

Degradation of free cyanide by photocatalytic oxidation

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ABSTRACT

Gold is normally recovered from its ores by cyanidation process, which is a well-known technique used worldwide. The merits of cyanide heap leaching technology of gold are well known, but environmental problems arise occasionally due to high toxicity of cyanide. Photocatalytic decomposition of cyanide was achieved using $\text{TiO}_2\text{-SiO}_2$ aerogel, $\text{V}_2\text{O}_5\text{-SiO}_2$ xerogel or ozone. The cyanide removal efficiencies were increased from 87 to 98.74% and from 85 to 99% by increasing loading wt% from 0.083 to 0.666 and from 0.083 to 0.166 for $\text{TiO}_2\text{-SiO}_2$ aerogel and $\text{V}_2\text{O}_5\text{-SiO}_2$ xerogel respectively. Also, the rates constant were increased from 0.020 to 0.044 min^{-1} and from 0.022 to 0.045 min^{-1} for $\text{TiO}_2\text{-SiO}_2$ aerogel and $\text{V}_2\text{O}_5\text{-SiO}_2$ xerogel respectively and the reaction kinetics were found to be first order. On the other hand the optimum conditions of Photocatalytic degradation of cyanide using ozone were found to be 2.5wt% ozone concentration, 1.14 m^3/h airflow as well as 36 Watt (W) UV light power. At these conditions, the cyanide removal efficiency was 99%, the rate constant was found to be 0.0075 min^{-1} and the reaction kinetic was found to be first order. © 2003 SDU. All rights reserved.

Keywords: Cyanide; Photocatalytic; Degradation; TiO_2 ; V_2O_5 ; Ozone

1. INTRODUCTION

Although cyanide leaching remains the overwhelming option for treating gold ores, because of its economy and simplicity of the process, it suffers from toxic and its use poses long-term environmental and disposal problems (Hiskey and Atluri, 1988; Dadgar, 1989). Cyanides are used in a number of chemical synthesis and metallurgical processes (as simple salts or cyanide complexes). Cyanides are highly toxic and must be destroyed or removed from wastewaters prior to discharge. The most common method for treating free or simple cyanide is the alkaline chlorination process. However, chlorination of cyanide results in highly toxic intermediates cyanogen chloride). These compounds, together with the residual chloride create additional environmental problems. Consequently, there is a growing need for alternative, non-chlorine methods for destroying cyanides. The photocatalytic degradation processes are effective alternatives alkaline chlorination for destroying free and complexed cyanides. The mechanism for the photocatalytic oxidation of compounds by oxygen at semiconductors has been illustrated (Harold, 1989). Irradiation of semiconductor with band gap light results in creation of holes in the semiconductor valence band by excitation of an electron to conduction band. The valence band hole is scavenged by solution species before electron-hole recombination can occur within the semiconductor. Electroneutrally within the semiconductor is maintained by reduction of dissolved oxygen or other solution species by the conduction band electron (Sara *et al.*, 1994).

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. Ozone might also decompose to generate hydroxyl radical (OH), 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). Therefore this research aims to detoxify cyanide from waste streams using UV in the presence of $\text{TiO}_2\text{-SiO}_2$, $\text{V}_2\text{O}_5\text{-SiO}_2$ or ozone and will attempt to explain the experimental results in view of kinetic models presented for the three processes.

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2. EXPERIMENTAL

2.1. Materials

All chemicals used in this study were analytical grade reagents; the following high purity raw materials were used for TiO₂-SiO₂ preparation: Titanium (IV) isopropoxide, (TIIP) 97% Ti[OCH(CH₃)₂]₄ and tetraethylorthosilicate, (TEOS) 98% Si[OC₂H₅]₄ Aldrich Chemical Co. and Ammonium metavanadate (AMV).

