

Degradation of phenol by photocatalytic oxidation

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ABSTRACT

Phenol is a major environment contaminated from various industries such as coke, pesticides, insecticides, fungicides and dyes due to high toxicity on the skin, eyes and mucous membrane in humans. Industrial wastewater containing phenols are conventional treated by FeSO_4 and H_2O_2 to oxidize phenol to CO_2 and H_2O . FeSO_4 is converted to $\text{Fe}_2(\text{SO}_4)_3$ and H_2O_2 is decomposed and then the reactants could not be recycled. In addition the ferric sulfate is dumped and water is not reused. A new process was developed based on treatment with $\text{V}_2\text{O}_5\text{-SiO}_2$ photocatalyst or ozone in presence of UV light. The process is advantageous as the photocatalysts could be recycled and water could be reused. The process was successfully applied for treatment of wastewater produced from coke plant. The percent degradation of the phenol is increased from 47.31 to 72% using $\text{V}_2\text{O}_5\text{-SiO}_2$ xerogel loading from 0.333 to 1.333 wt.% in presence of UV light. The rate constant was increased from 0.0025 to 0.0036min^{-1} using different $\text{V}_2\text{O}_5\text{-SiO}_2$ xerogel loading and the reaction kinetics were found to be first order. On the other hand, the optimum conditions of photocatalytic degradation of phenol using ozone were obtained as the following: 1.6 wt.% ozone concentration and $0.85\text{m}^3/\text{h}$ airflow. The phenol removal efficiency using these conditions was 99% and the reaction was found to obey first order reaction. © 2003 SDU. All rights reserved.

Keywords: Photocatalytic; Degradation; Phenol; Ozone

1. INTRODUCTION

Most organic compounds are resistant to conventional chemical and biological treatments. For this reason, other methods are being studied as an alternative to biological and classical physico-chemical processes. Of these, Advanced Oxidation Processes (AOPs) will probably constitute the best option in the near future. Peyton *et al.* (1987) have explored other possible ways of ozone activation, giving a precise explanation of the beneficial effect of UV light upon ozone reaction. The use of UV light is a well known technique for improving the reactivity of ozone toward the organic species and, for that reason, many water treatment systems based on the use of ozone take advantage of such a light source. However, the use of highly energetic UV photons is hampered by their relatively high economic cost. Any other way of effectively activate ozone while preserving a low cost would be interesting from an applied point of view, justifying the development of related research. In the usual fenton-type reaction using hydrogen peroxide, the key step is the formation of hydroxyl radicals from H_2O_2 and Fe(II) . These are known to be responsible for oxidizing the organic material RH present in the wastewater, yielding Fe(II) and R. But, the use of metallic salts as catalysts induces an additional pollution. The semiconductor materials when irradiated by UV-light, from the solar or a lamp generated spectrum, can oxidize/degrade most of dissolved organic compounds and cyanide in water (Matthews, 1986; Ahmed and Ollis, 1984; Chandrasekharaiah and Margrave, 1993). Also, ozone has been used successfully for removal of various synthetic organic compounds from waters. Ozone is quite selective in its reaction with organic substances in presence of sunlight (Laura *et al.*, 2003). Ozone might also decompose to generate hydroxyl radical ($\text{OH}\cdot$), which is a non-selective and highly reactive oxidant, and hence might significantly improve the oxidation efficiency for organic substances, which might be resistant to direct molecular attack of ozone. Ozonation coupled with UV radiation (O_3/UV) has been demonstrated to be a much more effective process than ozonation alone for the removal of many organic compounds (Peyton *et al.*, 1982; Kusakabe *et al.*, 1991; Santiago *et al.*, 2002). Cristina *et al.* (2002) observed that mineralization of phenol solution is faster with the use of $\text{O}_3/\text{UV}/\text{Fe}^{3+}$ than with simple ozonation.

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Therefore this research have aimed to detoxify phenol from wastewater using UV in the presence of V_2O_5 - SiO_2 or ozone, find out optimum condition of use ozone as a oxidant agent and explain the experimental results in view of kinetic models presented for the two processes.

