PHOTOCATALYTIC DEGRADATION OF NITROBENZENE USING TITANIUM DIOXIDE DOPED WITH COPPER PHTHALOCYNINE

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ABSTRACT

The effect of doping titanium dioxide with copper phthalocyanine (CuPc /TiO$_2$) in presence of H$_2$O$_2$ was investigated in the degradation of nitrobenzene (NB) in batch system using a mercury lamp (λ>250 nm). The doped catalysts were prepared with different complex loadings of 1.0, 1.4, 1.8 and 2.2 wt.% .The catalyst sample with loading of 1.4 wt.% was the most active one. Complete degradation of NB was achieved after 135 min using 40 mg / L from the optimum catalyst sample and 7500 mg / L of H$_2$O$_2$. The catalyst samples were characterized by XRD and FTIR spectroscopy. From the kinetic study of the photocatalytic degradation of NB, it was concluded that the rate of reaction increased by increasing catalyst weight. In addition, the effect of the initial concentration of NB was examined. The effect of doping CuPc / TiO$_2$ on the efficiency of TiO$_2$ was discussed. Oxidation and reduction pathways were investigated.

KEY WARDS:

Photocatalytic degradation, Nitrobenzene, Copper phthalocynine, Titanium dioxide, HPLC and UV-spectroscopy.

NOMENCLATURE:

CuPc (Copperphthalocynine), H$_2$O$_2$ (Hydrogen peroxide), NB (Nitrobenzene), TiO$_2$ (Titanium dioxide), nm (Nanometer), hv (Photo radiation), λ (The wave length of light).

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1. INTRODUCTION

Nitrobenzene (NB), a carcinogenic pollutant, is widely used in the production of different types of products, such as dyes [1, 2], explosives and pesticides [3]. Even at low concentrations, NB may present high risks to environment [4]. The electron deficient character of nitro-group prevents mineralization of nitrobenzene by microorganisms [5]. Therefore, conventional biological treatment processes are not effective for the treatment of NB-rich wastewaters [6]. During the last two decades various advances oxidation processes, such as ozonation and O_3 /UV processes [7], photocatalysis [8], photoassisted Fenton oxidation [9], supercritical oxidation [10] and other methods [11] have been applied for the degradation of NB-rich wastewaters. Recently, other catalytic systems have been studied using zero-valent iron [12-14], or nickel catalysts [15]. However, these methods are either expensive or ineffective for the treatment of NB-containing wastewaters. TiO_2, owing to its excellent photocatalytic activity, has been widely studied as an effective photocatalyst for environment purification. Numerous studies have been focused on its unique performance in photocatalytic degradation of toxic organics [16-19]. In aqueous solutions, a preponderance of evidence, as summarized by Turchi and Ollis [20], indicate that oxidative degradation of aromatic compounds occurs primarily via either bound or free hydroxyl radicals formed through the oxidation of adsorbed H_2O, hydroxide or surface titanol groups by photogenerated holes trapped at the semiconductor surface [21].

$$TiO_2 + h\nu \longrightarrow e^-_{cb} + h^+_{vb} \tag{1}$$

Direct oxidation by trapped holes has also been reported [22]. The predominant initial reductive step in aerated systems is a transfer of the photoexcited electron to adsorbed molecular oxygen to create a superoxide radical anion that may then form other activated oxygen species such as $HO_2\cdot$ and H_2O_2 [23-25].

Soluble and insoluble metal phthalocynine are known for their catalytic activities in many reactions, such as degradation [26 and 27], polymerization [28] and other reactions. They are also known as photosinsitizer [29].

The destruction of hazardous pollutants by the so- called Advanced Oxidation Processes (AOPs), where strong oxidizing agents (e.g. H_2O_2) are combined with the UV light (wavelength of light λ <320 nm) to generate the highly reactive species, hydroxyl radicals (e.q.2), have been thoroughly studied [30].

$$H_2O_2 \xrightarrow{h\nu} 2\,^{\cdot}OH \tag{2}$$
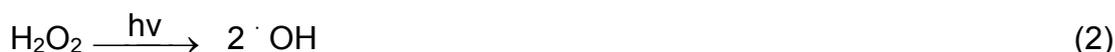
In this work, the effect of the initial concentration of NB and TiO_2, CuPc, and different loadings of CuPc / TiO_2 were investigated as photocatalysts for nitrobenzene degradation in presence of H_2O_2.

2. EXPERIMENTAL METHODS

2.1. Preparation of Catalyst

Copper phthalocynine doped TiO_2 was prepared using modified impregnation technique [28], with loading % of 1.0, 1.4, 1.8 and 2.2 % w / w. This process was affected by refluxing CuPc (0.1, 0.14, 0.18 and 0.22 g) in excess of n-butylamine (200 ml) for 1 h., after which TiO_2 (10 g) was added. This mixture was refluxed for additional 2 h. after which n- butylamine was distilled off, the catalyst was dryied for 9 h. at $190^{o}C$ in flow of nitrogen.