2.2. Preparation of titania-silica aerogel (Adel, 2001)

TEOS was added to ethyl alcohol and H₂O and HNO₃ (1M) as catalyst. The solution was magnetically stirred under inert gas in glove dry box. Then calculated amounts of TIIP was added to complete the reaction then forming TiO₂-SiO₂ sol. The optimum conditions for preparation of TiO₂-SiO₂ gel are Ti: Si mole ratio is 1:6, H₂O:Si(OC₂H₅)₄ mole ratio is 8, H₂O: Ti (iOC₃H₇)₄ mole ratio is 8, C₂H₅OH:Si(OC₂H₅)₄ mole ratio is 10, HNO₃ (1M): Si(OC₂H₅)₄ mole ratio is 0.25 for 90min reaction time, at 25°C reaction temperature. The mixed solution TiO₂-SiO₂ was kept still in order to form a rigid gel. The produced gel was dried under supercritical conditions (105 bar, 295°C) to produce TiO₂-SiO₂ aerogel.

2.3. Vanadia -silica xerogel (Reda, 2001)

Preparation of V₂O₅-SiO₂ xerogel via sol-gel technique was performed by dissolving ammonium metavanadate (AMV) and tetraethyl orthosilicate (TEOS). The optimum conditions for preparation V₂O₅-SiO₂ gel are 0.04V:Si mole ratio, H₂O:Si(OC₂H₅)₄ mole ratio is 8, C₂H₅OH: Si (OC₂H₅)₄ mole ratio is 4, H₂SO₄ (8M): Si(OC₂H₅)₄ mole ratio is 0.81, NH₄F (1M):Si(OC₂H₅)₄ mole ratio is 2.04 at 30°C for 10 minutes. The vanadia - silica alcogel was dried at 450°C under atmospheric pressure conditions to produce xerogel.

2.4. Photocatalytic Evaluation

All the experiments were 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 wave length after passing through a reaction suspension was 365nm. The experiments were performed by suspending 0.083 to 0.666wt% of TiO₂-SiO₂ aerogel or V₂O₅-SiO₂ xerogel into 300ml Potassium cyanide (100ppm) at pH 8.5 because at lower pH toxic HCN gas can be produced. The reaction was carried out isothermally at 25°C and samples of the reaction mixture were taken at different intervals for 6hrs total reaction time. The CN⁻ content in the solution after reaction time was analyzed by volumetric titration with AgNO₃ (Vogel, 1978). The removal efficiency of CN⁻ was calculated by applying the following equation.

$$\% \text{ Removal efficiency} = [(C_0 - C) / C_0] \times 100 \quad (1)$$

where: C₀ the original cyanide content and C the retained cyanide in solution.

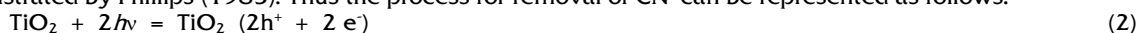
2.5. Photodegradation of cyanide using ozone

Ozone gas was produced from an ozone generator (OZONIA- OZAT, type CFS-1 using air. The ozone production is dependent on the airflow and electrical power. The gas stream was bubbled through a tank filled with 80 liter cyanide ion solution (100ppm). Ozone concentration (wt%) was calculated and adjusted with the aid of air scale division in the apparatus and gas flow diagram CFS-1 provided in the appendix of the apparatus catalogue. A container of about 100L was used to carry out the experimental work. The used UV lamps was 18W lamp with 59cm length. For kinetic study, either two or three 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 360 minutes to calculate the cyanide removal efficiency and kinetic of reaction.

3. RESULTS AND DISCUSSION

3.1. Photocatalytic degradation with semiconductor

The mechanism for the photocatalytic oxidation of compounds by oxygen at semiconductors has been illustrated by Phillips (1983). Thus the process for removal of CN⁻ can be represented as follows:





Overall reaction:



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

3.1.1. Photocatalytic degradation of CN using TiO₂-SiO₂ aerogel

Photocatalytic degradation of cyanide using different loading weight percent of TiO₂-SiO₂ aerogel were performed for different time ranging from 10 to 360 minutes. The findings are summarized in Table 1. It is clearly seen that, 87% of the cyanide content was degraded after 5 hours by using 0.083wt% of the TiO₂-SiO₂ aerogel. By increasing aerogel loading to 0.666wt%, the removal efficiencies were increased to 98.74% after 3 hours only. In spite of at 0.166wt% loading is good enough to degrade almost cyanide but at 0.166wt% loading longer time is needed reaching to 5h.

