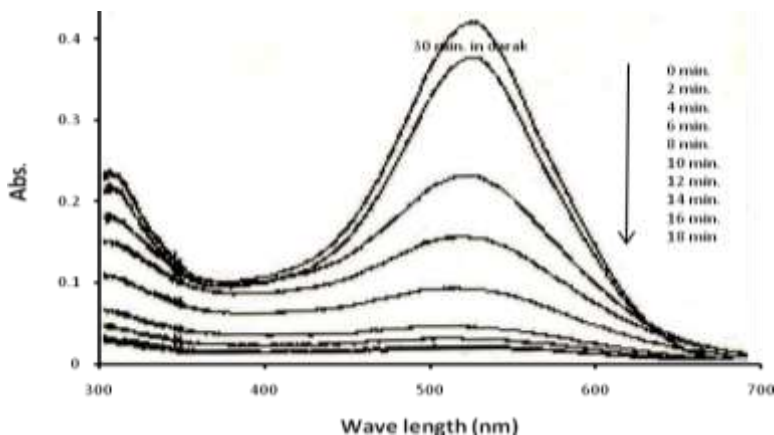
Fig.7: UV – Visible spectral changes showing the effect of UV light on direct violet 4-azodye (20 mg/L) in the presence of 22.66 mg/L of H_2O_2 and presence of 3 glass slides coated with Fe_2O_3 thin films.

Figure 8 shows the variation of dye concentration as a function of UV irradiation time under different experimental conditions. It shows that addition of Fe_2O_3 thin films does not cause enhancement of the photo-degradation process upon using UV irradiation. The dye has been degraded completely within about eighteen minutes in presence of H_2O_2 (22.66 mg/L) either in presence or absence of Fe_2O_3 thin films.
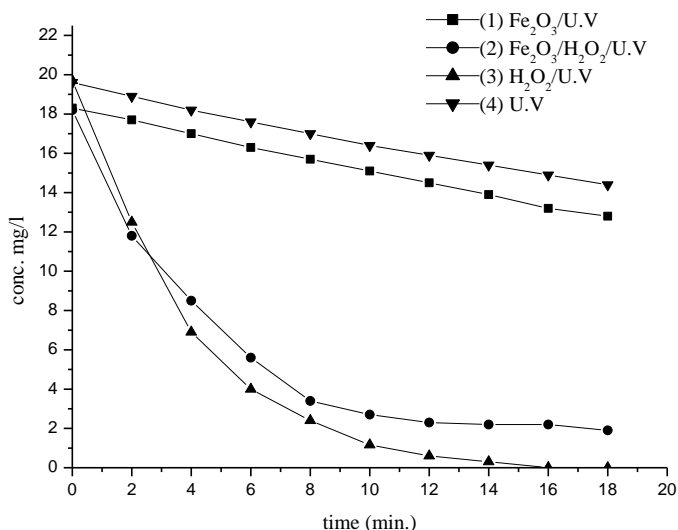

Fig. 8: The variation of direct violet 4-azodye concentration as a function of UV irradiation time under different experimental conditions.

3. 2. 1. B. Using tungsten lamp

The degradation process has been investigated using a tungsten lamp as a source of white light. The results obtained by using white light in presence of H_2O_2 are illustrated in Fig 9. The data indicate that the dye solution did not show significant degradation behavior under the used experimental conditions even in the presence of hydrogen peroxide. This behavior changed dramatically in presence of Fe_2O_3 thin films. Insertion of Fe_2O_3 thin films under the same experimental conditions caused about 31 % degradation of the dye in presence of 22.66 mg/L of H_2O_2 as shown in Figure 10.
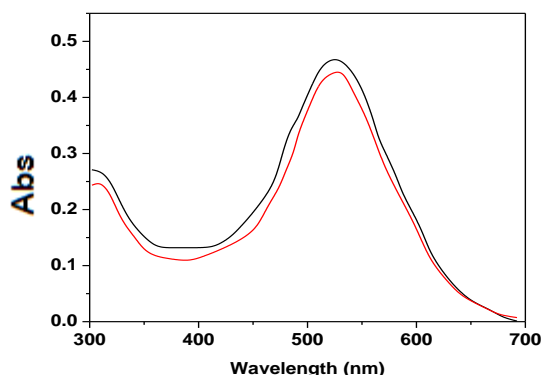

