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Removal of 2, 4 dinitrophenol pesticide from wastewater using zinc-doped TiO_2 nanoparticles under solar light illumination

Mounir Zaky[1], Ibrahim Elmehasseb[2], Saleh Kandil[1]* Khaled Elgendy[1]

[1]Chemistry Department, Faculty of Science, Zagazig University, Zagazig, Egypt
[2]Chemistry Department, Faculty of Science, Kafrelsheikh University, Egypt
Corresponding author: abosalah281182@gmail.com

ABSTRACT **: 2, 4 dinitrophenol is one of the common pesticides that are used widely in agriculture to combat harmful pests and organisms. As a result of its usual use, there is a great accumulation of its levels in aquatic media. Zinc-doped TiO_2 nanoparticles can serve in this field and have achieved excellent results in the detoxification of water using solar light irradiation. Zinc-doped TiO_2 nanoparticles have been fabricated by the sol-gel method. The new catalyst has been examined in the detoxification of wastewater by removing the dissolved toxic 2, 4 dinitrophenol. According to the treatment results, Zn-doped TiO_2 can remove about 85% of toxic material within 17 minutes only. The characterization of synthesized Zinc-doped TiO2 nanoparticles was carried out by Fourier transform infrared (FTIR), X-ray diffraction (XRD), and scanning electron microscopy (TEM), and the evaluation of the efficiency of the nanomaterial in the removal of toxic organic residues was carried out by UV-vis spectrophotometry.**

KEYWORDS: 2, 4 dinitrophenol; Zinc-dopedTiO$_2$, Pesticides, detoxification, Characterization; Solar light

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I. INTRODUCTION

Pesticides are versatile compounds and are used every time in agriculture to kill the harmful pests that cause harmful effects on the plants. But these organic compounds are extremely toxic. The environment cannot face its accumulation as it can affect the soil and water with toxic effects.(Abdennouri, Baâlala et al. 2016). The harmful toxic effect can extend to human health through the accumulation of these compounds in the plants themselves, causing harmful diseases.

2, 4-Dinitrophenol is one of these organic pesticides and herbicides, which is an alkyl dinitrophenol. Its removal faces great difficulty due to its stability and slow rate of biodegradability under the action of microorganisms, leading to the rise of its levels in the environment and posing a danger to human society. It has a low molecular weight and high toxicity and can be considered a carcinogenic compound.(Bagal and Gogate 2013).

It was a remarkable requirement to develop a technology that can serve in the removal of 2,4-dinitrophenol. Nanotechnology can achieve efficient results in the elimination of 2,4-dinitrophenol and various organic toxins in wastewater. Advanced oxidation processes (AOPs), which are employed by nanoparticles, serve effectively in the removal of different accumulated impurities. According to AOPs, the nanoparticles generate highly oxidative components like hydroxyl radicals, which can enter an effective oxidation mechanism to degrade organic pollutants.(Shiraishi, Miyawaki et al. 2015).

Titanium dioxide nanomaterial is an efficient nanopowder that has many properties, including the fact that it can be prepared easily, is nontoxic, and not expensive. TiO2 can be synthesized by the sol-gel method, which is a simple technique that can prepare TiO2 at ambient temperatures without needing to meet any specific conditions. TiO_2 has high photocatalytic efficiency and is used widely in the removal of toxic material. TiO_2 can be used in the treatment of wastewater for the removal of different organic pollutants like pesticides, drugs, dyes, and much more harmful compounds through their degradation by its high photoxidative activity(Zhang, Wang et al. 2016).

The only limitation of titanium dioxide nanomaterial was its wide band gap (3.2e.V). This high value limits its application to ultraviolet illumination only due to the required high energy to excite the electrons from the valence band to the conduction band. This problem was solved by the incorporation of different component in the crystal lattice of titanium dioxide in a chemical process which is called doping. Doping is the involving small amounts of metallic or nonmetallic impurities in the lattice of TiO_2. Doping by zinc species causes distortion of the titanium dioxide crystal lattice, which results in a decrease in its band gap. This decrease in the band gap value is due to the effect of dopants, which serve as electron scavengers which retard the fast recombination between electrons and holes, which led to the decreasing of the band gap value to a lower value(Aware and Jadhav 2016). The zinc doped TiO_2 nanoparticles with lower band gap can be utilized in the removal of toxic pollutants such as sever and harmful pesticides such as 2,4 dinitrophenol from wastewater under the illumination of solar light with a simple and wide use procedure in the water treatment plant technology as an advanced tools. The chemical structure of 2,4 dinitrophenol is illustrated in figure 1.

