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A Novel Catalyst from Water Treatment Sludge for Catalytic Ozonation to Degrade Phenol

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Abstract

Water treatment sludge (WTS) from a water treatment plant has been successfully converted into a novel catalyst. Catalytic ozonation using the WTS as a catalyst for degradation of phenol was studied. Water treatment sludge was dried naturally for 7 days, then grounded and sieved through a standard mesh with a size no. of 100, equivalent to less than 150 micron in size. The WTS was characterized by X-ray fluorescence spectrometer (XRF) and X-ray diffractometer (XRD). The XRF analysis showed that water treatment sludge contained silica of 49.90%, Al_2O_3 of 24.40 %, and Fe_2O_3 of 10.40 %. The XRD analysis illustrated that the structure of water treatment sludge was similar to that of kaolin clay. Factors affecting phenol removal efficiency including reaction time (0, 5, 10, 15, 30, 60, 90 and 120 min), pH (3, 7, and 11) and catalyst dosage (1, 3 and 5 g/L) were investigated. At the optimum conditions, i.e. reaction time of 120 min, pH of 11, and catalyst dosage of 3 g/L, the removal efficiency of phenol was 59.16% which was higher than that of sole ozonation (44.61%). According to kinetic analysis, it was found that the experimental data fit well with pseudo-first order kinetic model with a rate constant (K_{obs}) of 0.0347 min^{-1} while that of sole ozone was 0.0162 min^{-1}.

Keywords: Catalytic ozonation; Degradation; Phenol; Water treatment sludge

1. Introduction

Phenol is known as a hazardous pollutant found in aqueous effluents from various industries such as petrochemical plant, petroleum refinery, manufacturing of resins and plastics, pharmaceutical industry. It is considered as a refractory organic compound by the US EPA with high toxicity and carcinogenic properties (He *et al.*, 2008). Several technologies are available to remove industrial organic wastes, such as thermal, chemical and biological treatments. Thermal treatments present many drawbacks, such as considerable emission of other hazardous compounds. Chemical treatments, which include flocculation, precipitation, adsorption on activated carbon, air stripping or reverse osmosis, are not resolving requiring a post-treatment. Conventional biological processes represent an environmentally friendly way of treatment with reasonable costs, however, they are not adequate to treat non-biodegradable wastewaters and, usually, require a long residence time for micro-organisms to degrade the pollutants. Thus, there is a need to use effective strategies of treatment to achieve high quality of effluent prior to discharge to natural receiving water. (Farzadkia *et al.*, 2014).

Ozonation is one of the oxidation processes widely used for industrial wastewater treatment. Ozone, a strong oxidant, can break down recalcitrant and toxic organic compounds into smaller molecules. Ozone can react with various organic and inorganic compounds in solution in two ways including direct molecular ozone with a redox potential of 2.07 V and radical-type reaction involving hydroxyl radicals induced by ozone decomposition with a redox potential of 2.33 V (Li *et al.*, 2018).

However, ozonation has some limitations such as high energy demand and incomplete mineralization of recalcitrant organics (Shahamat *et al.*, 2014). The molecular ozone reacts especially reactively with specific functional groups such as amino group, double bonds and nucleophilic positions but lead to the formation of aldehydes and carboxylic acids, both of which are inert with ozone, thus total mineralization is not always achievable (Liotta *et al.*, 2009). For these reasons, improving the ozone efficiency by implementation of radical process might be overcoming the weakness of the single ozonation process.

Catalytic ozonation is one type of advanced oxidation processes which can be divided into two types including homogeneous catalytic ozonation and heterogeneous catalytic ozonation. Homogenous catalytic ozonation is the process that utilize ozone decomposed by metal ions such as Mn^{2+}, Fe^{3+}, Fe^{2+} and Co^{2+} (Li *et al*, 2018). However, using metal ion has several disadvantages such as insufficient active sites and limited specific surface area (Li *et al*, 2018), high consumption of the catalysts and complexity of these technologies. Moreover, this technology is to introduce ions and result in the secondary pollution, which lead to increase cost of water treatment. For this reason, it is rarely selected as a promising method (Farzadkia *et al.*, 2014).

