

Degradation of Nitroaromatic Pollutant by Titanium dioxide/Zinc Phthalocyanine: Study of the Influencing Factors

Houda Ben Yahia Smida¹, Bassem Jamoussi²

¹Laboratoire de Physicochimie des Matériaux, IPEST, BP51, La Marsa 2070, Tunisia

²Laboratoire de Chimie Analytique & Environnement .Institut Supérieur de l'Education et de Formation Continue, Tunis, Université Virtuelle de Tunis

Abstract: This study suggests that Effective photocatalyst ZnPc/TiO₂ based in the association between a semiconductor titanium dioxide TiO₂ and zinc phthalocyanine (ZnPc) can be applied successfully for the photocatalytic degradation of 4-Nitrophenol that has been classified as first-degree toxic pollutants. ZnPc/TiO₂ composite was prepared. Complete degradation was achieved after irradiation with solar light. Zinc phthalocyanine and ZnPc/TiO₂ photocatalyst were synthesized. The effect of various parameters, such as photocatalyst loading, 4-Nitrophenol concentration, type of catalyst, pH of aqueous solution, type current gas and addition of H₂O₂ on photocatalytic oxidation were investigated. The degree of mineralization was tested by Total Organic Carbon experiment indicating that 4-Nitrophenol was completely mineralized. This composite ZnPc/TiO₂ is able to perform efficiently degradation of 4-nitrophenol using solar irradiation.

Keywords: 4-Nitrophenol, Photocatalytic degradation, Solar light, Titanium dioxide, Zinc phthalocyanine.

I. Introduction

Nitroaromatic compounds are recognized as environmentally hazardous. 4 – Nitrophenol (4-NP) is a nitroaromatic pollutant used for manufacturing pesticides, herbicides, explosives, dyes and pharmaceuticals (e.g. synthesis of the aspirin and acetaminophen) [1, 3]. These compounds are widely distributed in the environment and have been detected in wastewater, rivers and soils [4, 6]. 4-NP can be released into soil as a result of hydrolysis of several organophosphates pesticides such as parathion and methyl parathion [7]. It is designated a major pollutant by US-Environmental Protection Agency (US-EPA) [8]. It has carcinogenic, mutagenic and toxic properties [9]. The presence of nitro group reduce electron intensity of the nitro aromatic ring thereby impeding electrophilic attack by oxygenase and oxidative degradation of 4-NP [3]. However, 4-NP is highly toxic to plants, animals and microorganisms [3]. A rapid acclimation is thus needed for the treatment process. Advanced oxidation process (AOP) could provide a solution for such environmental problem. Titanium dioxide (TiO₂) assisted photocatalysis is a well known emerging AOP for the removal of organic pollutants. TiO₂ as photocatalysis shows relatively high activity but only under ultraviolet (UV) light which exceed the band-gap energy of 3.0 or 3.2 eV [10, 11] in the rutile or anatase crystalline phase, respectively. Consequently, the use of sunlight, indoor light, or other rays from artificial sources has been an appealing challenge for extending the applicability of these techniques. Attachment of dyes to the TiO₂ surface is a convenient way to use solar light for sensitization of photocatalytic degradation reactions. Several attempts have been made in this direction by attaching dyes including Rose Bengal, chlorophylls, porphyrins, phthalocyanines, a ruthenium bipyridyl complex [12]. The electronic and photocatalytic properties of zinc phthalocyanine dyes have been widely studied [13]. The composite prepared by association between zinc phthalocyanine (ZnPc) [14] and TiO₂ is a finely divided bluish powder with improved photocatalytic activity^[15], insoluble in water, capable to give stable suspensions in this solvent. The solar light intensity should be capable to photoexcite ZnPc/TiO₂ composite, generating e⁻/h⁺ pairs in both species, and consequently favoring the electron injection from ZnPc excitons to TiO₂ conduction band. In this work, TiO₂ particles were coated with ZnPc for studies on photocatalytic degradation of 4-NP, with solar light. Thus the prime objective of the present work was to improve the efficiency of photocatalytic process using photosensitizers ZnPc/TiO₂.