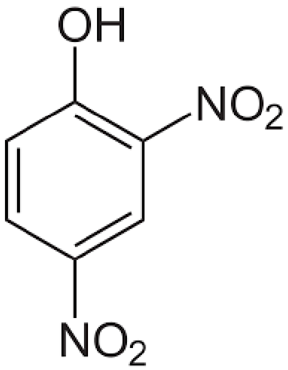


Fig.1: The chemical structure of 2, 4 dinitrophenol

II. MATERIALS AND METHODS

Reagents and chemicals

Titanium precursor of (titanium tetrachloride TiCL4) reagent grade, 97%, ethanol ≥99.8%,(C_2H_5OH), Cetyl trimethyl ammonium bromide (CTAB) [($C_{16}H_{33}$) $N(CH_3)_3$]Br, Zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$), citric acid, 2,4 dinitrophenol from Sigma-Aldrich, double deionized water was used through the work.

Instrumentation

FTIR spectra (6800 JASCO – Japan) adjusted in the range 4000-400 cm^{-1}. X-ray diffraction (XRD) lab type (6000 SHIMADZU Japan), scanning electron microscope (SEM) provided by energy dispersive spectroscopy (EDX) (JSM IT 100 JEOL Japan) for the characterization of surface morphology, UV-VIS double beam spectrophotometer (UV-2450 SHIMADZU Japan) for the evaluation of the nanoparticles and determination of the band gaps according to reflectance data.

Synthesis of TiO_2 nanoparticles by sol-gel technique:

15 ml of titanium precursor solution (titanium tetrachloride TiCL4) was dissolved in an alcoholic medium of 20 ml absolute ethanol with stirring until the formation of a yellowish-colored solution. A second solution was prepared by dissolving 2 g of CTAB in 75 ml of double-deionized water in the presence of 0.1 ml of citric acid to avoid agglomeration. Then the first solution was added carefully to the second solution. White suspended particles started to be formed during addition with vigorous stirring. Isolation of the precipitate was carried out by centrifugation at 6000 rpm for 10 min at each run with repeated washing with a mixed solvent of water and alcohol. The obtained powder was dried for 12 hours at 70 oC before calcination at controlled 450 oC, and the obtained powder was kept prior to use(Elgendy, Elmehasseb et al. 2019).

Synthesis of zinc doped TiO_2 nanoparticles by sol-gel technique:

15 ml of pure TiCL4 solution was dissolved in 20 ml absolute ethanol with stirring till pale-yellow color was obtained. Then the total solution was added carefully to the second solution: 2 gm of CTAB prepared in 75 ml DDI (0.1 M) citric acid to prevent agglomeration of the network structure. At the same time, 3 wt. % of zinc nitrate in-situ formation to produce Zinc doped TiO_2, the off-white suspended particles were centrifuged

at 6000 rpm for 10 min at each run with repeated washing with mixed solvent. The obtained powder was dried for two days at 70 ^{o}C, before calcination at a controlled 450 ^{o}C and the obtained powder was kept before use(Elmehasseb, Kandil et al. 2020).

Characterization of Zn doped TiO_2 nanoparticles:

FTIR characterization of Zn doped TiO_2:

The doping by zinc affects the shape of the peak between 450 cm^{-1} and 650 cm-1as it causes its broadening as a result of doping. The hydroxyl group has a peak at 1650 cm-1 representing bending vibration mode. Broadband between (3400 – 3650) cm^{-1} refers to the hydrolysis of titanium precursor by alcohol in addition to the reaction between nanoparticles surface and water(Silva, Martins et al. 2016, Elmehasseb, Kandil et al. 2020).

