



Kinetics of Phenol Degradation in Aqueous Solution Oxidized under Low Frequency Ultrasonic Irradiation

Kinetika Penguraian Fenol dalam Air Secara Oksidasi dengan Iradiasi Ultrasonik Frekuensi Rendah

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Abstract

Phenol is categorized as a refractory pollutant and its presence in water stream is strictly limited according to the government regulation. The present study investigated the degradation of phenol in aqueous solution by the effect of ultrasound. The process took place in a 500 ml glass reactor equipped with magnetic stirring and irradiated by low frequency (28 kHz) ultrasound from a horn type probe. Ultrasonic irradiation was found to enhance oxidation rates at ambient conditions, compared to other approaches. Optimum conditions were observed at a stirring speed of 400 rpm and temperature of 30°C in acidic solution. It was revealed that the phenol degradation was the first order kinetics with respect to phenol. A low value of the activation energy 6.04 kcal/mol suggested that diffusional steps were rate determining during the phenol decomposition. It also confirmed that phenol was mostly degraded in the film region and less occurred in the bulk solution.

Keywords: oxidation, phenol, wastewater, ultrasound, sonochemistry

Abstrak

Fenol tergolong polutan yang sulit diuraikan dan keberadaannya dalam aliran air sangat dibatasi berdasarkan peraturan pemerintah. Penelitian ini mengkaji penguraian fenol di dalam air dengan dibantu efek ultrasonik. Proses berlangsung di reaktor gelas 500 ml yang dilengkapi pengaduk magnetik dan pembangkit iradiasi ultrasonik frekuensi rendah (28 kHz) tipe *horn*. Iradiasi ultrasonik dapat meningkatkan laju oksidasi pada kondisi ruangan dibandingkan beberapa metode lain yang juga dicoba. Hasil optimal diperoleh pada kecepatan pengadukan 400 rpm dan suhu 30°C dalam suasana asam. Penelitian ini juga membuktikan bahwa penguraian fenol mengikuti kinetika reaksi orde pertama terhadap fenol. Nilai energi aktivasi yang rendah yaitu 6,04 kkal/mol menunjukkan bahwa perpindahan massa menjadi tahap pengendali laju reaksi keseluruhan selama proses penguraian fenol. Juga disimpulkan bahwa sebagian besar fenol terurai di daerah film sekitar gelembung kavitasi dan selebihnya berlangsung di larutan.

Kata kunci: oksidasi, fenol, air limbah, ultrasonik, sono-kimia

1. Introduction

Advanced oxidation processes by which highly oxidative free radicals are generated have been considered as alternative approaches to degrade and remove refractory pollutants from wastewaters. One of them uses ultrasound effect to stimulate the process and have gained significant attention because of the relatively mild reaction condition required and their success in conversion of several organics containing strong chemical bonds (Hagenson and Doraiswamy, 1998; Pham *et al.*, 2013). The true chemical effects of ultrasound are mainly because of the implosive collapse of microbubbles which are formed during the negative pressure period of soundwaves.

The temperature in the collapsing bubbles can reach 3000-5000K and the pressure to 500-10.000 atm (Suslick and Hammerton, 1986; Mason and Cordemans, 1996). Under such extreme circumstances, molecules of the vaporized reaction mixture within the bubbles are broken, forming small species including highly reactive free radicals such as OH* and H* (Neis, 2000; Bagal and Gogate, 2014). Entrapped molecules of dissolved gases and solutes can be also brought to an excited state and dissociate. These free radicals may further stimulate or accelerate some secondary reactions.

Phenol is categorized as a refractory pollutant and according to regulation released by Indonesian State Ministry for

Environmental Affair its maximum allowable presence in aquatic bodies is 1 ppm. Most studies on phenol oxidation employed advanced oxidation processes, in addition to conventional high pressure and/or temperature systems. Effect of ultrasound has been reported to decompose phenol in more effective and efficient processes (Okouchi *et al.*, 1992; Trabelsi *et al.*, 1996; Ku *et al.*, 1997; Peng *et al.*, 2014). Peng *et al.* (2014) summarizes that effect of cavitation is determined by a number of factors such as ultrasonic frequency, intensity, density, liquid temperature, type of solutes, presence of gas, external pressure, viscosity, and surface tension.

