

**OXIDATION OF ORGANIC COMPOUNDS WITH UV RADIATION
AND HYDROGEN PEROXIDE : TOLUENE IN AQUEOUS SOLUTIONS**
*(Oksidasi Senyawa Organik dengan Radiasi UV dan Hidrogen Peroksida :
Toluen dalam Larutan)*

I Made Bendiyasa*, Sarto, and Aprodhita Kusumaningtyas**

Chemical Engineering Department, Faculty of Engineering
Gadjah Mada University, Jln. Grafika, No.2, Yogyakarta, 55281

*Email : imbendiyasa@chemeng.ugm.ac.id,

**Email : sarto@chemeng.ugm.ac.id

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Abstract

Generally, waste water contains a large variety of organic and inorganic compounds. Most organic compounds are resistant to conventional chemical and biological treatments. Among them are aromatic compounds, such as toluene. This paper presents the results of experimental oxidation of toluene with combinations of UV and H_2O_2 which are usually called Advanced Oxidation Processes (AOPs). The experiments were performed in a batch system at room temperature. The experimental results exhibit that both initial concentration of hydrogen peroxide and initial pH affect the degree of oxidation. It is found that the order of reaction is pseudo first order with regard to toluene. The value of $k_{apparent}$ is observed linearly with respect to the initial hydrogen peroxide concentration and exponentially with regard to the initial pH. The effect of the initial hydrogen peroxide concentrations on $k_{apparent}$ is expressed as $k_{apparent} = 0,0015 C_{initial} + 0,0204 \text{ min}^{-1}$ and of the initial values of pH is $k_{apparent} = 0,0309 \cdot 10^{-0,027} (pH) \text{ min}^{-1}$. The effect of $C_{initial}$ and pH on $k_{apparent}$ can be expressed as $k_{apparent} = (0,0374 + 0,0009 C_{initial}) e^{-0,0316 (pH)} \text{ min}^{-1}$.

Keywords: toluene, UV radiation, hydrogen peroxide, wastewater

Abstrak

Umumnya limbah cair mengandung bermacam-macam senyawa organik dan anorganik. Sebagian besar senyawa organik, diantaranya adalah senyawa-senyawa aromatis, seperti toluene, tidak dapat dikenakan proses kimia maupun biologis konvensional. Tulisan ini menyajikan hasil penelitian yang terkait dengan oksidasi toluen dengan gabungan UV (ultra violet) dan H_2O_2 yang sering disebut Advanced Oxidation Processes (AOPs). Percobaan dilakukan di dalam sebuah reaktor batch pada suhu kamar. Hasil penelitian menunjukkan bahwa konsentrasi awal H_2O_2 maupun pH, mempengaruhi tingkat oksidasi toluen. Order reaksi yang sesuai dengan sistem ini adalah reaksi order satu semu terhadap toluen. Hubungan nilai $k_{apparent}$ dengan konsentrasi awal H_2O_2 adalah linier sedangkan hubungan $k_{apparent}$ dengan pH adalah eksponensial. Pengaruh konsentrasi awal H_2O_2 terhadap $k_{apparent}$ dapat dituliskan dalam bentuk persamaan: $k_{apparent} = 0,0015 C_{initial} + 0,0204 \text{ min}^{-1}$ dan pH awal terhadap $k_{apparent}$ adalah sebagai berikut $k_{apparent} = 0,0309 \cdot 10^{-0,027} (pH) \text{ min}^{-1}$. Pengaruh gabungan konsentrasi H_2O_2 dan pH awal dapat dinyatakan dalam persamaan $k_{apparent} = (0,0374 + 0,0009 C_{initial}) e^{-0,0316 (pH)} \text{ min}^{-1}$.

