Oxidation of cyanide in aqueous solution by chemical and photochemical process

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Abstract

Cyanide waste is found predominantly in industrial effluents generated from metallurgical operations. The toxicity of cyanide creates serious environmental problems. In this paper, oxidation of cyanide in aqueous solution was investigated using chemical and photochemical process. Chemical oxidation was studied at room temperature using H_2O_2 as oxidant and Cu^{2+} as catalyst. Photochemical oxidation was studied in an annular type batch photoreactor of 1 l capacity using 25 W low-pressure (81.7% transmission at 254 nm wavelength) ultraviolet (UV) lamp along with H_2O_2 as oxidant. The effect of Cu^{2+} catalysis was also studied. It was observed that in absence of UV source, the degradation of cyanide by H_2O_2 alone was very slow, whereas copper ions accelerated the rate of reaction thereby acting as catalyst. Copper formed a complex with cyanide ion, i.e. tetracyanocuprate which had greater affinity for H_2O_2. Cyanate hydrolysis was also favoured by copper ions. As Cu^{2+} ion concentration was increased, rate of degradation also increased. Photochemical oxidation by H_2O_2 and Cu^{2+} was found to be the best system for cyanide degradation. CN^- (100 mg/l) was degraded to non-detectable level in 9 min at pH 10.0 with optimum H_2O_2 dose of 35.5 mM and Cu^{2+} dose of 19 mg/l. Reaction kinetics of cyanide oxidation was found to be pseudo-first order and the rate constant has been determined for different processes.
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1. Introduction

Cyanides are highly toxic in nature and have adverse effect on humans if not taken care off. Cyanide wastes are generated from electroplating, photographic, metal processing and petroleum refineries. Alkaline cyanides are used in steel cementing by heat treatment. Here, the metal parts are dipped in molten alkaline carbonate and chloride salt baths containing alkaline cyanides. The treated parts are quenched in water baths and the salt crust dissolves, resulting in a cyanide-polluted waste. Many gold mining operations employ NaCN solutions to extract gold from pulverized ore followed by zinc precipitation. Due to their high eco-toxicological potential, cyanide may lead to regulatory issues and environmental concerns.

Conventional treatment methods like caustic chlorine treatment have certain drawbacks. These methods do not destroy the pollutants completely [1]. In caustic chlorine treatment, cyanide is converted to cyanate which is also toxic. Complete destruction of cyanate is difficult. The chlorination process also produces secondary by-products such as trihalomethanes, which are highly toxic and carcinogenic [2]. The treated water contains huge amount of dissolved chlorine. Considering the nature of the cyanide effluents, there is a need for better treatment methods, which can completely destroy cyanides. Advanced photo-oxidation process (AOP) using ultraviolet (UV) radiation in combination with various oxidants like H_2O_2, Fenton's reagent and ozone is a highly promising technology for the treatment of toxic compounds which

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are refractory in nature and difficult to oxidize completely by conventional methods [3–5]. In AOP technology, hydroxyl radicals are produced and these radicals are powerful oxidizing agents ($E_0 = 2.8$ V). Hydroxyl radical is second most oxidizing agent after fluorine ($E_0 = 3.06$) [6]. The oxidizing power of these hydroxyl radicals is used to degrade organic and inorganic molecules. It has been seen that using this process organics are converted into CO_2, water and other gaseous products. It does not produce any secondary pollutants. Thus, it is a clean technology, and if treated properly the discharge water can be recycled or reused.

Ronald [7] has carried out cyanide removal from wastewater by catalytic oxidation and reported that CN^- was removed from wastewater by oxidation at 0–200 °C and pH 6–10.5 using 30–70% commercial grade H_2O_2 in a H_2O_2/CN^- of 2–4:1 with aqueous $CuSO_4$ solution as catalyst. Stsiner et al. [8] have reported that CN^- was oxidized with peroxide compounds at pH 8–12. Chen and Ling [9] have carried out experimental studies for treatment of wastewater containing cyanide by peroxide oxidation. They have reported that cyanide content of wastewater (5–50 mg/l) was reduced to <0.5 mg/l.

Present study was carried out for treatment of cyanide by hydrogen peroxide and Cu^{2+} catalyst at room temperature and in combination of UV irradiation. Various process parameters like pH, H_2O_2 concentration and copper concentration were studied.

2. Materials and methods

2.1.1. Materials and reagents

NaCN (A.R. grade) was obtained from S.D. Fine Chemicals. All other reagents like 4-dimethylaminobenzylidinerhodanine, silver nitrate, sodium hydroxide, potassium titanium oxalate, barbituric acid, sodium acetate trihydrate and pyridine were obtained from E. Merck Ltd.

