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Research Article

ZnO DOPED TIO_2 NANOCOMPOSITE SYNTHESIS AND INFLUENCE OF PARAMETERS ON THE HETEROGENEOUS PHOTOCATALYTIC DEGRADATION OF PHENOL IN WASTEWATER

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ABSTRACT

ZnO doped TiO_2 nanocomposite was synthesized by the Sol-gel method. The synthesized nanocatalyst was characterized by XRD, SEM, FT-IR, UV-Vis to evaluate the crystal patterns and size, Band-gap energy, morphology, surface area into the ZnO doped TiO_2. Degradation of phenol was carried out under UV-Visible light irradiation by varying the reaction parameters such as initial phenol concentration, Catalyst loading and pH with an irradiation time of the solution.

Keywords: Photocatalyst, Photo Degradation, Phenol, Sol-Gel method, ZnO doped TiO_2

1. INTRODUCTION

Nowadays, non-biodegradable organic compounds are causing serious environmental issues. Among those organic compounds, phenol is one of the most dangerous non -biodegradable toxic substances which is both corrosive and toxic. The emission of phenol takes place mainly from pulp and paper industries, refining of petroleum, food processing, steel, tanning, fiber wood and pharmaceutical industries [1]. Continuous emission of phenol may affect the respiratory tract and eyes. It may affect CNS and heart also. So the degradation of phenol is the toughest task for today's researchers. Many conventional methods are having discrepancies. Photocatalysis is a current promising scenario for the degradation of many toxic organic compounds [2]. Total deterioration of the pollutant and low expenses are some of the markable advantages of the photocatalysis. Heterogeneous photocatalysis is one of the trendy and widely utilized methods for degradation or bleaching of dyes [3-5]. Many Researchers reported the application of semiconductor materials (TiO_2, $SrTiO_3$, ZnO, WO_3, Fe_2O_3) as a photocatalyst on degradation. Among semiconductor nanomaterials, ZnO and TiO_2 have shown amazing results on degradation [6]. ZnO is a harmless material and it shows better photocatalytic activity against many dyes and pesticides. Even though it's high photosensitivity nature, the rapid recombination rate of ZnO reduces degrading efficacy. To overcome the issues, ZnO nanoparticles are doped with transition metal oxides. Generally doping of transition metal cations in semiconductor catalysts successively narrowing the band-gap hence it triggers the catalyst to be active under visible light [7]. The doped metal oxide enhances its photocatalytic nature. The doping also enhances the electron-hole pair and increasing photocatalytic efficiency. The size of the nanocatalyst plays an indispensable role in the photocatalytic activity of photocatalysts. The tiddly photocatalyst can easily migrate to the reaction sites on the surface resulting in decreased recombination probability [7]. To the best of our knowledge, there are minimal studies about the degradation of phenol using ZnO as a doping material in TiO_2 under UV-Visible light irradiation. In this current investigation, the nanocatalysts were synthesized by the Sol-gel technique. The effect of different operational parameters like initial concentration of phenol, Catalyst dosage, pH was examined.

2. EXPERIMENTAL

The Zinc and Titanium precursor solution was prepared separately. TiO_2 precursor sol was prepared by mixing 30 ml of titanium tetrachloride ($TiCl_4$) with 100 ml absolute ethanol, forming solution A. The solution was stirred for half-an-hour. To obtain ZnO precursor sol, 0.04g of Zinc acetate and 90 ml of deionized water

were mixed with 10 ml acetic acid to form solution B. The solution was then stirred until zinc acetate was completely dissolved. The starting material ratio was equal to the ZnO/TiO_2 (molar ratio) of 0.75 % of dopant concentration. Then solution B was added drop-wise into solution A under vigorous stirring for 2 hours to increase the solubility. The mixed sol was aged for 24 hours at room temperature until formation of a gel. The product dried in an oven at 100°C for about 24 hours to evaporate the solvent and to remove the residuals. The crystal form of the sample was then grounded using mortar and pestle before calcination for 3 hours with the heating rate of 5°C at 600°C [8].