Fig. 9: Change in UV – Visible absorption spectrum of direct violet 4 dye (20 mg/L) in presence of 22.66 mg/L of H_2O_2 before (top) and after (bottom) illumination for using white light from a 100 W tungsten lamp for 60 min.
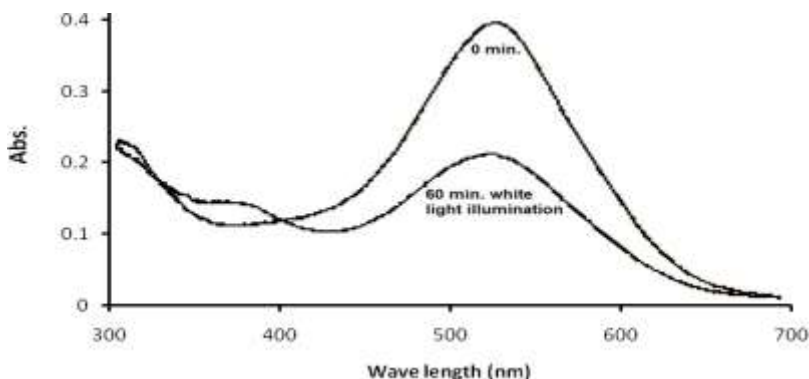

Fig. 10: Changes in UV – Visible spectra of direct violet 4-azodye (20 mg/L) in presence of 22.66 mg/L H_2O_2 at pH=7 with 3 slides of Fe_2O_3 thin films immersed in the illumination medium and using 100 W tungsten lamp as a source of white light.

3.2.2. Effect of pH

Wastewater containing dyes is discharged at different pHs, therefore, it is important to study the role of pH on decolorization process. In order to study the effect of pH on the decolorization efficiency, experiments were carried out at various pH values, ranging from 4 to 12 with a fixed dye concentration (20 mg/L) and using three slides of coated catalyst in presence of 68 mg/L of H_2O_2. It is clear in Figures 11- 14 that the degradation of direct violet 4-azodye has maximum rates at pHs 4, 7 and 12. At pH 10, the degradation process nearly stops. The interpretation of pH effects on the efficiency of the photocatalytic degradation process is a very difficult task, because of its multiple roles. First, it is related to the acid base property of the metal oxide surface. The adsorption of water molecules at surficial metal sites is followed by the dissociation of OH^- charge groups, leading to coverage with chemically equivalent metal hydroxide (M-OH) [17]. Due to amphoteric behavior of most metal hydroxides, the following two equilibrium reactions are considered:

$$M - OH + H^+ \rightleftharpoons M - OH^+OH_2 \qquad (1)$$

$$M - OH \rightleftharpoons M - O^- + H^+ \qquad (2)$$

Fe_2O_3 surface is positively charged below pH 7.8 and above this pH, its surface is negatively charged. The presence of large quantities of OH^- ions on the surface, as well as, in the reaction medium favors the formation of $^\bullet OH$ radicals, which are widely accepted as principal oxidizing species responsible for decolorization process at neutral or high pH levels, and results in enhancement of the efficiency of the process [18].

The results show that high degradation rate was also observed in acidic medium of pH 4. This may be attributed to the electrostatic interactions between the positive catalyst surface and dye anions leading to strong adsorption of the latter on the metal oxide support.