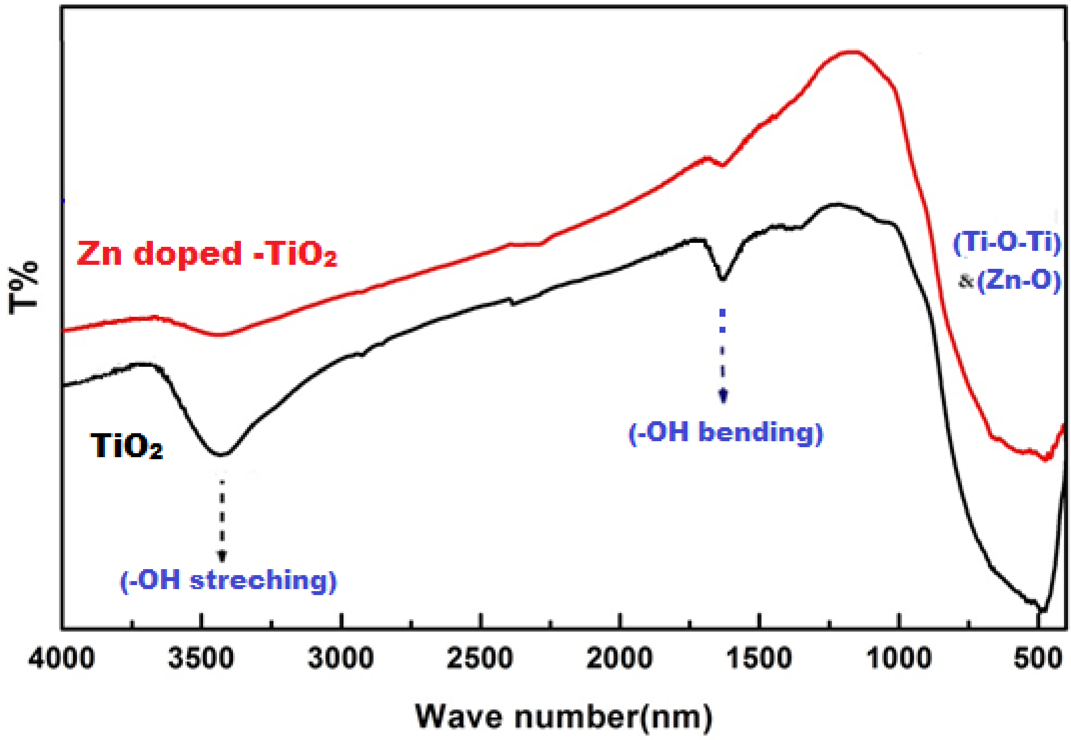


Fig.2 The FTIR curves of Zn doped -TiO_2

X-ray diffraction characterization (XRD)

The XRD pattern of the prepared TiO_2 represents the preparation of anatase phase with sharp peaks at 2θ= 25.2, which is proved by XRD patterns for TiO_2 and Zinc doped -TiO_2. The doping process even with a small number of zinc species retards the transformation of anatase phase to any other phase and affects the particle sizes to smaller sizes which can be calculated by Scherer's equation Scherer's equation:

$$D=K\lambda / \beta \cos \theta \qquad (1)$$

Where:

λ is wavelength of X-Ray (0.1540 nm)

& β is FWHM (full width at half maximum)

