Environment and Natural Resources Journal 2019; 17(2): 87-95

Catalytic Ozonation using Iron-Doped Water Treatment Sludge as a Catalyst for Treatment of Phenol in Synthetic Wastewater

Apiradee Sukmilin[1], Banjong Boonchom[1] and Chalor Jarusutthirak[2*]

[1]Department of Chemistry, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang,
Bangkok 10520, Thailand
[2]Department of Environmental Technology and Management, Faculty of Environment, Kasetsart University,
Bangkok 10900, Thailand

ARTICLE INFO

Received: 16 Nov 2018
Received in revised:
14 Dec 2018
Accepted: 17 Dec 2018
Published online:
28 Jan 2019
DOI: 10.32526/ennrj.17.2.2019.15

Keywords:
Catalyst/ Ozonation/ Phenol/ Trivalent iron/ Water treatment sludge

*** Corresponding author:**
E-mail: ecclj@ku.ac.th

ABSTRACT

In this study, iron (Fe)-doped water treatment sludge, designated as Fe/WTS, was prepared by a hydrothermal method using phosphoric acid and impregnation with ferric nitrate. The results from X-ray diffraction (XRD) confirmed the presence of Fe loaded on the WTS support, while Brunauer-Emmett-Teller (BET) analysis indicated an increase of specific surface area of the WTS from 37.37 m^2/g to 118.51 m^2/g after acid modification. The Fe/WTS was successfully used as a catalyst in catalytic ozonation for degradation of phenol in synthetic wastewater. Factors affecting phenol removal efficiency including reaction time, pH, catalyst dosage, and Fe content were investigated. At the optimum condition, i.e., reaction time of 120 min, pH of 11, catalyst dosage of 1 g/L, and Fe content of 2% (w/w), the removal efficiency of phenol was 99.16% which was higher than that of sole ozonation (44.61%). The results of kinetic analyses indicated that the reactions of catalytic ozonation in the presence of Fe/WTS and WTS catalysts followed pseudo-first order kinetic model with rate constants of 0.0362 and 0.0065 min^{-1}, respectively, while that of sole ozone was 0.0046 min^{-1}. This finding presented the potential use of Fe/WTS as a novel catalyst for catalytic ozonation.

1. INTRODUCTION

Water treatment sludge (WTS) is a by-product from water treatment process. Usually, WTS is classified as a waste material. The management of WTS has become an increasingly important environmental issue. A large amount of WTS from water supply process causes high cost of disposal. Therefore, the utilization of WTS for more valuable application is still challenging. Many researchers have attempted to use WTS as a beneficial material for various applications such as agriculture, ceramic production, and geo-polymer because its properties are similar to clay (Vinitnantharat et al., 2010; Kizinievic et al., 2013). The study of WTS composition found that the properties of WTS were equivalent to those of kaolin (Sirifhognugoon, 2000). Kaolinite is one type of clay with a major mineral component of kaolin, containing quartz, mica, and feldspar (Panda et al., 2010). From the literature, kaolinite can be used as a catalyst in catalytic ozonation which accelerates ozone mass transfer compared with ozone alone, leading to enhancement of organic degradation (Li et al., 2009). Porous materials such as granular activated carbon, zeolite, and acid activated clay can be used as supports for metal oxides. These materials as catalysts have shown satisfactory applications for enhancing the performance of ozonation (Lan et al., 2013). Thus, as the structure of WTS is similar to that of kaolin, it is interesting to utilize the WTS as a catalyst support in catalytic ozonation. However, modification of the WTS surface properties is required to achieve better performance of the WTS as a catalyst support.

Acid activation has been widely used as a chemical treatment method to improve the surface and catalytic properties of fibrous clay such as kaolin and smectite (Panda et al., 2010). The method involves leaching of the clays with an inorganic acid such as hydrochloric, nitric, and phosphoric acids causing disaggregation of clay particles, elimination of mineral impurities, and dissolution of the external layers (Shahidi et al., 2015). Hence, this process will change the chemical composition and the structure of clay (Belver et al., 2002). The acid treatment is beneficial in terms of increased surface area, porosity, and the number of acid centers with respect to the parent clay. From a previous study, acid activation using sulfuric acid provided more increased porosity

https://doi.org/10.32526/ennrj.17.2.2019.15

than using hydrochloric acid (Panda et al., 2010). However, both sulfuric and hydrochloric acids may cause environmental problems. Phosphoric acid is interesting to use for acid activation of clay because it opens up pores, increases surface area, reduces or eliminates diffusion resistance in the catalysts, and especially, it is environmental friendly (Ayodele et al., 2012). For these reasons, phosphoric acid was selected to modify WTS.

