Toluene degradation using aqueous absorption and Fenton’s oxidation in pilot plant

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Abstract
In pilot plant, the absorption column comprises a 2 m long by 75 mm diameter mass transfer section which was packed with 16 mm plastic Pall rings. The reactor has a capacity of 50 litres. The pressure drop at liquid and gas loading used in this study showed the system to be in the loading region. The mass transfer coefficient is a function of both the liquid and gas flow rates. The height of a transfer unit is in the range of Onda’s prediction toleration. Toluene absorption by water was observed to be 30 to be 37%. The percent toluene degradation is affected by sampling shaking time, operating time and the increasing of \([H_2O_2]\) and \([FeSO_4]\) at the beginning of reaction. The results show that toluene is absorbed and oxidized at the same time the packed column. The concentration toluene is 60 ppm in aqueous solution. The percent toluene degradation by mole than 95% measured at the reactor outlet indicates that the continuous operation gives agreement with the batch operation at the molar ratio of \([H_2O_2]/[Toluene]/[FeSO_4]\) of \([30]/[1]/[3]\), a pH of 3 and an operating time of 1 hr. The absorption combines with chemical oxidation using Fenton’s reagent to achieve optimum and cost-effective treatment for air contaminated with organic aqueous solution with a short time and a single treatment.

Key words: Toluene, absorption, Fenton’s oxidation.

Introduction
The emission of volatile organic compounds (VOCs) in effluent gas from industries contributes to smog and to air toxicity. Many of these compounds are highly toxic, carcinogenic, and/or mutagenic, therefore, they must be effectively destroyed in industrial wastes before these are disposed of. Toluene is one of the common toxic volatile organic pollutants in industrial water and air, being a member of 129 priority pollutants listed by the Environmental Protection Agency (EPA) in the USA. Of particular interest are the airborne volatile organic compounds which of absorbed into water need further rapid oxidation for the overall process to be effective. The organics wastes can be degraded by either biological methods or physicochemical processes. The biological treatment process usually takes from several hours to days to complete degradation, especially for aromatic compounds. Recently, physicochemical treatment processes for organic pollutants have been actively investigated. These processes include the photo-catalytic oxidation process, ozone/UV process, and the Fenton reaction. The oxidation processes involve hydroxyl radicals (\(HO^+\)), which is the second strongest oxidant (with an oxidation potential of 2.8 volts) next only to fluorine (3.0 volts) 4.

Absorption can be used to remove VOCs from gas streams by contacting the contaminated air with a liquid solvent. Any soluble VOCs will transfer to the liquid phase. It has proven to be a technically and economically feasible method for the removal of hydrocarbons from a contaminated air stream. In general, it is less costly than the other available methods, such as adsorption, condensation and combustion 5. Two important physicochemical parameters affecting absorber performance are the Henry’s law constant of the contaminant and overall mass transfer coefficient used to describe the gas-to-liquid-contaminant transfer. Mass transfer coefficients are often estimated from empirical correlations on Onda et al. 6 and calculated overall height of a transfer unit on Sinnott 7. Whereas values for Henry’s law constant are measured in the laboratory 8,9 selected from prior measurement reported in the literature, or calculated from published values of vapor and solubility 10,11.

The modified EPICS method 12 for measuring Henry’s law constant \((H)\) of toluene is an accurate and convenient procedure for practical use in the design and operation of absorption process. It is a combination of EPICS 10 (equilibrium partitioning in closed system) method with the simple calibration method 13. The EPICS method uses two headspace gas chromatograph peak areas to determine \(H\) but requires a saturated solution to be prepared for at least 2 weeks. The simple method uses a calibration curve to determine \(H\) from direct toluene injection. The modified EPICS method uses the two headspace peak areas, a direct toluene injection and equilibrium time of about 1 h. The dimensionless Henry’s Law Constant of toluene is calculated 12 as:

\[
H = \left( \frac{G_{a1}}{G_{a2}} \frac{W_{a1} - V_{a2}}{V_{a2} - \frac{G_{a1}}{G_{a2}} W_{a1}} \right)
\]

where \(C\) and \(V\) represent the concentration of the organic compound and the volume of the gas \((G)\) or liquid \((L)\) phase, respectively. The subscripts 1 and 2 identify the two closed
systems, namely, Modified EPICS bottle containing 20 and 200 mL of water in the 264 –mL glass bottles, respectively. To convert \( H \) into \( H_{\text{r}} \) in units of kPa.m\(^3\).mol\(^{-1}\), the factor \( RT \) was used to multiply \( H \), in which \( R \) is the gas constant (8.3145 Pa.m\(^3\).mol\(^{-1}\).K\(^{-1}\)) and \( T \) is the experimental temperature (K).