2. EXPERIMENTAL

2.1. Materials and procedure

All chemicals used in this study were analytical grade reagents. The following high purity raw materials were used to formulate V_2O_5 - SiO_2 xerogel preparation: tetraethyl orthosilicate, (TEOS) 98% $Si[OC_2H_5]_4$ Aldrich Chemical Co. and Ammonium metavanadate (AMV) and phenol (99%) Aldrich chemical Co. Preparation of V_2O_5 - SiO_2 xerogel via sol-gel technique by dissolving ammonium metavanadate (AMV) and tetraethyl orthosilicate (TEOS) has been achieved. The optimum conditions for preparation of V_2O_5 - SiO_2 must contain the following conditions 0.04V: Si mole ratio and C_2H_5OH : $Si(OC_2H_5)_4$: H_2O : HCl (8M) : NH_4F (1M) mole ratios are 4 : 1 : 8 : 0.36 : 0.15 respectively at 30°C for 10min. The vanadia – silica alcogel was dried at 450°C to produce xerogel (Ismail *et al.*, 2003). Photocatalytic degradation of phenol using V_2O_5 - SiO_2 xerogel was carried out using a horizontal cylinder annular batch reactor. A blacklight- blue florescent bulb (F18W- BLB) was positioned at the axis of the reactor to supply UV illumination. The wavelength after passing through a reaction suspension was 365nm. The experiments were performed by suspending 0.333 to 2 wt.% of V_2O_5 - SiO_2 xerogel into 300ml phenol (100ppm). The reaction was carried out isothermally at 30°C and samples of the reaction mixture were taken an interval for a total reaction time 8h.

Photodegradation of phenol using ozone was carried out using ozone gas produced from an ozone generator (OZONIA- OZAT, type CFS-1. The ozone production is dependent on the airflow and electrical power. The gas stream was bubbled through a tank filled with 80 liter phenol solution (100ppm) . There is appendix “ gas flow diagram CFS-1/ air to estimate airflow (m^3/h) based on air scale division and then calculate the ozone concentration (wt.%). A container of about 100L was used to carry out experimental work using UV and ozone. The UV lamp consumes approximately 18W by drawing 0.37A, and the lamp length is 59cm. For kinetic study, either one or two lamps are horizontally connected. The reaction was carried out isothermally at 30°C and samples of the reaction mixture were taken after different reactions intervals varies from 10 to 300 minutes to calculate the phenol removal efficiency and reaction kinetic. The phenol content in the solution after reaction time was analyzed by the reaction with 4 –aminoantipyrine. Diluted sample of phenol was treated with 2ml of 4N NH_4OH , 1ml of 1.5% 4 – aminoantipyrine, and 1ml of 4% $K_3[Fe(CN)_6]$ and quantitatively diluted to 100ml with H_2O . After 5min. the reaction was determined colorimetrically at (Cecil 7200) 510nm (John, 1975). The removal efficiency of phenol was calculated by applying the following equation.

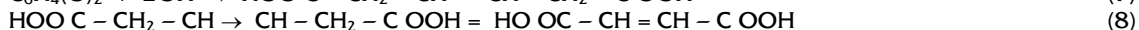
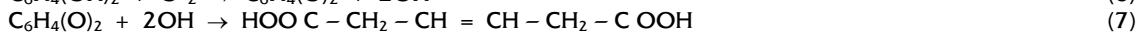
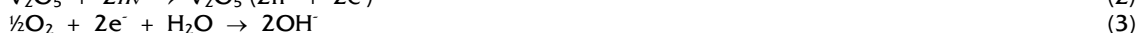
$$\% \text{ Removal efficiency} = [(C_o - C)/C_o] \times 100 \quad (1)$$

Where C_o the original phenol content and C the retained phenol in solution

3. RESULTS AND DISCUSSION

3.1. Photocatalytic degradation of phenol using V_2O_5 - SiO_2 xerogel

The mechanism for the photocatalytic oxidation of compounds by oxygen at semiconductors has been illustrated. Thus the process for removal of phenol can be represented as follows (Masakazu *et al.*, 1980; Zeevalkink, 1979; Tseng, 1990).



By further oxidation



Where h is plank's constant and ν is the frequency

The experiments were conducted under the following condition: phenol concentration, 100ppm; volume of phenol, 300ml at 30°C for 8h. The results indicate that the increase in the V_2O_5 - SiO_2 loading from 0.333 to 2 wt.%, tended to increase phenol removal efficiency from 47.31 to 72%. Experimental studies have revealed that a catalyst loading of 1.333 wt.% is the optimal dose for the degradation of 72mg/l of the phenol after 8h. irradiation period. Beyond the optimal dose the phenol photodegradation percent is slightly

increased about 2%. This can be rationalized in terms of availability of active sites on V_2O_5 surface and the penetration of photoactivating light into the suspension. At high catalyst concentration availability of excess active sites outweighs the diminishing photo-activated volume and significantly greater rate of degradation is achieved at increased V_2O_5 loading (Matthews, 1990). Therefore, the optimum condition is 1.333 wt.%.