& θ is diffraction angle

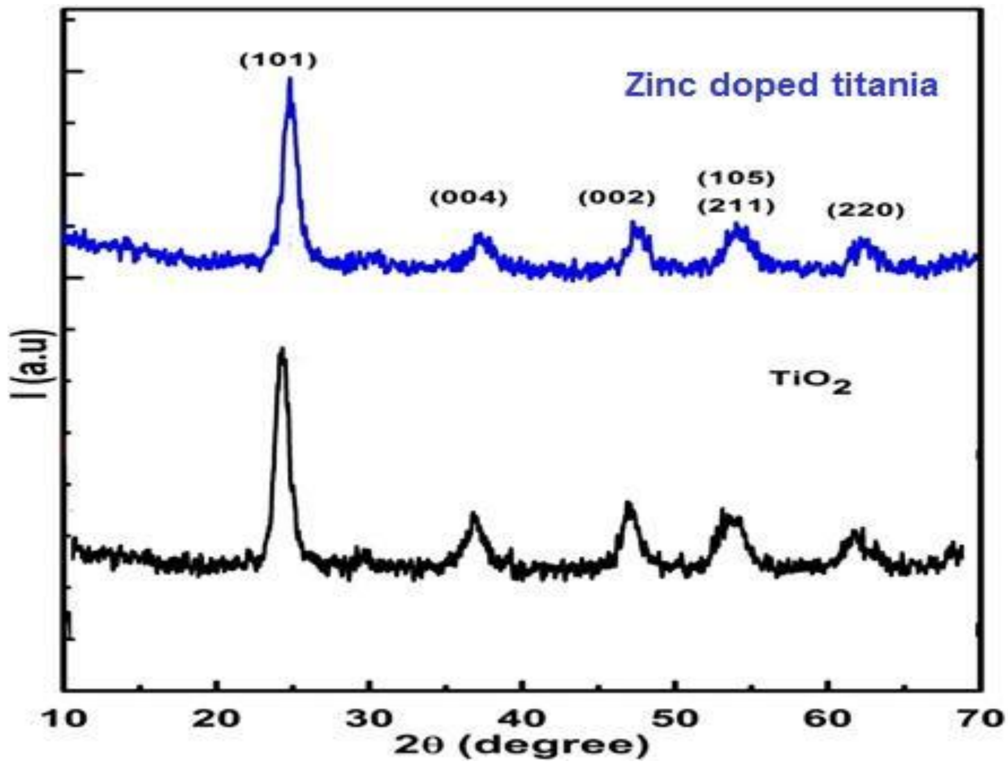


Fig.3 XRD of Zn doped -TiO_2 nanoparticles

The particles sizes were found to be in the range of between 20-25 nm at the more intense x-ray beaks at 25.2^{o}, 48.0^{o} and 54.9^{o} which were smaller than that of bare TiO2(Imran, Riaz et al. 2015, Elgendy, Elmehasseb et al. 2022).

Morphological characterization studies of Zn doped -TiO_2 nanoparticles:
Scanning electron microscope gives valuable feedback and sufficient study about the material's surface and the morphology of the synthesized nanoparticles and their shape. The particles have mainly spherical shapes nearly the similar particle size(Estrada-Flores, Martínez-Luévanos et al. 2020). Doping with species with smaller ionic radii like zinc which replace the titanium ions in the crystal lattice causes their retraction to lower dimensions due to the distortion of crystal lattices of the nanoparticles(Kamani, Nasseri et al. 2016).

