

The Influence of Ozone on The Photocatalytic Degradation of Phenol using TiO₂ Photocatalyst Supported by Bayah Natural Zeolite

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Abstract. Effect of ozone on the photocatalytic degradation of phenol using TiO₂ photocatalyst which supported Bayah Natural Zeolite has been investigated. Phenol (merk Pro analys) was used as waste solution. TiO₂ photocatalyst was obtained from Titanium isopropoxide using sol gel method which supported by Bayah Natural Zeolite. The influence of temperature of calcination and catalyst loading have been conducted. The calcination temperature of photocatalyst was 450 °C, 500 °C, 550 °C dan 600°C while the catalyst loading of 0,1g/L; 0,3 g/L; 0,6 g/L; 1 g/L dan 1,2 g/L. Analysis of phenol concentration was used Hach Spechtrophotometer. To determine the effect of ozone on photocatalytic degradation during process ozone was flowed into reactor. The result showed the optimum calcination temperature was obtained at 500°C. The optimum catalyst loading to degrade the phenolic compounds was equal to 1g/L. In these optimum condition the conversion of phenol degradation was 87% after 5 hours. By adding ozone during the degradation process, the conversion reached 100% after 2 hours.

Keywords: Bayah Natural Zeolite, Phenol, Photocatalyst, TiO₂, ozone

INTRODUCTION

TiO₂ is currently considered the most promising catalyst to completely decompose harmful organic compounds into CO₂ and H₂O under UV light irradiation. It has been widely studied for purification water, air and soil polluted with organic compounds [1-2] Some modifications on TiO₂ have been made to improve the photocatalytic activity, such as made into nanotubes morphology [3-4] for increasing their specific surface area and high surface free energy [5]. However pure TiO₂ nanoparticles are difficult to be recycled during their practical application [6,7]. Therefore some researchers has proposed to immobilized TiO₂ nanoparticles on a carrier to overcome shortcomings before mentioned [6,7]

Various substrates have been used as photocatalyst support for degradation of polluted water, such as alumina beads [7], glass and stainless steel [8], activated carbon [9-10], and zeolite [11-13], Illinoiu, E.C., et al 2013, Kamegawa, T., 2013). The combination of TiO₂ with adsorption properties of organic molecules onto some adequate adsorbent such as clays, zeolites with large surface areas, a synergims is gained, which leads to an enhancement of the reaction rate [6,12-13]. Among the mentioned supports, zeolites are supposed to provide an effective separation of photogenerated electrons and holes due to the electric field of their framework [14-15](Carp, O.et al, 2004, Nikazar, M., 2008)

This study has selected Bayah natural zeolites as the photocatalyst support due to their advantages over other conventional support material and also natural zeolite are cheap, abundant and easily available. In this paper, we report the photocatalytic oxidation of phenol over TiO_2 supported on zeolite and the effect of addition of ozone respectively.

MATERIALS AND METHODS

2.1. Catalyst Preparation

Activation of Bayah's Zeolite can be done by dilution in HF 2% (aqueous) to strip impurities. Followed by reflux of HCl 6 M and dilution with NH_4Cl 0.1 M. Filtered Bayah's Zeolite then calcined for 5 hours at 500°C . Activated Bayah's zeolite then combined with TiO_2 catalyst to get TiO_2 /zeolite composite using standard sol-gel route prepared from TEOS solution.

2.3. Photocatalytic Activity

Photocatalysis was performed inside a square batch reactor complemented with a magnetic stirrer under UV illumination from 6 Black Light Lamps (10 watt each). Evaluation was taken to seek influence of calcined temperature, catalyst loading, initial concentration of phenol liquid, addition of activated Bayah's zeolite as a support for TiO_2 catalyst, and also implementation of ozonation process. C/C_0 parameter was used as a starting point to make the difference of decreasing concentration become clear.