Table 1
 Effect of vanadia – silica xerogel loading on phenol removal efficiency

Time min	V_2O_5 - SiO_2 loading, wt.%. Phenol removal efficiency, %			
	0.333	0.666	1.333	2
10	11.22	17.20	20.00	24.10
30	17.44	21.40	24.00	26.92
45	22.80	27.10	30.00	32.40
60	27.21	30.91	38.00	39.20
120	30.82	34.00	44.10	44.80
180	34.34	38.00	50.20	50.50
240	38.11	41.00	55.00	56.00
300	41.20	45.00	57.00	59.00
360	45.10	50.95	60.00	63.00
420	46.23	57.23	65.00	67.00
480	47.31	66.38	72.00	74.00

3.2. Kinetic photocatalytic degradation of phenol using V_2O_5 - SiO_2 xerogel

The reaction order with respect to phenol was determined by plotting reaction time versus \log [phenol] according to the following equation for various vanadia – silica loading.

$$\log [C]_t = -kt + \log [C]_0 \quad (10)$$

$$t_{1/2} = 0.693/k \quad (11)$$

Where $[C]_0$ and $[C]_t$ represent the concentration (ppm) of the substrate in solution at zero time and t time of illumination respectively, and k represents the apparent rate constant (min^{-1}). The findings represented in Figure 1 and Table 2 have been seen that the reaction followed first order kinetics with respect to phenol and this results are in agreement with Yong *et al.* (1999) and the rate constants were ranged from 0.0025 to 0.0039min^{-1} .

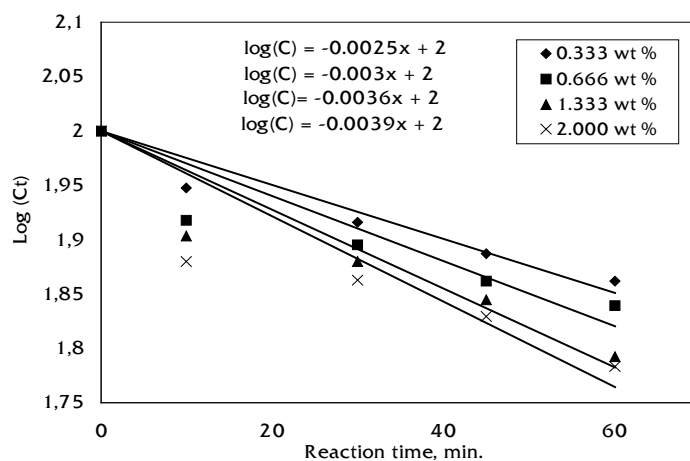


Figure 1. Reaction kinetic of vanadia - silica xerogel with phenol

The plot of natural logarithm of the normalized concentration of phenol versus irradiation time shows a good approximation over the range of 0.333 to 2 wt.% (Figure 1). k values obtained from the slopes of the plots Figure 1 and $t_{1/2}$ values obtained from the equation 2 are presented in Table 2. k values increase with increasing V_2O_5 - SiO_2 loading. This suggests that as photocatalyst loading increases, the requirement of catalyst surface needed for the degradation increase. Since the initial concentration of the phenol is constant, the O_2^- and $\cdot OH$ radicals formed on the surface of V_2O_5 are increased. Hence the relative number of $\cdot OH$ and O_2^- attacking the phenol molecules increases with increasing photocatalyst loading (Matthews, 1990; Mohamed, 2003). Hence the rate of degradation increases from 0.0025 to 0.0039min^{-1} with increase V_2O_5 - SiO_2 loading from 0.333 to 2 wt.%.

Table 2
 Rate constant of reaction kinetic of phenol with vanadia – silica xerogel

V ₂ O ₅ -SiO ₂ loading, wt.%	k x 10 ⁻⁴ , min ⁻¹	t _{1/2} , min
0.333	25	277
0.666	30	231
1.333	36	192
2.000	39	178

3.3. Photocatalytic degradation of phenol using ozone

It was decided to evaluate the use of ozone and UV irradiation to investigate the technical feasibility of the UV-aided oxidation using ozone as an oxidant for removing phenol and comparing this method with V₂O₅-SiO₂ xerogel.