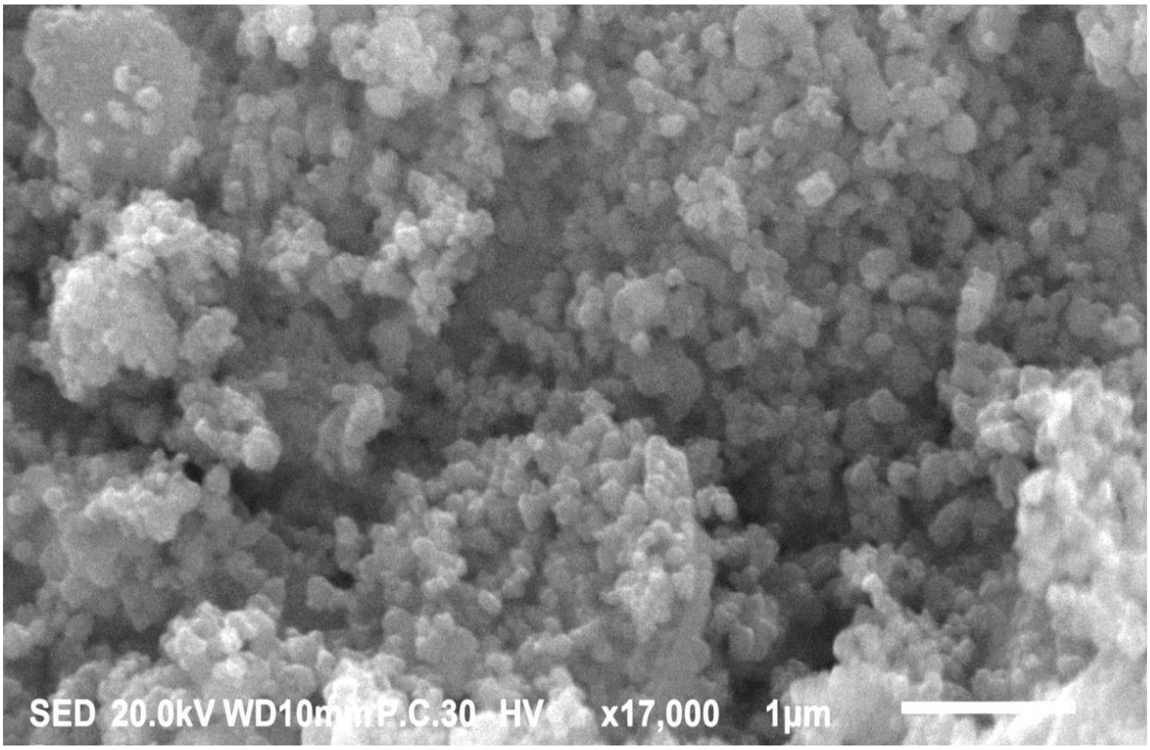
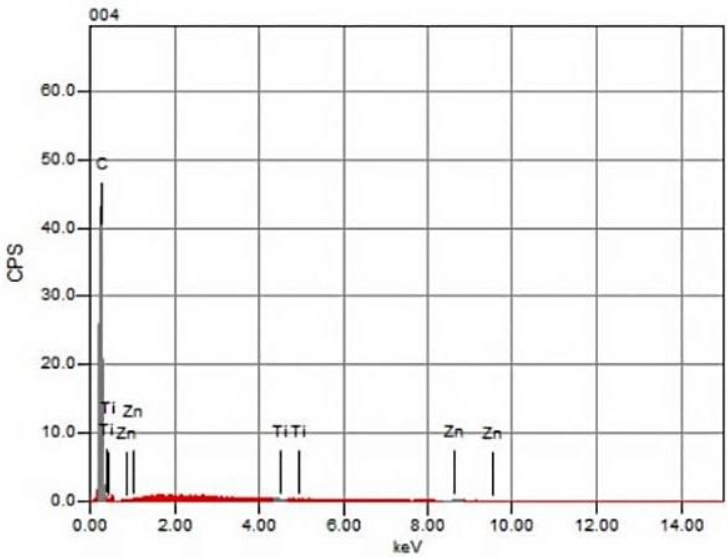


Fig.4 SEM images Zn doped -TiO_2 nanoparticles



Acquisition Condition
Instrument : IT100LA
Volt : 20.00 kV
Current : ---
Process Time : T3
Live time : 50.00 sec.
Real Time : 50.18 sec.
DeadTime : 0.00 %
Count Rate : 520.00 CPS

Formula	mass%	Atom%	Sigma	Net	K ratio	Line
C	97.84	99.59	0.09	50115	0.0075853	K
Ti*	0.10	0.03	0.06	103	0.0000444	K
Zn*	2.05	0.38	0.18	579	0.0008109	K
Total	100.00	100.00				

Fig.5 EDX image of doped TiO_2 by zinc

Band gap calculation by UV Spectrophotometer

The improvement of the photocatalytic activity of the nanoparticles can be carried out by the incorporation of small amounts of impurities within the crystal lattice of TiO_2. The incorporation of foreign species causes retarding in the recombination rate between electrons and holes. This retarding of electrons extended the lifetime of electrons causing more photoactivation of the catalyst. This enhancement can be determined by the calculation of band gap values by ultraviolet-visible Spectrophotometer. The smaller value of band gap is the more active photocatalyst and extending of the catalytic efficiency region to the visible region of longer wavelengths(Aware and Jadhav 2016).