Heterogeneous catalytic ozonation using solid catalysts such as metal, metal oxide, metal on support, activated carbon and clay, is a powerful treatment method, which increases the efficiency of ozonation process (Shahamat *et al.*, 2014). In this process, ozone is decomposed to generate hydroxyl radicals, which possess high rate constants with phenols (He *et al.*, 2008).

Kaolinite is one type of clay that can be used as catalytic ozonation. Kaolinite is the major mineral component of kaolin, which may contain quartz, mica and feldspar (Panda *et al.*, 2010). From previous study, catalytic ozonation with kaolin could accelerate ozone mass transfer compared with ozone alone, leading to enhancement of cationic dye degradation (Li *et al.*, 2009). Thus, kaolin is interesting to apply as a catalyst in catalytic ozonation because it is widely abundant in nature and inexpensive.

Water treatment sludge is a by-product from water treatment process. Usually, water treatment sludge is classified as a waste material. However, this waste includes a lot of useful chemical compositions, such as iron, silicon, and alumina (Kizinievic *et al.*, 2013). Large amount of sludge from water supply process causes the cost of disposal. Many researchers tried to recycle water treatment sludge by various applications such as plantation, ceramic production (Kizinievic *et al.*, 2013), and geo-polymer because its properties are similar to clay (Vinitnantharat *et al.*, 2010). However, the recycle of the water treatment sludge for more valuable application is still challenging. Suasamserm (2002) investigated the properties of water treatment sludge from Metropolitan Waterworks Authority, Bangkok, Thailand, and found that the properties of water treatment sludge were equivalent to those of kaolin. The core of the novelty of the present study resides in correlating these interactions with water treatment sludge and ozonation process. This issue has never been tackled and not even been envisaged so far.

In this research, water treatment sludge was introduced as a novel catalyst in ozonation because it can generate hydroxyl radical which was a powerful active species in oxidation reaction. The objective of this study was to study feasibility of water treatment sludge as a catalyst in catalytic ozonation for degradation of phenol. Factors affecting catalytic ozonation, including pH, time and catalyst dosage were investigated. Reaction kinetics of catalytic ozonation were analyzed and compared to sole ozonation. The catalytic ozonation by using water treatment sludge as catalyst can be applied to other phenolic compounds containing in wastewater and can be used as a pretreatment method for conventional biological processes.

2. Materials and Methods

2.1 Preparation of catalysts

Water treatment sludge, designed as WTS, was obtained from sludge belt of water treatment plant. It was dried naturally for 7 days, then grounded and sieved through the standard mesh with size no. of 100, equivalent to particle size less than 150 microns. The WTS sample was characterized by X-ray diffractometer (XRD) with Cu Kα radiation (Philips X-Pert-MPD) and X-ray fluorescence (XRF) spectrometer (Horiba XGT-2000W), and kept in desiccators until used.

2.2 Materials

All reagents such as phenol, sodium hydroxide, sodium thiosulfate, potassium iodide, and hydrochloric were analytical grades which were obtained from Sigma Aldrich. The scavenger, tert-butanol, was used as $OH^{\cdot}$-scavenger to confirm the performance of $OH^{\cdot}$ radical in degradation of phenol. Sodium thiosulfate was used to quench residual ozone, while potassium iodide was used to trap unreacted ozone.

