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PILOT SCALE SYSTEM FOR REMOVAL OF PHENOL IN PHENOLIC WASTEWATER OF OLEFIN PLANT

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Elimination of phenol from phenolic wastewater of an olefin plant using ozone is reported. In this work a bench-scale semi-batch ozonation system was set up in the Environmental Engineering Research Center (EERC). A venturi injection and a circulation system was used for injection of ozone into the ozonation contactor. Samples were taken from buffered aqueous phenol solutions at different pH values with an initial concentration of 80 ± 5 ppm. Experimental results revealed that phenol removal efficiency increased with increasing pH and reached >99.5% after 15 min ozonation at a pH of 11. With increasing pH, ozone consumption (i.e. mol O_3 per mol phenol) decreased from 6.1 to 5.1. The results were compared with Roth's model, which was used to describe the global reaction rate of ozonation of phenol. Using Roth's model and results of bench-scale system a pilot scale ozonation system was designed and set up in a petrochemical complex. From the results of steady-state pilot scale tests, it was shown that ozonation could significantly reduce phenol concentration to the desired level in actual wastewater.

Keywords: ozone; olefin plant; phenol; scale-up; phenolic wastewater.

INTRODUCTION

The petrochemical industry is a prominent and rapidly developing industry throughout the world. Production of phenolic wastewater is one of the environmental problems in the olefin plant of a typical petrochemical complex. Nearly $20\,m^3\,h^{-1}$ of boiler feed water (BFW) grade treated water is converted to phenolic wastewater in an average sized olefin plant. In addition to phenol, there are other hydrocarbon components such as polycyclic aromatic hydrocarbons (PAH) in the phenolic wastewater. In most of the petrochemical complexes, phenolic wastewater is often discharged into the biological wastewater treatment unit of the complex. Because of the adverse effects on microorganisms, phenolic wastewater usually reduces the performance of the treatment facilities. With elimination of the pollutants in phenolic wastewater, the treated water can be used in the plant for different purposes, or its harmful effects on wastewater treatment operation can be minimized. Onsite specialized treatment of the phenolic wastewater can have environmental and economical benefits. Typically there is about 30–60 ppm phenol in the phenolic wastewater of the olefin reactor, whereas the standard maximum limit of phenol concentration in effluent streams is less than 1 ppm. A review of the previous studies for elimination of phenol using ozone indicates that ozonation is a technically viable treatment alternative for treatment of phenolic wastewater. Besides phenolic compounds, ozone treatment has proven to be an effective method for destruction of other pollutants in phenolic wastewater such as PAH (Kommuller *et al.*, 1997).

Studies show that the reaction between ozone and phenol is complex owing to the existence and generation of various intermediates during ozonation (Eisenhauer, 1971). Based on the previous studies, the important parameters in the reaction between ozone and phenol are pH, temperature and mass transfer resistance in the gas–liquid reaction (Roth *et al.*, 1982; Mokrini *et al.*, 1997; Zhou and Smith, 2000; Hsu *et al.*, 2001). Eisenhauer (1971) reported that the effect of pH on the destruction rate of phenol by ozone was negligible at low pH levels, but at pH higher than 11 the destruction rate was doubled. Gould and Weber (1976) reported that there was an increase in the destruction rate of phenol by ozone at pH values between 4 and 7.5 with a slight increase at pH of above 8. Furthermore, an increase of the reaction rate constant with increase of pH has been reported by Li (1979). The results reported by Auguglirao and Rizzuti (1978) showed that pH had a minimal influence on the reaction rate of ozone with phenol. From these studies, it can be concluded that, with rising pH, the rate of elimination of phenol increases but the extent of this effect depends on the reaction system and operating conditions.

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The majority of the researchers have stated that temperature has a minor effect on the reaction rate at temperature range of 20–50 C (Eisenhauer, 1971, Li, 1979, Boncz *et al.*, 1997). It seems that the increase in the rate of reaction with rising temperature is compensated by the decrease in solubility of ozone in water and the increase in rate of ozone self destruction.

Moreover, Eisenhauer (1971) observed that the amount of ozone required to destroy each mole of phenol was about 5 mol (2.55 g O_3 g^{-1} phenol). Gould and Weber (1976) also reported that 4–6 moles of ozone were required to eliminate each mole of phenol. The results obtained by Roth *et al.* (1982) verified Gould's conclusions.