This interpreted that at 0.083wt% loading weight is not enough to degrade almost of cyanide due to small percentage of TiO₂. Increasing weight loading to 0.666wt% is good enough to decompose most of cyanide in the aqueous solution at 3 hours only, due to the presence of sufficient amount of TiO₂ as a semiconductor material. This behavior has been frequently observed in photocatalyst and interpreted that with sufficient loading all UV light is absorbed by TiO₂. Therefore 0.666wt% TiO₂-SiO₂ aerogel loading is considered to be the optimum dose.

Table 1
 Influence of reaction time on photocatalytic activity at different TiO₂-SiO₂ aerogel loading

Time, min.	TiO ₂ -SiO ₂ aerogel loading, wt%				
	0.083	0.166	0.333	0.5	0.666
	Cyanide removal efficiency, %				
3	11.07	17.77	25.01	40.02	40.02
5	25.01	27.55	28.05	45.04	46.04
10	38.76	42.45	52.02	58.02	62.67
15	53.01	50.11	71.02	75.50	78.62
20	58.02	58.02	79.10	84.15	86.51
30	59.10	64	84.20	84	85
45	68.04	66.7	86.05	87	89
60	74	80.8	91	92.3	93
90	79.20	90	94	94.40	95
120	81.10	91.7	95	95	97
150	84	92.5	96	96	98
180	85.4	95.8	96.7	97	98.74
240	86	96.3	97	97	98.74
300	87	97	97	97	98.74
360	87	97	97	97	98.74

3.1.2. Photocatalytic degradation of CN using V₂O₅-SiO₂ xerogel

Photocatalytic degradation of cyanide using different loading weight percent of V₂O₅-SiO₂ xerogel were conducted for different time intervals up to 360 minutes. The findings are summarized in Table 2. It is clearly seen that with the smallest loading 0.083wt% the cyanide removal efficiency is 85% after 3h. By increasing xerogel loading to 0.666wt% the removal efficiency is increased to 98.5% after 2.5 hours. In spite of at 0.166wt% loading is good enough to degrade almost cyanide but it requires 3hr. This means that, with increasing xerogel loading from 0.166 to 0.666wt% the reaction time is decreased from 3 to 2.5h. This interpreted that loading at 0.083wt% is not enough to degrade almost of cyanide due to small percentage of V₂O₅, but increasing loading to 0.166wt% is good enough to decompose most of cyanide in the aqueous solution, due to V₂O₅ is the effective semiconductor material. So from economic point of view 0.166wt% is considered the best xerogel loading.

3.1.3. Kinetic photocatalytic degradation of CN using TiO₂-SiO₂ aerogel and V₂O₅-SiO₂ xerogel

By applying the following expression which represent first order kinetic reaction. The loss of the substrate was fitted to the corresponding expression: (Yiming *et al.*, 1995).

$$\text{Log [C]}_t = -kt + \text{Log [C]}_0 \quad (8)$$

Where $[C]_0$ and $[C]_t$ represent the concentration (ppm) of the substrate in solution time zero and time t of illumination respectively, and k represent the apparent rate constant (min^{-1}). It is noticed that, by depicting $\log[C]_t$ versus time, straight lines are obtained with slope equal to the apparent rate constants (k , min^{-1}) and intercepts equivalent to $\log[C]_0$. The findings are represented in Figures 1 and 2 and the apparent rate constants (min^{-1}) are summarized in Tables 3 and 4.