A reaction mechanism for the ozonation of phenol can be summarized as follows (Zeevalkink, 1979; Tseng, 1990).



The hydroxyl radical attacks the phenol and the mechanism was aforementioned.

3.3.1. Effect of ozone concentration

The experiments have been carried out to study the effect of ozone concentration on the phenol removal efficiency under the following conditions. UV light power, 36W; Airflow, 0.44m³/h; phenol concentration, 100ppm, volume of solution, 80 liter, reaction time, 0-5h at 30°C. The findings are shown in Table 3 and the results indicate that increasing ozone concentration from 0.5 to 2.1 wt.% the phenol removal efficiency is increased from 1.41 to 96% respectively after 5h. It is known that ozone is powerful oxidizer that can be effective for degradation of many pollutants (Yong *et al.*, 1999). It is also noticed that, the increase of ozone concentration more than 1.6 wt.% is not economically feasible due to the phenol removal efficiency increased 2 percent only. So the optimum ozone concentration is 1.6 wt.% giving 94.28% phenol removal efficiency.

Table 3
 Effect of ozone concentration on phenol removal efficiency

Time min	Ozone concentration, wt.%			
	0.5	1	1.6	2.1
	Phenol removal efficiency, %			
10	0.78	19.10	20.00	21.6
30	0.78	20.00	21.90	40.00
45	1.00	27.20	42.85	52.00
60	1.10	38.40	52.38	68.00
120	1.20	49.60	67.61	78.00
180	1.30	68.80	77.14	94.20
240	1.40	72.80	94.28	95.00
300	1.41	73.00	94.28	96.00

3.3.2. Effect of airflow

The effect of airflow on the phenol removal efficiency has been conducted. The data are shown in Table 4 and the findings emerge that with increasing airflow from 0.33 to 0.85m³/h, the phenol removal efficiency was increased from 92.15 to 99% after four hrs. This may be attributed to at high airflow rate sufficient ozone generation was performed and good mixing and diffusion in the solution is also achieved. Therefore, the optimum airflow rate is 0.85m³/h with 1.6 wt.% of ozone concentration.

3.3.3. Effect of UV light power

UV irradiation of water generated hydroxyl radical that was responsible for the oxidation of phenol and water as according to the following equation (Gurol and Woodman, 1989).



Therefore, the effect of UV light power on photocatalytic degradation of phenol was investigated by varying its light power from 0–36 Watt. The results are displayed in Table 5 and the findings reveal that by increasing UV light power from 0 to 18W, the phenol removal efficiency was slightly increased from 98.2 to 99%. Therefore, UV illumination is not necessary to complete this reaction. So the optimum conditions for degradation of phenol by ozone are, ozone concentration, 1.6 wt.% and air flow, 0.85m³/h without UV light power.

Table 4
 Effect of airflow rate on phenol removal efficiency

Time min	Airflow rate, m ³ /h			
	0.33	0.44	0.55	0.85
	Phenol removal efficiency, %			
10	18.11	20.00	23.00	25.60
30	19.82	21.90	30.00	36.00
45	40.02	42.85	42.22	52.00
60	49.99	52.38	53.42	60.80
120	65.23	67.61	78.20	83.20
180	75.02	77.14	88.90	98.30
240	92.15	94.28	96.00	99.00
300	92.15	94.28	97.00	

Table 5
 Effect of UV light power on phenol removal efficiency

Time min	UV illumination, Watt		
	0	18	36
	Phenol removal efficiency, %		
10	24.20	25.60	25.80
30	35.40	36.00	36.20
45	51.82	52.00	52.21
60	58.99	60.80	61.00
120	82.00	83.20	83.50
180	97.21	98.30	98.70
240	98.20	99.00	99.00
300	98.70		

3.4. Kinetic of phenol with ozone

The reaction order with respect to phenol was determined by plotting reaction time versus log [phenol] according to the equations 1 and 2 mentioned before. The findings are represented in Figures 2, 3 and 4 and the apparent rate constants and $t_{1/2}$ are summarized in Table 6. The results show that the reaction follows first order kinetics with respect to phenol and the rate constants increase with increasing ozone concentration and airflow rate. In addition, $t_{1/2}$ decrease with increasing ozone and airflow whereas UV light power is insignificant and the rate constants are ranged from 3.4×10^{-3} to $7.8 \times 10^{-3} \text{ min}^{-1}$.