The other important factor influencing the reaction rate is mass transfer resistance. Ozonation is a simultaneous mass transfer and chemical reaction kinetics phenomenon. This phenomenon has been recognized in some previous studies (Li, 1979; Augulalirao and Rizzuti, 1978). For ozonation of phenol, the chemical reactions network is very complex. Ozone decomposes simultaneously in aqueous solution while reacting with phenol. The subsequent phenol decomposition products are further oxidized by ozone. Roth *et al.* (1982) modelled this mass transfer/chemical reaction system as a function of operating parameters using a semi-empirical model:

$$-r_{\Phi OH} = -\frac{d[\Phi OH]}{dt} = k_n[\Phi OH]^n \quad (1)$$

and

$$k_n = \alpha\left(\frac{G}{V}\right)^{\beta}[\Phi OH]_0^{\gamma}[OH^-]^{\delta} \quad (2)$$

where $-r_{\Phi OH}$ is the global rate of phenol disappearance (gmol phenol l^{-1} min^{-1}); k_n is the global rate constant, min^{-1} (gmol phenol l^{-1})$^{1-n}$; $[\Phi OH]_0$ is the initial concentration of phenol (gmol l^{-1}); $[OH^-]$ is the hydroxyl ion concentration (gmol l^{-1}); G is the ozone feed molar flow rate (gmol min^{-1}); V is the volume of liquid reaction medium (l); n is the apparent order of phenol decomposition reaction; and α, β, γ and δ are constants determined from experimental data. They analysed different kinetic data using integral method to determine the rate constant, k_n. Their kinetic analysis showed that a first-order kinetic fitted reasonably well the experimental data with correlation parameters ranging from 0.94 to 1. Then they fitted the experimentally determined rate constants and re-analysed the literature data using first order kinetics and the model given in equation (2) and multilinear regression analysis.

In the present work an experimental study was conducted for elimination of phenol in phenolic wastewater with ozone in both semi-batch and continuous modes. A venturi system was used for injection of ozone into the liquid phase, which was circulated by a circulation pump. Buffered aqueous phenol solutions were used in semi batch laboratory experiments (batch with respect to phenol) to determine the reaction kinetics and to study the effects of important operating parameters. For continuous operations, actual phenolic wastewater produced in the olefin plant (effluent of the cracking reactor) was used as the feed to the pilot-scale system. It is believed that the findings of this work can be used in design and operation of larger scale-ozonation systems.

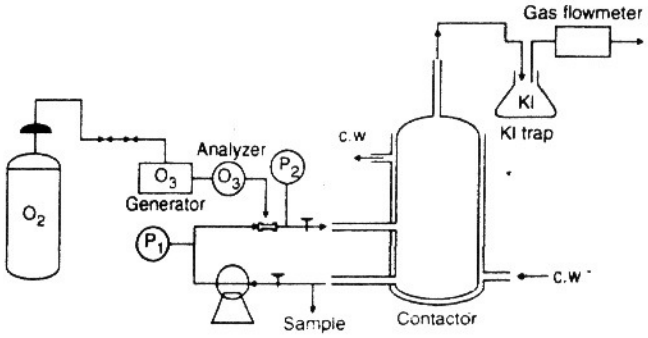

Figure 1. Schematic diagram of the bench-scale batch set-up (P_1, upstream pressure; P_2, downstream pressure of the injector).

METHODS AND MATERIALS

All laboratory experiments were carried out in a bench-scale set-up. A schematic diagram of the bench scale system is shown in Figure 1. Ozone was generated using an ozone Lab generator (Ozomatic Lab 802, Wedeco, Germany) with the production rate of 1–4 g h^{-1}. Pure oxygen was used as the feed to the ozone generator. Using a flow meter and an ozone analyser (BMT, Press version), the gas flow rate and ozone concentration were monitored in the ozone-rich gas stream. For the gas-phase injection, a venturi injector (Lab 802) was used. A stainless steel circulation pump (CRN2-30) was used to circulate liquid phase reaction medium in the system. The ozonation reactions took place in a 3 l batch contactor made of glass (i.d. = 70 mm). The temperature of the contactor could be controlled by a water jacket circulation. The total reaction volume of the system was 5 l. This is the volume of the contactor and the volume of reaction loop. The outlet gas from the contactor passed through a KI trap containing 100 ml of 1% KI solution to trap the unreacted ozone.