This paper presents the results of aqueous phenol degradation under low frequency (28 kHz) ultrasonic irradiation, instead high frequency and high power as used other researchers. Some reports suggested that the best result is not always at the use of maximum ultrasonic power. Moreover, the present work includes introduction of gaseous oxygen, which is believed probably playing an important role on the mechanism involved for sono-degradation of phenol.

2. Methodology

Reagent grade phenol (>99%, Sigma - Aldrich) and sulfuric acid (95-98%, Sigma-Aldrich) were used as obtained. Oxygen gas was purchased from Aneka Gas (Medan) with purity of 99%. Reagents for phenol determination by the 4-aminoantipyrine method are as prescribed in APHA (1985). The reactions were carried out in a 500 ml glass reactor (see Fig. 1), made entirely of Pyrex glass fitted with 4 baffles.

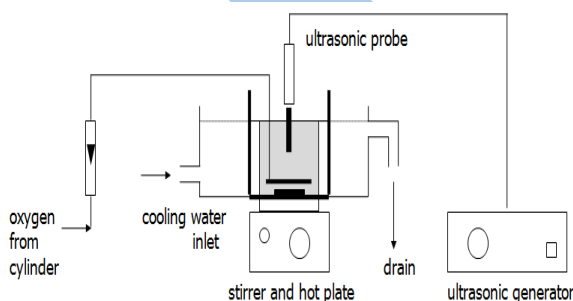


Figure 1. Experimental setup

Aqueous phenol solution (200 ml) of a given concentration was prepared and transferred to the reactor. It was then immersed into a water bath to maintain its temperature. Mixing and heating was facilitated by a hot-magnetic stirring device. The solution was adjusted to acidic by adding sulfuric acid.

Acidic solution is required to maintain phenol in molecular state in the solution, while the phenol tends to dissociate into ionic form in base solution. In the molecular state, phenol more easily enters the gas-water interfaces of bubbles and even vaporizes into cavitation bubbles; thus it can react both inside by thermal cleavage and outside with OH^* radicals (Okouchi *et al.*, 1992; Wu *et al.*, 2001). Oxygen was introduced through a diffuser placed at bottom of the reactor at rate of 0.25 L/min. During the reaction, the reactor was irradiated by an ultrasonic wave transduced by a horn type probe with tip surface of 2 cm². The ultrasonic wave is supplied at frequency of 28 kHz and power of 50 W by a generator (Model US-50, Nihonseiki Kaisha Ltd.) Liquid samples were collected at times of 15, 30, 45, and 60 minutes, and then directly analyzed for phenol by the 4-aminoantipyrine method (APHA, 1985). The influence of ultrasonic irradiation was observed at different initial phenol concentrations (25 to 100 mg/L), reaction temperature (30 to 60°C), and stirring speed (200 to 500 rpm). The reaction with initial phenol concentration of 32 mg/L was also performed as concentration based on the phenol content in effluent of a wastewater treatment in one of field gas exploration units operating in Aceh.

3. Results and Discussion

3.1. Influence of Sonication

The effect of ultrasonic wave presence on the phenol degradation was determined. Table 1 shows that no conversion was observed for oxidation without ultrasound because a less active oxidant such as oxygen or air was not able to react with the phenol. When sonication was applied, even without dispersing oxygen a conversion of 2% was obtained after one hour of the reaction, probably because of utilization of OH^* free radical. Such low conversion is because of less availability of OH^* in the system. Use of low frequency sonication (28 kHz) in the present work led to limited release of OH^* . Petrier *et al.* (1994) found release of OH^* is enhanced at high frequency, and at low frequency (20 kHz) they reported low is conversion where only 2% of carbon recovered in the gaseous phase, but at high frequency (487 kHz) carbon recovery is about 15%.

The occurrence of cavitation bubbles was observed in the region around tip of the ultrasound probe. The bubbles moved away and then disappeared, indicating the collapse

sing of bubbles. The bubbles continuously appeared suggesting that the solution evaporated in the cavitation bubbles. An increase in solution temperature was observed when fresh cool water stopped to flow into the water bath. This suggests that hot spot effect happened during bubble collapses. When oxygen was introduced via a diffuser, sono-oxidation took place at better conversion (41.7%) compared to the previous two as shown in Table 1.