2.1. Characterization of ZnO doped TiO_2

Synthesized ZnO doped TiO_2 were characterized using different techniques to know about obtained properties. The powder XRD (Hitachi, Model S -4000, Japan) was used to identify the crystalline structure and particle size with Bragg's angle ranging from 10-70 with a speed of 3/ minute using nickel-filtered Cu Kα radiation source and obtained results were ratified by comparing JCPDS file. The structural elucidation and functional groups were identified by FT-IR (JASCO 460 PLUS, JAPAN). Morphological studies of ZnO doped TiO_2 nanoparticles were identified by Scanning Electron Microscope (Hitachi, Model S-4000, Japan). Finally, a diffusive reflective UV-Vis Spectrophotometer (Shimadzu UV-2501PC) was used to measure the band-gap of the catalysts.

2.2. Photocatalytic experiments

The photocatalytic degradation of Phenol by Zinc oxide doped TiO_2 photocatalysts was performed under Visible light irradiation. The photocatalytic degradation was monitored using UV-VIS light irradiation at λ max > 420 nm as a light source using a 250 Watt Xenon lamp. In the experiments, the calculated amount of catalyst was suspended in 100 ml of 10ppm Phenol solution in a conical flask. The flask was wrapped with aluminum foil then placed in the dark, for an hour for adsorption to take place. The system was then irradiated with visible light from a lamp that was fixed in the middle of the system and 12 cm above the surface of the solution. To detect changes in concentration, aliquots of phenol solution (5 ml) were taken after every 30 minutes and centrifuged followed by measuring the absorbance of the clean solution by UV-Vis spectrometer. The concentration of Phenol was proportional to its absorbance according to Beer-Lambert's law, so the degradation efficiency of phenol was calculated as formula,

Degradation Efficiency = {(C0-C) /C0} X 100

Where Co and C concentrations before and after degradation respectively [9].

3. RESULTS AND DISCUSSIONS

3.1. XRD

The XRD images of ZnO doped TiO_2 were illustrated in Fig. 1. The grain size of ZnO doped TiO_2 was calculated using the Scherrer formula by the Full width at half maximum of the (102) diffraction peak of TiO_2 after subtraction of the equipment broadening [7]. The doping elements did not affect the crystalline structure. The 2θ values for synthesized nanoparticles (102), (005),(200),(105), (210), (203), (116), (218), (215). The estimated powder grain size of synthesized ZnO doped TiO_2 was about 16 nm.