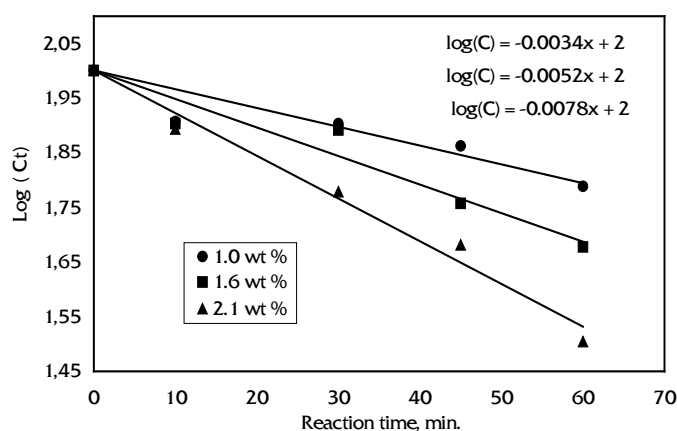


Figure 2. Reaction kinetic of ozone concentration, wt.% with phenol

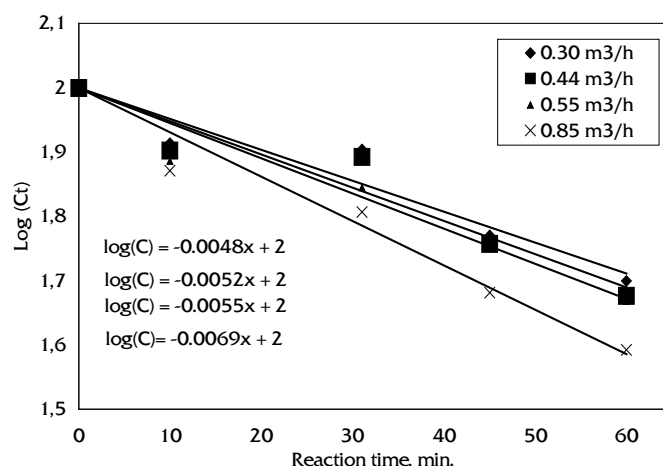


Figure 3. Reaction kinetic of air flow with phenol

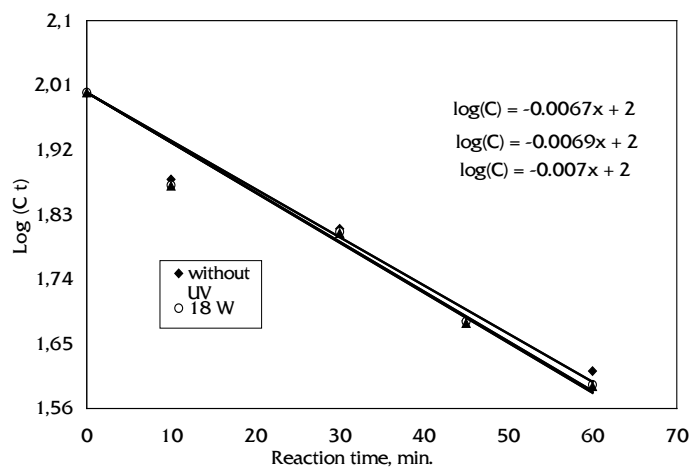


Figure 4. Reaction kinetic of UV light power with ozone

Table 6
 Rate constant of reaction kinetic of phenol with ozone

Item	$k \times 10^{-3}$ min^{-1}	$t_{1/2}$ min
Ozone concentration, wt.%		
1.0	3.4	204
1.6	5.2	133
2.1	7.8	89
Airflow, m^3/h		
0.33	4.8	144
0.44	5.2	133
0.55	5.5	126
0.85	6.9	100
UV light power, Watt		
0.0	6.7	103
18	6.9	100
36	7	99

4. CONCLUSIONS

Different AOPs (ozone and photocatalyst) in presence of UV have been studied and compared with a view to the decrease in the pollutant concentration, the first order kinetic constant for the degradation of phenol in aqueous solution. It has been found 72% phenol removal efficiency was achieved by using 1.33% wt.% V₂O₅-SiO₂ xerogel after 8 hours whereas 98.2%, phenol removal efficiency was found by using 1.6 wt.% ozone concentration and 0.85m³/h airflow after 4h. The reaction kinetic of photocatalytic decomposition of phenol using V₂O₅-SiO₂ xerogel or ozone was found to be first order. Whereas the rates of photocatalytic degradation of phenol using ozone are faster than using V₂O₅-SiO₂ xerogel about two times.