Kata kunci: toluen, radiasi UV, hidrogen peroksida, limbah cair

INTRODUCTION

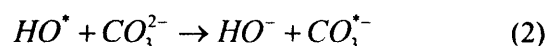
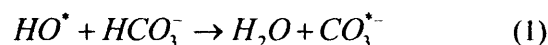
Environmental issue is becoming a global issue. Advanced oxidation processes (AOPs) have gained increasing interest in the treatment of wastewater to remove organic and inorganic compounds. This is because most of industrial wastes are not suitable to conventional treatment processes whose effluents are so very toxic so that they inhibit the microbiological processes involved in the treatment system. AOP's have been applied to special liquid effluents, particularly, to those of difficult biodegradability, and high toxicity (Mokrini *et al*, 1997; Martins, 1998). Overall organic content in the waste water, measured as COD (chemical oxygen demand), must be reduced in concentration before it is discharged to the environment. The main problems of AOPs lies in the high cost of reagents, such as ozone, H_2O_2 or energy-light sources like ultraviolet radiation, UV (Boncz, *et al*, 1997). The use of solar radiation as an energy source has a potential to reduce costs (Esplugas *et al*, 2002). The combination of UV as an energy source with H_2O_2 as an oxidant is a commonly studied AOP (Juang *et al*, 1997; Beltran-Heredia, *et al*, 2001, Dilmeghani & Zahir, 2001; Ghaly *et al*, 2001).

All AOPs produce hydroxyl radical, which is extremely reactive, and possesses a very high oxidation potential (Martins, 1998). Hydroxyl radicals produced by AOPs are used to oxidize organic compounds to the preferred end products of carbon dioxide and water. Hydrogen peroxide which is strong oxidizing agent has been applied as one of popular oxidizing agent in textile, electronic, and pulp and paper industries (Kirk-Othmer, 1995). The use of H_2O_2 for oxidizing nitrous acid was studied by Thomas *et al*, (1995). It was found that overall order was three with reaction rate constant was $k=3012 \text{ L}^2 \text{ mol}^{-2}\text{s}^{-1}$.

The use of H_2O_2 as an oxidant has a number of advantages compared to other methods of chemical or photochemical methods (Legrini *et al*, 2001). H_2O_2 is a commercial available oxidant, thermally stable and possible to store

on site. It has infinite solubility in water where two hydroxyl radicals are formed from each molecule of H_2O_2 photolyzed; $H_2O_2 + h\nu \rightarrow 2 \text{ OH}^*$. Peroxyl radicals are generated after a HO^* attack on most organic compounds leading to subsequent thermal oxidation reactions.

One of the disadvantages of the H_2O_2 /UV process is the oxidation of the contaminants is limited by the rate of formation of hydroxyl radicals. In system contains HCO_3^- and CO_3^{2-} ions, both ions will trap hydroxyl radicals to form carbonate radical ions (Legrini, *et al*, 2001) as follows:



Although, the generated carbonate radical anion has been shown to be an oxidant itself, its oxidation potential is less positive than that of the HO^* radical.

Bendiyasa *et al*, (2007) have studied the effects of initial hydrogen peroxide and pH on oxidation of benzene in aqueous solutions using combination of UV and hydrogen peroxide. It was found that the reaction was first order and the value of kapparent was observed linearly with respect to the initial hydrogen peroxide concentration and exponentially with regard to the initial pH. The effect of the initial hydrogen peroxide concentrations on k_{apparent} is expressed as $k_{\text{apparent}} = 0.0015 C_{\text{initial}} + 0.0204, \text{ min}^{-1}$ and of the initial values of pH is $k_{\text{apparent}} = 0.0303 e^{-0.0143 (\text{pH})}, \text{ min}^{-1}$.

Toluene is an aromatic hydrocarbon that is widely used as an industrial feedstock and as a solvent. It is water-insoluble liquid with the typical smell of paint thinners. Its solubility in water is 0.053 g/100 mililiters (20-25 °C). The methyl group makes it around 25 times more reactive than benzene.