RESULTS AND DISCUSSION

3.1. Characterization

The BET surface area of natural zeolite and synthesized photocatalysts are summarized in Table 1. An increase in the surface area of the natural zeolite is observed after the activation process. This is due to the process of soaking with acid (HCl) which caused the zeolite to become acidic and contain Cl^- ions, and then Cl^- ions reacted with aluminum to form AlCl_3 . This process caused dealumination, which reduced the aluminum [16-17]. The specific surface areas of the composites increased with the presence of TiO_2 as presented in Table 1.

Table 1. Summary of the BET surface area of natural zeolite and photocatalysts

Sample	Surface Area (m^2/g)
Natural Zeolite	34
Natural Zeolite after Activation	124
TiO_2 sol gel	200
TiO_2 Supported Zeolite	225

The comparative SEM images of the natural zeolite before and after the activation process are presented in Fig. 1.

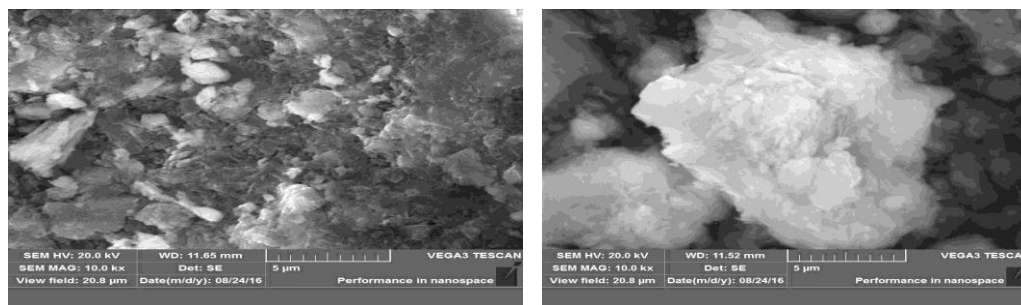


Fig. 1. SEM image of natural zeolite (a). Before activation, (b) after activation.

Fig. 1 shows significant difference between zeolite before activation and after activation. It seems zeolite after activation had more pores than zeolite without activation. It also presented at Table 1, before activation process the surface area of zeolite was $34 \text{ m}^2/\text{g}$, and after activation process the surface area was increasing 4 times higher than before.

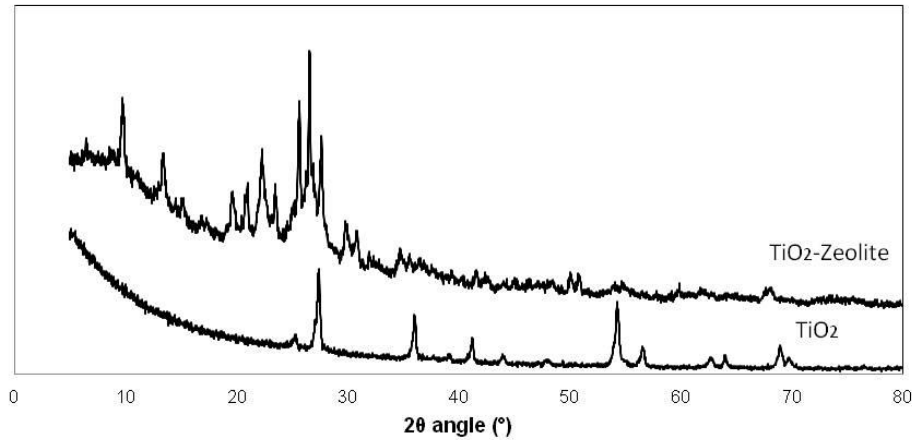


Fig. 2. XRD patterns of TiO_2 and TiO_2 supported zeolite

Fig 2 shows pattern of TiO_2 sol gel and TiO_2 supported zeolite. The TiO_2 from sol gel process showed typical defraction patterns to attributed to the (101) phase of an anatase structure at around 26° .

3.2. Adsorption tests.

Adsorption tests were examined by determinng effects of activation process in order to phenol waste adsorption. 0.3 gram of zeolite sample diluted in 300 ml of phenol aquous (10 mg.L^{-1}) at square batch reactor for 5 hours operation. For every 1 hour, sample of waste taken to analyzed.