Table 2
 Influence of reaction time on photocatalytic activity at different $\text{V}_2\text{O}_5\text{-SiO}_2$ xerogel loading

Time, min.	$\text{V}_2\text{O}_5\text{-SiO}_2$ xerogel loading, wt%				
	0.083	0.166	0.333	0.5	0.666
	Cyanide removal efficiency, %				
3	11	21.7	25	40	40
5	25	30.5	28	45	46
10	38.7	50.4	52	58	60
15	53	53	71	75	80
20	58	62	79	80	84
30	59	67	84	84	85
45	68	69.7	86	87	89
60	74	83.8	91	92.3	93
90	79	93	94	94	95
120	81.10	91.7	95	95	97
150	83	96	98.2	98.2	98.3
180	85	98.5	99	99	99
240	85	99	99	99	99.1
300	85	99	99	99	99.1
360	85	99	99	99	99.1

The results indicate that, photodegradation in presence of $\text{TiO}_2\text{-SiO}_2$ aerogel or $\text{V}_2\text{O}_5\text{-SiO}_2$ xerogel photocatalysts kinetics were satisfactorily fit to a first order rate law (Yiming *et al.*, 1995). Moreover the rate constant is increased from 0.0203 to 0.0444min^{-1} and from 0.0222 to 0.0459min^{-1} with increasing loading weight of $\text{TiO}_2\text{-SiO}_2$ aerogel and $\text{V}_2\text{O}_5\text{-SiO}_2$ xerogel respectively from 0.083 to 0.666wt%.

Furthermore Janet *et al.*, (1997) concluded that, the hydroxyl radical produced on the surface of the TiO_2 is nominally bound in the form of surface titanol functionality Ti-OH . Hydroxyl radical that is not consumed by reactions with substrates within the electrical double layer may self-react to form hydrogen peroxide. In which the small steady state concentration of surface-bound hydroxyl radical controls the reaction rate with an observed first order dependence on the substrate.