2.3 Ozonation experiment

Ozone was generated by a laboratory ozone generator using oxygen from air pump as raw material. The generation rate of ozone was 0.57 mg/min. Ozonation experiments were performed in a cylindrical reactor and carried out in a batch mode. In typical catalytic ozonation procedure, 1 g/L of WTS was mixed with 2.7 L of phenol sample (initial concentration of phenol was 50 mg/L). Then, the ozone flow was introduced into the reactor via air diffusers. Samples of 50 mL were collected at the specified time. The residual ozone was quenched by sodium thiosulfate solution while potassium iodide was used to trap unreacted ozone. The concentration of ozone was measured by standard iodometry (Rice *et al.*, 2017). Phenol was determined by colorimetric method by using 4-aminoantipyrine in a formation of phenol complex, then determined by UV-Vis spectrophotometer (UV-1700, Shimadzu) at a wavelength of 510 nm (Li *et al.*, 2018). The phenol removal efficiency was calculated by the equation of $[(A_o - A) / A_o] \times 100$ where A_o is an initial absorbance at the wavelength of 510 nm, and A is an absorbance at the wavelength of 510 nm after phenol removal.

3. Results and discussion

3.1 Characterization of water treatment sludge

Characteristic of water treatment sludge (WTS) was analyzed by XRD, as shown in Figure 1. The result exhibited two well-defined characteristic peaks of kaolinite at 2θ value of 12° and 25°, corresponding to the reflections from [0 0 1] and d value of 7.154 Å was observed (Sachan and Penumadu, 2007). Other peaks corresponding to the 2θ values of 34–36°, 38–42°, 45–50°, and 54–63° were also visible but possibly varied for kaolinites from different origins (Ayodele *et al.*, 2012). The structure of WTS sample showed the sharp diffraction peak combined with noised peak that indicated crystalline and amorphous phases, respectively. The result from XRF analysis indicated that major components of WTS were silica, alumina (Al_2O_3), and ferric oxide (Fe_2O_3) at percentages of 49.90%, 24.4%, and 10.4%, converted from their relevant atomic compositions, respectively.

These finding evidences proved that the water treatment sludge was equivalent to kaolin clay, corresponding to Vinitnantharat *et al.* (2010). However, aluminum content (Al) in water treatment sludge was higher than that found in natural kaolin because aluminum was originated from alum used in coagulation and flocculation processes. According to Li *et al.* (2009), kaolin was efficiently used as a catalyst to degrade cationic dye methylene blue in catalytic ozonation. For this reason, water treatment sludge whose chemical structure was similar to kaolin could be used as a catalyst to accelerate catalytic ozonation process. The performance of WTS as a catalyst in catalytic ozonation was further investigated.

3.2 Effect of initial pH

Hydroxide ion (OH−) was found to be an initiator of the chain reaction in ozone decomposition (Qi *et al.*, 2012). Therefore, the solution pH is an important factor affecting ozone decomposition process. In this research, the effect of solution pH on the degradation of phenol by catalytic ozonation and sole ozone at pH 3, 7, and 11 were investigated, as shown in Figure 2 (a)-(c) respectively. It was found that, as the solution pH increased, the degradation of phenol became increased. The results illustrated that increasing time from 0, 5, 10, 15, 30, 60, 90 and 120 min, the removal of phenol increased. At 120 min and pH of 3, 7, and 11, removal efficiencies of phenol by sole ozonation were 29.85, 35.20 and 47.79%, respectively. While the catalytic ozonation using WTS as a catalyst provided the removal efficiencies of 37.67, 43.07, and 59.28 % at pH of 3, 7, and 11, respectively. It can be explained that the direct reaction of molecular ozone with phenol was dominant in acidic condition. Increasing pH promoted ozone decomposition and formation of hydroxyl radical ($OH^{\cdot}$) which was very powerful radical and reacted with phenol in non-selective mode (Li *et al.*, 2009). However, the presence of WTS in catalytic ozonation facilitated the ozone decomposition which eventually produced $OH^{\cdot}$ at low pH. In case of WTS as catalyst, apart from OH-, the surface charge properties of water treatment sludge could also initiated $OH^{\cdot}$ production from ozone. For this reason, hydroxyl radicals played a key role in the degradation of phenol by catalytic ozonation in the presence of WTS.