For absorption operation, it is customary to use \( K_c \) values because the overall gas phase resistance dominates the mass transfer rate; the liquid phase resistance can often be removed by chemical reaction. The prediction of gas–film mass transfer coefficient was obtained by Onda’s equation \(^6\) that correlated available data on gas absorption in packed columns for a range of packing as following:

\[
k_{\text{g},RT} = \left( \frac{G}{a \mu_g} \right)^{\frac{3}{8}} \left( \frac{\mu_g}{\rho_\text{g} D_\text{g}} \right)^{\frac{1}{8}} (a d_i)^{-\frac{3}{2}}
\]

where \( k_{\text{g},RT} \) is gas-phase mass transfer coefficient, \( a \) is total surface area per unit packed volume, \( D_\text{g} \) is gas diffusivity, \( d_i \) is packing nominal diameter, \( \mu_g \) is gas viscosity and \( \rho_g \) is gas density. The constant \( C \) is 5.23 for packing sizes above 15 mm except for small Raschig rings and Berl saddles and 2.00 for sizes below 15 mm. The eq. (2) was found to predict experimental gas-side volumetric mass transfer used within \( \pm \)30%.

The overall height of a transfer unit (HTU\(_{\text{OG}}\))\(^7\) can be calculated from the volume of tower packing for the absorber. According to the relationship between the individual gas and liquid film height of transfer units with HTU\(_{\text{OG}}\) by equation (3) to (5) as following:

\[
\text{HTU}_{\text{OG}} = \text{HTU}_a + m(G_m - \rho_\text{L})\text{HTU}_l
\]

\[
\text{HTU}_l = \frac{L_m(MW_{\text{solution}})}{k_a a \mu_\text{L} \rho_\text{L}}
\]

\[
\text{HTU}_a = \frac{G_m}{k_a a \mu_\text{g} \rho_\text{g}}
\]

where \( m \) is equilibrium line slope, \( MW \) is molecular weight, \( L_m \) is liquid molar flux, \( G_m \) is gas molar flux, \( a \) is wetted surface area of the packing, \( \rho_\text{L} \) is liquid density and \( P \) is total pressure.

Chemical oxidation of wastes is a well-established technology that is capable of destroying a wide range of organic molecules, including chlorinated VOCs, mercaptans, phenol and inorganics such as cyanide \(^{14}\). Fenton’s reagent is a mixture of hydrogen peroxide an a ferrous ion (Fe\(^{2+}\)) that produces hydroxyl radicals (HO\(^•\)). It has three attractive features for treating organic compounds in water \(^{15}\). First, the HO\(^•\) radicals have proved to effectively react with a variety of organic substances such as chlorinated phenol\(^{16}\), and polycyclic aromatics \(^{15}\), in aqueous solutions and wastewater. Second, the products are easy to handle and environmentally friendly since the final decay materials (water, oxygen, carbon dioxide, and ferric hydroxide) introduce no further pollution. Third, costs of the hydrogen peroxide and ferrous ion are quite, so the treatment is economical and practical for a single treatment system. Kinetic scheme for hydrogen peroxide and ferrous ions are usually stable in a strong acid, but if hydrogen is added to an aqueous system containing an organic substrate and excess ferrous in a strong acid, a complex redox reaction \(^{17-20}\), as in equation (6)-(9), will occur:

\[
\text{Fe}^{2+} + \text{HO}^• \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{HO}^• \quad k_1 = 76 \text{ M}^0\text{s}^{-1}
\]

\[
\text{Fe}^{2+} + \text{HO}^• \rightarrow \text{Fe}^{3+} + \text{OH}^- \quad k_2 = 3 \times 10^4 \text{ M}^0\text{s}^{-1}
\]

\[
\text{RO}^• + \text{RH} \rightarrow \text{H}_2\text{O} + \text{R}^\cdot \quad k_3 = 10^7 - 10^{10} \text{ M}^0\text{s}^{-1}
\]

\[
\text{R}^\cdot + \text{Fe}^{2+} \rightarrow \text{R}^- + \text{Fe}^{3+} \quad k_4
\]

where eq. (6) and eq. (7) are chain initiation and termination and eq. (8) and eq. (9) the chain propagation steps. The most likely side reactions in the redox system are:

\[
\text{H}_2\text{O}_2 + \text{HO}^• \rightarrow \text{H}_2\text{O} + \text{HO}^• \quad k_3 = 2.7 \times 10^3 \text{ M}^0\text{s}^{-1}
\]

\[
2\text{R}^\cdot \rightarrow \text{R}^- + \text{R} \quad k_5
\]

Since \( k_3 = 10^3 \text{ M}^0\text{s}^{-1} \) while \( k_4 = 10^7 - 10^{10} \text{ M}^0\text{s}^{-1} \), eq. (10) can be reduced in importance by maintaining a high [RH] : [H\(_2\)O\(_2\)] ratio, the reaction rates of \( k_3 \) eq.(9) and \( k_4 \) eq.(11) depend on the structure of organic compound and eq. (11) can be suppressed by maintaining as low a radical concentration as feasible in the system.