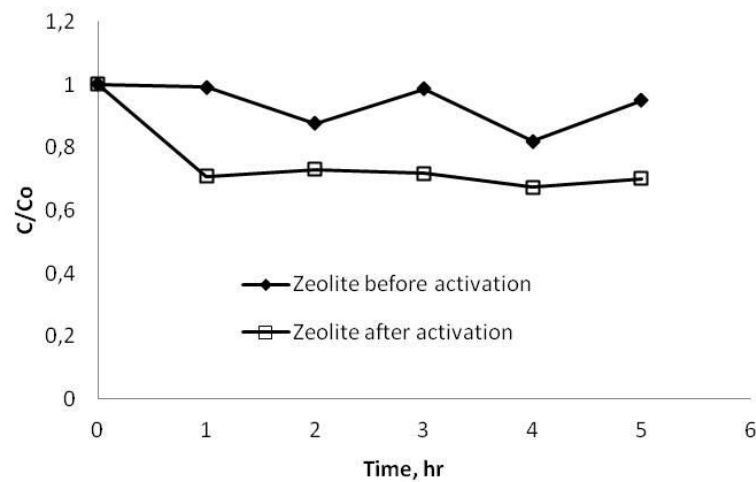


Fig. 3 Effect of activation process on phenol adsorption

As depicted in Fig. 3, activation of Bayah's zeolite significantly impacted adsorption of phenol liquid. First hour is the highest rate of waste adsorption whereas for the next hours adsorption of phenol remained constant. On the contrary, non-activated Bayah's zeolite proved instabilisation of adsorption process. Instabilisation exhibited to due adsorption – desorption process, once active site of Bayah's zeolite surface saturated, there are several phenol were desorpted from surface and left zeolite active site and increasing waste concentration.

Higher adsorption rate at Fig. 3 also proved that activation process could leached zeolite impurities at its surface by acid dilution (HF 2%). Impurities were diluted among acid solution and left zeolite surface. Activation process effected a higher number of active site due to impurities free. Dimension of activated zeolite surface also influenced adsorption process. When diameter of zeolite active site less than phenol molecule, waste molecules were harder to adsorpted. Conversely, when diameter of zeolite active site existed bigger after activation process, phenol molecules were easier to penetrate zeolite active site .

Leached zeolite surface could increasing hydrophobicity of bayah's zeolite. Among the impurities of bayah's zeolite surface, alumina compound were diluted by acid solution which made Si/Al ratio bayah's zeolite rose. Elevated Si/Al ratio caused an isomorphiic substitution that opted nonpolar molecules such as phenol to be adsorpted rather than polar molecules like water.

3.3. Photocatalytic reaction

Composite TiO₂/zeolite prepared by standard sol-gel route using TEOS as precursor of TiO₂. Degradation rate of phenol evaluated for 300 ml waste volume and 0.3 grams of activated bayah's zeolite.