Toluene may enter the human system not only through vapor inhalation from the liquid evaporation, but also following soil contamination events, where human contact with soil, ingestion of contaminated groundwater or soil vapor off-gassing can occur. As toluene has

very low water solubility, it cannot exit the body via the normal routes (urine, feces, or sweat). It must be metabolized in order to be excreted. The methyl group of toluene is more easily oxidized by cytochrome P450 than the benzene ring. Therefore, in the metabolism of toluene, 95% is oxidized to become benzyl alcohol (Nakajima *et al.*, 1997). The toxic metabolites are created by the remaining 5% that are oxidized to benzaldehyde and cresols (Hanioka *et al.*, 1995). Most of the reactive products are detoxified by conjugation to glutathione but the remainder may severely damage cells (van Doorn *et al.*, 1981).

United States Environmental Protection Agency (EPA) has set for both the maximum contaminant level goals (MCLG) and maximum contaminant level (MCL). The MCLG for toluene has been set at 1 part per million (ppm) and the MCL has also been set at 1 ppm. Toluene, in short term, has potentially cause minor nervous system disorder such as fatigue, nausea, weakness, and confusion when people are exposed to toluene at levels above the MCL for relatively short periods of time. While in long term, toluene can cause more pronounced nervous disorder such as spasms, tremors, impairment of speech, hearing, vision, memory, coordination; liver and kidney damage.

Because concentration of toluene is very low compared to hydrogen peroxide concen-

$$-\frac{dC}{dt} = k_{\text{apparent}} C \quad (3)$$

or

$$\frac{dX}{dt} = k_{\text{apparent}} (1 - X) \quad (4)$$

where $X = \frac{C_{(t=0)} - C_{(t=t)}}{C_{(t=0)}} = \text{conversion}$

of toluene, $t = \text{time}$, $k_{\text{apparent}} = k_r C_{H_2O_2} =$

tration, the H_2O_2 concentration changes are neglected. Therefore, the rate of toluene consumed is affected only by toluene concentration. By assuming the order of reaction is first order with respect to toluene concentration, in a batch system, mole balance of toluene becomes apparent reaction rate constant, $C_{(t=0)}$ and $C_{(t=t)}$ are initial concentrations of toluene and at any time, respectively. By integrating equation (4), it is found

$$-\ln(1 - X) = k_{\text{apparent}} t + I \quad (5)$$

where $I = \text{integration constant}$, If $-\ln(1 - X)$ is plotted against, it will give a linear line with slope of k_{apparent} . From equation (3) it can be

seen that if $-\frac{dC}{dt}$ is plotted against, it will

give a straight line with slope of k_{apparent} (reaction rate constant).

The main goals in the present study are to determine the order of reaction and the reaction rate constant of oxidation of toluene with combinations of UV and initial H_2O_2 concentrations.

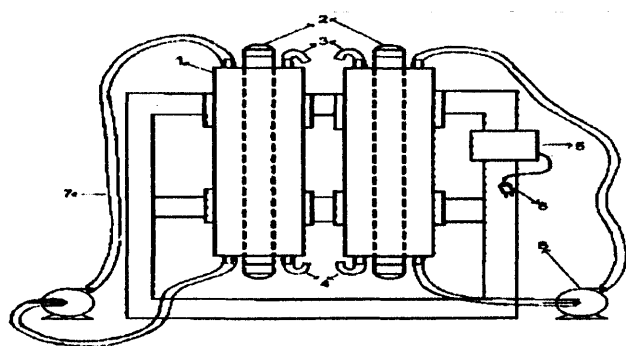
EXPERIMENTAL METHOD

Materials

Toluene of 99.85 % purity, hydrogen chloride (HCl), sodium hydroxide (NaOH), and aquadest. Hydrogen peroxide of 50 % purity was supplied by PT. Peroxide Indonesia Pratama.