Hence the doped nanoparticles with improved band gap can be easily utilized under visible or solar light with a simple application. For TiO_2 nanoparticles, the doping process was carried out by zinc species in order to improve and minimize the larger band gap of TiO_2 with the absorption shift to longer wavelengths in the visible region. The band gaps of the TiO_2, TiO_2/Zn were calculated by Kubelka–Munk (KM) method using the following equation (2)

$$\alpha h\upsilon = A\,(h\upsilon - Eg)\ 1/2 \qquad (2)$$

Where α is the absorption coefficient, h is Planck's constant, υ light frequency, Eg is the band gap and A is a constant.

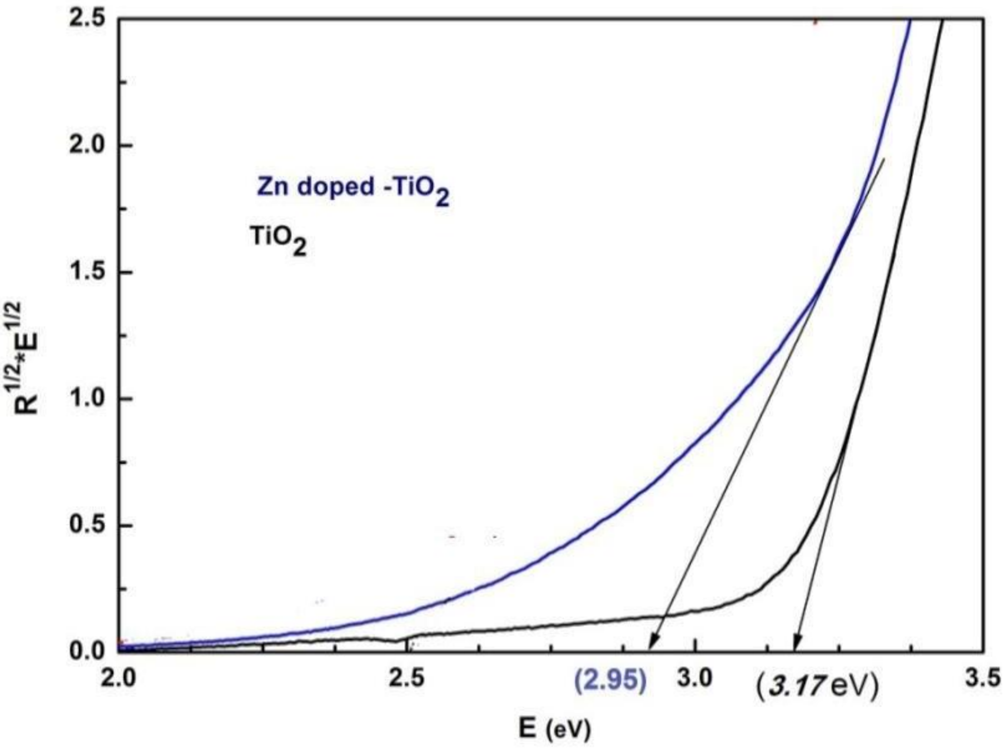


Fig.6 Band gap calculation of TiO_2, TiO_2/Zn respectively

From the past data of the band gap, it is clear that pure TiO_2 is not applicable in visible light due to the large band gap, so the application was carried out using TiO_2/Zn nanocomposites in the photodegradation of the pesticides under solar light due to modified band gap. When plotting a curve between (αhυ) 0.5 versus energy (hυ), the value of the band gap energy can be estimated from the intercept of the tangent. From the curves, the band gap was 3.2 e.V and 2.95 e.V for TiO_2, and TiO_2/Zn respectively and the improvement has a red shift hence more photocatalytic performance(Benjwal and Kar 2015).

III. Results and discussion

Using UV- visible light spectroscopy, the evaluation of the photocatalytic efficiency of the synthesized Zn doped -TiO_2 nanoparticles in the removal of different pesticides. Figure 7 represents the removal of 2, 4 dinitrophenol from wastewater. The results were obtained when treating of 10 ml of 10 ppm of polluted wastewater under the illumination of solar light. Using the UV-vis spectroscopy, the blank reading of the solution was taken at 0 time of illumination and then the absorbance were gradually recorded with successful photodegradation curves.