The synthetic phenol solutions with phenol concentration of 80 ppm were prepared using distilled water at different pH levels. The pH values were adjusted to 2.4, 4.4, 6.3, 7.8, 9.0 and 11.0 (±0.2), using buffer solutions.

For every experiment, about 3.5 l of the synthetic phenol solution was charged into the system. Flow rate and concentration of the ozone gas were 50 l h^{-1} and 36–37 g m^{-3}, respectively. All experimental runs were isothermal at 21 ± 2 C. The reaction volume varied from 3.2 to 3.5 l and the phenol concentration was 80 ± 5 ppm (G/V of between 0.00017 and 0.0002). Samples were taken from

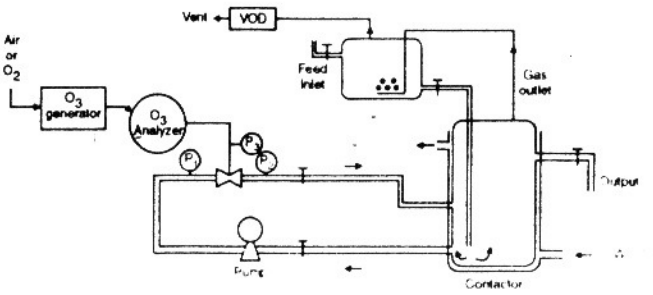

Figure 2. Schematic diagram of the continuous pilot-scale set-up (P_1, upstream pressure; P_2, downstream pressure of the injector; P_3, ozone stream pressure).

Table 1. Test conditions for continuous flow pilot-scale runs in the olefin plant

Test series	Volume of reaction medium, l	Liquid feed flow rate, $l\,h^{-1}$	Phenol concentration in the liquid feed, ppm	Ozone gas inlet concentration, g Nm^{-3}	Ozone flow rate, $Nl\,h^{-1}$	P_1, bar	P_2, bar	Feed pH	T (°C)
1	45	23–27	54.9	38	50	1.1	0.55	5.8	25
2	45	23–27	54.9	65	50	1.1	0.55	6	30
3	45	15–19	37.5	65	50	1.1	0.55	6	30

the reactor at different time intervals (e.g. 0, 5, 10, 15, 25 and 40 min). Phenol concentration in the liquid phase was determined by HPLC (Merck) and ozone inlet and outlet concentrations were determined by ozone analyser and iodometric methods, respectively.

Figure 2 shows a schematic diagram of the pilot-scale set-up, which was used in the olefin plant site. The system was operated in the continuous mode. The phenolic wastewater was collected from the boot of the receiver vessel and was cooled by a heat exchanger to 25–30°C. Contactor, valves, pipes and tubings were made from polyethylene and polytetrafluoroethylene.

Table 1 summarizes the test conditions of the experiments of the continuous pilot-scale set-up in the olefin plant under steady state conditions. As in the batch experiments, inlet ozone concentration was measured by ozone analyser and the amount of outlet ozone was determined by iodometeric titration (APHA, 1989). Concentration of phenol in the liquid phase was determined by standard methods (ASTM Standards, 1991). The chemical oxygen demand (COD) of untreated and treated wastewater was determined by using a thermal reactor (VELP Scientifica, Italy) for 2 h at 150°C (APHA, 1989).

RESULTS AND DISCUSSION

Roth *et al.* (1982) developed a model that could empirically incorporate effects of mass transfer, kinetics and operating parameters to predict a kinetic rate constant for ozonation of phenol. This model is mostly based on first-order kinetics and it can be applied to both semi-batch and well-mixed modes of operation. Three main operating parameters in the model are $[\Phi OH]_0$, G/V and $[OH^-]$. Figures 3–5 compare profile of the first-order reaction rate constant (k_1) vs effective operating parameters for the models of Roth, Eisenhauer and Gould. Figure 3 shows that for operating parameters of constant pH and G/V the rate constant, k_1, decreases exponentially with phenol initial concentration ($[\Phi OH]_0$). However the trend of Eisenhauer's curve is sharper. Indeed, the curves based on both Roth's and Gould's data have almost identical trends.

Figure 4 shows that at constant $[\Phi OH]_0$ and pH, reaction rate constant increases linearly with increase of G/V. The reaction rate constants increase with almost the same slope for all three curves.