Methods

All experiments were conducted in a reactor as shown in Figure 1. Each reactor consists of two cylindrical glasses; the smaller one is inserted inside the bigger one,



Legends

1. Annular Reactor
2. UV lamp
3. Inlet hole for fresh feed
4. Drainage hole
5. Voltage regulator
6. Pump
7. Flexible pipe
8. Plug

Figure 1. Schematic of annular reactor for advanced oxidation process

so it looks like an annulus. In each reactor, a UV lamp of 10 W is placed inside the smaller cylinder to avoid any contact with the wastewater. The intensity of lamp during the experiment was not monitored. To keep the solution in the reactor homogeneous, the solution was circulated by the pump.

Two hundred fifty milliliters of H_2O_2 of required concentration was mixed with 250 milliliters aqueous solution containing 0.1% toluene, and then the mixture was poured into the reactor. Subsequently, the UV light and the pump were switched on. Every five minute interval, since the UV light and pump were put on, 10 mL of sample was drained from the reactor via drainage hole and then the toluene content in the sample was analyzed using GC (Gas Chromatography) equipped with FID (Flame Ionization Detector). The initial pH was adjusted using NaOH or HCl solution depending upon the initial pH that was needed.

RESULTS AND DISCUSSION

Effects of initial hydrogen peroxide concentration

Figure 2 shows that the concentrations of toluene decrease with the increase of concentration of H_2O_2 . When the concentration of H_2O_2 rises from 30 % to 40 %, the concentration of toluene does not change markedly. Thus, the H_2O_2 concentration that is higher than 30% does not have any significant effects in increas-

ing the degree of toluene removal. This is because the changing of toluene concentration is very small.

According to Figure 3, relationship between $-\frac{dC}{dt}$ versus C exhibits a linear correlation. On this basis, it can be deduced that the reaction rate is first order regarding to toluene. Slope for each line, as can be seen in Figure 3, indicates the value of reaction rate constant, k_{apparent} . In addition, Table 1 also indicates that the ratio of mole of H_2O_2 to toluene is so very high that the changes of hydrogen peroxide can be neglected.

Figure 4 exhibits the correlation of k_{apparent} versus initial concentration of hydrogen peroxide. It can be seen that k_{apparent} is linear with respect to C_{initial} and can be expressed as:

$$k_{\text{apparent}} = 0.001C_{\text{initial}} + 0.034, \text{ min}^{-1}, \quad (6)$$

Equation (6) holds for C_{initial} ranging from 1.4706 to 5.8824 (mol.L^{-1}). If equation (6) is used to calculate the value of apparent reaction rate constant, it will give the maximum deviation from the experimental value equal to 1.49 %. Table 3 shows the values of k_{apparent} for both benzene (Bendiyasa *et al*, 2007) and toluene in aqueous solutions for pH=3. From Table 2 it can be seen that the value of k_{apparent} for toluene system is higher than that of benzene system. This means that toluene is more reactive.

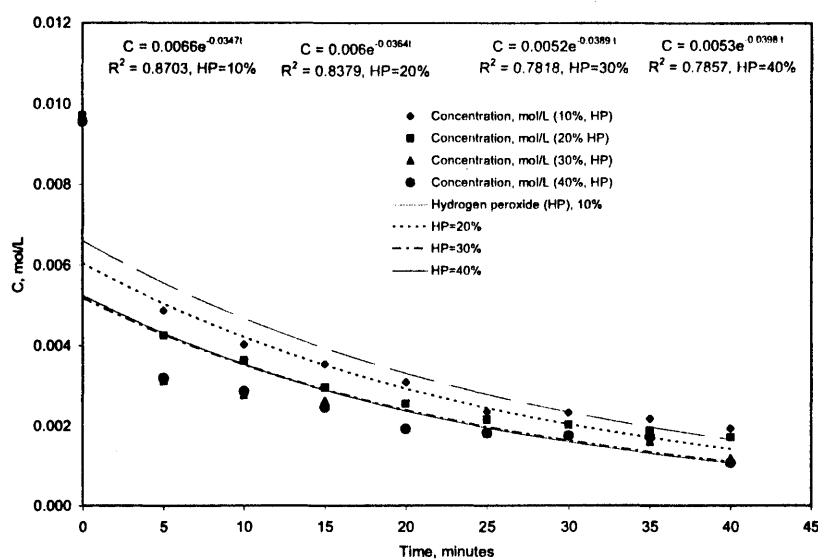


Figure 2. Concentration of toluene versus time for different initial H_2O_2 concentration (t =room temperature)