Table 1. Comparison of different degradation systems ($T = 30^{\circ}\text{C}$, time = 1 h, $N = 400$ rpm, $[\text{PhOH}]_0 = 100$ mg/L).

System	[PhOH] mg/L	Conversion %
Only dispersed oxygen	99.9	0.0
Sonication without dispersed oxygen	97.9	2.1
Sonication with dispersed oxygen	58.3	41.7

In comparison to other works, it is interesting to find that the present works exhibit a comparable conversion. Trabelsi *et al.* (1996) obtained only 5% conversion after 3 hours of sonication with oxygen saturation done prior to the reaction. This study also obtained a low conversion of 2.1% but solely utilizing dissolved oxygen in the original solution. With oxygen sparging system, Ku *et al.* (1997) reported a 2-chlorophenol conversion of 50% after 3 hours of sonication at optimized conditions. Both reported works use an ultrasonic frequency of 20 kHz. Higher conversion is possible when using higher frequency of ultrasonic irradiation. Trabelsi *et al.* (1996) reported a phenol conversion of 80% after 1 hour of sonication with ultrasonic frequency of 540 kHz.

The presence of dissolved oxygen in aqueous solution was reported to play a very important role on the generation of highly oxidative hydroxyl free radicals (Wu *et al.*, 1992; Serpone *et al.*, 1994; Rooze *et al.*, 2012), and it might enhance the phenol degradation. Gogate *et al.* (2014) also reported beneficial effect of gaseous flow in the reactor in sonolitic oxidation of potassium iodide. Ku *et al.* (1997) indicates that most phenol breakdown by sonication may occur in the gaseous region inside cavitation bubbles and in film region, an interface between the gaseous phase and the bulk solution. This is because of free radical attack and pyrolysis which both only occur on these two regions. Free radical attack of

phenol is supposed to be negligible in the bulk solution region because the free radical produced in the cavitation bubbles are hardly moved to the room temperature bulk solution region through the much higher temperature film region. Gultekin *et al.* (2009) suggests that only small fraction of free radical OH^* diffuses from the interface into the bulk solution. Moreover, phenol is hydrophilic moderately soluble compound with relatively low vapor pressure. These properties prevent transfer of phenol molecules into the cavitation bubble, so they remain in the film or in the bulk of the solution during cavitation (Peng *et al.*, 2014). When oxygen exists in the solution in form of dissolved ones, however, oxygen molecules were decomposed in the cavitation holes to produce atomic oxygen and compete with some intermediates resulted from water molecules breakdown, leading to the formation of hydroxyl and hydrogen radicals (Wu *et al.*, 1992). Higher concentration of the radicals in the cavitation bubbles and the film region enhances transport of the OH^* radicals toward the bulk solution, promoting phenol and the radical interaction in the film region and bulk solution. This could be the reason of the increasing phenol degradation in the presence of dispersed gaseous oxygen in the solution with the degradation predominantly taking place in the film region, and to some extent in the bulk solution.

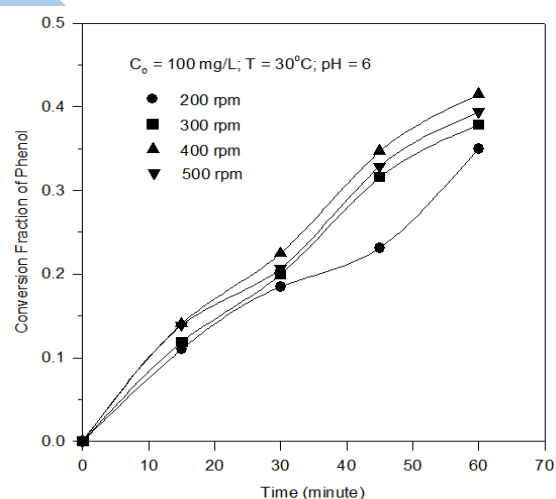


Figure 2. Phenol conversion at different stirring speeds.