Fenton’s oxidation \(^{21}\) is capable of oxidizing toluene by more than 95% in a period of ten min at a concentration ratio of [H\(_2\)O\(_2\)]/[C\(_6\)H\(_5\)CH\(_3\)]/[FeSO\(_4\)] of 30:1:3 (molar) at a temperature of 25 \(\pm\)C. The optimum pH is found to be 3 which is required for the catalytic decomposition of toluene. The rate equation for toluene degradation is derived from experimental data for predicting the residual concentration of toluene from the contact time. It is found to follow a pseudo first-order reaction at a temperature of 25 \(\pm\)C that can be expressed as:

\[
\ln C = \ln 0.095 - 0.14 (t)
\]

This research work attempts to use the Fenton’s oxidation in the liquid-phase to degrade toluene in the effluent gas on pilot plant at a concentration ratio of [H\(_2\)O\(_2\)]/[C\(_6\)H\(_5\)CH\(_3\)]/[FeSO\(_4\)] of 30:1:3 (molar). It can provide valuable information for reaction kinetics, mass transfer, start-up and shutdown operations and operability studies.

Materials and Methods

A schematic diagram of the experimental setup for the toluene absorption and Fenton’s oxidation process is depicted in Fig. 1. The main apparatus consists of a packed column, a reactor with a capacity of 50 litres, a peristaltic pump, a centrifugal pump, a water column (2 litres) with inside diameter 6 cm. by 70 cm long., a bubbler to deliver toluene vapor and fixed with two checkvalves for protecting against back pressure, u-tube/manometer, three air rotameters, a liquid rotameter, five thermometers with accuracy \(\pm 0.1 \text{ \degree C}\), an amber bottle of hydrogen peroxide and two gas sample bombs. The absorption column has a 2 m long by 75 mm (3 inch) inside diameter packed section, with liquid distributor at the top column and re-distributor between the packed section. The column is packed with 16 mm (5/8 inch) plastic Pall rings.

Toluene absorption: Feed tap water (ambient temperature 18 \(\pm\)C) directly into the reactor is approx. 20 litres by observing water level in the reactor. Then turn switch on the centrifugal pump, it draws the aqueous solution from the reactor and delivers it to the top of column with flow rate to 1, 2, 3 and 4 L/min, respectively. Next, start supplying toluene and air mixture into the system by control air mixture at various values. Finally, read the pressure drop from u-tube/ manometer in unit of mm water. At steady state, approximately 30 min. after feeding toluene/air mixture into column,
taking two gas sample bombs at column inlet and outlet to analyze with gas chromatography.

**Toluene absorption with subsequent chemical oxidation:** Feed tap water directly into the reactor is approx. 20 litres by observing water level in the reactor, turn off tap water valve. Then, pour 68, 210 mL of 0.75 N sulphuric acid and 197, 600 mL of 0.2 N ferrous sulphate into reactor and circulate the aqueous solution 30 min, meanwhile the control range of pH 2.6-3.0. Next, the centrifugal pump draws the aqueous solution from the reactor and delivers it to the top of column with flow rate to 2L/min. about 20, 60, 120 and 180 min. Start supplying toluene and air mixture into the system until air mixture flow rate is reached to 38.8 L/min. Turn on peristaltic pump switch, it is used to feed hydrogen peroxide from an amber storage bottle into the reactor. When the first drop of hydrogen peroxide contacts the surface of aqueous solution (start the reaction), press stopwatch button. The flow rate of hydrogen peroxide is 2.4 L/h. Wait for 20, 60, 120 and 180 min. and then taking two gas sample bombs at the column inlet and column exit and the gas samples, and two bottles of aqueous solution at reactor inlet and outlet for toluene analysis.

The optimum conditions of Philips Gas Chromatograph (GC),
model PU4550, obtained for toluene are as follows; Flame Ionisation Detector (FID), flow rate of He gas at 30 mL/min., injector and detector temperature at 250 °C, oven temperature at 130 °C, DB-Wax column, approx. residence time 4 min.

Results and Discussion

Pressure drop along the packed column: The logarithm of the ΔP/Z against the logarithm of the G for Pall rings with various liquid loading 0 to 14.61 kg/s.m² is shown in Fig. 2.

As may be found from this figure, the slope of the dry pressure drop is 2.35 Pa.s.m/kg, the ΔP/Z increases with increasing gas rate at constant liquid loading and increasing liquid rate at constant gas loading. Each of liquid loading curves shows no indication of sudden change in the slope at flooding point.

Effect of gas (G) and liquid (L) rates on mass transfer coefficient:

The plot of effect of gas and liquid loading on the $K_{G,a}$ was shown in Fig. 3 (a) and (b).