2.2. Photo Reactor

Photocatalytic degradation reaction was conducted in a batch reactor as in fig.1. This reactor consists of a cylinder glass reactor vessel with an effective volume of 200 ml, cooling water jacket. A mercury lamp of λ >250 nm(15 W with intensity of 1.26 mW cm^{-2}) positioned axially at the center of the reactor in quartz tube which fitted with inlet and outlet to pass a stream of N_2 gas for cooling the quartz tube. The reaction temperature was kept at $25^{o}C$ by cooling water. Reaction mixture was inserted into the reactor and reaction samples were expelled from the reaction mixture through two special glass fit using a syringe.

2.3. Materials and Method

2.3.1. Chemicals

The chemicals TiO_2 (anatase phase), CuPc, and NB were purchased from Aldrich (with above 99% purity). Hydrogen peroxide was from Adwic Co. with 30 % w/v concentration. The transformation products such as azobenzene, resorcinol, phenol, m-nitrophenol and aniline were purchased from Aldrish Co.

2.3.2. Experimental Method

The operation started by stirring the catalyst, H_2O_2 and nitrobenzene in 100 ml deionized water for 15 min in absence of radiation to ensure the establishment of adsorption equilibrium, after which the Hg lamp was connected. The reactor temperature was kept at 25 ± $1^{o}C$ with circulation of water through the outer double jacket and passing N_2 gas inside the quartz tube containing the lamp. The samples of 10 ml were taken into UV and HPLC analysis after centrifugation and filtration through 0.45 μm, in brown vials covered with aluminum foil for protection against light interference [31].

Photocatalytic degradation of nitrobenzene (72.2 mg / L) was studied using 40 mg / L of TiO_2, CuPc, and doped samples of CuPc /TiO_2 with loading % of 1.0, 1.4, 1.8, and 2.2 %w/w. The optimum loading % 1.4 was studied with different concentrations, 20,

40, and 60 mg / L. The initial concentration of NB was studied using 36.1, 72.2and 120.3 mg / L in the presence of 40 mg /L from the optimum load, 1.4% and 7500 mg / L of H_2O_2.

2.4. Analysis

The nitrobenzene concentrations were detected by using UV-3101 PC UV-VIS-NIR spectrophotometer (Shimadzu). The intermediate compounds were identified using high performance liquid chromatography (HPLC) equipped with a C- 18 column (5µm particle diameter, Merck) and UV –Vis detector. Water : acetonitrile : methanol (1 :1 :1, by volume) was used as the mobile phase with a flow rate of 1 ml min $^{-1}$ and λ = 270 nm.

The crystalline phase of TiO_2, CuPc, and doped samples of CuPc /TiO_2 with loading % of 1.0, 1.4, 1.8, and 2.2 w/w were examined by X-ray powder diffraction (XRD) using a Philips X- ray diffractometer (PW3020) with Cu Kα radiation (λ=0.154060nm). The accelerating voltage of 40kV and an emission current of 30 mA were used. FTIR spectroscopy has been studied for pure CuPc, TiO_2 and doped CuPc/TiO_2 samples using ATI Mattson spectrophotometer.

3. RESULTS AND DISCUSSION

3.1. XRD- Analysis

The TiO_2, CuPc, and doped samples of CuPc /TiO_2 with loading % of 1.0, 1.4, 1.8, and 2.2 %w/w were examined by XRD. Fig.2. shows the XRD photograph of CuPc, TiO_2, 1.4 and 2.2 % w/w sample. The XRD pattern of TiO_2 samples showed the presence of three main peaks at 2θ = 25.4, 37.89 and 48.1^o, respectively, regarded as an attributive indication of anatase TiO_2. A diffraction peak corresponding to rutile TiO_2 also appear on the pattern of the optimum sample 1.4% w/w at 2θ =27.35^o with intensity of 1%. The characteristic peaks of CuPc disappeared on the pattern of all the doped samples. It is concluded that CuPc penetrates the matrix of TiO_2 which have no effect on TiO_2 phase in all samples except the optimum sample in which a small amount of TiO_2 changed from anatase to rutile phase. This interaction increased the photocatalytic activity of TiO_2 and/ or CuPc in NB degradation reaction [32].

3.2. FTIR Analysis

The absorption FTIR spectrum for pure CuPc, TiO_2 and doped CuPc/TiO_2 samples indicated that TiO_2 have absorption bands at 508.6, 670, 1046.6 and 1113.8 cm^{-1}. The characteristic bands of CuPc (741, and 1117 cm^{-1}) show a masking effect by TiO_2 due to the high dilution effect of the complex moieties over the support. It was noticed that some deviation occurs for the absorption bands 1046.6 and 1113.6 cm^{-1}due to the effect of increasing CuPc concentration in all the doped samples. A

characteristic band of CuPc appears at 1117.2 cm^{-1} in the chromatogram of 1.4% sample. These observations are in agreement with XRD analysis. It is concluded that there is some interaction between CuPc and TiO$_2$, which may improve the photocatalytic activity of the doped sample.