3.3 Effect of catalyst dosage

Catalyst dosage is an important parameter in the catalytic ozonation. Figure 3 exhibited the effect of catalyst dosage on phenol degradation. As the WTS dosages of 1,3, and 5 g/L, were applied, catalytic ozonation for phenol degradation efficiencies were 42.78, 53.12, and 56.16%, respectively, while that of sole ozonation was 26.27 %. As mentioned earlier, in the presence of WTS as a catalyst, hydroxyl radicals played a key role in the degradation of phenol.

More catalyst dosage provided more active sites for the catalytic reaction, leading to more formation of $OH^{\cdot}$. Many literatures reported that the surface hydroxyl groups of the metal oxides were the active sites of catalytic ozonation (Qi *et al.*, 2009; Peng *et al.*, 2018). Higher dosage of catalyst provided more surface hydroxyl groups for catalytic ozonation, leading to high performance on phenol degradation.

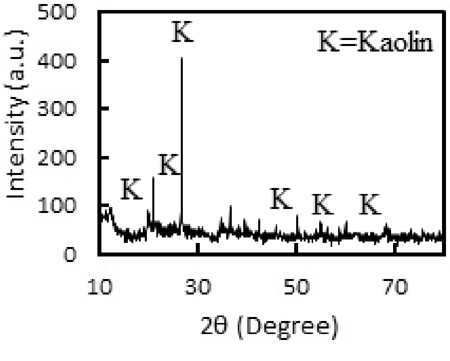
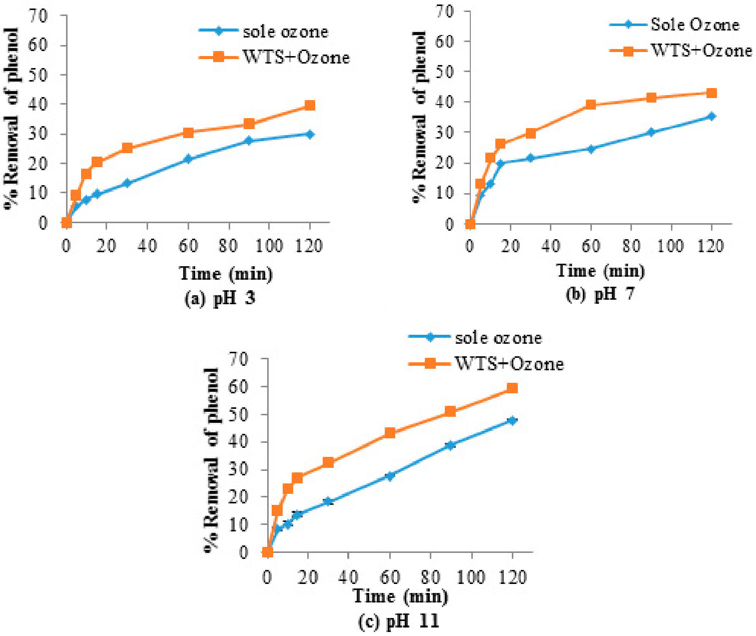


Figure 1. XRD pattern of water treatment sludge



(a) pH 3

(b) pH 7

(c) pH 11

Figure 2. Effect of solution pH on catalytic activities of water treatment sludge (a) pH 3, (b) pH 7 and (c) pH 11 (Experimental conditions: O_3 generation = 0.57 mg/min, [phenol] = 50 mg/L, [WTS] = 1 g/L)