Table 1. Ratio mole of H_2O_2 to toluene

No.	Concentration of H_2O_2	Initial concentration of H_2O_2 in the system, mol/L	Ratio mole of H_2O_2 to toluene
1.	10 %	1.4706	151.3
2.	20 %	2.9412	303.0
3.	30 %	4.4118	461.6
4.	40 %	5.8824	615.4

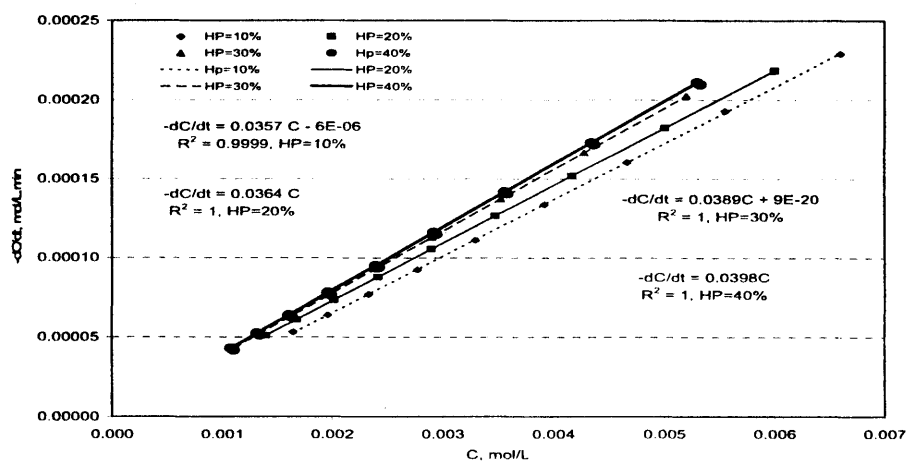


Figure 3. versus C for different initial hydrogen peroxide concentration. (t = room temperature)

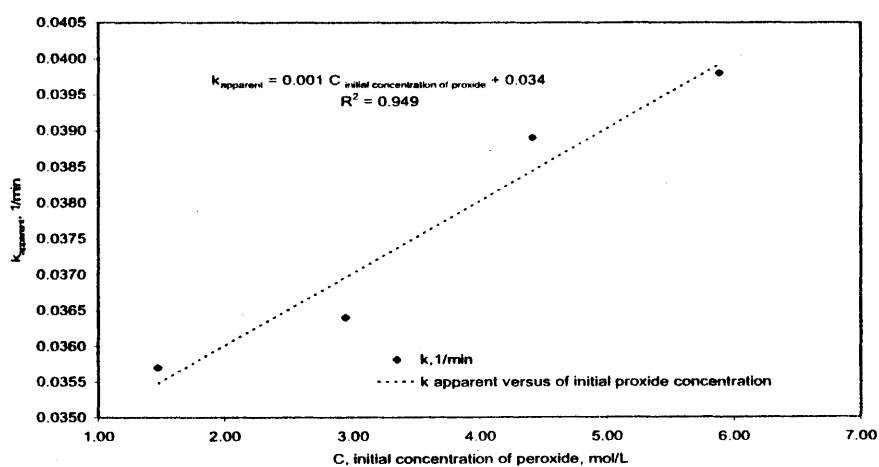


Figure 4. Plot of kapparent versus initial concentration of hydrogen peroxide (t=room temperature)