3.3. Photocatalytic Degradation of NB Using CuPc /H$_2$O$_2$ /UV

Photocatalytic degradation of NB (72.2 mg / L) using 40 mg / L CuPc in presence of 7500 mg / L H$_2$O$_2$ leads to degradation percentage of 32.6% after 60 min. This result may be due to the oxidative degradation of NB initiation by hydroxyl radicals produced by uv- photolysis of H$_2$O$_2$ [30], eq. 2 and or by hydroxyl radicals produced due to the fact that Cu reacts with H$_2$O$_2$ as both Cu^{II} and Cu^{I} [31 (a, b)] and esq. 3-5.

$$Cu^{II} + H_2O_2 \longrightarrow Cu^{I\cdot}OOH + H^+ \tag{3}$$

$$Cu^{I\cdot}OOH + H_2O_2 + H^+ \xrightarrow{+H^+} Cu^{I} + O_2 + 2\ ^\cdot OH + H_2 \tag{4}$$

$$Cu^{I} + H_2O_2 \longrightarrow Cu^{II} + \ ^\cdot OH + \ ^-OH \tag{5}$$
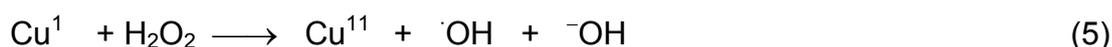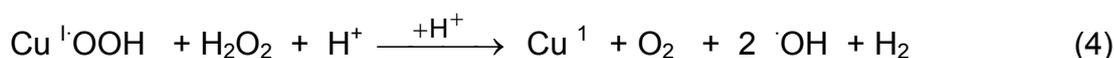
Otherwise, copper phthalocynine is an efficient photosinsitizer in photocatalytic reactions. As a result, photocatalytic degradation of NB by CuPc may be due to type 1 mechanism in which the longer lived triplet state of ^{3}CuPc$_1$ directly oxidizes NB (eqs. 6 and 7) or due to type 11 mechanism, in which CuPc transfers energy to H$_2$O$_2$ or molecular oxygen (the reaction medium is not deariated) which thus becomes exited [32].

$$^1(CuPc)_0 \xrightarrow{h\nu} \ ^1(CuPc)_1 \longrightarrow \ ^3(CuPc)_1 \tag{6}$$

$$^3(CuPc)_1 + NB \longrightarrow \ ^1(CuPc)_0 + \ ^1NB \tag{7}$$

3.4. Photocatalytic Degradation of NB Using TiO$_2$ /H$_2$O$_2$/UV

The energy from light (λ < 497nm) is large enough to promote valence band electrons to the conduction band of the semiconductor and the creation of positive holes in the valence band in TiO$_2$ particle, Fig.3 and eq.1. The electrons and holes thus separated migrate to the surface of the particles where they can either recombine or participate in interfacial oxidation and reduction reactions [33]. Water also acts as a donor and acceptor of electrons, thus on hydrated and hydroxylated TiO$_2$ surface, the holes trap $^\cdot$OH radicals linked to the surface, eq. (8).

$$(TiO^{IV}\text{-}O^{2-}Ti^{IV})\text{---}OH_2 + h^+_{BV} \longrightarrow (TiO^{IV}\text{–}O^{2-}\ ^-Ti^{IV})\text{----}OH + H^+ \tag{8}$$

The presence of hydrogen peroxide (an electron acceptor) avoid the recombination of electron / hole pair through its reaction with the conduction band electrons eq. (9).

$$H_2O_2 + e^- \longrightarrow OH + OH^- \qquad\qquad (9)$$

Photocatalytic degradation reaction of NB (72.2 mg / L) using TiO_2 (40 mg / L) and H_2O_2 (7500 mg / L) is shown from the catalytic curve Fig.4 and kinetic curve Fig.5. It is concluded that the degradation of NB divided into three stages. Firstly, fast initial reaction rate in the first 25 min due to the competitive effect between the adsorption of NB molecules on TiO_2 surface and its oxidative degradation due to the catalytic efficiency of $^-$OH free radicals. In this step, the reaction followed first order kinetic equation ($k = 0.0133$ min $^{-1}$). In the second step, the rate of reaction decreased to $k = 0.0093$ min $^{-1}$ due to the competitive effect between the desorption and degradation of NB.This step is pseudo-first order. The third step, the concentration of free radicals increased and as a result, the rate of reaction increased to $k = 0.42$ min^{-1}.