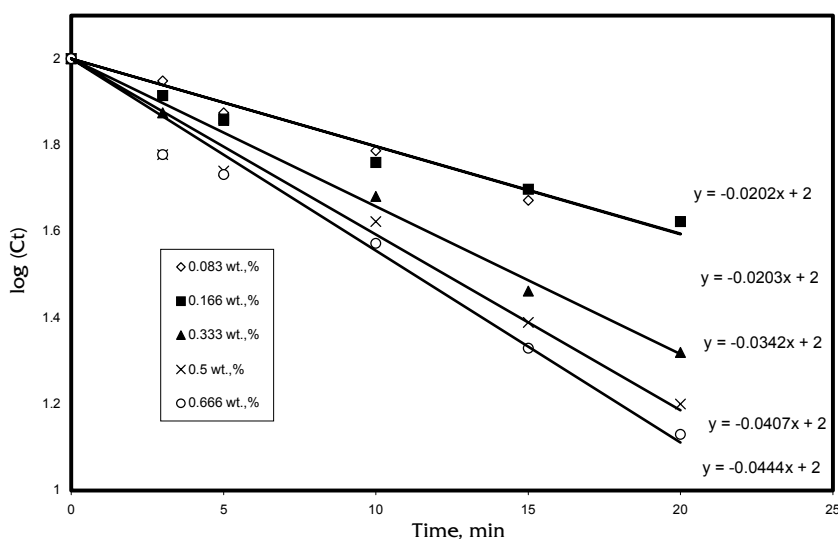


Figure 1. Reaction kinetic of Titania-Silica aerogel with cyanide ion

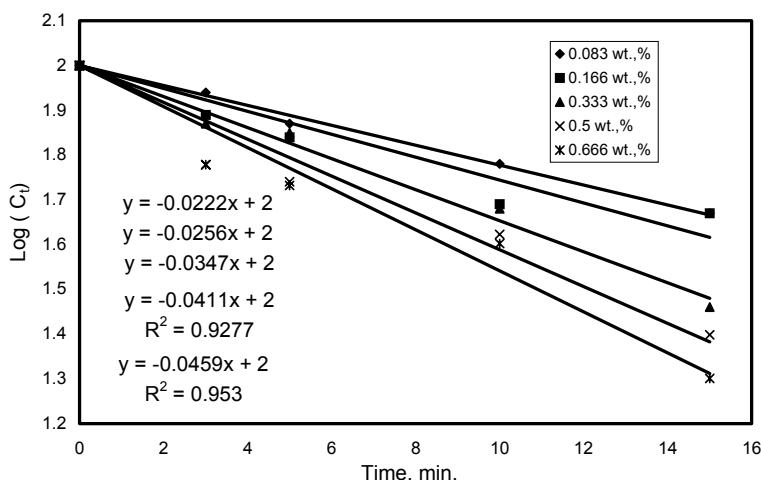


Figure 2. Reaction kinetic of vanadia -silica xerogel with cyanide ion

Table 3
 Apparent rate constant (k) at different TiO₂-SiO₂ aerogel loading

TiO ₂ -SiO ₂ aerogel loading, wt %	K, min ⁻¹ x 10 ⁻³
0.083	20.20
0.166	20.30
0.333	34.20
0.500	40.70
0.666	44.40

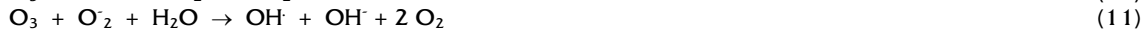
Table 4
 Apparent rate constant (k) at different V₂O₅-SiO₂ xerogel loading

V ₂ O ₅ -SiO ₂ xerogel loading, wt %.	K, min ⁻¹ x 10 ⁻³
0.083	22.2
0.166	25.6
0.333	34.7
0.500	41.1
0.666	45.9

3.2. Photocatalytic degradation of cyanide ion 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 cyanide and comparing this method with TiO₂-SiO₂ aerogel and V₂O₅-SiO₂ xerogel.

A reaction mechanism for the ozonation of cyanide can be summarized as follows (Zeevalkink, 1979).



Continued ozonation of cyanide results in consecutive reactions of the primarily formed cyanate. Tyler *et al.*, (1951) and Selm (1959) postulate the oxidation of the cyanate to nitrogen and carbon dioxide according to.



3.2.1. Effect of ozone concentration

A series of experiments has been carried out to study the effect of ozone concentration on the cyanide removal efficiency. The experiments have been performed under the following conditions: UV light power, 36W; air flow, 0.52m³/h; CN⁻ conc., 100ppm; volume of solution, 80L; reaction time, 0-6h; at 30°C.

The findings are shown in Table 5. The results indicate that UV irradiation alone could remove 29% after 6hr. which is in agreement with findings by Gurol and Woodman (1989) and Kim *et al.*, (1998). However, this is not consistent with the findings by other researchers; (Zaidi and Carey, 1984) which reported no significant destruction of cyanide with UV irradiation alone.

It is clearly seen that with increasing ozone concentration from 1.6 to 2.5wt% the cyanide removal efficiency was increased from 66 to 95.5% respectively. It is known that ozone is powerful oxidizer that can be effective for degradation of many pollutants (Yongquiang *et al.*, 1999). This process utilizes the hydroxyl radical for contaminant degradation and is typical in conjunction with ultraviolet photolysis (Zappi *et al.*, 1993). This attributed to the free cyanide is oxidized by ozone and hydroxyl radical (Zeevalkink, 1979).

It is also noticed that, the increase of ozone concentration more than 2.5wt% is not economically feasible due to the cyanide removal efficiency increase only about 1% so the optimum ozone concentration is 2.5wt%.