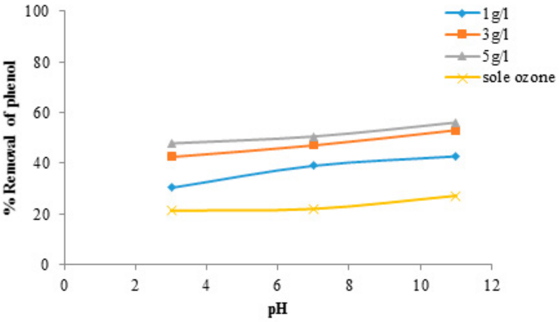


Figure 3. Effect of catalyst dosage on the catalytic activities of water treatment sludge (Experimental conditions: O_3 generation = 0.57 mg/min, [phenol] = 50 mg/L, time = 60 min)

However, it slightly increased in percent removal from 3 to 5 g/L. This result can be explained that excess $OH^{\cdot}$ generated by high catalyst dosage could be quenched each other, as expressed in Eq. (1) (Peng *et al.*, 2018).

$$OH^{\cdot} + OH^{\cdot} \rightarrow H_2O_2 \qquad (1)$$

As a part of $OH^{\cdot}$ was quenched, the performance of catalytic ozonation on phenol degradation was limited.

3.4 Effect of radical scavengers

In general, the key active species in catalytic ozonation were $OH^{\cdot}$ generated during ozone decomposition. In this study, tert-butanol (TBA) as a radical scavenger at varied concentrations of 1-3 mM were used to prove the formation of $OH^{\cdot}$ from ozone decomposition and its performance on phenol degradation during catalytic ozonation process. As shown in Figure 4, when the concentration of TBA increased, the percent phenol removal

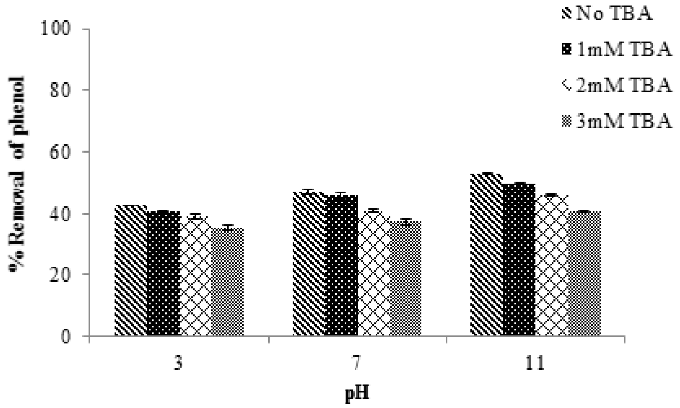


Figure 4. Effect of tert-butanol as OH˙ scavenger on degradation of phenol. (Experimental conditions: O_3 generation = 0.57 mg/min, [phenol] = 50 mg/L, [WTS] = 1g/L, time = 60 min)

simultaneously decreased. The presences of tert-butanol obviously inhibited the degradation rate of phenol in catalytic ozonation with WTS. The result was corresponding to several researchers (Zhang *et al.*, 2018; Lan *et al.*, 2013). This finding confirmed that hydroxyl radicals played an important role in the catalytic ozonation.

3.5 Reaction kinetics of catalytic ozonation using WTS as a catalyst

Kinetic of catalytic ozonation using WTS as a catalyst was analyzed. Plots of ln [C]/[C0] versus reaction time of the sole ozonation and catalytic ozonation by WTS, are shown in Figure 5. A good linear fitting was observed for each of ozonation reaction. The experimental data fit well with pseudo first order kinetic model, where [C] was assigned to the concentration of phenol, $[O_3]$ and $[OH^{\cdot}]$ are the concentrations of ozonation and hydroxyl radical. K_{obs} was an apparent reaction rate coefficient (Qi *et al.*, 2012). The degradation rate of phenol in both ozonation and catalytic ozonation by WTS can be expressed as follows:

$$-\frac{d[C]}{dt} = k_{O_3}[O_3][C] + k_{OH^{\circ}}[OH^{\circ}][C] \qquad (2)$$

where k_{O3} and k_{OH} are constants for ozone and $OH^{\cdot}$ reacting with phenol, respectively. Eq (2) can be transformed to Eq (3)