Heterogeneous catalytic ozonation is a powerful treatment method which increases removal efficiency of ozonation. This process is catalyzed by solid catalysts, such as metals, metal oxides, and metals on supporting materials (Shahamat et al., 2014). In this process, ozone is decomposed to generate hydroxyl radicals ($OH^{\bullet}$), which possess high rate constants with phenols (He et al., 2008). Among these, Fe-based catalyst exhibits high activities for decomposition of ozone and generation of hydroxyl radicals (Lolita et al., 2009). Fe-based catalysts have been widely used in wastewater treatment because it is efficient and environmentally friendly (Li et al., 2018a). In this study, Fe-doped WTS (Fe/WTS) prepared by wet impregnation was used as a catalyst in catalytic ozonation.

Phenol is known as a hazardous pollutant found in aqueous effluents from various industries such as petrochemical plants, petroleum refining, and plastics industries. It is considered as a refractory organic compound by the U.S. EPA with high toxicity and carcinogenic properties (He et al., 2008). Conventional biological processes represent an environmentally friendly way of treatment with reasonable cost, however, they are not adequate to treat such a toxic and refractory compound, otherwise, a long residence time for microorganisms is required. Thus, there is a need to use effective strategies of treatment to achieve a high-quality effluent prior to discharge to natural receiving water (Farzadkia et al., 2014).

In this research, phenol was used as a model pollutant in synthetic wastewater to be degraded by catalytic ozonation in the presence of the Fe/WTS catalyst. The WTS was modified with phosphoric acid during a hydrothermal process and trivalent iron as ferric nitrate was loaded into the WTS support. The prepared Fe/WTS was used as a catalyst in catalytic ozonation for degradation of phenol in synthetic wastewater. The objective of this study was to evaluate the feasibility of Fe/WTS as a catalyst in catalytic ozonation for the degradation of phenol. Factors affecting catalytic ozonation, including pH, % of Fe doped, and catalyst dosage, were investigated. The reaction kinetics of catalytic ozonation catalyzed by Fe/WTS and WTS were analyzed and compared with that of sole ozonation. The results from this research demonstrate the successful utilization of Fe/WTS in catalytic ozonation which might be applicable to degrade other phenolic compounds contained in wastewater and can be used as a pre-treatment method for conventional biological processes.

2. MATERIALS AND METHODS

2.1 Materials

All reagents used in this experiment including phenol (C_6H_5OH), ferric nitrate ($Fe(NO_3)_3$), sodium hydroxide (NaOH), sodium thiosulfate ($Na_2S_2O_3$), potassium iodide (KI), phosphoric acid (H_3PO_4), and hydrochloric acid (HCl) were analytical grade. Tert-butanol (C_4H_9OH), was used as a free radical scavenger to confirm the performance of hydroxyl radical ($OH^{\bullet}$) in degradation of phenol. Sodium thiosulfate was used to quench residual ozone, while potassium iodide was used to determine ozone concentration and to trap unreacted ozone.

2.2 Catalysts preparation and characterization

WTS was collected from the sludge dewatering process of a water treatment plant. After seven days of natural drying, the WTS was pulverized and sieved through a mesh, equivalent to a particle size less than 150 microns. The prepared WTS was used as a catalyst in control experiments of catalytic ozonation and as a support for doped iron. The so-called iron-doped WTS (Fe/WTS) was prepared by treating 10 g of WTS with 25 mL of 5 M phosphoric acid and then treated by a hydrothermal method at 100 ^{o}C for 2 h. The reaction was immediately quenched by adding iced water. The acid-modified WTS was centrifuged and washed several times with distilled water to remove unspent acid until the solution pH became 4.5 to 5. The acid-modified WTS sample was dried in an oven at 60 ^{o}C for 16 h prior to grinding into a powder form. Trivalent iron was loaded onto WTS support by wet impregnation method. Ferric nitrate at varying concentrations of 1, 2 and 3% (w/w) was added into 10 g of acid-modified WTS samples, then sonicated for 30 min. After that, samples were calcined at 550 ^{o}C for 2 h and stored in a desiccator before use. WTS and Fe/WTS catalysts were characterized by X-ray diffraction (XRD, Philips X-Pert-MPD, Malvern Panalytical, UK) for investigation of crystalline materials and by Brunauer, Emmett, and Teller (BET, Autosorb-1-C, Quantachrome, USA) analysis for specific surface area.