REFERENCES

- Ahmed, S. and Ollis, D.F., Photo-assisted catalytic decomposition of the chlorinated hydrocarbons trichloroethylene and trichloromethane. *Solar Energy*, 1984, **32**, 597-601.
- Chandrasekharaiah, M. and Margrave, L., Proceedings of waste stream minimization and utilization. Vol. 2 – Industrial Liquid and Gaseous Waste Processing, Lee, V. E. (Ed.), Austin, Texas, 1993, 5.1–5.6.
- Cristina, C., Santiago, E., Juan, C., Mineralization of phenol in aqueous solution by ozonation using iron or copper salts and light. *Applied Catalysis B: Environmental*, 2002, **1320**, 1–11.
- Gurrol, M.D. and Woodman, J.H., Removal of iron cyanide by photolysis and chemical oxidation. *Hazard Ind. Wastes, Proc.*, 21 st Mid-Atlantic Industrial Waste Conf., Technomic Pub. Co., Inc., Lancaster, 1989, 282-290.
- Ismail, A.A., Ibrahim, I.A., Mohamed, R.M., Sol-gel synthesis of vanadia-silica for photocatalytic degradation of cyanide. *App. Catal. B: Environmental*, 2003 (in press).
- John, R.P., Retention of preservative levels of phenol in desiccated biological products. *Journal of Clinical Microbiology*, 1975, 147-148.
- Kusakabe, K., Aso, S., Wada, T., Hayashi, J.I., Morooka, S., Isomura, K., Destruction rate of volatile organochlorine compounds in water by ozonation with ultraviolet radiation. *Water Res.*, 1991, **25**(10), 1199-1203.
- Laura, S.A., Xavier, D.E., Juan C. and, J.E.P., Solar activated ozonation of phenol and malic acid. *Chemosphere* 2003, **50**, 1085–1093.
- Masakazu, A., Ichiro, T., Yutaka, K., Photoluminescence and photoreduction of V₂O₅ supported on porous vycor glass. *J. Phys. Chem.*, 1980, **84**, 3440-3443.
- Matthews, R.W., Photo-oxidation of organic material in aqueous suspensions of titanium dioxide. *Wat. Res.*, 1986, **20**(5), 569-578.
- Matthews, R.W., Purification of water with near-u.v. illuminated suspensions of titanium dioxide. *Water Res.*, 1990, **24**(5), 653.
- Mohamed, K., Sarra, B.A., Semia, C., Elimame, E., Ammar, H., Mouhieddine, E., Photodegradation of lignin from black liquor using a UV/TiO₂ system. *J. of Photochemistry and Photobiology A: Chemistry*, 2003, **154**, 211–218.
- Peyton, G.R., Huang, F.Y., Bureson, J.L., Glaze, W.H., Destruction of pollutants in water with ozone in combination with ultraviolet radiation. 1. General Principal and Oxidation Tetra-chloroethylene. *Environ. Sci. and Tech.*, 1982, **16**, 448-453.
- Peyton, G.R., Smith, M.A., Peyton, B.M., Photolytic ozonation for protection and rehabilitation of ground water resources; a mechanistic study. University of Illinois, Water Resources Center, 1987, Research Report No. 206.
- Santiago, E., Jaime, G., Sandra, C., Esther, P., Miguel R.G., Comparison of different advanced oxidation processes for phenol degradation. *Water Research*, 2002, **36**, 1034–1042.
- Tseng, M.J. and Huang, P.C., Removal of chlorophenols from water by photo-catalytic oxidation. *J. Am. Water Assoc.*, 1990, **76**, 60-70.
- Yongqiang, Q., Mark, E.Z., Chiang, H.K., Elizabeth, C.F., Kinetic and mechanistic study of ozonation of dichlorophenols in aqueous solutions. *J. of Environ. Eng.*, 1999, **125**(5), 441-450.
- Zeevalkink, A.J., Visser, C.D., Arnoldy, P., Boelhouwer, C., Mechanism and kinetics of cyanide ozonation in water. *Water Res.*, 1979, **14**, 1375-1385.