$$-\frac{d[C]}{dt} = (k_{o_3}[O_3] + k_{OH}[OH^{\circ}])[C] \qquad (3)$$

By defining $k_{obs}=k_{O3}[O_3\ ]+k_{OH}[OH^{\circ}]$ can be transformed to Eq.(4)

$$-\frac{d[C]}{dt} = k_{obs}[C] \qquad (4)$$

As shown in Eq. 4, it indicated that phenol degradation in both ozonation and catalytic ozonation was described by the pseudo first order kinetic model (Qi *et al.*, 2012). According to Figure 5, two-stage reactions occurred in both sole ozonation and catalytic ozonation. The initial phase, instantaneous ozone demand (IOD), was explained by the fast consumption of ozone by phenol in water or by catalyst. In the stage of IOD, a fast oxidation reaction between ozone (or •OH) and phenol took place. The second phase was a slow oxidation process where residual ozone molecular contained to oxidize phenol (Qi *et al.*, 2012).

The use of WTS as a catalyst in the ozonation process enhanced the phenol degradation rate and efficiency. As listed in Table 1, rate constants (k_{obs}) with both initial and second phases are shown. It was found that the rate constant of catalytic ozonation at pH 11 was 0.0347 min^{-1}, which was higher than sole ozone at the same pH (0.0162 min^{-1}). Moreover, rate constants in initial phase of catalytic ozonation were exhibited to be higher than those of sole ozonation at all pH, indicating good performances of catalytic ozonation using WTS as a novel catalyst on phenol degradation.

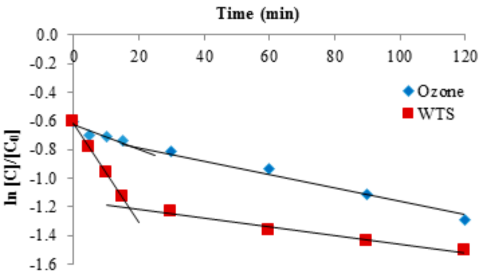


Figure 5. Degradation kinetic for phenol by catalytic ozonation in the presence of water treatment sludge. (Experimental conditions: O_3 generation = 0.57 mg/min, [phenol] = 50 mg/L, [WTS] = 3 g/L, pH= 11)

Table 1. Pseudo-first order rate constants of phenol degradation in the different processes

Experiment	Initial phase		Second phase	
	Rate constant (k_{obs}, min^{-1})	R^2	Rate constant (k_{obs}, min^{-1})	R^2
Ozonation pH 3	0.0077	0.9762	0.0021	0.9657
Ozonation pH 7	0.0085	0.9968	0.0020	0.9963
Ozonation pH 11	0.0162	0.9968	0.0055	0.9762
Catalytic Ozonation pH 3	0.0203	0.9687	0.0030	0.9122
Catalytic Ozonation pH 7	0.0254	0.9970	0.0024	0.9474
Catalytic Ozonation pH 11	0.0347	0.9998	0.0030	0.9647

4. Conclusions

Based on experimental data the following conclusion can be drawn:

(1) Water treatment sludge (WTS) has been efficiently used as a novel catalyst to enhance degradation of phenol in catalytic ozonation.

(2) In catalytic ozonation using WTS, as a catalyst, hydroxyl radical ($OH^{\cdot}$) mechanism was proved to play a dominant role on phenol degradation.

(3) At the optimum conditions of catalytic ozonation, i.e. pH of 11, time of 120 min, and catalyst (WTS) dosage of 3 g/L, phenol degradation achieved 59.16% while sole ozonation provided 44.61% in removal efficiency.

(4) The experimental data of catalytic ozonation using WTS as a catalyst and sole ozonation fit well with pseudo- first order kinetic model with rate constants of 0.0347 and 0.0162 min^{-1}, respectively, at the pH of 11.

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