Solid State Science and Technology, Vol. 25, No 2 (2017) 30-36
ISSN 0128-7389 | *http://journal.masshp.net*

THE EFFECT OF pH AND CATALYST LOAD ON THE PHOTOCATALYTIC PERFORMANCE OF $ZnO/TiO_2/N$ UNDER VISIBLE LIGHT EXPOSURE FOR PHENOL DEGRADATION

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ABSTRACT

ZnO/TiO_2 codoped N was synthesized by modified sol gel method with N molar ratio of 0.75% in order to study catalyst performance.The photocatalytic degradation of phenol was performed in lab scale reactor under 24 W visible light irradiation.The effect of pH and catalyst loading were studied. The degradation efficiency of phenol reached maximum of 56% and 70% within three hours light exposure at pH 5 and 3g/l catalyst load respectively. At optimum condition, the influence of catalyst load was posibbly contributed by an availability of active site that promote higher adsoprtion on catalyst surface.

Keywords: Photocatalysis; phenol degradation; $ZnO/TiO_2/N$ catalyst,visible light;

INTRODUCTION

Harmful effect of industrial phenolic effluent which heavily toxified water streamsand drinking water sources prompted scientis and environmentalists to look for sustainable remediation of this bio-recalcitrant substances . In the past few decades, the used of TiO_2 based photocatalytst culminated a sustainable technology that transforms the phenol and its derivatives into CO_2 and water. The destruction of the pollutant is basically governed by the combined actions of a semiconductor, an energetic radiation source and an oxidizing agent [1]. TiO_2 has been extensively used as a photocatalyst due to its highly potential photocatalytic activity but its downside is contributed by wide band gap and low quantum efficiency which requires intensive photon energy such as UV light to promote its photoexcitation [2]. Therefore, modification of photocatalyst is imperative to harness more abundant light source such as visible light to render its economical and sustainable application.

Several approaches have been proposed to enhanced sensitivity of TiO_2 to visible light largely by narrowing its band gap as well as increasing charge separation for efficient photocatalytic activity. In particular, doping with co-material such as ZnO, an anoxide semiconductor induced excess elextron hole pairs leading to superior photocatalytic activity, which in turns boosted oxidative and reductive reactions for mineralisation of

pollutant. However, ZnO experienced anodic dissolution under light exposure resulting rapid recombination of photogenerated electron hole pairs which curtailed its optimum performance [3]. Hence, studies tounted nitrogen as additional component in the composite to improve overall photocatalytic activity. Jintao et al.[4] demonstrated higher methyl orange degradation by N doped TiO_2/ZnO compared to TiO_2/ZnO due the to capability of N co-dopant to hinder the state transformation of anatase to rutile which is crucial in obtaining higher photocatalytic activity. Furthermore, nitrogen known to restrain recombination of the photoinduced electron thus enhancing the eficiency of the photocatalyst itself [5]. In this work, the photocatalytic activities of the photocatalyst ZnO/TiO2/N synthesis were demonstrated by the degradation of phenol under visible-light irradiation. The effect of catalyst loading and pH value on phenol removal were reported. Finally, the optimum conditions of these factors were determined.

EXPERIMENTAL

TTIP, phenol and concentrated ammonia were purchased from Sigma Aldrich Chemicals. Zinc acetate,ammonium nitrate acetic acid glacial and absolute ethanol were obtained from Merck. 4-aminoantipyrine and Potassium ferricyanide(III)($C6FeK_3N_6$) were obtained from PubChem.

Synthesizing TiO_2/ZnO doped N catalysts via sol gel method.
The zinc and titanium precursor solutions were prepared separately. TiO_2 precursor sol was prepared by mixing 30 mL of titanium(IV) isopropoxide with 100 mL ethanol absolute to form solution A. The solution was stirred for half an hour. In order to obtain ZnO and N precursor sol, a fixed amount of zinc acetate and ammonium nitrate were mixed with 90 mL deionized water and 10 mL acetic acid to form solution B then followed by stirring until all component dissolved completely. The starting materials ratio was equalised to 0.75% N dopant concentration. Then, solution B was added dropwise into solution A under vigorous stirring for 2 h in order to increase the solubility. The mixed sol was aged for 24 h at room temperature to form gel. The product was dried in an oven at 100°C for about 24 hours to evaporate the solvent and to remove the organic residuals. The crystal form of sample was then ground using mortar and pestle before calcination for 3 hours at 600°C with the heating rate of 3C°/minutes.