II. Experimental

2.1 Materials and methods

Titanium dioxide, P25, was kindly provided by Degussa Chemicals (Hanau, Germany). 4-Nitrophenol (purity 99%) (GR, Merck, Germany) (Molecular formula C₆H₅O₃N, molecular weight 139.11), phthalic anhydride (≥99%), ammonium chloride (≥99.5 %), urea (95%), ammonium molybdate (99,98 %), zinc acetate (≥99 %), ethanol (≥99.5 %), nitrobenzene (≥99.0 %), methanol (≥99 %), dimethylformamide (DMF) (99.8 %), dimethylsulfoxide (DMSO) (≥99.7 %), NaOH (≥98 %), H₂SO₄ (95.0-98.0%) were commercially purchased from Sigma-Aldrich (Germany). The pH of the solution was adjusted before irradiation using NaOH or H₂SO₄.

The experiments under solar irradiation were performed in July 2011 from 12 to 4 p.m. The irradiation, were measured using the radiometer (PMA 2100 Solar Light Co), with the sensor positioned horizontally. The irradiation measured during the experiments varied from 15 to 20 W m⁻². The intensity was nearly constant during the experiments.

2.2 Apparatus and instruments

UV spectral analysis was done using UV-Visible Spectrophotometer Shimadzu 1650PC. The pH of the solution was measured by using HANNA pHeP (model H 198107) digital pH meter. The specific surface area of the composites was estimated from BET (Brunauer, Emmett, and Teller) isotherms, based on the adsorption of gaseous nitrogen, using a MICROMERITICS ASAP 2000 system.

2.3 Preparation of ZnPc and ZnPc/ TiO₂ composite

Phthalic anhydride (4.32 g, 16 mmol) ammonium chloride (0.47 g, 9 mmol), urea (5.8 g, 97mmol), ammonium molybdate (0.34 g, 0.03 mmol) and zinc acetate were thoroughly mixed. The mixture was added slowly to heated (180°C) nitrobenzene (10 mL). The mixture was heated for 6 hours at 180°C. The crude product obtained was a dark solid cake. The product was treated in a Soxhlet extraction apparatus with methanol for 24 hours. Finally, the product was heated under reflux in 20 mL ethanol for 4 hours. Thereafter, cooled, filtered and dried in oven at 120°C for 12 hours.

According to the literature [14], the composite was prepared coating TiO₂ particles with ZnPc. The necessary amount of TiO₂ (P25 Degussa) was gradually added in a mixture of 100 mL (50% DMSO, 20% ethanol, and 30% DMF) of a solution of ZnPc (2M)), stirring and heating, resulting in a suspension with a homogeneous appearance. After evaporation, the composite is dried at a temperature between 70 and 80° C, for 24 hours. Then, the composite is reduced to a powder finitely divisible that will get stable in water suspensions.

2.4 Characterization

The UV-vis absorption spectrum of ZnPc is shown in Fig. 1. The ZnPc spectrum in DMF is similar to that of the literature [15] with two groups of absorption at 600- 700 nm (Q band) and at 336 nm (Soret band or B band).

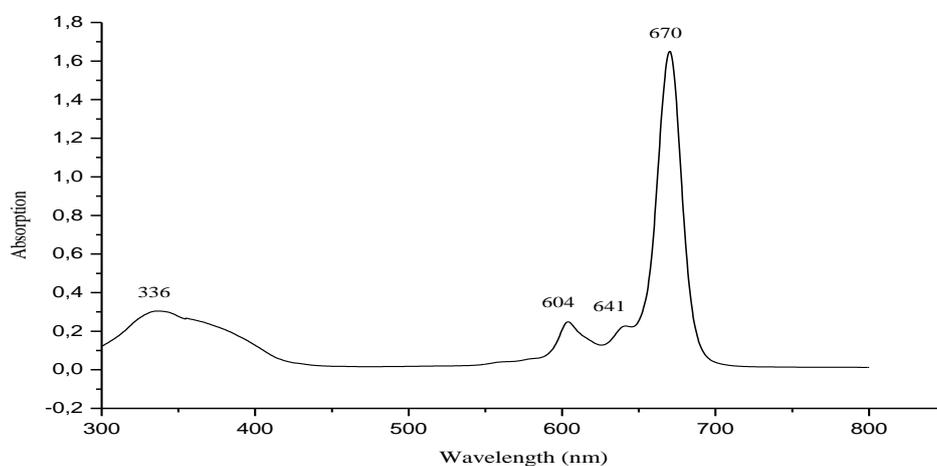


Fig. 1. UV-Vis spectrum of ZnPc in DMF solution at room temperature.

Table 1 shows the specific surface area (SSA) of pure TiO₂ and of ZnPc/TiO₂. For pure TiO₂ and composite, the peak positions and lattice parameters of the anatase and rutile phases (not shown).