A profile of the reaction rate constant with the same $[\Phi OH]_0$ and G/V values at different pH values is shown in Figure 5. As is shown, the reaction rate constant increases with increasing pH for the correlations of Roth and Gould and it is constant for that of Eisenhauer.

In this study a semi-batch bench scale system was used to develop chemical kinetics for scale up using a 3 l contactor with a venturi injection system. Most of the previous studies used 2–2.5 l agitated vessels and a ceramic porous diffuser, or they were performed using 0.5–1 l unagitated vessels. Because of the complex interaction of chemical kinetics and transport phenomena, it is believed that the kinetic parameters determined under conditions close to a scaled-up system would give more reliable results.

Figure 6 shows a plot of $-\ln(C/C_0)$ vs reaction time for a laboratory semi-batch system. It can be observed that the data points fall on a reasonably straight line. The integral method for kinetic analysis of the first-order reaction kinetics led to a good fit of the experimental data. Comparison with other kinetic models of ozonation of phenol verified that reaction rate follows first-order kinetics.

Comparison of the experimental reaction rate constants with Roth's model indicates that the experimental results are comparable to predictions of the model. Based on the experimental data shown in Figure 7, it can be observed

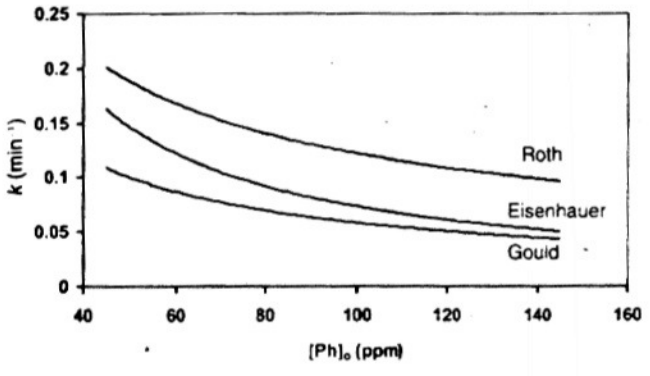

Figure 3. Profile of the first-order reaction rate constant (k_1) vs initial phenol concentration using different models (pH = 4.4 and $G/V = 0.0002$ gmol $min^{-1}\,l^{-1}$).

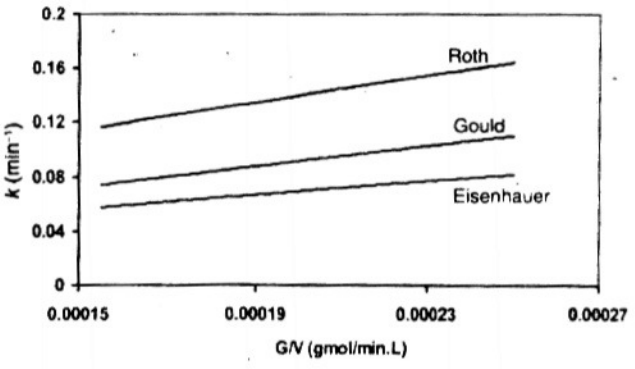

Figure 4. Profile of the first-order reaction rate constant (k_1) vs G/V using different models (pH = 4.4 and $[\Phi OH]_0 = 80$ ppm).

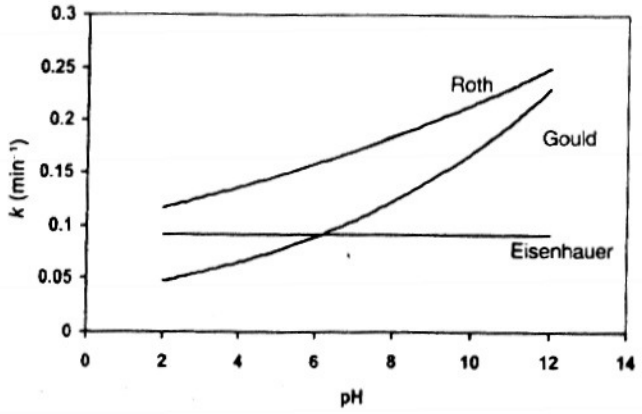

Figure 5 Profile of the first-order reaction rate constant (k_1) vs pH using different models ($[\Phi OH]_0 = 80$ ppm and $G/V = 0.0002$ gmol min^{-1}l^{-1}).