Photocatalysis experiment in batch stirred reactor
The photocatalytic activity of the synthesized catalyst was simulated with phenol as a model pollutant at atmospheric pressure and room temperature. Initially, a 100 ml of phenol solution with initial concentration of 10 ppm was mixed with 0.1 g of the catalyst in the photoreactor where pH of solution was adjusted to required value (pH 3, pH 5, pH 7) by adding of 0.1 M NAOH or 0.1 M HCI. In order to study the effect of catalyst loading, batch experiment were conducted with different catalyst loading between 0.2 g/l and 0.3/l g with initial pH of 5. The catalysts were later suspended in an aqueous solution of phenol in 100 ml beaker. The suspension was illuminated by a 24

Watt tornado lamp in a closed box. Prior to irradiation, the suspension was magnetically stirred in dark for 30 minutes to attain the adsorption-desorption equilibrium between the catalyst and the solution. Later, 5 ml of sample was taken out and analyzed. In order to maximize the energy exchange between the source of irradiation and reaction mixture, the lamp was positioned at the centre of the reactor with distance of 10 cm from phenol solution. After 30 minutes irradiation, 5 ml sample was taken out and centrifuge for 10 minute at 10000 rpm to separate catalyst and phenol solution. Consequently, the procedure was repeated after every 30 minutes until complete 3 hours reaction of lamp illumination.

Analytical method

The phenol concentration was analyzed by measurement absorbance at a wavelength of 510 nm following 15 min colour changing by 4-aminoantypyrine method. Then, the photodegradation efficiency can be calculated from the equation 1: All experiments were performed in triplicates. The phenol degradation efficiency can be calculated using formula as below:

$$\eta = \frac{[(c_0 - c_t)]}{c_o} \; x \; 100\% \qquad [1]$$

Where
η : phenol degradation efficiency
Co: concentration of phenol at initial time(before illuminate)
Ct : concentration of phenol at specific time

RESULTS AND DISCUSSION

Effect of pH on batch photocatalytic degradation of phenol under visible light

Previous study reported that the refinement in pH values influence the rate of photodegradation mainly by sorption–desorption process which took place at catalyst surface [6]. In this study, the degradation of phenol was investigated by varying pH from 3 to 7 using TiO_2-ZnO-N as catalyst with maximum dose of 1 g/L. The results in Figure 1 shows that percentage of phenol degradation increased with increasing pH value and then decreasing at pH 7. The highest photodegradation of phenol was observed at pH 5 which show 56.86% of degradation. However, decrease in pH value to 3, backroll the photocatalytic activity. It is believed that the declining activity in this condition reflects the abrupt fall-off in oxidation potential of catalyst itself.

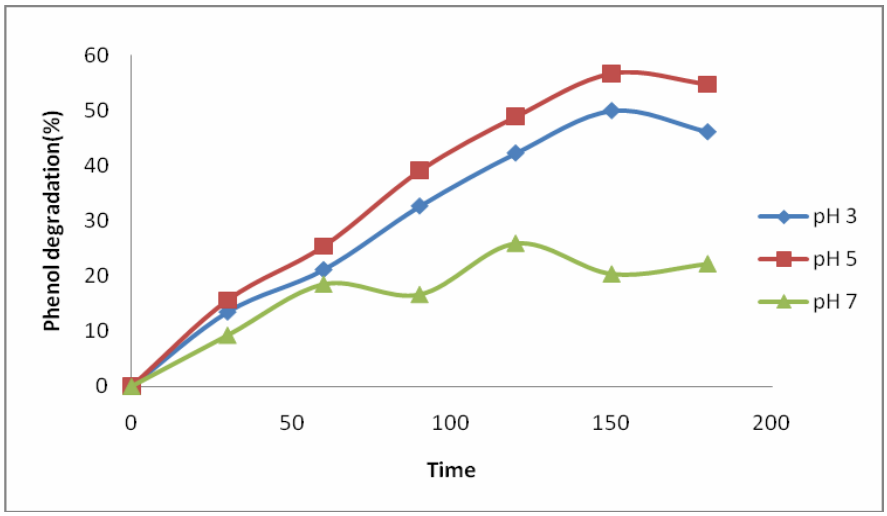

Figure 1: Effect of pH suspension on the percentage degradation of phenol after 180 min irradiation time under visible light.Condition:catalyst loading =1g/l;Co=10 ppm

These results are similar to those reported by [2] on the effect of pH on the photocatalytic degradation of phenol over TiO_2 photocatalyst under UV illumination. The observed trend were attributed to the oxidation species present (mainly positive holes) at lower pH. These oxidation species then reacted with hydroxide ions generated on TiO_2 surface to produce hydroxyl radicals. Therefore, reducing electron- hole recombination by these surface adsorbates trapped mechanism. Thus, the efficiency of the process is logically increased at acidic pH. Similar results also have been reported by [3][4]. The study determined that the rate of phenol degradation is faster at acidic pH condition under visible light irradiation.