3.5. Photocatalytic Degradation of NB Using Different Loading Percentage of Cupc/TiO$_2$/H$_2$O$_2$/UV

The addition of a photosinsitizer to a semiconductor could modify the photocatalytic properties by changing the semiconductor surface properties and increasing the efficiency of the excitation process [34]. Vohra et al.[35] reported that Pt has been considered to promote the transfer of conduction band electrons to oxygen species, which should suppress the electron / hole recombination. Thanaka et al.[36] reported that by controlling the TiO_2 surface charge the photocatalytic activity for the degradation of cationic compounds could be increased. Sadek et al. [28] reported that supported CuPc on bentonite in presence of $^-$HNO$_3$ has a controlling effect in methyl methacrylate polymerization through living free radical mechanism. So we can suggest that CuPc (Cu^{11}) contacted with TiO_2 surface, can capture electrons of the conduction band and reduces to Cu^1.Since, after excitation, the electron migrates to CuPc where it becomes trapped and e -/h + recombination is avoided. The hole is then free to migrate to the surface where oxidation of NB can occur. Also the valence band have the ability to produce $^-$OH free radicals, Fig.3. Then CuPc (Cu^1) can transfere electrons to H_2O_2 adsorbed on TiO_2 surface to produce $\cdot$OH free radicals and oxidize NB, Fig.6.

Fig.7, shows the photocatalytic degradation percentage of NB (72.2 mg / L) using 40 mg / L of doped CuPc/TiO_2 with different loading percentage (1.0, 1.4, 1.8 and 2.2% w/w) and H_2O_2 (7500 mg / L) after 1h. It is concluded that 1.4 % is the optimum loading % which achieve the maximum photocatalytic rate, affecting the distribution of electrons in the system [35]. Above the 1.4 %, the efficiency decreases because once negatively charged, Cu^1 formed become attractive for holes, which recombine with electrons into inefficient energy [34] According to all these studies and our results, we concluded that CuPc have a controlling effect and undergo a redox reaction between electrons of the conduction band and H_2O_2 producing $\cdot$OH free

radicals, on the other hand prevent recombination of e-/h+, and as a result free holes migrates to the surface of TiO_2 undergoing NB oxidation reactions [34].

3.6. Photocatalytic Degradation of NB Using Different Concentrations of the Optimum Loading % of Cupc / TiO_2 and H_2O_2.

Photocatalytic degradation of NB (72.2 mg / L), using 20, 40 and 60 mg / L from the optimum doped sample (1.4 % w/w) and 7500 mg / L H_2O_2, are shown in Figs. (8, 9). The photocatalytic degradation % of NB increases with concentration of catalyst. The kinetic study in Fig.9, indicates that 20 mg follows first order kinetic whereas 40 and 60 mg are pseudo-first order .The rate of reaction increases from $0.0047min^{-1}$ to 0.0227 and $0.1044min^{-1}$by increasing the catalyst weight respectively, i.e. the rate of reaction increases about 4.7 times by increasing the catalyst weight 20 mg each time. The comparison between the kinetic curves of NB degradation using 40 mg from TiO_2 without CuPc and from the optimum sample (1.4%) indicates that doping of TiO_2 with CuPc increases the efficiency of the catalyst. So, the reaction rate increases about two times due to the effect of CuPc. All previous studies reported that the rate of the degradation process increases with catalyst concentration as shown in our present results.

3.7. Photocatalytic Degradation Using Different Initial Concentrations of NB.

Different initial concentrations of NB (36.1, 72.2 and 120.3 mg / L) have been studied. Figs. (10 and 11) show the degradation % and the kinetic curves of photocatalytic degradation of NB using 40 m gm from the optimum doped sample (1.4%) and 7500 mg /l H_2O_2. It is found that the degradation of NB can be divided into two stages. There was a rapid initial reaction rate (k=0.0308 min $^{-1}$) using 36.1 mg of NB as an initial concentration which decreases to 0.0193 and 0.0118 min $^{-1}$ corresponding to 72.2 and 120.3 mg NB respectively as shown from table 2. In the second stage the rate of reaction is in direct proportion to the initial concentration of NB. These results are in agreement with other studies [19]. It is concluded that, as the initial concentration of NB decreased, its adsorption on TiO_2 surface is increased but in the second stage as the concentration of NB increased, its desorption increased. At high concentration of NB, it's contacted with ˙OH free radicals which adsorped on catalyst surface and also which present free in water and as a result the rate of reaction increase with increasing the initial concentration of NB.

3.8. Mechanism of NB Photocatalytic Degradation

The mechanism of the photocatalytic degradation of NB using 1.4 % CuPc/ TiO_2 (40 mg / L), 72.2 mg / L of NB and 7500 mg / L of $H_2O_2$was investigated using HPLC by identifying the intermediate compounds. The HPLC chromatographic analysis indicated that the concentration of nitrobenzene decreased with time whereas the concentration of intermediates increased. By using authentic samples it is found that m- nitrotoluene, resorcinol and phenol were reported with high concentration relative to aniline and azobenzene as intermediates.