Table 5
 Effect of ozone concentration on cyanide removal efficiency (UV light power: 36W, Air flow: 0.52m³/h)

Time, min.	ozone concentration, wt%				
	0	1.6	2.5	3	3.35
	cyanide removal efficiency, %				
10	5.80	8.30	13.10	16.82	18.71
30	11.60	20.56	33.62	36.75	37.91
45	12.50	27.05	42.98	37.48	41.56
60	14.60	32.39	49.88	50.68	52.46
120	16.70	34.6	63.3	65.7	67.6
180	18.43	57.14	72.3	74.86	77.14
240	22.90	64.10	84.5	89	88.6
300	29	65.33	92.5	95.6	95
360	29.20	66	95.5	96	96.7

3.2.2. Effect of airflow

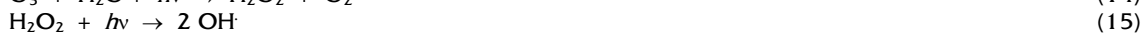
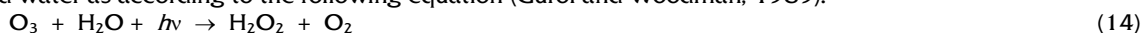
A series of experiments has been carried out to study the effect of airflow on the cyanide removal efficiency under the following conditions: Ozone concentration, 2.5wt% and UV light power, 36W. The data are shown in Table 6. The findings emerge that with increasing airflow from 0.22 to 1.14m³/h the cyanide removal efficiency is increased from 53 to 99% respectively after six hrs. This may be attributed to at high airflow rate sufficient ozone generation is performed and good mixing and diffusion in the solution is also achieved. Therefore, the optimum airflow rate is 1.14m³/h with 2.5wt% of ozone concentration.

Table 6
 Effect of airflow rate on cyanide removal efficiency (Ozone concentration: 2.5wt%, UV light power: 36W)

Time, min.	Airflow rate, m ³ /h				
	0.22	0.52	0.7	0.94	1.14
	Cyanide removal efficiency, %				
10	7.1	13.10	20.56	23.79	27.05
30	12.4	33.62	36.02	41.65	44.02
45	16.01	42.98	41.38	48.47	53.22
60	20.56	49.88	55.02	58.31	62.84
120	25	63.3	66.7	68.5	70.54
180	30	72.3	72.4	76	78
240	36	84.5	85.5	87.5	90
300	50	92.5	93.76	94.6	97
360	53	95.5	96.58	96	99

3.2.3. Effect of UV light power

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



Therefore, a series of experiments has been carried out to study the effect of UV light power on the cyanide removal efficiency under the following conditions: Ozone concentration, 2.5wt% and air flow,

1.14m³/h. The results are displayed in Table 7. The findings reveal that by increasing UV light power from 18 to 36W the removal efficiency is slightly increased from 96.7 to 99%. It is also noticed that, increasing UV light power more than 36W has no effect on cyanide removal efficiency. So the optimum conditions for degradation of cyanide ion by ozone are, ozone concentration, 2.5wt%, air flow, 1.14m³/h as well as UV light power 36W.

Table 7
 Effect of UV illumination on cyanide removal efficiency (Ozone concentration: 2.5wt%, Air flow: 1.14m³/h)

Time, min.	UV illumination, W		
	18	36	54
	Cyanide removal efficiency, %		
10	15.47	27.05	27.052
30	26.03	44.02	44.40
45	31.45	53.22	53.22
60	38.34	62.84	63.41
120	56.7	70.54	69.89
180	70.8	78	76.67
240	86.5	90	85.96
300	94.6	97	97.9
360	96.7	99	98.7

3.2.4. Kinetic of cyanide degradation with ozone

The reaction order with respect to cyanide was determined by plotting reaction time versus log [CN] according to the following equation for various ozone concentration, airflow and UV light power.

$$\text{Log } [C]_t = -kt + \text{Log } [C]_0 \quad (16)$$

Where [C]₀ and [C]_t represent the concentration (ppm) of the substrate in solution time zero and time t of illumination respectively, and k represent the apparent rate constant (min⁻¹).