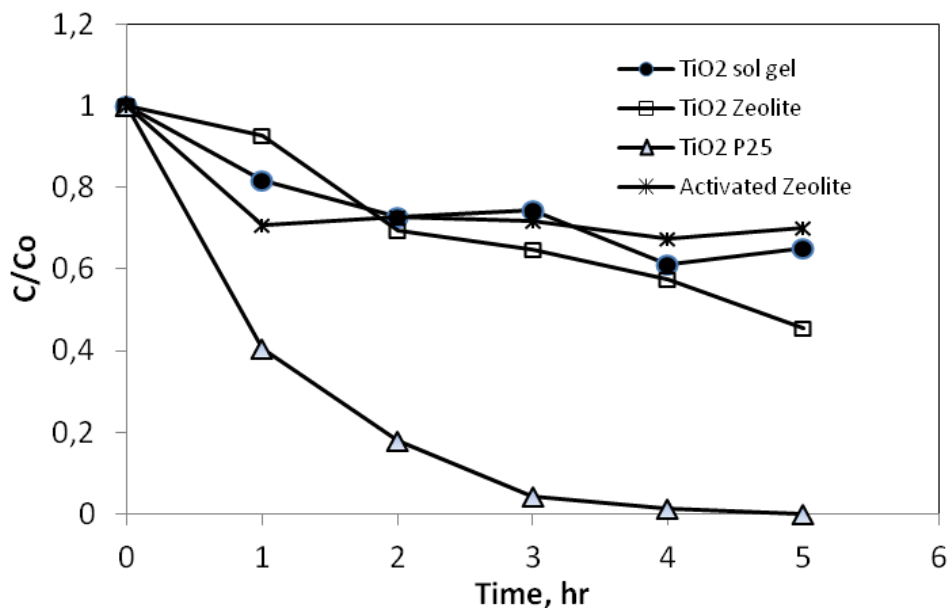


Fig. 4. Photocatalytic degradation of phenol over TiO₂ sol gel, TiO₂ Zeolite, TiO₂ P25 and adsorption of phenol over activated zeolite.

Fig 4 shows composite TiO₂/zeolite performed better compared to activated bayah's zeolite (29.9%) only or TiO₂ made from sol-gel path (34.9%) with total degradation of phenol reached 54.44%. Both of activated bayah's zeolite and TiO₂ sol-gel has poor capability for phenol degradation. Combining material instead, necessary improved potential of phenol degradation. Since activated bayah's zeolite had a good adsorption capability to collect phenol molecules onto zeolite surface, TiO₂ particles which bound to zeolite surface could directly oxidized phenol molecules into CO₂ and H₂O and made activated zeolite last longer to be saturated.

The trend also happened on others work [15] that proved zeolite was a good adsorbent for photodecomposition of propylamide, propionaldehyde, and pyridine. Composite $\text{TiO}_2/\text{zeolite}$ could not surpass commercial TiO_2 performances because of the impurities either from zeolite or other phase TiO_2 growth by sol-gel path.

The effects of calcined temperature of TiO_2 sol-gel catalyst are also shown in Fig 5. Calcined temperature required to be evaluated were 450°C, 500°C, 550°C, 600°C for TiO_2 catalyst made from standard sol-gel route.

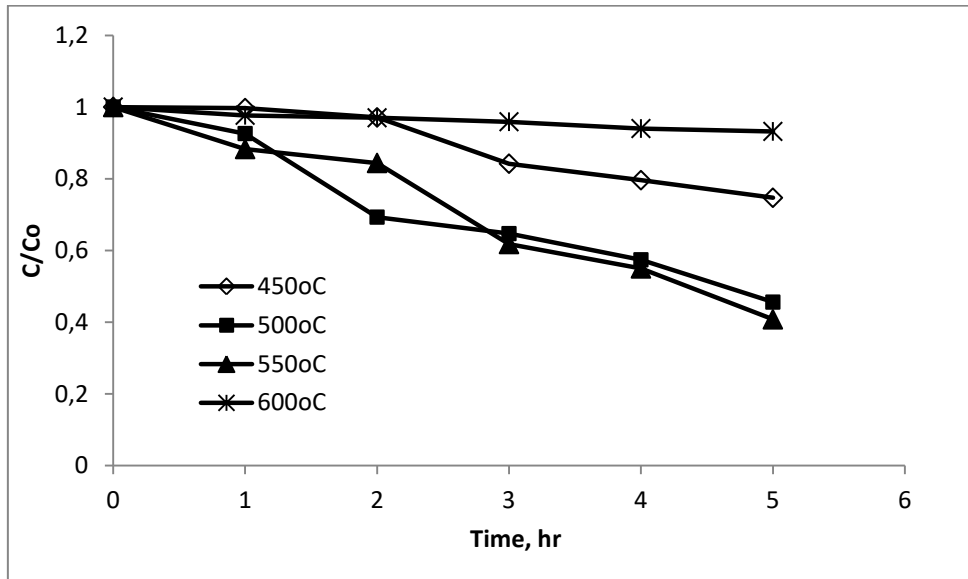


Fig.5. Effects of calcined temperature on photocatalytic degradation of phenol

Crystal growth of TiO_2 played important roles in order to phenol degradation. TiO_2 particles has various phase involving : Anatase, Rutile, and Brooklite. TiO_2 photocatalysis performed best by anatase phase. Anatase phase initially growth from temperature of 120°C to 500°C, whilst rutile could be found when its calcined at 700°C.