The nitrogroup is an electron-withdrawing group so, it is strongly deactivate the ortho and para positions and favoring the electrophilic substitution of the ˙OH radicals at meta positions, so it is a meta directing group producing m-nitrophenol. The nitrogroup is a good leaving group and as a result, it can be easily eliminated. So, it can be suggest that m- nitrophenol undergo a further oxidation giving resorcinol [33](scheme.1).
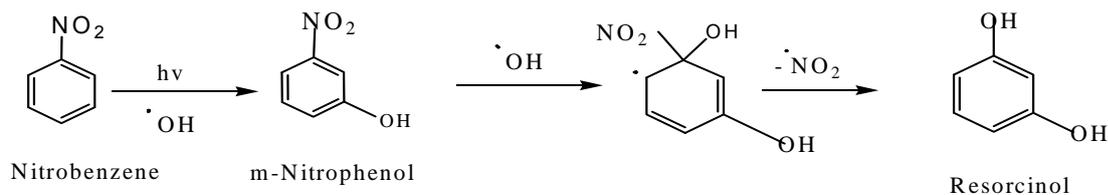
Scheme .1

Phenol can be produced due to the direct attack of ˙OH free radicals at the same position which carrying NO_2 group or by heterolytic cleavage of ˙NO_2 group followed by oxidation as reported by Paolo et al. (2003) (scheme. 2).
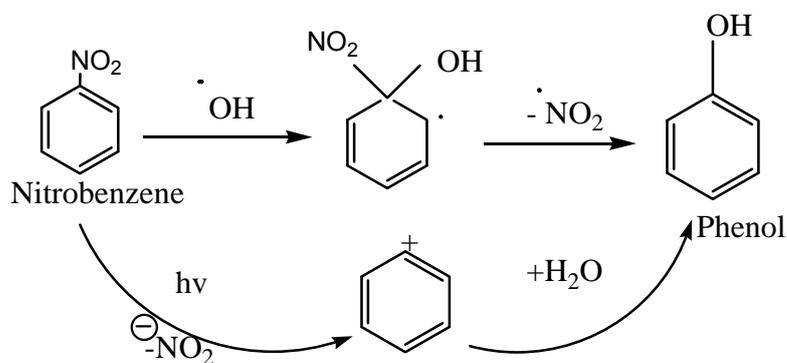
Scheme. 2

The formation of aniline implies that reduction pathway are also significant under the experimental conditions used in this study due to the presence of $^{.}$H (scheme.3).

Nitrobenzene   Nitrosobenzene   Hydroxyaminobenzene   Aniline
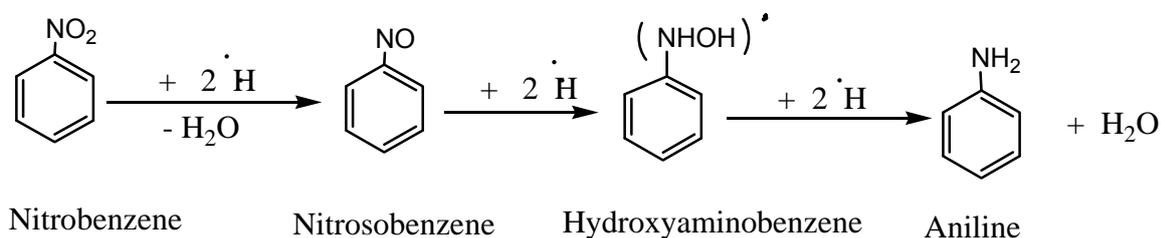
Scheme.3

The combination of two species from the pathway of aniline formation produces azobenzene (scheme.4).

Hydroxyaminobenzene   Azobenzene
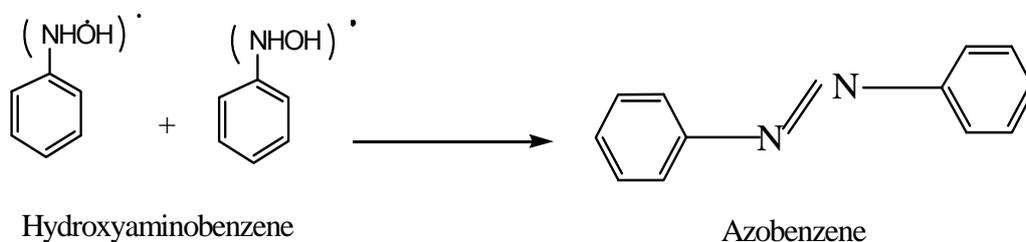
Scheme.4