Table 1: Specific surface area values for TiO₂ and ZnPc /TiO₂ composite.

Composition	SSA (m ² g ⁻¹)
TiO ₂	52
TiO ₂ /PcZn	35

X-ray powder diffraction patterns of TiO₂ and the ZnPc /TiO₂ composite only show peaks due to the anatase and rutile phases (figure not shown) [16].

2.5 Procedure

A recirculating photocatalytic reactor was constructed as shown in Fig. 2. The reaction vessel consists of a small cylinder constructed of Pyrex glass. It is connected to a reactor of 25 cm length and 5 cm diameter glass cylinder. A pump (Masterflex, Cole Parmer, USA) was used to circulate the solution. Under solar light irradiation, ZnPc/TiO₂ composite (1 g) was added in 4-NP solution (1 × 10⁻⁴ M, 50 mL), was circulated continuously under O₂ (flow rate 300 mL min⁻¹). At certain time intervals, small aliquots (2 mL) were withdrawn and filtered (0.45 μm Millipore filter) to remove the catalyst particles. All photocatalytic experiments were carried out at pH 6. The concentration of 4-NP in each degraded sample was determined with UV-Visible Spectrophotometer Shimadzu 1650PC at λ_{max}=316 nm. A calibration plot based on Beer-Lamberts law was established by relating the absorbance to the concentration. Degradation rate was calculated using the following equation 1

$$\text{Degradation rate (\%)} = \{(C_0 - C_t) \div C_0\} \times 100 \quad (1)$$

Where C₀ is the initial concentration of 4-NP and C_t is the instant concentration in the sample at time t.

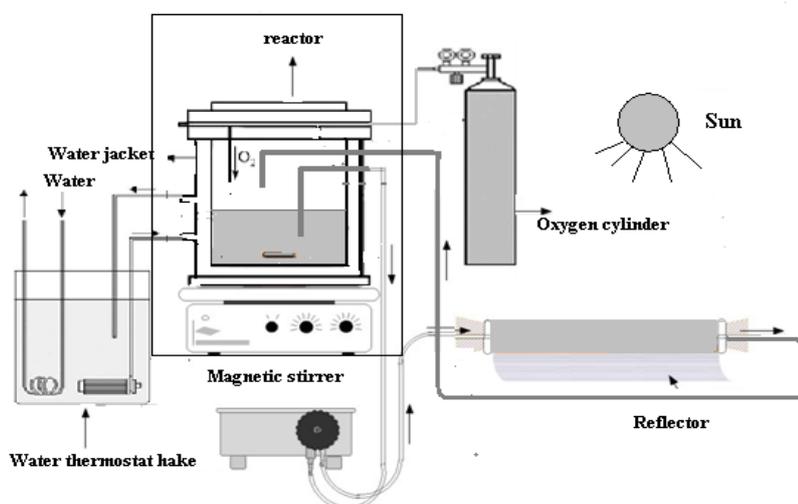


Fig. 2. Schematic diagram of the solar photocatalytic reactor system.

2.6 Total Organic Carbon Analysis.

The oxidative mineralization was therefore examined by measuring the Total Organic Carbon (TOC) in the solution [17]. The TOC measurements were made using Analytik jena TOC multi N/C 3100 analyzer by direct injection of the aqueous solution after centrifugation.

III. Result And Discussion

3.1 Photodegradability

The results of photodegradation with and without ZnPc/TiO₂ are shown in Fig. 3. The 4-NP is not degradable with solar light in the absence of catalyst ZnPc/TiO₂ and by ZnPc/TiO₂ in dark. The 9% decrease in 4-NP concentration with ZnPc/TiO₂ in dark is due to the adsorption of 4-NP; about 99% of 4-NP is removed after 80 min of solar irradiation. This reveals that the 4-NP can be degraded only in the presence of ZnPc/TiO₂ and solar light.