2.3 Ozonation experiment

Ozone was generated by a laboratory ozone generator using oxygen from air pump as raw material. The ozone generation rate measured by iodometric method was 0.57 mg/min. Ozonation experiments were carried out in batch mode using a cylindrical reactor. In a typical catalytic ozonation procedure, 1 g/L of Fe/WTS catalyst was mixed with 2.7 L of phenol sample at an initial concentration of 50 mg/L. Then, the ozone flow was introduced into the reactor via air diffusers. Aliquot samples of 50 mL were collected at the specified time. A few drops of sodium thiosulfate solution were added to quench the residual ozone. Ozone concentration was measured by standard iodometry (Rice et al., 2017), whereas phenol concentration was determined by colorimetric method using a spectrophotometer at a wavelength of 510 nm (Li et al., 2018a). All experiments were performed in triplicates. Data presenting in figures and tables were average calculated from three initial values.

2.4 Analytical method

The prepared catalysts were characterized by X-ray diffraction (XRD, Philips X-Pert-MPD, Malvern Panalytical, UK) for investigation of crystalline materials. BET surface area of catalysts was determined by BET (Autosorb-1-C, Quantachrome, USA). Ozone generation rate was measured by an iodometric method using 2% KI solution for the absorption of ozone gas, then, subsequently measuring the ozone using sodium thiosulfate titrant. The concentrations of phenol were determined by a 4-aminoantipyrine procedure using colorimetric quantitation with a UV-vis spectrophotometer (Shimadzu UV-1700, Japan) at a wavelength of 510 nm pH was measured using a pH meter.

3. RESULTS AND DISCUSSION

3.1 Characterization of WTS and Fe/WTS

Characteristics of WTS and Fe/WTS were investigated by XRD, as shown in Figure 1. The XRD pattern of WTS exhibited two well-defined characteristic peaks of kaolinite at 2θ values of 25°, corresponding to the reflections from [0 0 1] and d values of 7.154 Å (Ayodele et al., 2012). According to Figure 1, the XRD pattern of Fe/WTS exhibited more crystallinity than WTS. It can be explained that acid modification of the WTS caused structural disorder which distorted the crystallinity of WTS and disintegrated its layered structure (Ayodele, 2013). Diffraction peak 2θ values of 33.14°, 35.61°, and 54.34° were observed which corresponded to Fe_2O_3 (Ma et al., 2009). This finding indicates that most of the Fe_2O_3 was attached to the WTS surface and changed its structure to crystalline. The results from BET analysis revealed that the specific surface area of Fe/WTS was 118.51 m^2/g while that of WTS was 37.37 m^2/g. The increase of surface area of Fe/WTS was caused by acid modification using phosphoric acid that opened up the WTS pore volume and increased WTS surface area (Ayodele et al., 2012). These results confirmed that acid activation of WTS led to higher specific surface area and turned WTS into a more crystalline structure with Fe-species loaded into the structure.