Table 2. Values of kapparent for benzene and toluene systems for pH=3

Benzene		Toluene	
$C_{\text{H}_2\text{O}_2}$, mol/L	k_{apparent} , (min) $^{-1}$	$C_{\text{H}_2\text{O}_2}$, mol/L	k_{apparent} , (min) $^{-1}$
1.4706	0.0226	1.4706	0.0319
2.9412	0.0248	2.9412	0.0333
4.4118	0.0270	4.4118	0.0348
5.8824	0.0292	5.8824	0.0363

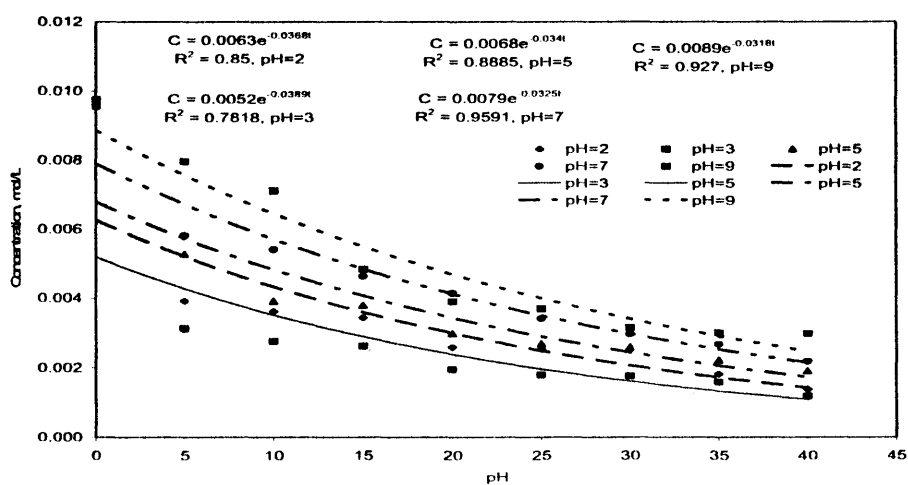


Figure 5. Concentration of toluene versus time for different initial pH (t=room temperature)

Effects of initial pH

As shown in Figure 5 the concentrations of toluene drop with the increase of the initial pH from 2 to 3 and then rise again. This is because when pH is high, hydrogen peroxide decomposes into oxygen and water, as follows (Beltran-Heredia, *et al*, 2001): $2H_2O_2 \rightarrow O_2 + 2H_2O$, $\Delta G = -56.9$ kcal/mole. Thus, it can be said that conversion of toluene becomes lower.

Figure 6 exhibits a linear correlation between $\frac{dC}{dt}$ and C. Each slope of the line provides a value of apparent rate constant. As shown in Figure 7, the trend of k_{apparent} (apparent reaction rate constant) decreases with initial pH and can be represented by equation (7).

$$k_{\text{apparent}} = 0.0399e^{-0.027[\text{pH}]}, \text{min}^{-1} \quad (7)$$

Equation (7) holds for pH from 2 to 9. If equation (7) is applied to estimate the value of k_{apparent} , it gives the maximum deviation 5.41% from the experimental value. As shown in Figure 7, the maximum value of k_{apparent} is 0.0389 min^{-1} at pH = 3. Table 3 exhibits the values of k_{apparent} for benzene (Bendiyasa *et al*, 2007) and toluene in aqueous solutions for 4.4118 mol/L of initial organic concentration. It can be seen from Table 3 that the values of k_{apparent} of toluene is higher than that of benzene. As has been mentioned before, this indicates that toluene is more reactive than that of benzene.