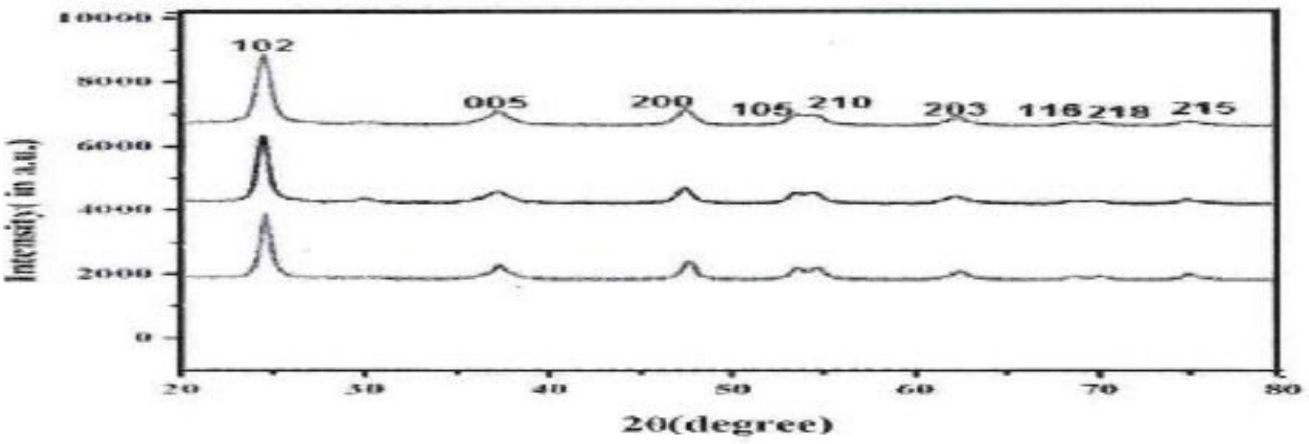

Fig. 1: XRD image of ZnO doped TiO_2

3.2. SEM (Scanning electron Microscope)

The SEM images of ZnO doped TiO_2 was as shown in Fig. 2. It was used to investigate the morphology of the synthesized nanocomposite. The agglomerated spherical shaped particles and its uniformity show the doping of ZnO doped TiO_2 nanoparticles. High surface and porosity is suitable for enhancing the photodegradation of dyes [10].

3.3. FT-IR

Fig. 3 shows the FT-IR spectrum of ZnO doped TiO_2 nanoparticles in which, some small peaks at 500-600 cm^{-1} are due to the stretching modes of Ti-O-Ti. The peaks at 3329.43 cm^{-1} in the spectra are due to the stretching vibration of the–OH group. The peak at 2924.25cm^{-1} shows the presence of asymmetric stretching vibration of CH_2. This spectra of the stretching vibration of C=O showed at 1621.61 cm^{-1}. The peak at 1384 cm^{-1} shows the atmospheric CO_2 absorption. A characteristic band with strong and wide absorption at below 1000cm^{-1} was attributed to the formation of ZnO doped TiO_2. The above result indicates the presence of Zn/ZnO as doping impurities in synthesized nanocomposites [1].

3.4. UV-VIS Spectroscopy

The bandgap energy was calculated from the Kubelka - Munk relationship. Here the graph is plotted against Absorbance and wavelength. From the UV-Vis results shown in Fig. 4, the bandgap energy of ZnO doped TiO_2 is 3.2eV, which leads to higher photocatalytic efficiency [11].