Although the adsorption of dye molecules is low at alkaline pH, the possible reason for high degradation rate may be the presence of higher proportion of hydrolyzed forms of dye and/or the higher concentration of hydroxide ions leading to the photogeneration of more reactive hydroxyl radical species [19].
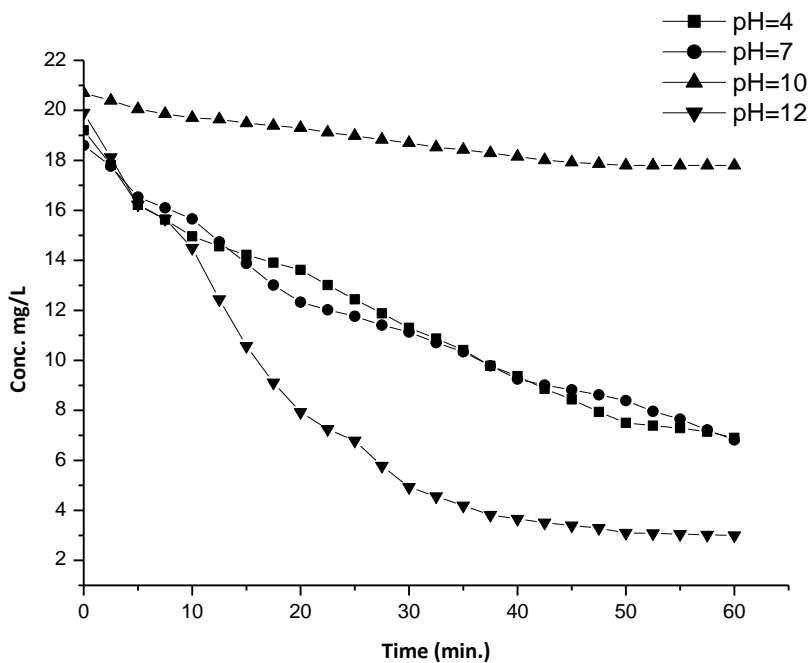
Fig.11: The pH effect on photodegradation of the direct violet 4-azodye by Fe₂O₃ thin film under the influence of white light.
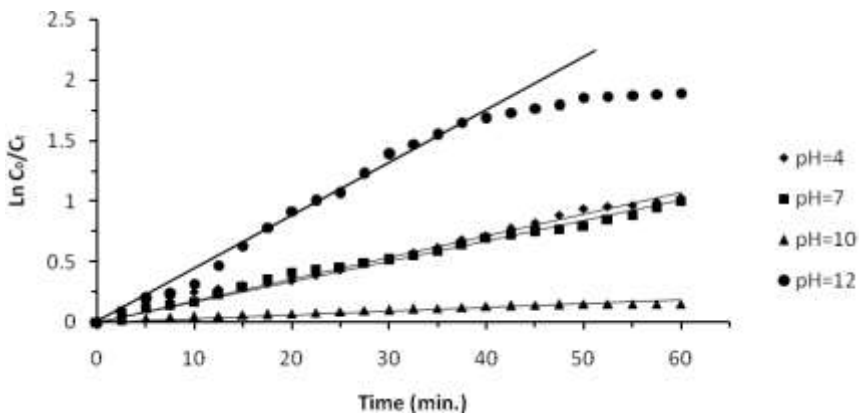

Fig.12: **First order plot for the photodegradation of the direct violet 4-azodye at different pH values.**
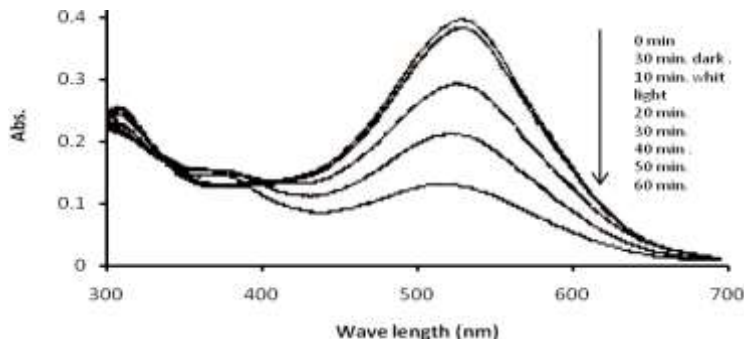
Fig.13: UV – Visible spectra of the degradation reaction of the direct violet 4-azodye (20 mg/L), (68 mg/L H_2O_2) in the presence of 3 slides of Fe_2O_3 thin film illuminated by white light at pH=4.
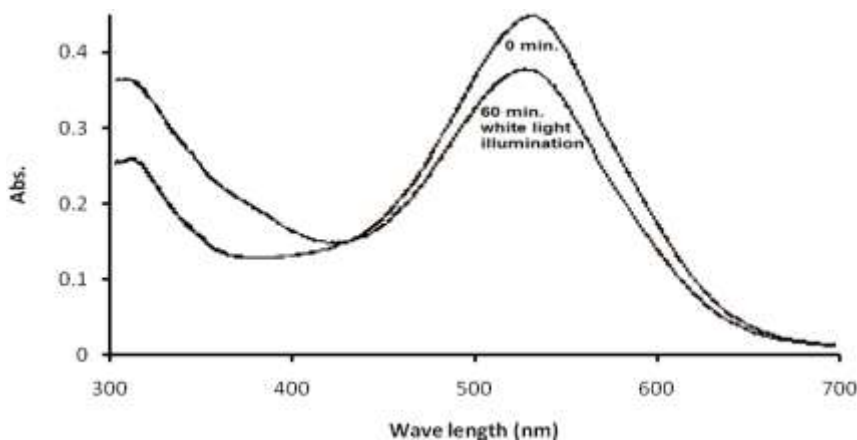