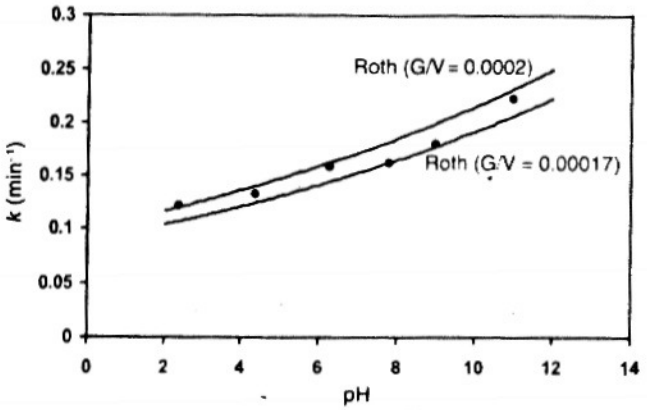

Figure 7 Comparison of experimental rate constants with Roth's model predictions.

that there is a good agreement between experimental k_1 values and Roth's model predictions under the conditions of G/V from 0.0002 and 0.00017 and initial phenol concentration of 80 ppm in the pH range 2–12. It can also be concluded that both the phenol destruction rate and phenol removal efficiency increase with increase in pH of the reaction medium.

Examination of the results for the bench scale batch system (Figure 8) reveals that there is a significant enhancement of phenol removal efficiency during the first 15 min of ozonation at all pH values. It also shows that phenol removal efficiencies are higher at high pH values and generally they have similar trends. It is well known that the ratio of direct molecular ozone reaction to free radical ozone reaction and therefore the regime of the ozonation is affected by pH of the reaction medium. It is interesting that at pH values higher than 7.8 there was a deepening of colour in the reaction medium due to polymerization of phenolics during the first phase of ozonation. To examine the stoichiometric ratio of the number of moles of ozone required to remove 1 mol of phenol, a plot of moles of ozone consumed per mole of phenol removed was made using semi-batch laboratory experiments (Figure 9). Figure 9 shows that, for almost complete removal of phenol (higher than 99.5%), between 5 and 6 mol of ozone were required for each mole of phenol. The results of this study agree with the results of other investigators (Roth *et al.*, 1982; Gould and Weber, 1976). It is also important to note that the amount of outlet O_3 (O_{3out}) decreases from 78.7 to 5.4 mg with increasing pH, and the ratio of consumption (mole O_3 consumed)/(mole [ΦOH]) reduces from 6.1 to 5.1. In practice this means that efficiency of ozone utilization is higher at higher pH levels. Results from the semi-batch experiments indicate that, under the operating conditions of the bench-scale system of this study, Roth's model can reasonably predict the reaction rate constant for ozonation of phenol.

Using Roth's model to predict the ozonation reaction rate constant and assuming a well-mixed reaction system and taking into account the maximum capacity of the ozone generator, a continuous pilot-scale ozonation system was designed and set up. The contactor volume was 45 l and a venturi system was used for ozone injection. The high circulation rate of the pump ensured a nearly well-mixed condition (Figure 2). The phenolic wastewater was collected from the boot of the receiver vessel of the effluent of the olefin reactor. It was cooled by a heat exchanger to 25–30 °C in the plant.

For the three sets of continuous pilot-scale runs, profiles of phenol concentration vs ozonation time are shown in Figures 10–12, respectively. The results obtained from the pilot scale series no.1 (refer to Table 1 and Figure 10) depict that, after about 3 h ozonation, the system reached a steady

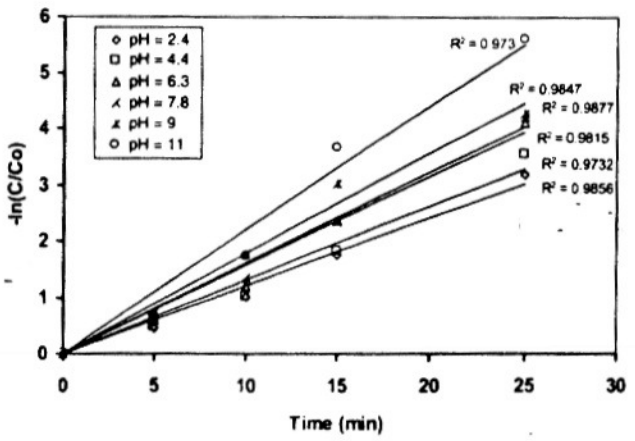

Figure 6 Values of $-\ln(C/C_0)$ vs reaction time at different pH levels.