3.2 Effect of catalyst type

The prepared 1% Fe/WTS and WTS catalysts were used during catalytic ozonation for degradation of phenol. Compared with the control experiment using ozonation alone, as shown in Figure 2, it was found that at 60 min and pH of 11, the use of Fe/WTS and WTS as catalysts in catalytic ozonation removed 64.30% and 42.77% of the phenol, respectively, while the percent removal using ozonation alone was only 27.78%. The presence of Fe in Fe/WTS catalyst facilitated ozone decomposition to enhance degradation of phenol. These results correspond with previous reports in the literature (Li et al., 2009; Chen et al., 2016; Peng et al., 2018). It can be explained that, in the presence of Fe/WTS as a catalyst, hydroxyl radicals ($OH^{\bullet}$) played a key role in the degradation of phenol according to Equation 1-3 (Chen et al., 2016; Wang and Bai, 2017). As a result, the Fe/WTS catalyst was successfully used to degrade phenol compared with using WTS catalyst and sole ozonation.

$$\equiv FeOH \longrightarrow \equiv FeO^{-} + O_3 \longleftrightarrow \equiv FeO(O_3)^{-} \quad (1)$$

$$\equiv FeO(O_3)^{-} \longleftrightarrow \equiv FeO^{\bullet} + {}^{\bullet}HO_3/{}^{\bullet}O_3^{-} \quad (2)$$

$$\equiv FeO^{\bullet} + H_2O \longleftrightarrow \equiv FeOH + OH^{\bullet} \quad (3)$$

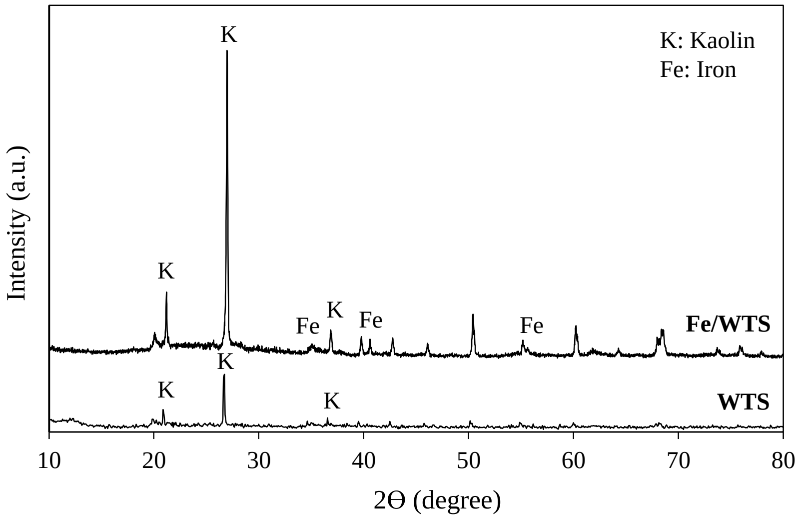

Figure 1. XRD patterns of WTS and Fe/WTS catalysts

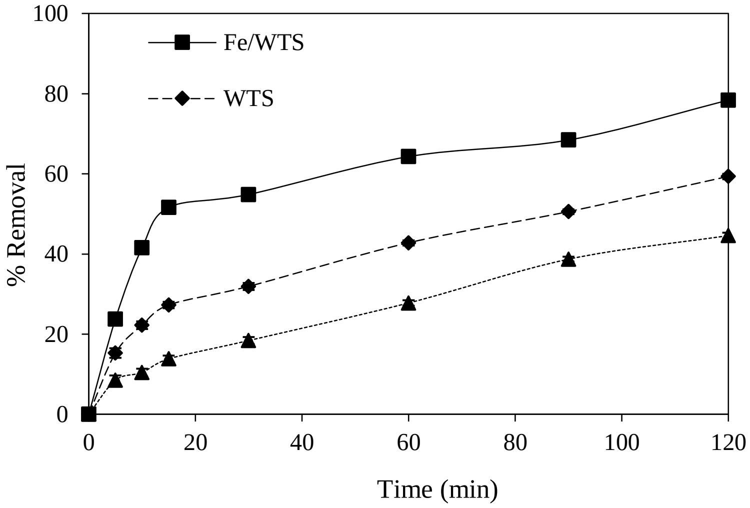

Figure 2. Degradation of phenol by catalytic ozonation using different WTS-based catalysts compared with sole ozonation (Experimental conditions: O_3 generation=0.57 mg/min, [Phenol]=50 mg/L, [Fe/WTS]=1 g/L, Fe content=1%, [WTS]=1 g/L, solution pH=11)