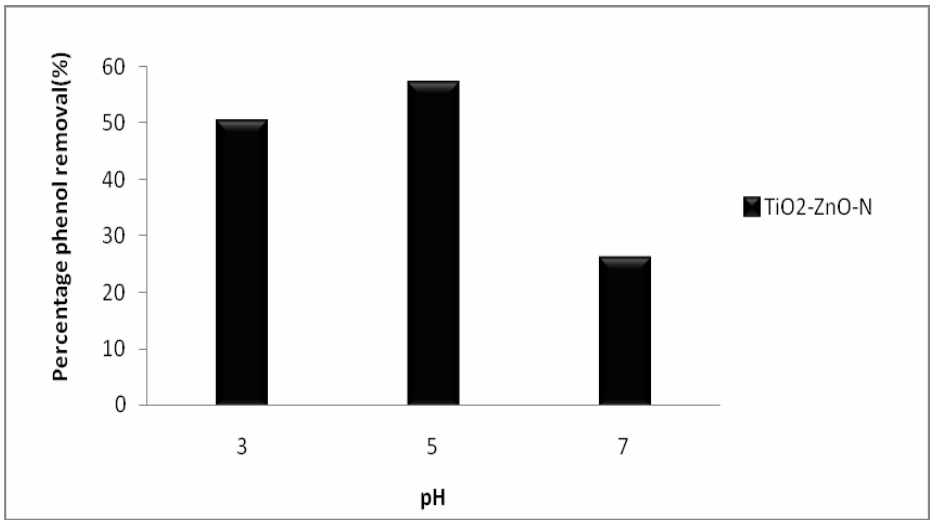

Figure 2: Percentage degradation of phenol obtained with different pH values under visible light.Condition:Co=10ppm;catalyst loading=1g/l

On the other hand, a significant loss of activity was observed at pH 7. Reduced photocatalytic activity in samples is observed under basic conditions as compared to acidic conditions. The catalyst performances was rapidly drop off up to 20 % . As in neutral condition, both of catalyst and pollutant will repel to each other as they bring the same charges. As in the basic conditions, surface of ZnO and TiO_2 is negatively charged as its point of zero charged lying at pH 8 and 6.5 respectively [7]. A possible reason for this trend is because the surface of catalyst would be positively charged at pH below its isoelctric point and negatively charged at pH higher than its isoelectric point [8]. As phenol molecules are also negatively charged, they will be experiencing repulsion leading to a lower adsorption of phenol on the surface of catalysts. As a result, the removal efficiency is retarded. These behavior may explain why that degradation seem to be slow in both acidic and neutral medium but optimum at pH 5. These results are in agreement with observations reported by [9].

Effect of catalyst loading on batch photocatalytic degradation of phenol under visible light

A number of studies indicated that the loading amount of catalyst is a significant factor in the photocatalytic degradation process. The photocatalytic efficiency could be strongly affected by the number of available active sites and rate of photoadsorption as extensively demonstrated in previous studies [10][11]. In this study, the amount of catalyst was varied from 1g/L to 3g/L per 100 ml of 10 ppm phenol solution. The effect is graphically depicted in Figure 3.