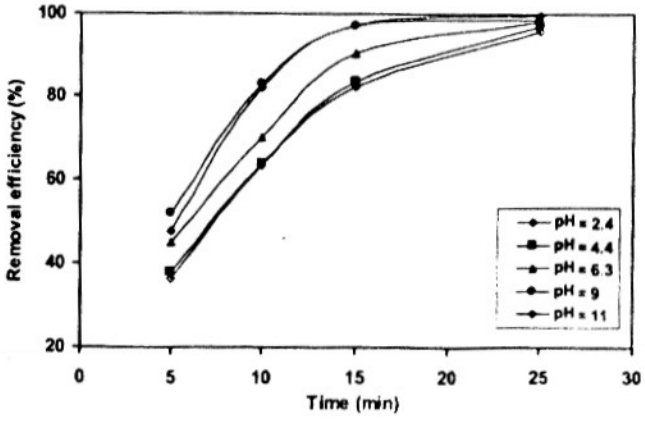

Figure 8 Phenol removal efficiency vs ozonation time at different pH levels.

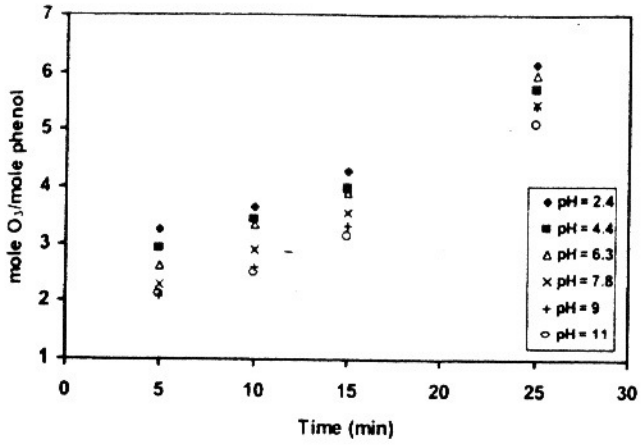

Figure 9. Mole of ozone consumed per mole of phenol removed vs ozonation time at different pH levels.

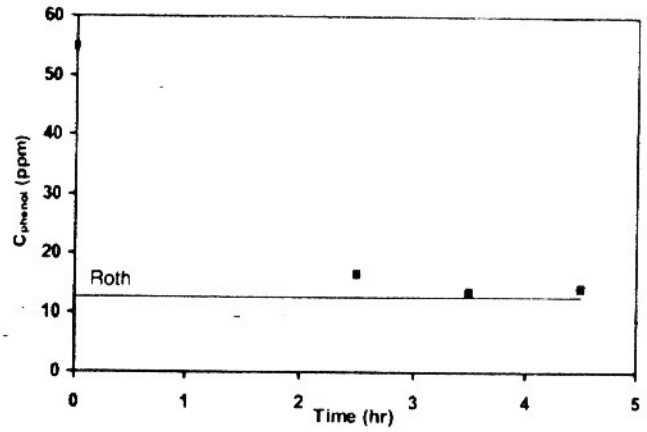

Figure 11. Profile of phenol concentration versus ozonation time for the test series no. 2 (continuous line represents phenol concentration predicted by Roth's model).

state and phenol concentration dropped below 11 ppm, pH also decreased by about 1 unit during ozonation. Figure 10 shows that prediction of Roth's model based on the operating conditions of this set of experiments is reasonable. Furthermore, for the test set no. 1, there was a reduction in COD from 333 to 220 ppm and an increase in electric conductivity from 204 to 222 $\mu S\,cm^{-1}$.

In the pilot test set no. 2 (Table 1 and Figure 11), the inlet ozone concentration was lowered to 38 $g\,m^{-3}$ and, after 2.5 h, samples were taken during 4.5 h ozonation. Similar to the results of the test set no. 1, after about 3 h, the phenol concentration dropped to about 13 ppm and the system reached a steady state. COD was reduced from 333 to 256 ppm and electric conductivity increased from 204 to 216 $\mu S\,cm^{-1}$. In the test series no. 3 (Table 1 and Figure 12), the volumetric flow rate of phenolic water was reduced to 5–19 $l\,h^{-1}$ and the inlet ozone concentration was increased to 65 $g\,m^{-3}$, whereas the other parameters remained constant. Examination of the results for the test set no. 3 reveals that there was a fall in phenol concentration down to 1.5 ppm during ozonation. For this set, COD decreased from 174 to 165 ppm and conductivity increased from 196 to 210 $\mu S\,cm^{-1}$. There was also a drop of 1 unit in pH for both test cases nos 2 and 3.