Fig. 5 shows relation between calcined temperature and degradation rate of phenol. Generally, degradation rate of phenol achieved good results at calcined temperature varies from 500°C to 550°C with total phenol degradation seized to above 50% (Figure 3b). Conversely, when calcined temperature attained 600°C degradation rate exhibited only around 6%. It has been proved that 550°C was the best calcined temperature of TiO_2 growth. For this particular experiment, temperature of 500°C was an optimum. Due to economical point of view, increasing 50°C degree for alter ~5% degradation rate was insufficient.

Fig 6 shows the effect of loading composite TiO_2 zeolite on photocatalytic degradation of phenol. Liquid phenol was degraded using catalyst which had been made from sol-gel path at calcined temperature of 500°C. Catalyst loading for evaluation range from 0.1 g.L^{-1} to 1.2 g.L^{-1} .

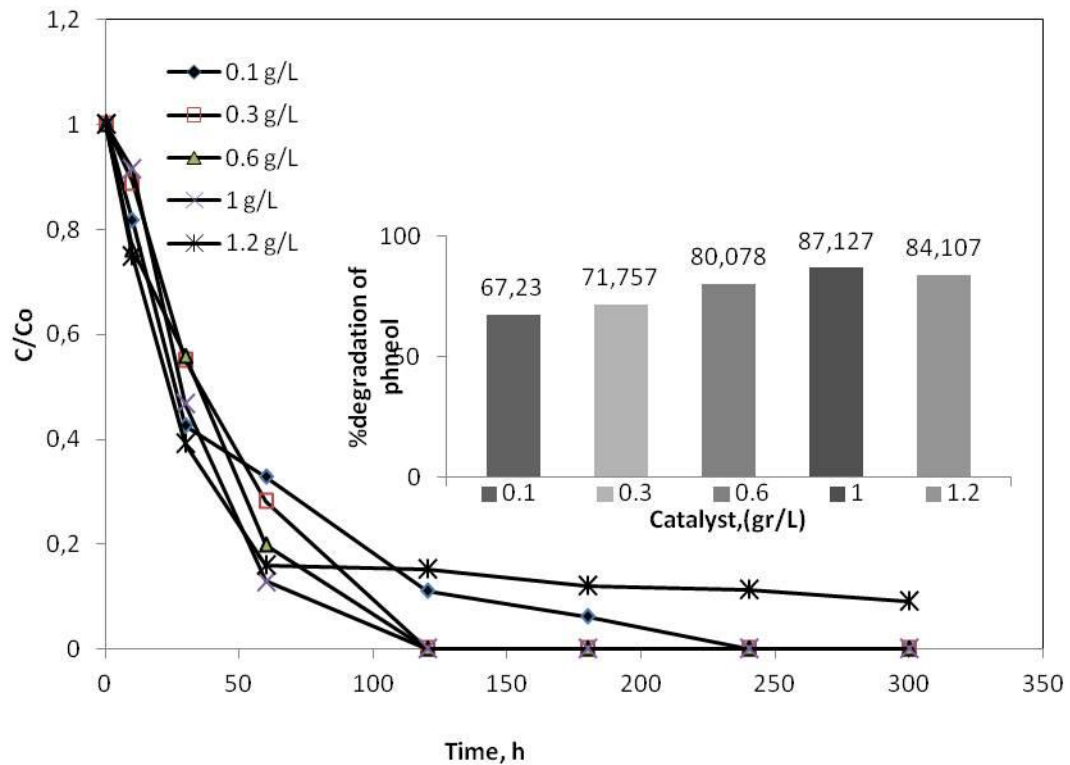


Fig. 6. Effects of catalyst loading on photocatalytic degradation of phenol

Fig 6 shows the optimum loading catalyst for phenol degradation was 1g/L with total phenol degradation achieved 87.1%. Increasing catalyst loading up to 1.2 g.L⁻¹ conversely total degradation phenol after 6 hours operation same as reducing catalyst loading down to 0.1 g.L⁻¹. Lowering catalyst loading impacted imbalance of number TiO₂ that could be attached on zeolite surface. Therefore, oxidation of phenol got slower. On the other hand, the higher catalyst loading intake on phenol liquid and catalyst