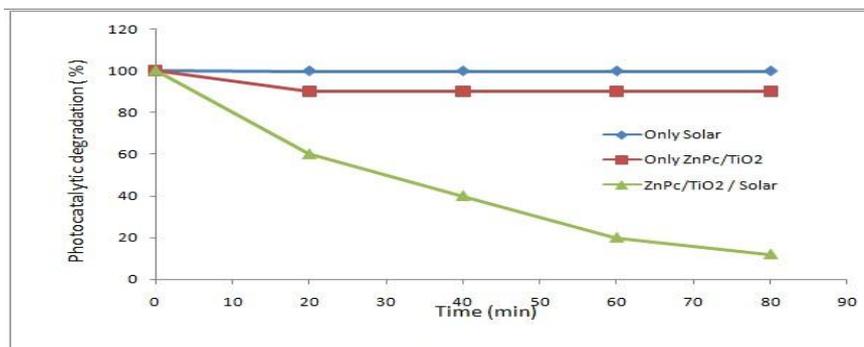


Fig. 3. Effect of solar light and ZnPc/TiO₂ on photocatalytic degradation of 4-NP [4-NP] = 1 × 10⁻⁴ M; pH 6.0 ± 0.1.

3.2 Effect of pH of the solution

The effect of pH on the photocatalytic degradation efficiency of AOP, according to some literatures [18], is one of the major factors influencing the rate of degradation of some organic compounds. The degree of photocatalytic degradation of 4-NP was found to be affected by a change in pH. Fig. 4 shows the effect of varying the pH from 2 to 12 on the degradation of 4-NP in the presence of ZnPc/TiO₂ under solar light irradiation. Increase of pH of 4-NP solution from 2 to 6 increases the degradation from 70.6% to 87% at 60 min. Degradation of 4-NP was high between pH 2 and pH 6, while the degradation efficiency was lower in the alkaline environment above 7 pH. Titania surface will remain positively charged in acidic medium (pH < 7) and negatively charged in alkaline medium (pH > 7). This behavior can be explained when the pH value of the solution is increased up to a maximum value and then decreased, this is because in alkaline medium the surface area of photocatalyst possesses much negative charge [19, 20].

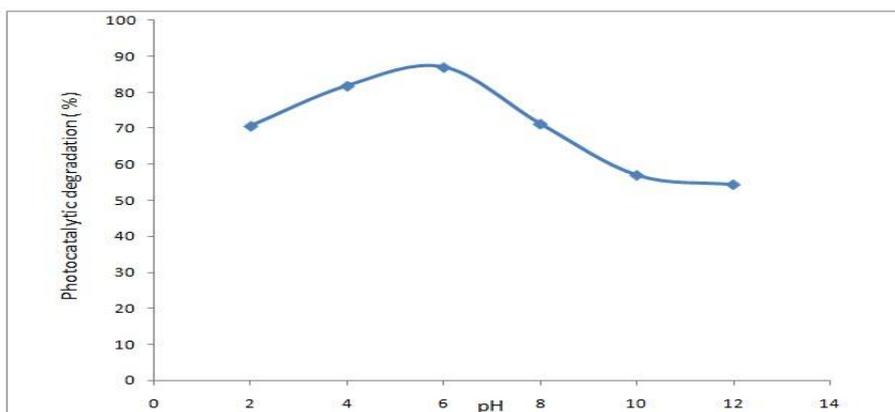


Fig. 4. Represent the effect of change in pH on photocatalytic degradation of 4-NP using solar light.

3.3 Effect of catalyst loading

The amount of catalyst is one of the main parameter for the degradation studies. The experiment was carried out by varying the catalyst loading from 25 mg/100 mL to 150 mg/100 mL. The results are shown in Fig. 5. The percentage degradation increases rapidly from 55% to 87% with the increase in the amount of ZnPc/ TiO₂ from 25 to 100 mg/100 mL at 60 min. This is due to an increase in the number of ZnPc/ TiO₂ particles, which increases the absorption of photons and adsorption of pollutant molecules. Further increase of ZnPc/ TiO₂ loading from 100 to 150 mg/100 mL, decreases the removal rate. At high solute concentration availability of excess active sites outweighs the diminishing photoactivated volume and significantly greater percentage is achieved at increased ZnPc/ TiO₂ loading. Thus, the decreased percentage degradation at higher catalyst loading may be due to deactivation of activated molecules by collision with ground state molecules. Hence, an optimum catalyst has to be added in order to avoid unnecessary excess catalyst and also to ensure total absorption of solar light photons [21] for efficient photomineralisation. The optimum amount of catalyst loading was found to be 100 mg/100 mL of the degradation of 4-NP. Hence, 100 mg/100 mL was used as the catalyst dosage for the photocatalytic reaction.