3.3 Effect of initial pH

The solution pH is an important factor affecting ozone decomposition because hydroxide ion (OH^-) was found to be an initiator of the chain reaction in the ozone decomposition process (Qi et al., 2012). In this research, the effect of solution pH on the degradation of phenol by catalytic ozonation using 1% Fe/WTS catalyst at a dosage of 1 g/L were investigated. As shown in Figure 3, as the solution pH increased, the degradation of phenol increased. At 120 min and pH of 3, 7, and 11 removal efficiencies of phenol by using Fe/WTS as a catalyst in ozonation were 42.23, 66.16, and 78.39%, respectively. It can be explained that the pH_{pzc} of Fe/WTS was 7.16, therefore, most of its surface hydroxyl groups are deprotonated when the pH was higher than 7.16. According to a previous study, a negatively charged surface had a strong reactivity to ozone, and hydroxyl radicals ($OH^•$) were generated from the reaction of deprotonated surface hydroxyl groups ($\equiv FeO^-$) and O_3 through Equation 1-3 (Chen et al., 2016). Therefore, increasing pH promoted ozone decomposition and formation of the powerful hydroxyl radical ($OH^•$) which reacted with phenol and its by-products in non-selective mode (Li et al., 2009).

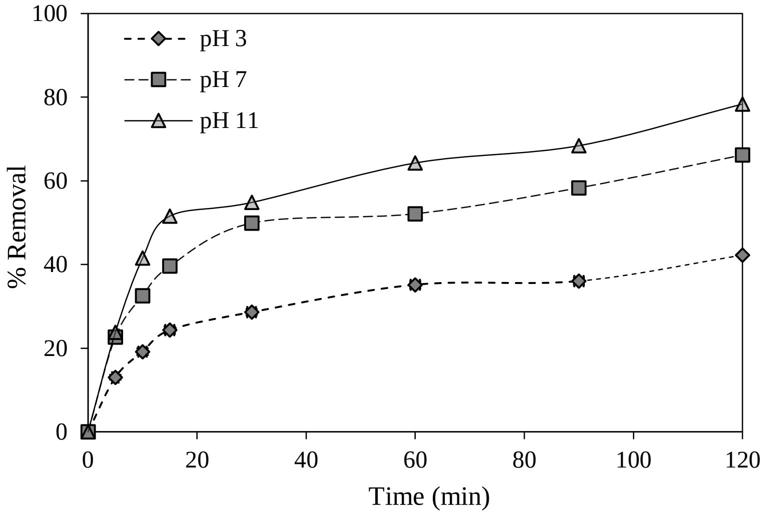

Figure 3. Effect of solution pH on catalytic ozonation using FE/WTS as a catalyst (Experimental conditions: O_3 generation=0.57 mg/min, [Phenol]=50 mg/L, [Fe/WTS]=1 g/L, Fe content=1%)

3.4 Effect of catalyst dosage

The effect of catalyst dosage in catalytic ozonation for phenol degradation was studied by adding 1% Fe/WTS at various dosages. Figure 4 exhibited that as the Fe/WTS dosages increased, the performance of catalytic ozonation in phenol degradation was reduced. At the Fe/WTS dosages of 1, 3, and 5 g/L removal efficiencies for phenol degradation were 65.24, 52.58, and 49.01%, respectively, while that of sole ozonation was 27.26% at 60 min. As mentioned earlier, in the presence of Fe/WTS as a catalyst, hydroxyl radicals played a key role in the degradation of phenol. High catalyst dosage provided more active sites for the catalytic reaction, leading to more formation of $OH^{\bullet}$. Many researchers have reported that the surface hydroxyl groups of metal oxides are the active sites of catalytic ozonation (Qi et al., 2009; Peng et al., 2018). Regarding to Equation 1-3, ≡FeOH on Fe/WTS catalyst reacted with O_3 to promote $OH^{\bullet}$ generation, leading to phenol degradation (Li et al., 2018b). However, excess $OH^{\bullet}$ generated by high catalyst dosage led to self-quenching. When higher Fe/WTS dosage was applied, some $OH^{\bullet}$ were quenched by itself according to Equation 4 and 5 (Peng et al., 2018). As the $OH^{\bullet}$ radicals were quenched, the performance of catalytic ozonation on phenol degradation was limited. Thus, removal efficiency decreased when the system was operated with 3 and 5 g/L of Fe/WTS catalyst. Based on this result, 1 g/L of Fe/WTS catalyst was selected for further study.