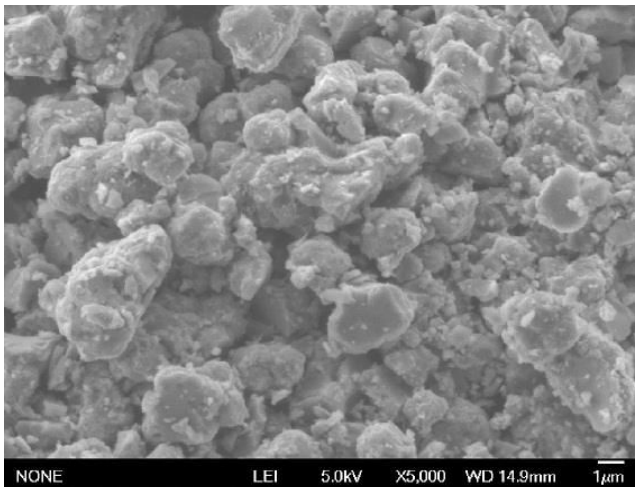

Fig. 2: SEM image of ZnO doped TiO_2

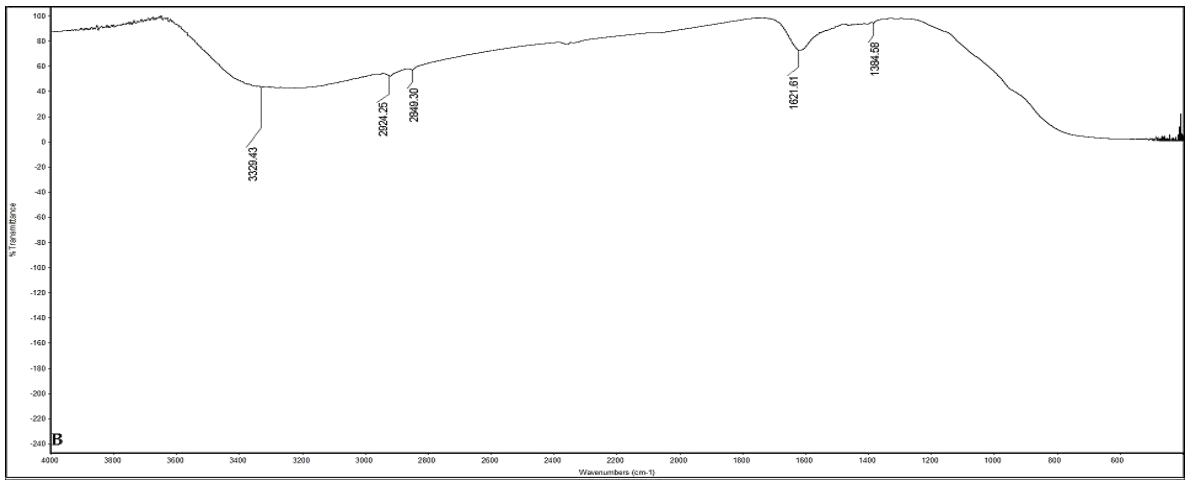

Fig. 3:FT-IR image of ZnO doped TiO_2

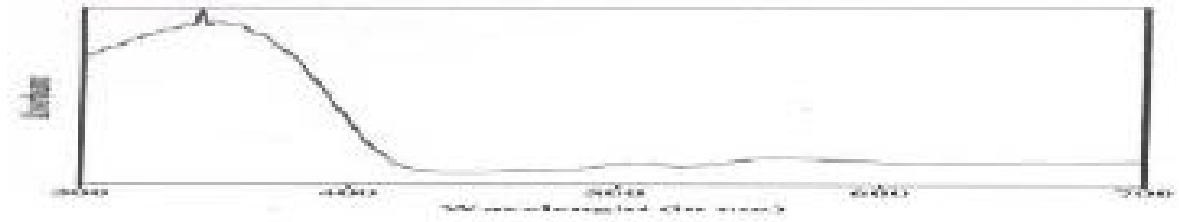

Fig. 4: UV-Vis image of ZnO doped TiO_2

3.5. Effect of initial ion concentration of Phenol

The effect of initial ion concentration of phenol concentration under UV light irradiation was investigated. The photocatalytic degradation was monitored using UV light irradiation at λ max 464 nm as a light source using 250-watt xenon lamp was investigated initial concentration from 10-50 mg/l with 10 mg of the photocatalyst. After irradiation of 50 min, the degradation efficiency was reached. Increasing the initial ion concentration of Phenol reduces photocatalyst degradation efficiency. Due to the squashed number of $OH^{\cdot}$ reduces the degradation capability. The path length of the photons entering the solution decreases as the initial concentration of phenol increases [12, 13]. From the observed results the photodegradation of phenol in the presence of ZnO doped TiO_2 decreases from 20 mg/L to 50 mg/l solution of Phenol. The maximum degradation of 70.86% is obtained at 10mg/L, so it was considered as an optimum level and it was prescribed for further studies.