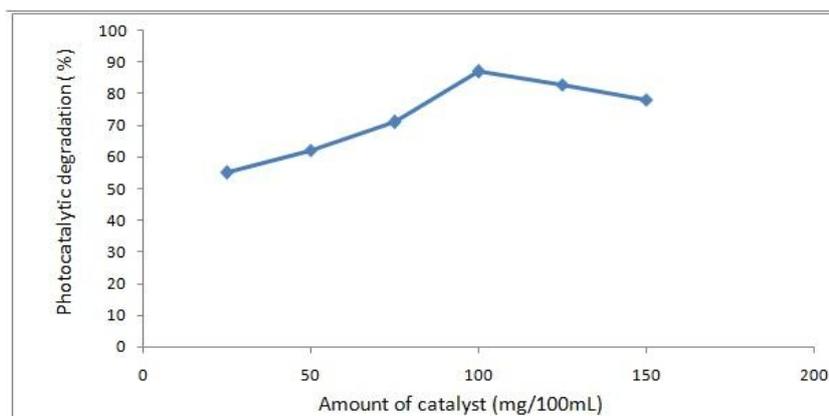


Fig. 5. Effect of catalyst weight on the degradation of 4-NP using solar light; [4-NP] = 1×10^{-4} M; pH 6.0 ± 0.1 ; irradiation time = 60 min.

3.4 Effect of 4- NP concentration

The effect of initial concentration of 4-NP on the percentage degradation was studied by varying the initial concentration from 1×10^{-4} to 6×10^{-4} M with optimum catalyst loading. The results are shown in Table 2. Increase in the concentration of 4-NP decreases the degradation of 4-NP from 98.81 % to 20.37 % in 60 min of irradiation time. The possible explanation for this behavior is that as the initial concentration of the 4-NP increases, the path length of photons entering the solution decreases and in low concentration the reverse effect is observed, thereby increasing the number of photon absorption by the catalyst in lower concentration [22]. The pollutant molecule rather than the catalyst may absorb a significant amount of solar light and this may also reduce the catalytic efficiency.

Table 2: Effect of initial concentration of 4-NP on the photocatalytic degradation of 4-NP using Solar light ZnPc/ TiO₂ = 100 mg/100 mL; pH 6.0±0.1.

Concentration of 4-NP (10 ⁻⁴ M)	Degradation (%)
1	98.81
2	72.19
3	57.24
4	46.12
5	35.64
6	20.37

3.5 Effect of Current Gas

The results in fig. 6 shows that the photodegradation efficiency for 4-NP increased with the presence the oxygen gas (O₂) but the decreases or was extremely slow in the presence the nitrogen gas (N₂). This behavior can be explained that in the presence of nitrogen gas (N₂) and ZnPc/TiO₂ will production grey-blue in color may be attributed to the sharing of lattice oxygen from the surface. The results indicated that the presence of oxygen necessary [23, 24]. The presence of oxygen in the solution plays an important role in the photocatalytic degradation of 4-NP. This behavior can be explained that the oxygen molecule acts as an electron acceptor and minimizes the chance of electron-hole pair recombination [25].

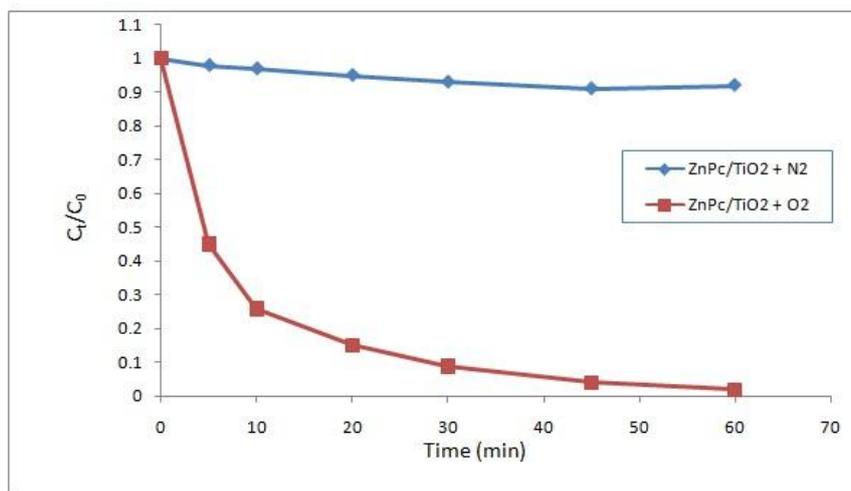


Fig. 6. Effect of type of gas on the degradation of 4-NP using solar light ZnPc/ TiO₂ = 100 mg/100 mL; [4-NP] = 1×10^{-4} M; pH 6.0±0.1; irradiation time = 60 min.