3.2. Influence of Stirring Speed

Fig. 2 indicates that an increase in stirring speed resulted in higher phenol degradation rate, while beyond 400 rpm the rate decreased. When stirring speeds were

increased up to 400 rpm, dissolved oxygen was also increased because of better oxygen transfer rate into the solution. At higher dissolved oxygen, phenol degradation rate was enhanced through mechanism described in previous section. It seems that at such speed, more oxygen is dispersed in the solution in the forms of bubble, thus increasing bubble density. Possibly, more dense bubble dispersion at stirring speed exceeding 400 rpm has reduced effectiveness of ultrasound irradiation. As known, dispersed oxygeneous bubbles and cavitation bubbles could limit the cavitation range (Martin and Ward, 1992; Gogate *et al.*, 2014). The stirring speed of 400 rpm, therefore, was an optimum condition in the present work.

3.3. Influence of Phenol Concentration

Fig. 3 shows that initial phenol concentration has a linear relationship with the rates, indicating the first order kinetics with respect to phenol. This is in good agreement with observation on most catalytic and non catalytic oxidation of aqueous phenol which is typically the first order in phenol (Chang *et al.*, 1995; Ku *et al.*, 1997; Nikolopoulos *et al.*, 2005). Li *et al.* (2010) observed the same trend at low initial phenol concentration and then tend to be zero order at high concentration, above 0.1 mmol/L.

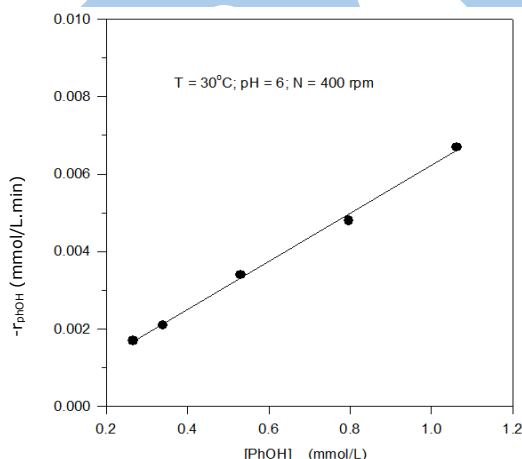


Figure 3. The effect of initial phenol concentration on reaction rates.

In present work, upper limit of the first order kinetics was higher (above 1.0 mmol) and this shift was probably enhanced because of free radical formation under oxygen rich solution. This trend also demonstrates that the intermediate products formed such as catechol, hydroquinone, and resorcinol did not inhibit the phenol degradation rate at least up to a conversion of around 40%.

3.4. Temperature Dependence of the Degradation Rate

Fig. 4 indicates that the conversion rates were found to decrease with increasing temperature. The conversion was reduced from 22.8% at 30°C to 10.0% at 60°C at one hour. Mason and Lorimer (1988) pointed out that the maximum sonochemical benefit obtained at such low temperature is feasible. At higher temperatures, the threshold intensity required to produce cavitation is lowered. This could be resulted from rising of vapour pressure, or lowering of viscosity or surface tension (Gogate *et al.*, 2014). On the other hand, increasing temperatures promote degassing of oxygen, leading to reduction in dissolved oxygen in the interface and the liquid bulk. As mentioned before, dissolved oxygen contributes significantly to the generation of highly oxidative hydroxyl free radicals.

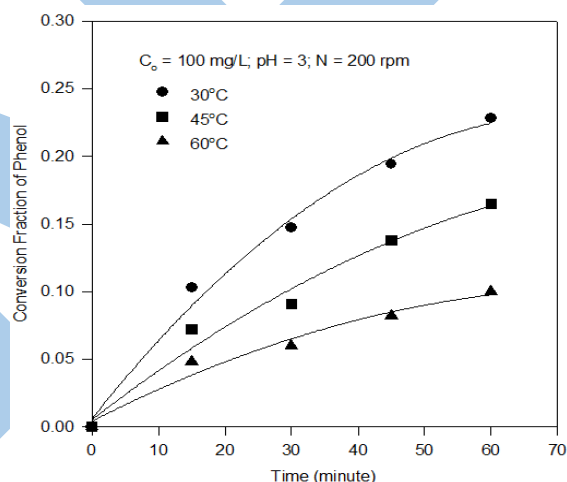


Figure 4. Phenol conversion at various sonication temperatures.