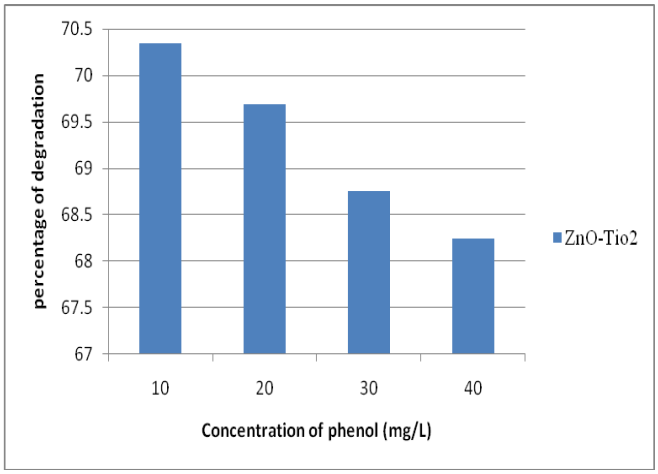

Fig. 5: Effect of phenol concentration

3.6. Effect of Catalyst Dosage on Phenol degradation

The photocatalytic degradation of phenol predominantly relies on the existence of a multitude of photocatalytic reactive sites taking part in the degradation reaction, so it is mandatory to find out the optimum amount of catalyst. To determine the effect of catalyst dose a set of studies was carried out by varying the amount of photocatalyst ZnO doped TiO_2 from 10-100mg/L.

From the above study, it was observed that degradation proceeding was substantially improved with increasing the amount of the photocatalyst up to a certain level, this is because of an increased number of active sites on ZnO doped TiO_2 surface. When UV irradiation occur with higher energy than the bandgap, the electron(e-) hole(h+) pair was generated in the valence and conduction band respectively [14,15]. These generated electron pairs can drift the surface of the catalyst where they degrade the adsorbed phenol molecules after oxidizing either by water to produce hydroxyl radical $OH^{\cdot}$. The higher amount of reactive hydroxyl radicals can be attributed to better degradation. The increased catalyst loading contributes a large number of binding with substrates (Phenol) molecules to adsorb on the catalyst surface so that 40mg/L ZnO doped TiO_2 photocatalyst degrade the 83.78 % of phenol and 40 mg is considered as optimum amount catalyst and it was recommended for further photocatalysis study.

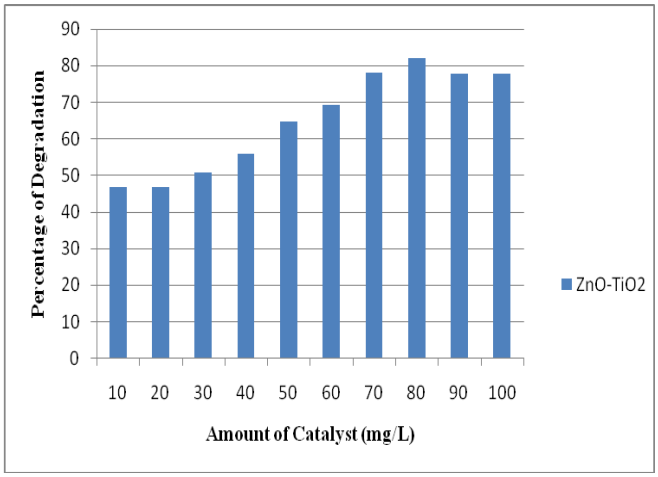

Fig. 6: Effect of Catalyst Dosage

3.7. Effect of pH with irradiation time on Phenol Degradation

The photodegradation of phenol was studied at three different pH (*i.e.* 3, 6 and 9) using ZnO doped TiO_2. The pH of the reaction mixture was adjusted using an aqueous solution of HNO_3 and NaOH. The degradation efficiency was increased with increasing pH and the degradation efficiency simply depends upon the Zero Point Charge (ZPC). pH (ZPC) of TiO_2 nanocatalysts is about 6 [16]. So the Catalyst surface is positively charged in acidic media, whereas it is negatively charged in alkaline pH. Generally, the hydrogen ion concentration changes will have a non-insignificant result not solely on the mode of sorption of the phenol substrate on TiO_2 surface, however conjointly on the property of the photo degradative reaction occurring on the particle surface chemical reaction reactions are sensitive to