$$OH^{\bullet} + OH^{\bullet} \longleftrightarrow H_2O_2 \qquad (4)$$
$$OH^{\bullet} + HO^{-}_2 \longleftrightarrow H_2O + O_2 \qquad (5)$$

3.5 Effect of iron content

The effect of Fe content in Fe/WTS on the degradation of phenol by catalytic ozonation is shown in Figure 5. The removal efficiencies by Fe/WTS catalyst with Fe contents of 1, 2, and 3% were 65.24, 81.75, and 55.71%, respectively. It was found that increasing Fe content in Fe/WTS from 1 to 2% caused the removal efficiency to increase, but the efficiency decreased when 3% Fe/WTS was applied. Higher content of Fe in WTS provided more active sites of ≡FeOH to accelerate O_3 decomposition, leading to the formation of $OH^{\bullet}$ as mentioned earlier in Equation 1-3. Moreover, the decomposition of ozone possibly generated several radicals such as $HO_2^{\bullet}$, $HO_3^{\bullet}$, and $O_3^{-\bullet}$ (von Gunten, 2003). On the one hand, the reaction of these radicals led to the generation of $OH^{\bullet}$ (Wang and Bai, 2017). On the other hand, high radical concentration possibly caused scavenging of $OH^{\bullet}$ as described in Equation 4-7 (Chen et al., 2016; Peng et al., 2018). As a result, the decreasing performance of catalytic ozonation on phenol degradation at higher Fe content was observed.

$$OH^{\bullet} + HO_3^{\bullet} \longleftrightarrow H_2O_2 + O_2 \qquad (6)$$
$$H_2O_2 + O_3 \longleftrightarrow H_2O + O_2 \qquad (7)$$

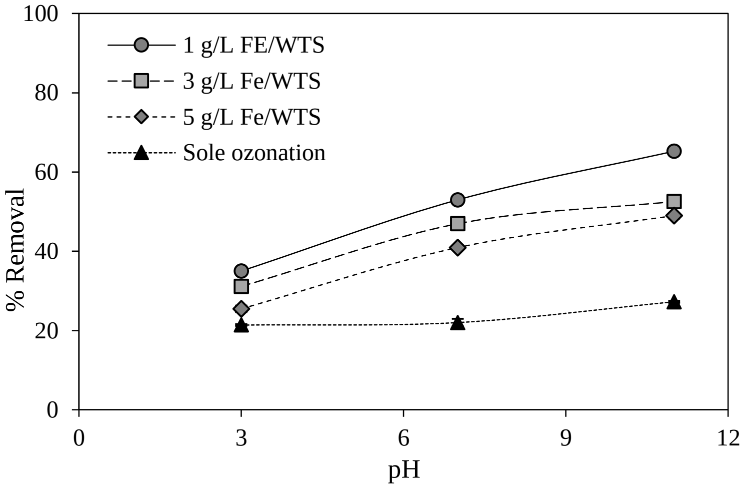

Figure 4. Effect of catalyst dosage on catalytic ozonation using Fe/WTS as a catalyst (Experimental conditions: O_3 generation=0.57 mg/min, [Phenol]=50 mg/L, Fe content=1%, Ozonation time=60 min)

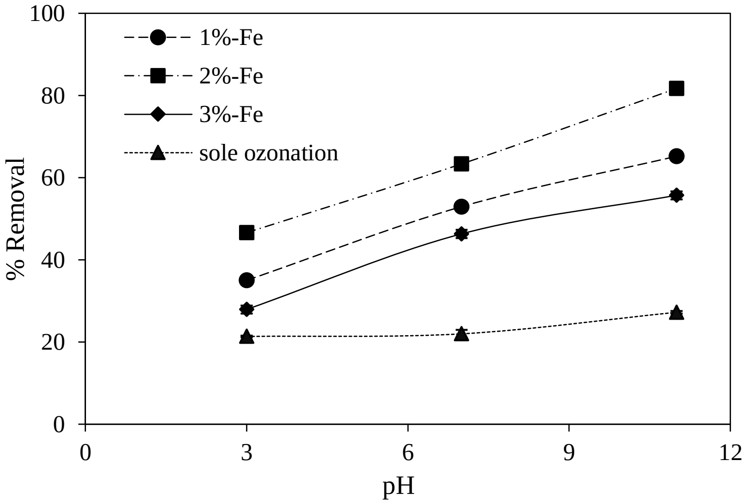

Figure 5. Effect of Fe content on catalytic ozonation using Fe/WTS as a catalyst (Experimental conditions: O_3 generation=0.57 mg/min, [Phenol]=50 mg/L, [Fe/WTS]=1 g/L, pH=11, Ozonation time=60 min)