mixture, the higher oxidation reaction performed. Oxidation of phenol would produced intermediates compound before transformed into CO₂ and H₂O. Higher oxidation rate would prevent UV illumination through TiO₂ particles in order of higher turbidity of liquid waste.

Fig 7 shows the effect of initial concentration of phenol on photocatalytic degradation. Composite TiO₂/zeolite were tested on various initial waste concentration to evaluate maximum amount of phenol waste which could be handled for 5 hours operation until 100% conversion to CO₂ and H₂O.

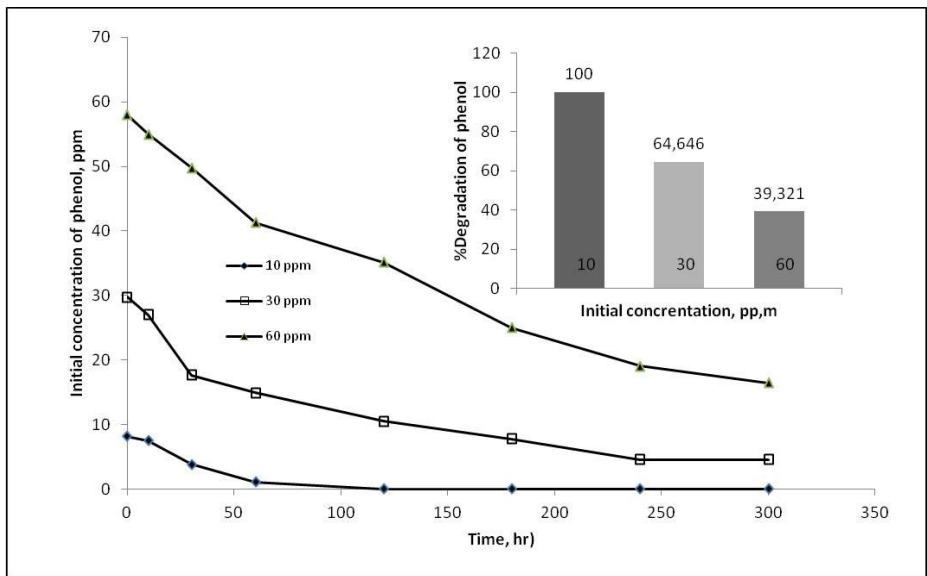


Fig.7. Effects of initial concentration of phenol on % photocatalytic degradation

As seen in Fig.7 increasing initial waste concentration will reduce effectiveness of TiO_2 /zeolite catalyst performance. Insufficient effectiveness caused by imbalance between the amount of waste (phenol aqueous) to number of catalyst agent (TiO_2 /zeolite). Smith et.al (1992) proved higher initial concentration was effected to molecular size of phenol as it turned intensified to the active site of zeolite surface which remain constant. Consequently, phenol molecules were harder to attached to zeolite surface and taken more time to react with TiO_2 particles. Also, high initial concentration could penetrate higher oxidation rate to produce intermediates compound that resisted UV lights to stimulate further reaction of photocatalysis. 100% degradation rate of liquid phenol obtained for 10 mg.L^{-1} initial concentration.