2.2. UV Lamp

Low-pressure UV lamp (25 W; intensity = 48.4 μW/cm^2) was used. In low-pressure lamp, about 81.7% UV radiation is emitted at 254 nm. This lamp was obtained from G.E. Electrical.

2.3. Experimental

Experiments were carried out in an annular type batch photoreactor (length = 550 mm, O.D. = 95 mm and wall thickness = 2.5 mm) made up of boro-silicate glass (Fig. 1). The effective volume of the photoreactor was 1000 ml. An immersion well made of high purity quartz was placed inside the glass reactor fitted with a standard joint at the top. UV lamp was kept inside the immersion well. Water was passed through the thin annular zone of the immersion well to re-
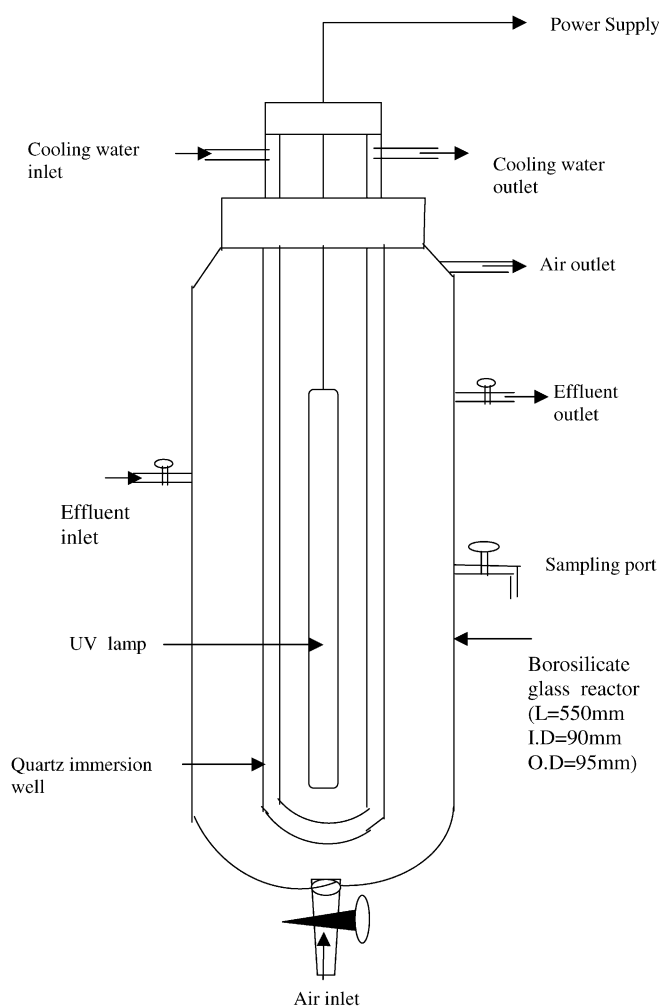

Fig. 1. Photoreactor.

move the heat generated by the UV lamp. Air was bubbled into the reactor through the bottom inlet for mixing the liquid uniformly. A sintered disc (Grade 2 Borosil, pore diameter 40–90 μm) was provided for producing small bubbles to enhance the mass transfer between the gas and liquid. There was a sampling port at the middle of the reactor, so that periodic samples can be withdrawn for analysis. A Teflon-coated thermocouple was introduced into the reactor solution and it was fitted with a temperature indicator outside. The reactor assembly was covered with a photoreactor safety hood, so the person working is not affected by harmful UV radiation. Moreover, safety goggles and proper safety clothes were used during experiments.

2.4. Analytical procedure

Cyanide concentration was determined by titrimetric method for high cyanide concentration (>1 mg/l) using silver nitrate and 4-dimethylaminobenzylidinerhodanine indicator and by colorimetric method for low concentration (<1 mg/l) using UV–vis spectrophotometer (GBC, Cintra 10).

Minimum detection limit (MDL) for CN^- by this method was 0.2 μg/l and the accuracy for both cases was $\pm 5\%$ [10]. Cyanate concentration was determined by hydrolysing it to ammonia at acidic pH (1.5–2.0) and ammonia was measured by Nesslerisation [10]. H_2O_2 concentration was determined colorimetrically using potassium titanium oxalate solution at 398.9 nm [11].

3. Results and discussion

3.1. Chemical oxidation of cyanide by H_2O_2

Hydrogen peroxide is a powerful oxidizing agent (oxidation potential 1.77 V). Chemical oxidation of the dissolved organics and inorganics present in industrial effluents and concentrated aqueous streams by H_2O_2 is a technique that has been applied to a broad spectrum of organic and inorganic compounds. Hydrogen peroxide is regarded as an isomer of following two structures:
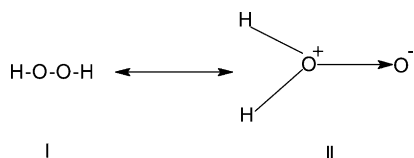
Structure (II) represents hydrogen peroxide as a molecule of water linked to an oxygen atom by a co-ordinate linkage. Being a very weak acid, hydrogen peroxide ionizes in alkaline solution and liberates molecular oxygen in the presence of trace of alkali. Due to this decomposition of hydrogen peroxide in alkaline solution, smaller amount of HOO^- are available in reaction mixture [12].