The findings are represented in Figures 3, 4 and 5 and the apparent rate constants are summarized in Table 8. The results show that the reaction followed first order kinetics with respect to cyanide concentration and the rate constants were ranged from 3x10⁻³ to 7.5x10⁻³min⁻¹ reaching its maximum value 7.5x10⁻³min⁻¹ at 2.5wt% ozone concentration, 1.14m³/h airflow and 36W UV light power.

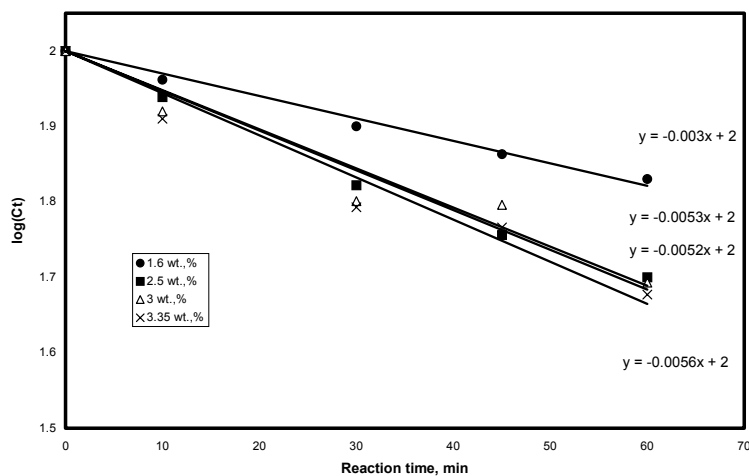


Figure 3. Reaction kinetic of cyanide ion with different ozone concentration

3.3. Comparison between TiO₂-SiO₂ aerogel, V₂O₅-SiO₂ xerogel and ozone methods for waste water treatment

The results of the cost analysis indication is summarized in Table 9. It is noticed that, the cost of cyanide removal by TiO₂-SiO₂ aerogel is the highest one followed by V₂O₅-SiO₂ xerogel whereas by using ozone the cheapest one. But some other technical points should be considered in order to have more accurate comparison:

- The treatment efficiency for the three methods is more or less similar and ranges between 98.5 – 100%. The price of chemical ingredients used in this analysis was a laboratory grade price for the first and second methods i.e. $\text{TiO}_2\text{-SiO}_2$ aerogel and $\text{V}_2\text{O}_5\text{-SiO}_2$ xerogel methods. Accordingly, it is expected that the cost of the chemical used in the $\text{TiO}_2\text{-SiO}_2$ aerogel and $\text{V}_2\text{O}_5\text{-SiO}_2$ xerogel methods to decrease sharply to around 50% of that mentioned in Table 9 when the price of the bulk large quantities is considered.
- The equipment cost for the $\text{TiO}_2\text{-SiO}_2$ aerogel and $\text{V}_2\text{O}_5\text{-SiO}_2$ xerogel methods is insignificant compared to that of ozone cyanide degradation one which requires an ozone generator unit.
- The time required for the waste water treatment is also different for the various techniques. The ozone method is 5 hours while retention time for $\text{TiO}_2\text{-SiO}_2$ aerogel and $\text{V}_2\text{O}_5\text{-SiO}_2$ xerogel methods are 3h for the same volume of effluent (1 m^3).