Addition of ozonation process performed to determined the impact of overall process and evaluate overall composite catalyst performances. Catalyst loading that had been used for experimentation was 1 g.L^{-1} for 300 ml phenol liquid. Batch reactor supplemented with ozonator as an ozone gas producer.

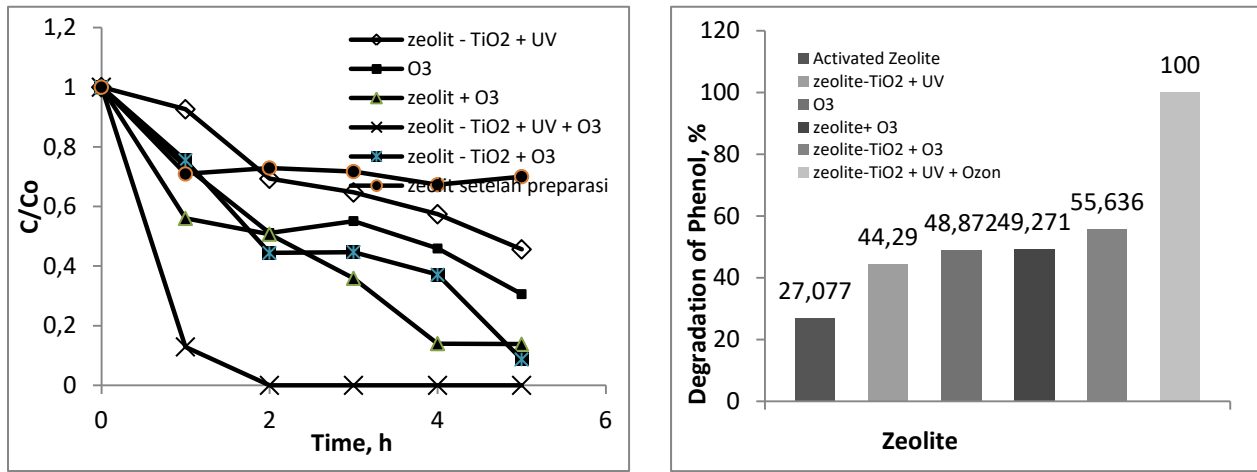


Fig 8. Effect of addition ozone on photodegradation phenol

Fig. 8 shows that combination of conventional oxidation process using TiO₂/zeolite composite with ozonation process exhibited most promising path to alter overall process effectiveness. Graph on Figure 6a showed after 2 hours operation, 100% of phenol aqueous were degraded into CO₂ and H₂O.

Upon photocatalytic ozonisation process (TiO₂/zeolite catalyst + UV + ozonator), ozone helped activated zeolite for degrading phenol compound and producing OH[•]. Phenol compound which had not been adsorbed to zeolite surface will immediately reacted with ozone. When desorption occurred at saturated condition of zeolite active site, OH[•] radicals produced by ozone helped phenol oxidation that will increase effectiveness of degradation process as observed in Sanchez-Polo et.al (2005) experiment.

Ozone had functioned as electron trapper and could directly transformed phenol molecules into CO₂ and H₂O as it prevented recombination of holes and electrons. The number of holes available could react with water molecules instead and produced OH[•] radicals. OH[•] radicals produced significantly increased as it continuously will degrade phenol molecules into CO₂ and H₂O molecules.

CONCLUSIONS

Activation process of natural bayah's zeolite as a support indeed altered overall performances of photocatalysis TiO₂/zeolite composite. Demonstration from several effects of variable also influenced overall photocatalysis TiO₂/zeolite performances, such as calcined temperature optimum at 500°C. 10 mg.L⁻¹ concentration of phenol aqueous could be completely degraded into CO₂ and H₂O molecules using catalyst loading of 1 g.L⁻¹ after 5 hours operation whilst combination of standard photocatalysis process with ozonisation significantly effected conventional method which resulted less than half normal operation time (2 hours operation) taken to degrade 100% of 10 mg.L⁻¹ phenol aqueous.

ACKNOWLEDGEMENT

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