Experiments were conducted with different doses of H_2O_2, i.e. 44.1, 88.2 and 132.3 mM at pH 10.0 at room temperature. It was seen that oxidation by H_2O_2 alone was very slow, 90% degradation of CN^- occurred in 24 h by 88.2 mM H_2O_2. Results are shown in Fig. 2. An increase in the hydro-

gen peroxide concentration results in the increased availability of the HOO^- in solution thereby increasing the rate of oxidation of cyanide compound. De et al. [12] have reported similar results for the oxidation of phenolic compounds.

In the present study, attempt was made to find out the intermediate products of cyanide oxidation by H_2O_2 process. Cyanate and ammonia were detected as intermediate products, which suggests that cyanide is first oxidized to cyanate, which further oxidized to ammonium and carbonate ions as follows:

$$CN^- + H_2O_2 \rightarrow CNO^- + H_2O \tag{1}$$

$$CNO^- + 2H_2O \xrightarrow{H_2O_2} NH_4^+ + CO_3^{2-} \tag{2}$$
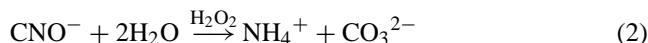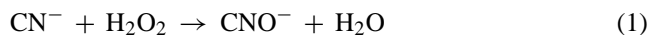
Knorre and Griffiths [13] also used hydrogen peroxide for removal of cyanide and reported that product formation depends upon the amount of hydrogen peroxide used. Lawes et al. [14] reported that cyanate is intermediate product for cyanide oxidation by H_2O_2 process. According to Goldstein [15] investigation, H_2O_2 reacts with cyanide to produce cyanate which further hydrolyses to ammonium and carbonate ion. Marsden and House [16] also reported that cyanide can be mineralized to bicarbonate and ammonia as follows:

$$CN^- + 2H_2O \xrightarrow{H_2O_2} HCOO^- + NH_3 \tag{3}$$
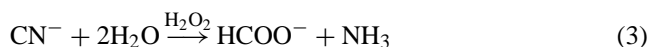
The kinetics of reactions (1) and (2) was studied and found to be pseudo-first-order reaction. The rate constants for cyanide and cyanate oxidation were found to be 0.61 and 0.074 h^{-1} for H_2O_2 dose of 35.3 mM. From the value of the rate constants, it is clear that the oxidation rate of cyanate is slower than cyanide.

Oxidation of cyanide to cyanate is kinetically slow when the cyanide ions are associated with alkaline cations such as sodium and potassium, faster for zinc and cadmium complexes and very fast for copper cyanide complexes [17]. The latter effect is the reason copper salts are employed for cyanide oxidation.

3.1.1. Effect of Cu^{2+} catalysis

The effect of Cu^{2+} catalysis was studied using different dose of Cu^{2+} ion, i.e. 12.5, 25, 50, 75 and 100 mg/l with a fixed dose of H_2O_2 (30%, w/v) 88.2 mM in the absence of UV. It was seen that with increasing Cu^{2+} dose, cyanide degradation rate also increased and the highest rate obtained at 75 mg/l of Cu^{2+} dose. The time taken for complete degradation of cyanide was 9 min at pH 6.0. Results are shown in Fig. 3. Different doses of H_2O_2 (35.3, 52.9, 70.5, 88.2 and 132.3 mM) in NaCN solution were studied along with fixed dose of 75 mg/l of Cu^{2+}. It was again seen that 88.2 mM H_2O_2 was the optimum dose along with 75 mg Cu^{2+}. Results are shown in Fig. 4.