3.6 Effect of radical scavengers

In general, the key active species in catalytic ozonation were $OH^{\bullet}$ generated during ozone decomposition. In this study, tert-butanol (TBA) was used as a radical scavenger at varied concentrations of 1-3 mM to prove the formation of $OH^{\bullet}$ from ozone decomposition and its performance on phenol degradation during catalytic ozonation process. As shown in Figure 6, when the concentration of TBA increased, the percent phenol removal simultaneously decreased. The presence of TBA obviously inhibited the degradation rate of phenol in catalytic ozonation using Fe/WTS. The results corresponded to previous studies (Zhang et al., 2018; Lan et al., 2013). This finding confirmed that hydroxyl radicals played an important role in the catalytic ozonation.

3.7 Reaction kinetics of catalytic ozonation using Fe/WTS as a catalyst

The optimum condition to achieve high performance of catalytic ozonation using Fe/WTS as a catalyst was achieved, i.e., 2% Fe/WTS, catalyst dosage of 1 g/L, pH of 11, and reaction time of 120 min. At this condition, the removal efficiency of phenol was 99.16% which was promisingly effective compared with using WTS as a catalyst (59.35%) and sole ozonation (44.61%). This optimum condition was further used in a kinetic study.

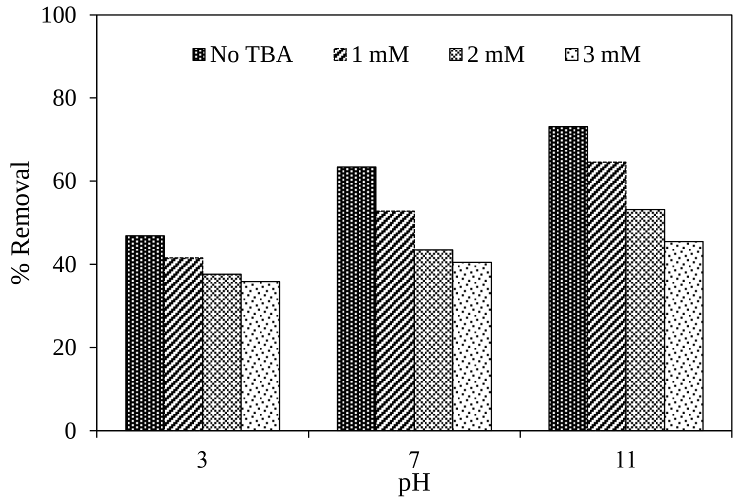

Figure 6. Effect of TBA on the catalytic activities of Fe/WTS catalyst (Experimental conditions: O_3 generation=0.57 mg/min, [Phenol]=50 mg/L, [Fe/WTS]=1 g/L, Fe content=1%, Ozonation time=60 min)

The reaction kinetics of catalytic ozonation using Fe/WTS as a catalyst was analyzed. Plots of $\ln([C]/[C]_0)$ versus reaction time of the sole ozonation and catalytic ozonation by Fe/WTS and WTS, are shown in Figure 7. A good linear fit was observed for each of these ozonation reactions. The experimental data fit well with a pseudo-first order kinetic model (Zhao et al., 2009), where [C] was the molar concentration of phenol, and $[O_3]$ and $[OH^\bullet]$ were the concentrations of ozone and hydroxyl radical, respectively. The value K_{obs} is an apparent reaction rate coefficient, which indicated that phenol degradation in both ozonation and catalytic ozonation was described by a pseudo-first order kinetic model (Qi et al., 2012). The degradation rate of phenol in both ozonation and catalytic ozonation by Fe/WTS is expressed in Equation 8,

$$-\frac{d\,[\text{phenol}]}{dt} = k_{O_3}[O_3][\text{phenol}] + k_{OH^\bullet}[OH^\bullet][\text{phenol}] \qquad (8)$$

where k_{O_3} and $k\ OH^\bullet$ are constants for ozone and $OH^\bullet$ reacting with phenol, respectively. Equation 8 is transformed to Equation 9,

$$-\frac{d\,[\text{phenol}]}{dt} = [k_{O_3}[O_3] + k_{\cdot OH}[\cdot\, OH]][\text{phenol}] \qquad (9)$$