Fig.14: UV – Visible spectrum of the degradation reaction of the direct violet 4-azodye (20 mg/L), (68 mg/L H_2O_2) by3 slides of Fe_2O_3 thin film illuminated by white light at pH=10.

3. 2. 3. The effect of H_2O_2 concentration

There is no degradation in absence of H_2O_2 even in the presence of 3 slides coated with Fe_2O_3 thin film at pH=7. Degradation begins in presence of H_2O_2 and increases by increasing the concentration of H_2O_2 as shown by figures 15 to 18. To explain the enhancement in degradation of the dye upon addition of H_2O_2, we have to understand the role of H_2O_2 in photodegradation. The role of H_2O_2 is to generate the $^\bullet$OH by accepting a photogenerated electron from the conduction band and thus promotes the charge separation. Thus H_2O_2 is considered here the only source of hydroxyl radicals required for catalytic oxidation of organic matter.

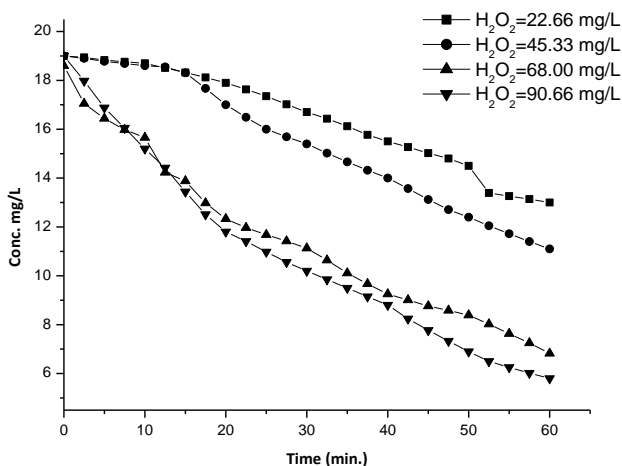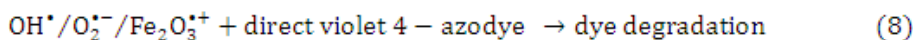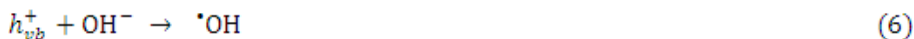The proposed mechanism of photoreaction is summarized as follows:

$$Fe_2O_3 + h\nu \rightarrow e_{cb}^- + h_{vb}^+ \tag{3}$$

$$e_{cb}^- + H_2O_2 \rightarrow {}^\bullet OH + OH^- \tag{4}$$

$$R\text{-}H + {}^\bullet OH \rightarrow R^\bullet + H_2O \tag{5}$$

$$h_{vb}^+ + OH^- \rightarrow {}^\bullet OH \tag{6}$$

$$e_{cb}^- + O_2 \rightarrow O_2^{\bullet -} \tag{7}$$

$$OH^\bullet / O_2^{\bullet -} / Fe_2O_3^{\bullet +} + direct\ violet\ 4 - azodye\ \rightarrow dye\ degradation \tag{8}$$