3.6 Effect of addition of H₂O₂

The photocatalytic degradation of organic pollutants depends upon their reactions with the hydroxyl radicals $\cdot\text{OH}$. Therefore, electron acceptors have been used to enhance the degradation rates since they generate $\cdot\text{OH}$ radicals [26]. Hydrogen peroxide (H₂O₂) plays an important role in the production of hydroxyl radicals. The effect of addition of hydrogen peroxide H₂O₂ on the degradation was studied for photocatalytic oxidation of the 4-NP. The results in fig. 7 show that the degradation increases from 82.1 to 87 % with increases concentration of hydrogen peroxide H₂O₂ from 4 to 16 mmol at 60 min. This behavior is due to the increasing the concentration of hydroxyl radical since it inhibits the hole-electron recombination according to the following equation 2.



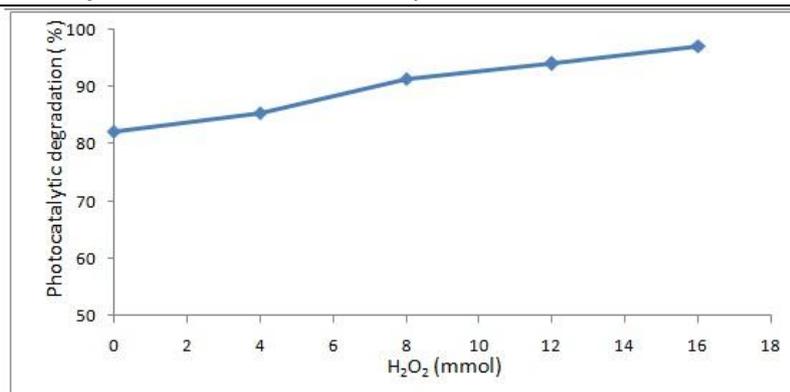


Fig. 7. Effect of addition of H₂O₂ concentration on the degradation of 4-NP using solar light ZnPc/TiO₂ = 100 mg/100 ml; [4-NP] = 1 × 10⁻⁴ M; pH 6.0±0.1; irradiation time = 60 min.

3.7 Total Organic Carbon (TOC) Analysis.

Fig. 8 show the results of the TOC experiment indicating that 4-NP was mineralized up to 87.7 % within the period of 80 min. This indicates mineralization of 4-NP. Mineralization of 4-NP was also revealed by the formation of carbon dioxide during photodegradation. Carbon dioxide formation was tested by passing the evolved gas during photodegradation into lime water.

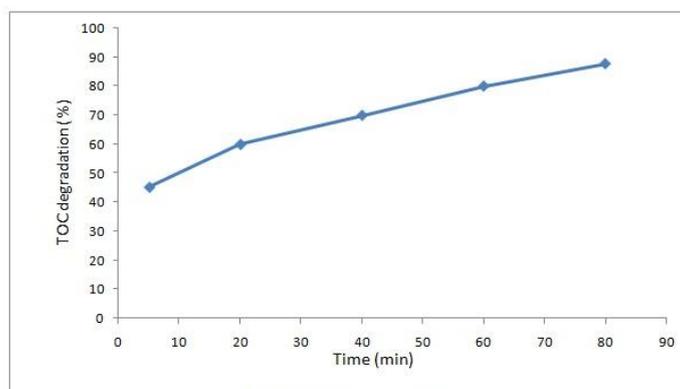


Fig. 8. Mineralization of 4-NP.

IV. Conclusion

In this study, Zinc phthalocyanine-modified titanium dioxide, ZnPc/TiO₂, as photocatalyst was synthesized. ZnPc/TiO₂ has been found to be most active catalyst, exhibiting high photocatalytic activity. 4-NP is successfully degraded by ZnPc/TiO₂ assisted photocatalysis in aqueous dispersion under irradiation by Solar light. Photocatalytic degradation of 4-NP depends on the amount of catalyst, initial concentration, pH. The optimum concentration of oxidant H₂O₂, for enhanced degradation is 8 mmol. Photocatalytic mineralization of 4-NP (97%) was achieved using ZnPc/TiO₂, after a period of 80 min. The solar assisted photocatalysis with ZnPc/TiO₂ can be used as a viable technique for the treatment of 4-NP (an organic pollutant).

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