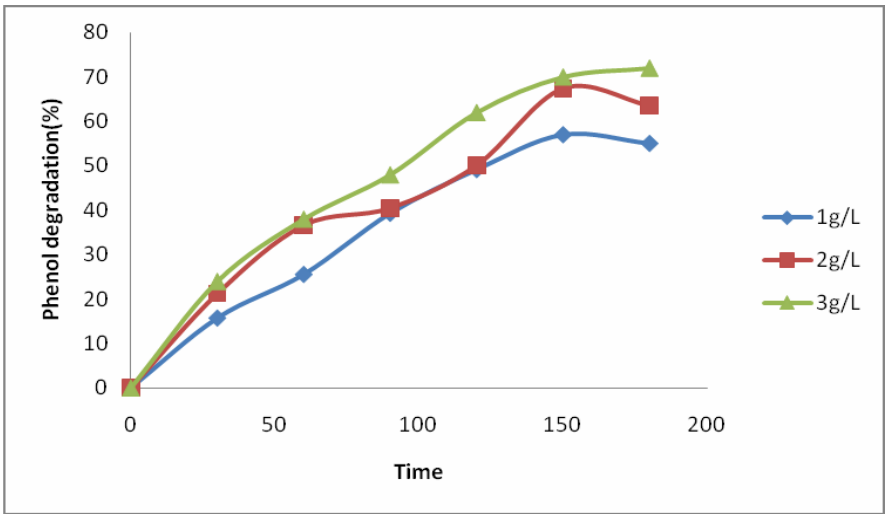

Figure 3: Effect of catalyst loading on the percentage degradation of phenol after 180 min irradiation time under visible light.Condition:pH =5;Co=10 ppm

With 1g/l catalyst, the rate of phenol degradation was 56%. When the catalyst loading was increased to 2g and 3 g/l, the rate of photocatalytic degradation was 67% and 70% respectively. The results indicate the significance increased in the rate of degradation

with the increase of catalyst loading from 1g/l to 2g/l. However, further increases in the catalyst loading up to 3g/l, did not show a significant increase in rate of degradation. A similar pattern was reported for photocatalytic degradation of phenol under visible light using various catalysts by [5][12].

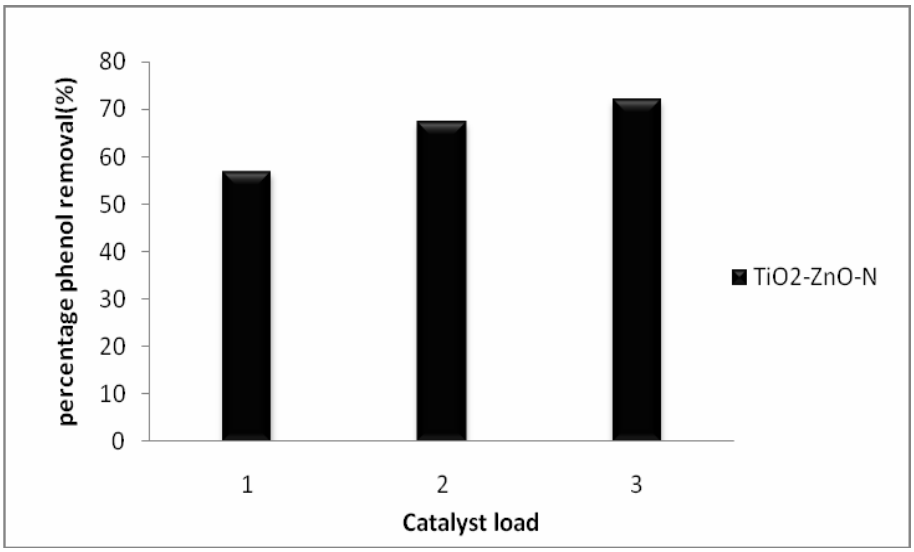

Figure 4: Percentage degradation of phenol obtained with different catalyst load under visible light.Condition:Co=10ppm;pH=5

Such efficient photocatalytic activity enhancement has been explained by a number of physical mechanisms.(i) The phenomenon is attributed to the increment of the average path length of a photon (the intensity of light that reaches the catalyst surface) as well as the enhancement of the unabsorbed photon dispersion. Thus, increase the rate of photo-adsorption of the utilized catalyst [10].(ii) The presence of abundant catalyst loading leading to greater absorption of pollutant molecules around the catalyst surface due to an availability of active sites. As a result, photodegradation is increased [13]. However, increasing catalyst concentration beyond the optimum value may minimize the rate of photodegradation. The phenomenon is attributed to the deactivation of activated molecules by collision with ground state molecules which consequently decrease the rate of radical production and less absorption of efficient photons was occurred. In particular, at some point, the presence of an excessive number of catalysts causes the particle to agglomerate which in turn reduce the surface area needed for photon absorption. In addition, the high solid suspension also impeded light penetration which is known as screening effect [14].

CONCLUSION

The study suggested that removal of phenol pollutant from synthetic wastewater during photocatalytic oxidation using synthesized photocatalyst were greatly affected by pH 5 and 3g/l catalyst loading. Hence, ZnO/TiO2/N catalyst could act as an excellent photocatalyst for phenol degradation under these optimum conditions.

ACKNOWLEDGEMENT

The work was fully funded by Ministry of Education Malaysia for research funding through RAGS GRANT (600-RMI/RAGS 5/3 (73 /2013)) .Authors would like thanks UiTM for facilities.

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