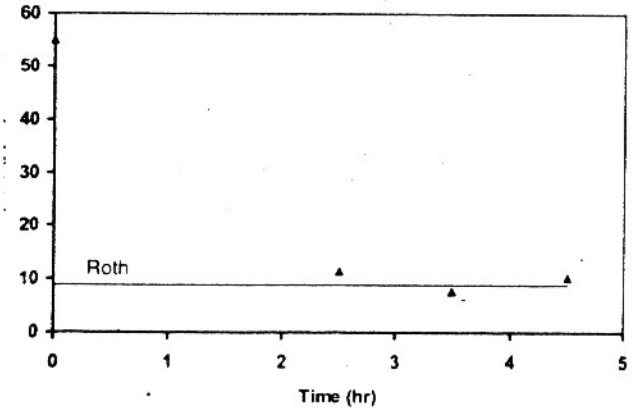

Figure 10. Profile of phenol concentration versus ozonation time for the test series no. 1 (continuous line represents phenol concentration predicted by Roth's model).

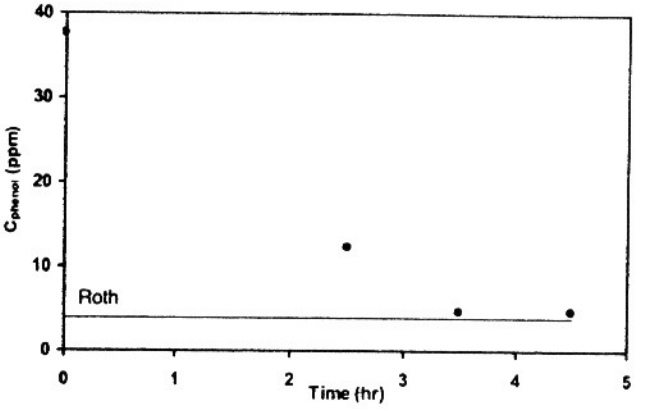

Figure 12. Profile of phenol concentration versus ozonation time for the test series no. 3 (continuous line represents phenol concentration predicted by Roth's model).

Using the results from pilot-scale system, it can be observed that actual concentrations of phenol in the effluent of the reactor were slightly higher than those predicted by Roth's empirical model. It is believed that this is due to the presence of other hydrocarbons in actual phenolic wastewater from the olefin plant, whereas the data used for development of Roth's model were based on synthetic phenol solutions in pure water.

CONCLUSIONS

In this work, a laboratory semi-batch set-up with a venturi injection system was used to examine the chemical kinetics of ozonation of phenol in industrial phenolic wastewater. The experimental results in the semi batch bench-scale treatment system show that at pH values 7 and above, higher phenol removal efficiency could be achieved. The kinetic parameters are reasonably consistent with Roth's empirical model used to describe the global rate of reaction of ozonation of phenol.

Experimental results in the continuous pilot-scale treatment system also indicate that Roth's model can be used to predict phenol ozonation under design and operating conditions of a pilot-scale wastewater treatment system.

The results from both semi-batch bench-scale and continuous pilot scale experiments show that Roth's model can be used for design of larger scale ozonation systems for destruction of phenol. However appropriate safety margins should be considered to account for the presence of other species that may consume ozone.

NOMENCLATURE

C_0	initial phenol concentration, mg l^{-1}
C	phenol concentration, mg l^{-1}
G	ozone feed rate, gmol min^{-1}
k_1	the first-order global rate constant, min^{-1}
k_n	global rate constant, min^{-1} (gmol phenol $l^{-1})^{1-n}$
n	apparent order of phenol decomposition rate
$-r_{\Phi OH}$	global rate of phenol disappearance (gmol phenol l^{-1} min^{-1})
t	time, min
V	volume of liquid reaction medium, l
$[\Phi OH]_0$	initial concentration of phenol, gmol l^{-1}
$[OH^-]$	hydroxyl ion concentration, gmol l^{-1}
$\alpha, \beta, \gamma, \delta$	constants determined from experimental

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