changes within the surface potential. Moreover, at High initial pH, the number of Hydroxide ions (OH^-) present in the solution persuades the generation of hydroxyl free radicals (OH^-) which was obtained from photo-oxidation of OH^- by holes forming on the catalyst's surface. This Hydroxyl free radical acts as a dominant oxidizing species in photocatalysis, the photocatalytic perish of phenol is stimulated in alkaline medium [17, 18]. Hence in pH 3, the degradation percentage was increased from 10.78-68.53% and the maximum percentage was attained within 80 minutes of UV irradiation. The irradiation time also simultaneously increased from 0-80 min. This experiment was repeated to analyze the degradation efficiency at pH 6 and the obtained results are from 18.18-78.03 %, here also the maximum degradation attained at 80 minutes of UV irradiation. Further increase in pH, *i.e.* pH 9, has examined the degradation efficiency from 07.45-57.96 %. Here the degradation was increased with increased irradiation time but the degradation was reduced when compared to pH 6. From the above results, we have concluded that in pH 6, degradation of phenol was up to 78.03 % with 80 minutes of UV irradiation. This shows that acidic pH gives the maximum degradation [2]. The photocatalytic activity of phenol is increased with an extended duration of UV irradiation. The maximum degradation was obtained at a maximum irradiation time is 80 minutes of UV irradiation. The elongated UV irradiation encourages the interaction of phenol with photocatalyst which increases the degradation percentage of phenol.

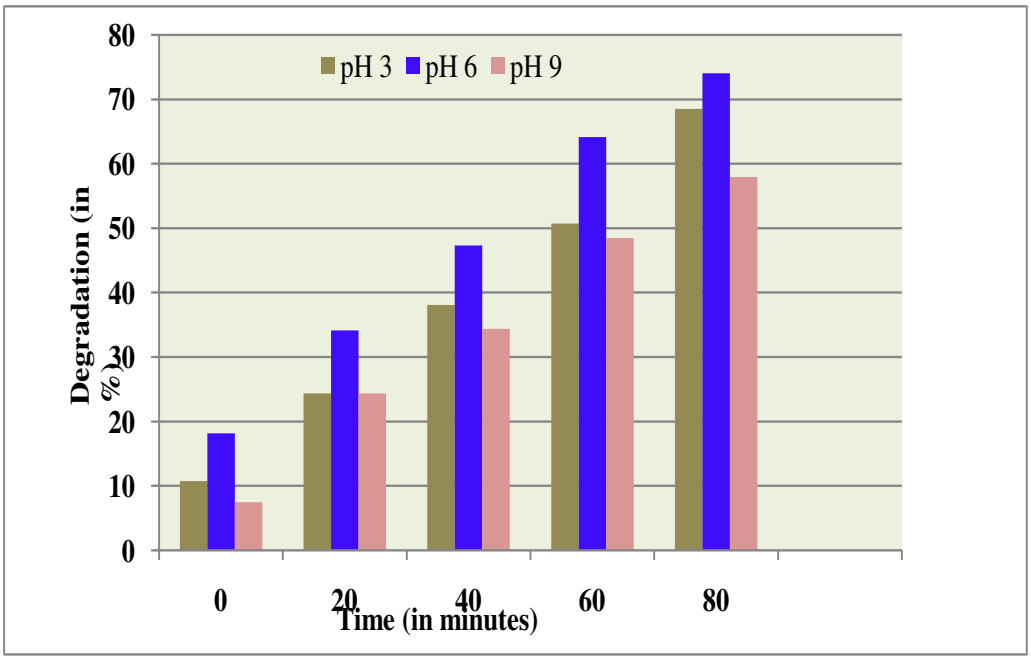

Fig. 7: Effect of pH with irradiation time

4. CONCLUSION

ZnO doped TiO_2 was successfully synthesized by the sol-gel method and characterized by XRD, SEM, FT-IR, UV-Vis spectroscopy. The presence of ZnO doped TiO_2 was confirmed by FT-IR. The ZnO doped TiO_2 nanoparticles were found to have high degrading efficiency of phenol, to analyze the degrading nature, the effect of initial ion concentration, effect of catalyst dosage, Effect of pH and irradiation time was examined. From the results, we came to know, at optimum phenol concentration 10mg/L it shows % degradation, at 40 mg of ZnO doped TiO_2 catalyst shows 83.78% of degradation, at optimum pH (pH 6) it shows 78.03 % degradation.

5. REFERENCES

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