4. CONCLUSION

The photocatalytic degradation of nitrobenzene in aqueous suspension containing doped $CuPc/TiO_2$ and H_2O_2 leads to complete degradation of nitrobenzene. The concentration of nitrobenzene was monitored using UV- spectrophotometer. The intermediate compounds were identified using HPLC. Doping of CuPc with TiO_2 plays important roles. The first rule is avoiding the recombination of e^-/h^+ because CuPc penetrates TiO_2 and trapped electrons of the induction band and reduced from Cu^{11} to C^1. The second rule is that Cu^{11} or Cu^1 may reacts with O_2 and / or H_2O_2 to produce free radicals. It is concluded that there is a synergism effect between CuPc as a photosinsitizer and TiO_2. The formation of m- nitrotoluene, phenol and resorcinol confirms that the hydroxyl radical oxidation is the major pathway in the present reaction. The formation of aniline and azobenzene implies that reductive pathway is also significant under the experimental conditions used in this work. The characterization of the doped catalyst samples indicated that CuPc penetrates the matrix of TiO_2 without changing its phase.

5- Figures

Quartze tube

Outlet of water

Double jacket reactor

Magnetic

Outlet of N$_2$ from cooling

Inlet of N$_2$ for cooling the

Glass

UV-Lamp

Inlet of water
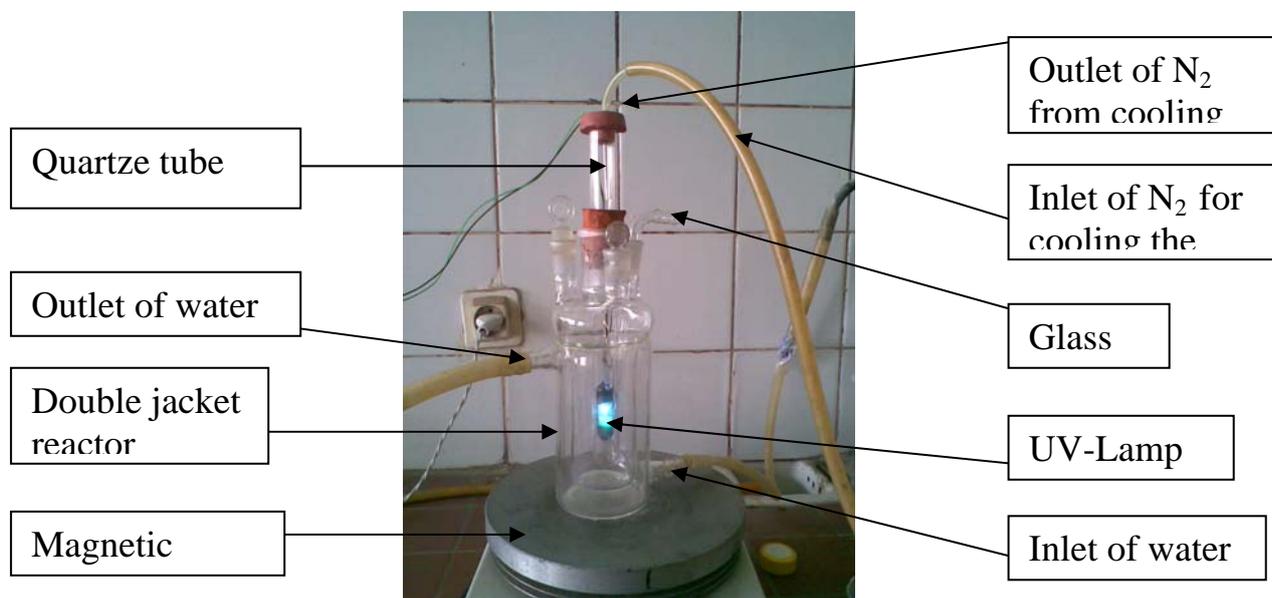
Fig. 1. The Photoreactor

Fig. 2. The XRD Photograph of the Photocatalysts.