By defining K_{obs} as an apparent reaction rate coefficient, Equation 9 is transformed to Equation 10 and 11,

$$k_{obs} = k_{O_3}[O_3] + k_{\cdot OH}[\cdot\, OH] \qquad (10)$$

$$-\frac{d\,[\text{phenol}]}{dt} = k_{obs}\,[\text{phenol}] \qquad (11)$$

According to kinetic analysis results as shown in Figure 7, it was found that the experimental data fit well with a pseudo-first order kinetic model with apparent rate constants (K_{obs}) of 0.0362 min^{-1} and 0.0065 min^{-1} for the use of Fe/WTS and WTS catalysts, respectively, while that of sole ozonation was 0.0046 min^{-1}. In comparison with a previous study, the rate constant of phenol degradation by Fe-hollow zeolite was 0.021 min^{-1} (Dai et al., 2017). The results confirmed that the use of Fe/WTS catalyst in catalytic ozonation was efficient for phenol degradation (Qi et al., 2012).

4. CONCLUSIONS

Iron-doped WTS was successfully used as a catalyst in catalytic ozonation for degradation of phenol. The structure of Fe/WTS was highly crystalline with a high BET surface area when compared with WTS. At the optimum conditions, i.e., reaction time of 120 min, pH of 11, Fe/WTS catalyst dosage of 1 g/L with 2% iron content, the removal efficiency of phenol was 99.16%, which was higher than that of sole ozonation (44.61%) at 120 min. Kinetic studies showed that the catalytic ozonation using Fe/WTS and WTS catalysts followed pseudo-first order kinetic models with the apparent rate constants (k_{obs}) of 0.0362 and 0.0063 min^{-1}, respectively. It can be concluded that acid modified WTS was able to be used as a catalyst support and that the Fe/WTS catalyst was successful in accelerating the reaction and improve the performance of ozonation process in the degradation of phenol.

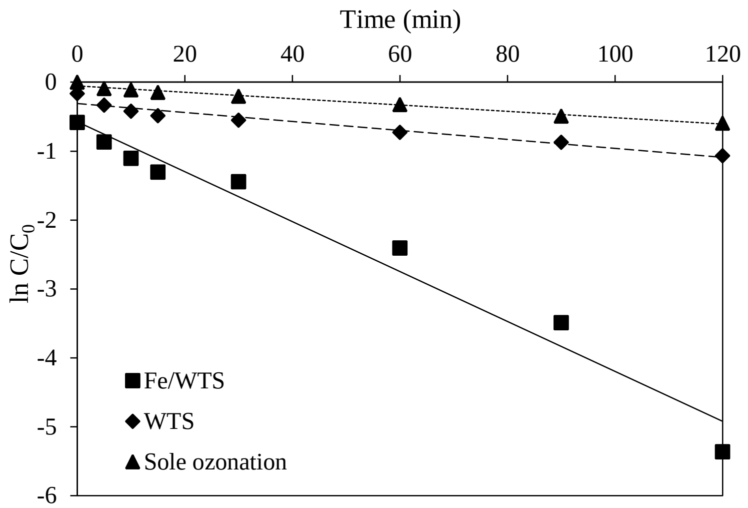

Figure 7. Kinetic study of phenol degradation by catalytic ozonation in the presence of Fe/WTS and WTS as catalysts compared with sole ozonation (Experimental conditions: O_3 generation=0.57 mg/min, [Phenol]=50 mg/L, [Fe/WTS]=1 g/L, Fe content=2%, [WTS]=1 g/L, solution pH=11)

ACKNOWLEDGEMENTS

The research was supported by the Office of the Higher Education Commission and Pranakhon Rajabhat University.

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