Fig.15: The effect of H$_2$O$_2$ concentration on the photodegradation of direct violet 4-azodye by Fe$_2$O$_3$ thin film under the influence of white light.
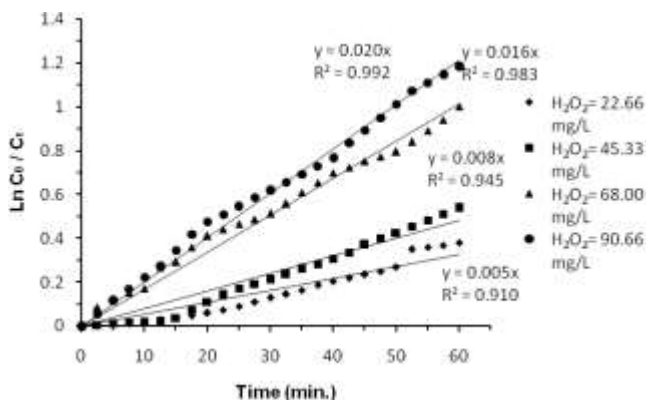

Fig.16: First order plot for the photodegradation of the direct violet 4-azodye at different H$_2$O$_2$ concentration.
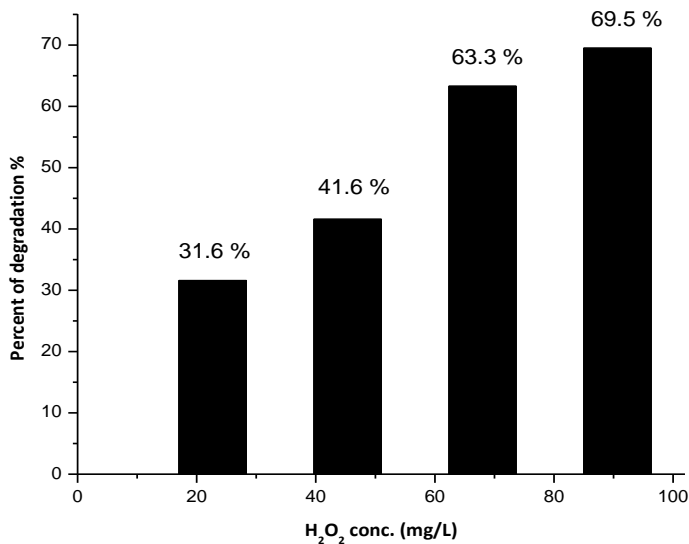
Fig.17: The percentage dye degradation as a function of increasing the concentration of H_2O_2 recorded after one hour of irradiation using white light in presence of Fe_2O_3 thin films.
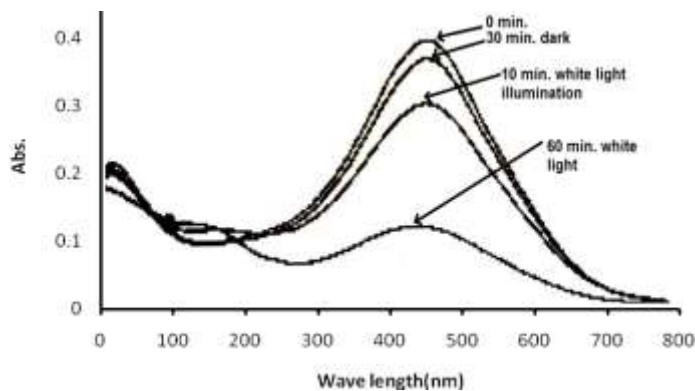

Fig.18: U.V – Visible spectrum of the degradation of the direct violet 4-azodye (20 mg/L), (68 mg/L H_2O_2) in presence of 3 slides of Fe_2O_3 thin film illuminated by white light at pH=7.

4. Conclusions

An immobilized photocatalyst has been made by inexpensive chemicals and by simple and fast method supported on cheap material (glass slide). Fe_2O_3 thin film has no marked activity as a photocatalyst when using UV irradiation in absence or presence of H_2O_2 as oxygen carrier material. H_2O_2 is necessary for the photodegradation of direct violet 4-azodye by using Fe_2O_3 thin film as a

photocatalyst in case of using white light irradiation from tungsten lamp 100 watt as a light source. Degradation increases by increasing H_2O_2 concentration. The pH has important role in photodegradation processes. The Maximum degradation has been observed at pH 12, less degradation at pH 10 and moderate degradation at pH 4, 7.

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