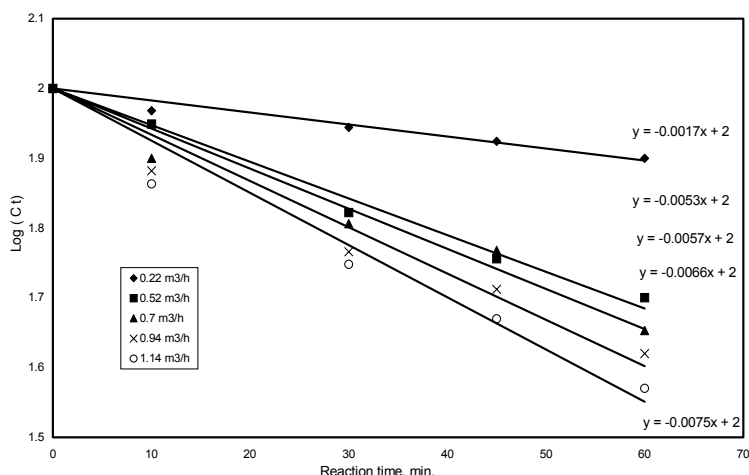


Figure4. Reaction kinetic of cyanide ion with ozone at different airflow

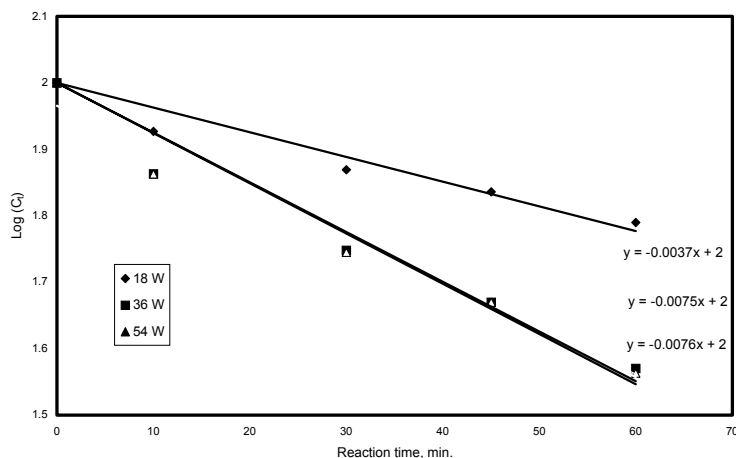


Figure 5. Reaction kinetic of cyanide with ozone at different UV light power

Table 8
 Rate constant of reaction kinetic of cyanide ion with ozone

Item	$K \cdot 10^{-3}, \text{min}^{-1}$
Ozone concentration, wt%	
1.6	3
2.5	5.3
3	5.2
3.35	5.6

continued

Item	$K \cdot 10^{-3}, \text{min}^{-1}$
Airflow, m^3/h	
0.22	1.7
0.52	5.3
0.70	5.7
0.94	6.6
1.14	7.5
UV light power, W	
18	3.7
36	7.5
54	7.6

Table 9
 Cost materials and power for the three methods of waste water treatment (Basis: Treatment of 1m^3 cyanide)

	Amount (gm)	Cost (\$)
TiO₂-SiO₂ aerogel		
Si(OC ₂ H ₅) ₄	28.66	1.38
Ti(OCH ₃) ₄	6.60	0.31
C ₂ H ₅ OH	72.77	0.34
UV lamp	0.9 K watt	0.10
Total		2.13
V₂O₅-SiO₂ xerogel		
Si(OC ₂ H ₅) ₄	20.33	0.970
AMV	0.051	0.002
C ₂ H ₅ OH	18.22	0.650
H ₂ SO ₄	7.73	0.010
NH ₄ F	4.2	0.010
UV lamp	0.9 K watt	0.100
Total		1.742
Ozone		
Ozone generator	1.35 K watt	0.11
Compressor	1.25 K watt	0.10
UV lamp	0.9 K watt	0.10
Total		0.31

4. CONCLUSIONS

TiO₂-SiO₂ aerogel, V₂O₅-SiO₂ xerogel or ozone is technically feasible. Increasing the TiO₂-SiO₂ aerogel or V₂O₅-SiO₂ xerogel loading for treatment of wastewaters reduces the treatment time and increases rate constant. The reaction kinetic of photocatalytic decomposition of cyanide using TiO₂-SiO₂ aerogel, V₂O₅-SiO₂ xerogel or ozone was found to be first order. Rate of photocatalytic degradation of cyanide using TiO₂-SiO₂ aerogel is much faster than using ozone 6 times.

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