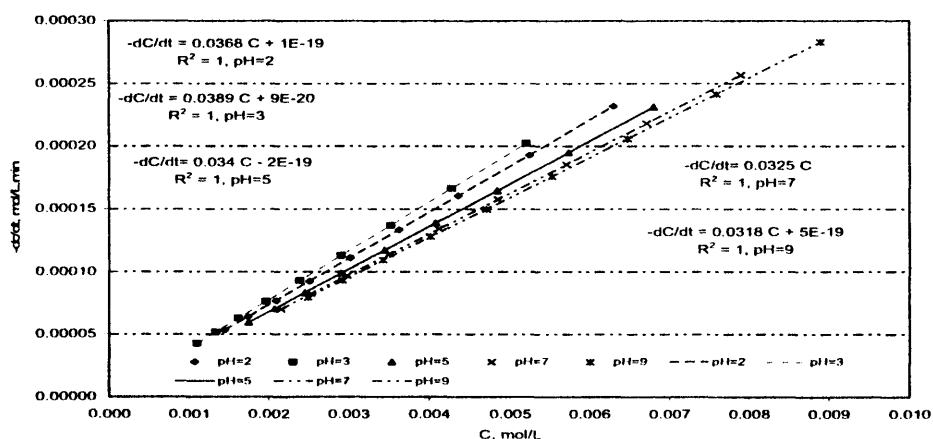


Figure 6. versus C for different initial hydrogen peroxide concentration. (t = room temperature)

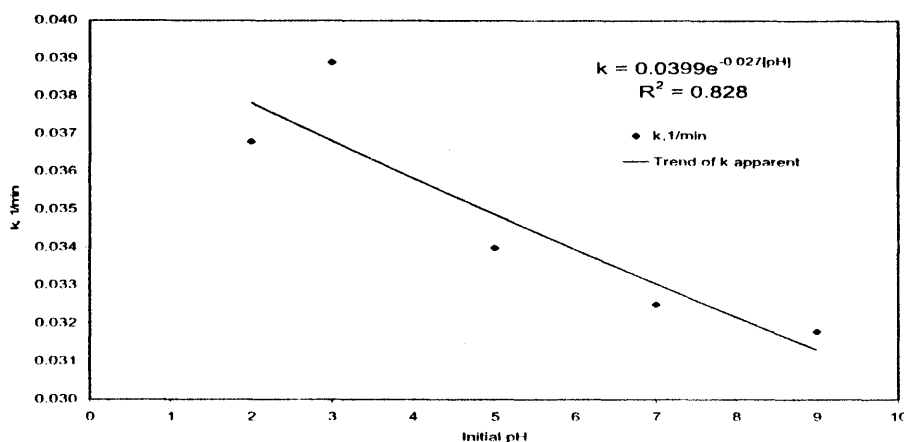


Figure 7. Plot of k_{apparent} versus initial pH (t=room temperature)

Table 3. Values of kapparent for benzene and toluene systems for 4.4118 mol/L of initial organic concentration

Benzene		Toluene	
pH	$k_{\text{apparent}}(\text{min})^{-1}$	pH	$k_{\text{apparent}}(\text{min})^{-1}$
2	0.0294	2	0.0378
3	0.0290	3	0.0368
5	0.0282	5	0.0349
7	0.0274	7	0.0330
9	0.0266	9	0.0313

The effect of C initial and pH on k_{apparent}

The can be expressed as

$$k_{\text{apparent}} = (0.0374 + 0.0009C_{\text{init}})e^{-0.0316(\text{pH})} \text{ min}^{-1}.(8)$$

If equation (8) is used to calculate the values of k_{apparent} , it gives the maximum deviation of 5.75 % from the experimental values.

CONCLUSIONS

Using combinations of hydrogen peroxide and UV radiation for oxidation of toluene have shown a promising process for removing the organic compounds. Both initial concentration of hydrogen peroxide and pH affect the degree of removal of toluene. The apparent reaction rate constant, kapparent, is observed linearly with respect to initial concentration of hydrogen peroxide and exponentially with regard to initial pH. The increase of initial concentration of hydrogen peroxide rises the value of kapparent. In contrary the value of kapparent declines with respect the increase of initial pH. The order of reaction is pseudo first order reaction.

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