The results showed that the effective utilization of 5 mg of Zn doped -TiO_2 nanoparticles in the treatment of water according to the AOPS mechanism and the generation of hydroxyl radicals and degradation of about 84% within 17 min only in solar light which is considered as excellent results for the treatment of water by the detoxification of harmful pesticides under the illumination of solar light using modified Zn doped -TiO_2 nanoparticles. The removal process by this method is considered as a superior technique because it enables the scientists to remove extremely toxic compounds and degrade them to safe degradation products of CO_2 and H_2O

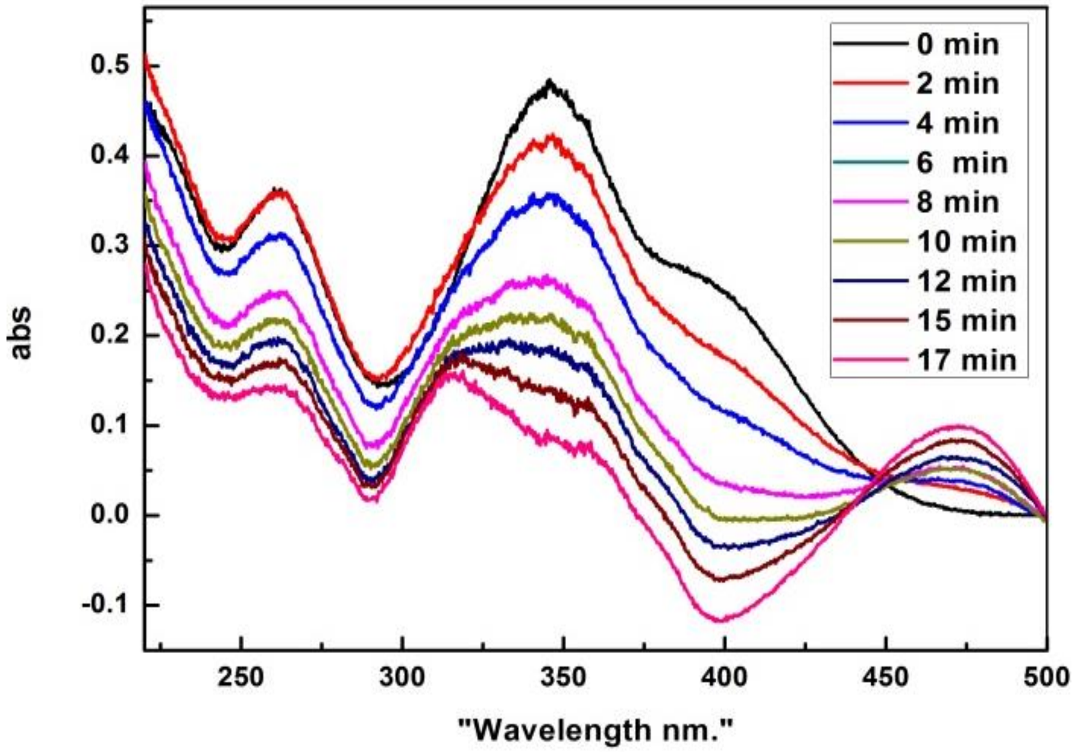


Fig.7 Efficient removal of 2, 4 dinitrophenol by Zn doped -TiO2 nanoparticles

IV. Conclusion

The doping of TiO_2 by zinc species decreases the bandgap from 3.17 to a lower value of 2.95e.V. This enhancement enables the utilization of doped nanoparticles under the irradiation of solar light. In addition to the improvement in the particle sizes of smaller particles 20-25 nm with more modification and increasing surface area of the nanomaterials. The application of nanomaterials especially Zn doped-TiO_2 nanoparticles an effective technique in the removal of nonbiodegradable pesticides such as 2, 4 dinitrophenol effectively via AOPS and degradation of 84% within 17 min for effective treatment of wastewater and degradation of toxic compounds to safe products.

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