For a given liquid loading, the overall volumetric mass transfer coefficient increases with increasing gas loading as indicated in Fig. 3 (a). The $K_{G,a}$ increases with increasing gas rate at constant liquid rate and the $K_{G,a}$ increases with increasing $L$ at constant $G$.

The effect of liquid loading ($L$) on the $K_{G,a}$ has the trend line same as effect of $G$ on the $K_{G,a}$ as viewed in Fig. 3 (b).

Effect of gas and liquid rates on overall height of a transfer unit:

The plot of the HTUOG versus gas and liquid loading was demonstrated in Fig. 4 (a) and (b).

At constant $L$, the HTUOG increases with increasing gas rate. On the contrary, the HTUOG decreases with increasing liquid rate at constant gas loading as found in Fig. 4 (a). The results of effect of liquid loading ($L$) on the HTUOG are indicated the trend line as effect of gas loading ($G$) on the HTUOG viewed in Fig. 4 (b).

Comparison between Onda’s correlation and the experimental data:

The prediction of the HTUOG for toluene absorption Pall rings between Onda’s correlation and the observed data is shown in Fig. 5.

As may be seen from this figure, the value of experimental HTUOG

![Figure 2](image-url)  
*Figure 2. Pressure drop per unit length of Pall ring versus gas loading.*

![Figure 3](image-url)  
*Figure 3. Effect of gas and liquid rates on $K_{G,a}$ for toluene absorption.*

![Figure 4](image-url)  
*Figure 4. Effect of gas and liquid rates on $K_{G,a}$ for toluene absorption.*

![Figure 5](image-url)  
*Figure 5. Deviation in prediction of toluene absorption using Pall rings by Onda’s correlation.*
are higher than that of Onda’s prediction by about 20%. Therefore, the experiment of toluene absorption using 16 mm. of plastic Pall ring in the following conditions is an acceptable operation: diameter of column was 75 mm., height of packing was 2 meters, and liquid and gas loading was in the range of 3.65-14.59 and 0.17-0.34 kg/s.m², respectively. For toluene absorption, most of the height of a transfer unit is due to the resistance in the gas phase. Because the results show that HTU is much higher than HTU).

**Toluene absorption with subsequent chemical oxidation**

**Effect of aqueous sample shaking time in modified EPICS bottle:** The effect of sample shaking time in EPICS bottle before injecting to GC is shown in Table 1.

When the time for shaking the sample bottle was changed from 1 hr to 5 min., percent toluene degradation reduced from 97 to 37%. Because the solution at the reactor outlet is recycled into the packed column, it still has H₂O₂ and FeSO₄, and is sufficient to oxidize toluene. From these results, a sample bottle at the reactor inlet and outlet need to be shaken for 5 min. before moving a gas injection into GC for measuring toluene degradation.

**Effect of operating time related to FeSO₄:** The effect on toluene absorption and degradation related to FeSO₄ solution at 197-mL and operating times as shown in Table 2.

The results showed that % toluene degradation increase with increasing time between 20 to 60 min. After at that times, it inverses to increasing time. According to the eq. (7) and (9) as:

The kinetic rate constant k₁ may be much faster than k₂ Ruppert et al. 22 and Murphy et al. 23 demonstrated that the initial rate of destruction of organic pollutants by the Fe²⁺/H₂O₂ reagent has been found to be much slower than that for the Fe³⁺/H₂O₂ reagent. Also after 60 min, it may be that the amount of ferrous ion (Fe²⁺) decreases, while ferric ion (Fe³⁺) increases.

**Effect of increasing H₂O₂ and FeSO₄ at the beginning of reaction:** The effect on toluene absorption and degradation by increasing H₂O₂ and FeSO₄ at the beginning of reaction is shown in Table 3. Comparing percent toluene degradation at reactor inlet for 197 mL of FeSO₄ and 600 mL of FeSO₄ and 400 mL of H₂O₂ at any time, the results showed that the higher amount of H₂O₂ and FeSO₄ at the start-up, the higher percent toluene degradation. It is caused by adding hydrogen peroxide at the beginning of reaction time increasing the number of hydroxyl radicals, ready to oxidize and accumulate in the recycled solution.

**Conclusions**

The absorption of toluene from air into aqueous phase is in the range of 30-37% of the gas phase values. The wet pressure drop values in the studied range of gas and liquid flow rates are in the loading region. The K,α values of toluene are a function of both the liquid and gas flow rates. However, the HTU is much higher than HTU, also toluene absorption is a gas-film-controlled system. The HTU of the experimental data is within the tolerance of Onda’s correlation. Also, the absorption of toluene vapor into aqueous solution with subsequent Fenton’s oxidation in a pilot plant is an acceptable for continuous operation by more than 95%.

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**References**