$$H_2O_2 \qquad ^-OH + \cdot OH$$

$$h\gamma > or = 3.0\ e\ V$$

e^-

h^+

$TiO_2\ particle$

$$H_2O \qquad \cdot OH + H^+$$
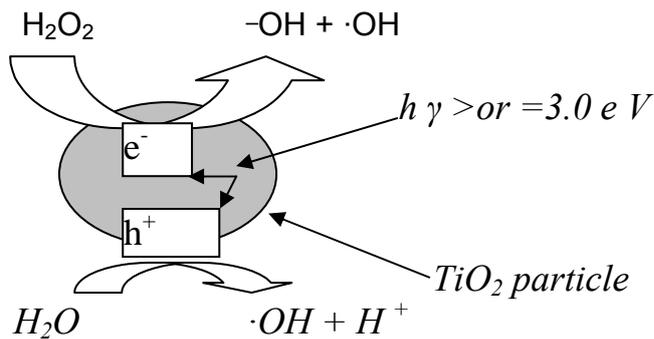
Fig. 3. Effect of UV radiation on TiO_2 particles dispersed in water in presence of H_2O_2
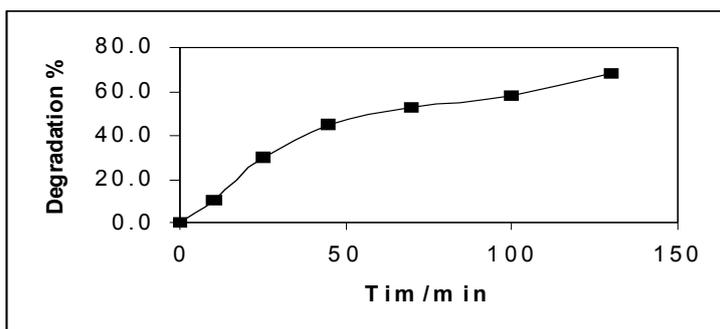
Fig. 4. Photocatalytic degradation of NB (72.2 mg / L) using 40 mg / L TiO_2 / 7500 mg / L H_2O_2
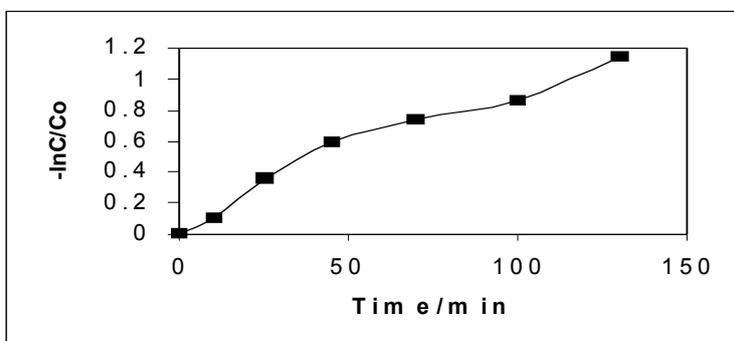
Fig. 5. Kinetic study of photocatalytic degradation of (72.2 mg / L) using 40 mg / L TiO_2 / 7500 mg / L H_2O_2

$CuPc$

e^-

h^+

hv
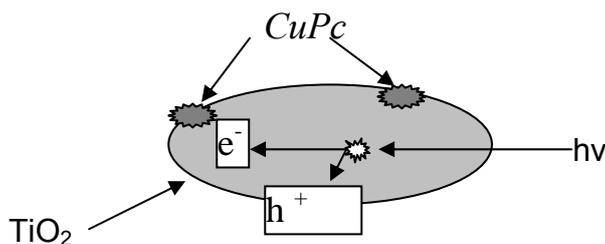
TiO_2

Fig.6. An illustration of the capacity of CuPc in contact with TiO_2 surface to capture electrons.
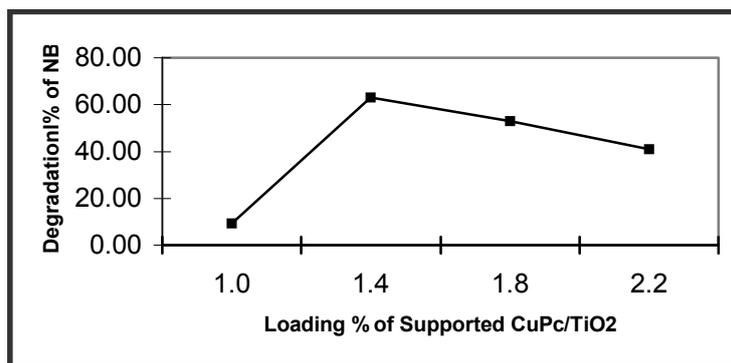
Fig.7 photocatalytic degradation of NB (72.2 mg / L) using 40 mg / L of different loading% of CuPc/TiO$_2$ and 7500 mg / L H$_2$O$_2$ after 1 h.
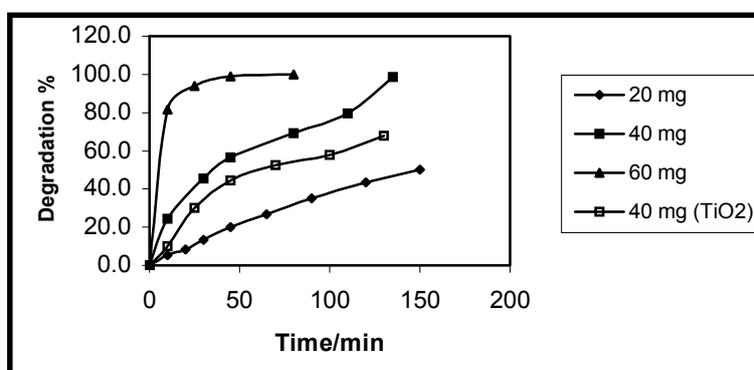
Fig.8. Photocatalytic degradation of NB (72.2 mg / L) using TiO$_2$ (40 mg / L), and different weights of the optimum doped CuPc/TiO$_2$ with loading % = 1.4 (20, 40, 60 mg / L) and 7500 mg / L H$_2$O$_2$.
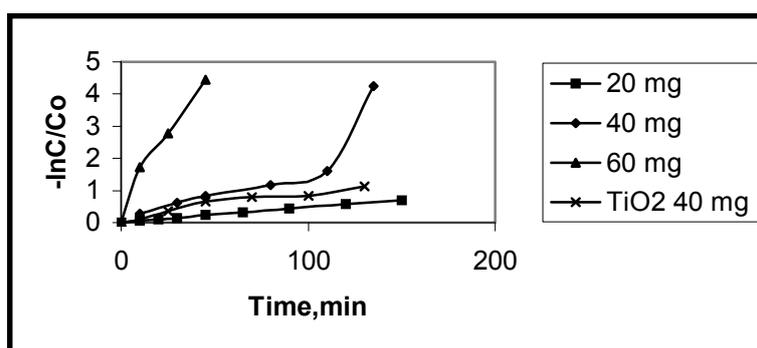
Fig.9. Kinetic study of photocatalytic degradation of NB (72.2 mg / L) using TiO$_2$ (40 mg / L), and different weights (20, 40, 60 mg / L) of the optimum doped catalyst sample (1.4% w/w) and 7500 mg / L H$_2$O$_2$.