The temperature-dependence of reaction rate is evaluated by Arrhenius relationship. In order to allow this evaluation, values of rate constant should be determined. The semi-log plots of phenol concentration shown in Fig. 5 were linear over the entire reaction durations suggesting the first-order kinetics with respect to phenol and expressed by the following simple equation:

$$-\frac{dC_{Ph}}{dt} = k_1 C_{Ph} \quad C_{Ph} = C_{Ph0} e^{-k_1 t} \quad (1)$$

where C_{Ph0} and C_{Ph} represent the initial concentration and the concentration at time t , respectively, and k_1 is the apparent pseudo first-order constant. This confirms finding discussed in previous section. Most catalytic and non catalytic oxidation of aqueous phenol has been reported typically

as first order in phenol (Chang *et al.*, 1995; Ku *et al.*, 1997; Nikolopoulos *et al.*, 2005). By a best fitting procedure against Equation (1), the value of k_1 can be determined and the results are shown in Table 2. The determination coefficients of the fitting indicate good correlation between data and the equation. The combined kinetics constant at the observed reaction conditions is as follows:

$$k_1 = 1.30 \times 10^{-8} e^{6.04/T} \quad (2)$$

where T is absolute temperature in Kelvin. Similar findings of pseudo first-order degradation were reported for various organic pollutants under ultrasonic treatment with k values decreasing for increasing initial concentration (Lastre-Acosta *et al.*, 2014). A combination of decreasing cavitation effects, hydroxyl radicals produced, and diffusional rate out of the film region contributed to this reduction at higher pollutant concentration (Bagal and Gogate, 2014; Gogate *et al.*, 2014).

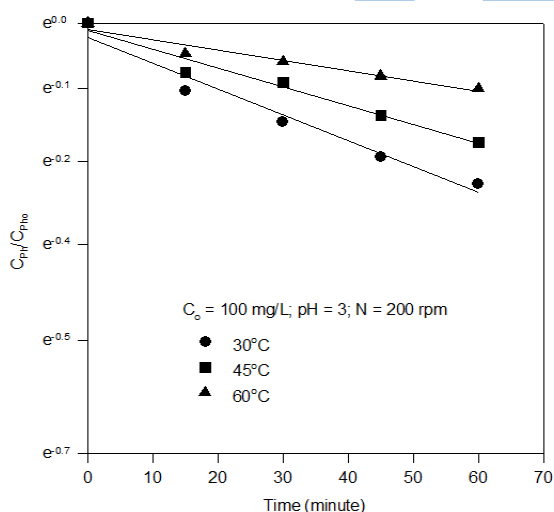


Figure 5. Semi-log plot for prediction of reaction order.

Table 2. Apparent pseudo first-order rate constants for sono-oxidation of phenol.

T (°C)	k_1 (min ⁻¹)	r^2
30	0.0047	0.9414
45	0.0033	0.9672
60	0.0019	0.9206

The rate controlling step of the reaction can be identified from the value of activation energy. The activation energy of the phenol degradation was determined from the straight line slope of Arrhenius plot and found to be 6.04 kcal/mol, suggesting

diffusional steps as rate determining during the decomposition of phenol by sono-oxidation. This diffusional steps refer to transport of reacting species, *i.e.* OH* free radicals from cavitation bubbles toward the film region.

4. Conclusions

The ultrasonic assisted oxidation of aqueous phenol carried out in a magnetically stirred glass reactor, demonstrates that phenol can be decomposed at ambient conditions which are milder than found in other AOPs. A 41.7% phenol conversion is achievable after one hour of sonication. Oxygen dispersed into the solution contributed to enhancement of degradation rate, by promoting formation of highly oxidative hydroxyl free radicals present in cavitation bubbles and the interfacial film. Phenol degradation was predicted predominantly occurring in the film region. The optimum reaction condition was found at a stirring speed of 400 rpm and temperature of 30°C. Kinetics analysis reveals that the phenol degradation was the first order with respect to phenol, and activation energy 6.04 kcal/mol suggests that diffusional step of OH* free radicals was rate determining during the phenol degradation by sono-oxidation.

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