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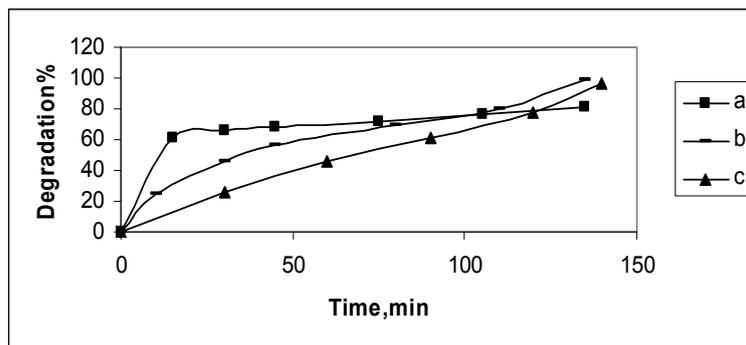
Fig. 10. Photocatalytic degradation of NB with different initial concentrations (■ (a) 36.1, — (b) 72.2 and ▲(c) 120.3 mg / L using (40 mg / L) from the optimum catalyst sample (1.4%w/w) and 7500 mg /L H_2O_2.
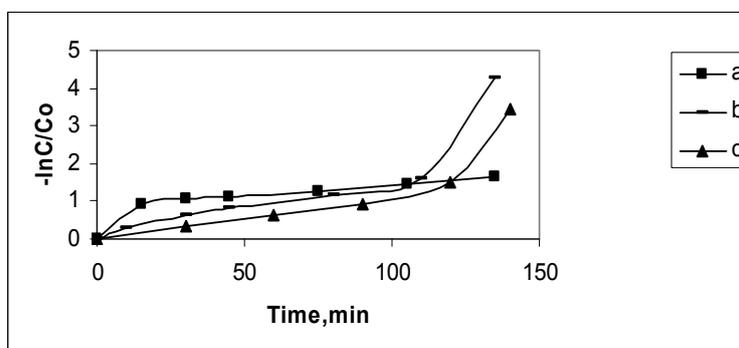
Fig .11. Kinetic curves of photocatalytic degradation of NB using different initial concentrations
(■ (a) 36.1, — (b) 72.2 and ▲(c) 120.3 mg / L using (40 mg / L) from the optimum catalyst sample (1.4 % w/w) and 7500 mg / L H_2O_2.

6. TABLES

Table.1. Photocatalytic degradation of NB (72.2 mg / L) using different weights from the optimum catalyst and 7500 mg / L H_2O_2 .

Catalyst weight (mg / L)	Rate of reaction (K) (min $^{-1}$)
40 mg TiO_2	0.0093
Doped CuPc /TiO_2 (1.4%)	
20 mg	0.0047
40 mg	0.0227
60 mg	0.1044

Table.2. Rate of photocatalytic degradation of NB using different initial concentrations of NB (36.1, 72.2 and 120.3 mg / L) using 40 mg / L of the optimum loading % (1.4) and 7500 mg / L H_2O_2.

Initial volume of NB (mg / L)	36.1	72.2	120.3
Initial reaction rate (k) min^{-1}	0.0308	0.0193	0.0118
Average reaction rate (K) min^{-1}	0.6305	0.975	0.9826

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