3.1.2. Effect of pH

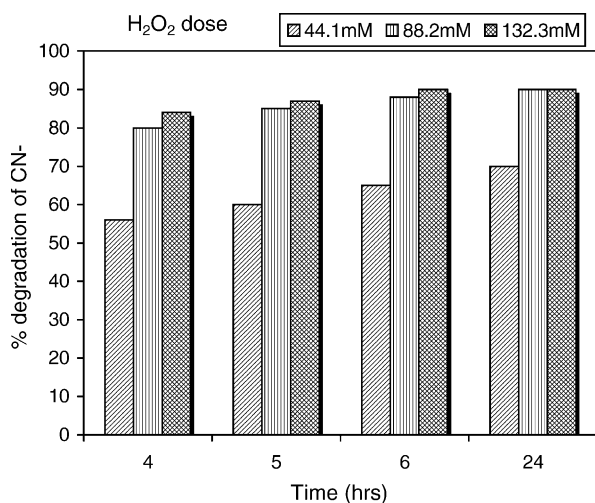The effect of pH was studied by varying the pH of the solution from 3.0 to 10.0. All experiments were carried out
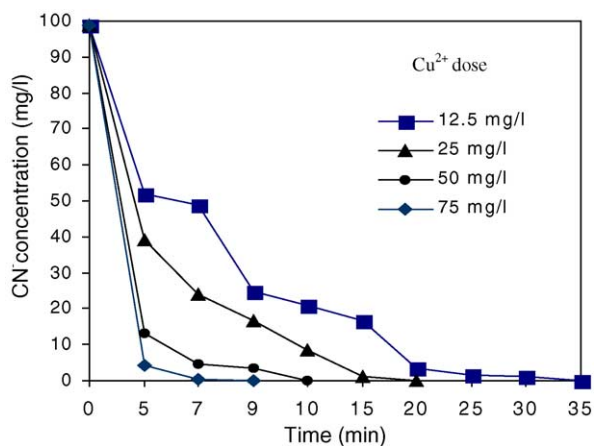

Fig. 2. Optimisation of H_2O_2 concentration at room temperature.

Fig. 3. Effect of Cu^{2+} concentration on chemical oxidation of CN^- ($H_2O = 88$ mM).
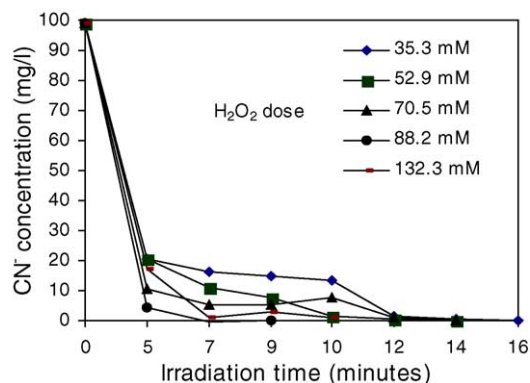
Fig. 4. Effect of H_2O_2 concentration on chemical oxidation of CN^- ($Cu^{2+} = 75$ mg/l).

with initial CN^- concentration of 100 mg/l and H_2O_2 dose of 88.2 mM and Cu^{2+} dose of 75 mg/l in the absence of UV radiation at room temperature. It was observed that alkaline pH was better for degradation of cyanide and at pH 10.0, complete degradation of CN^- occurred in 9 min. At pH 3.0, time taken for complete degradation was 120 min and at pH 7.0, it was 90 min. Results are reported in Table 1. In alkaline pH, cyanide is present as CN^- ions, so it reacts easily with H_2O_2 and Cu^{2+} ions. In acidic pH, cyanide is present mainly as HCN gas which is very difficult to oxidize. Moreover, HCN

is highly toxic and volatile. So cyanide treatment should be carried out in alkaline pH.

The reaction (2) is favourable at pH lower than 7 at room temperature in the absence of UV [14,18]. Ammonium ion is toxic which can be discharged by nitrification. Hydrogen peroxide dissociates in aqueous solution according to the following equation:

$$H_2O_2 \rightarrow HO_2^- + H^+ \tag{4}$$
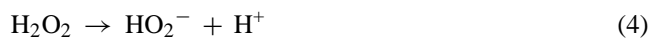
In alkaline conditions, the deprotonated HO_2^- species can be further consumed by the H_2O_2 molecules and OH^- ions [19,20]:

$$H_2O_2 + HO_2^- \rightarrow H_2O + O_2 + OH^- \tag{5}$$
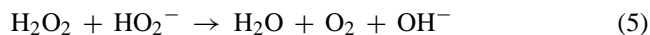
Significant enhancement of H_2O_2 decomposition was observed at pH 11.0 with the presence of Cu^{2+} ions, similar to the results reported by Parker [21]. It was possibly because that Cu^{2+} ions would consume OH^- to form hydroxyl complexes or hydroxide precipitate and accelerate the reactions (5) and (6) [21]:

$$HO_2^- + OH^- \rightarrow H_2O + O_2 \tag{6}$$
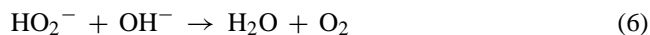
3.2. Photochemical oxidation of cyanide

Photo-oxidation experiments were carried out in 1-l annular batch photoreactor with 25 W low-pressure UV lamp. All experiments were carried out at pH 10.0 with an initial cyanide concentration of 100 mg/l. It was observed that with UV alone, the rate of cyanide degradation was very slow and only UV radiation was not effective. So further experiments were carried out along with H_2O_2 as oxidant.

3.2.1. UV/H_2O_2 system

The combination of H_2O_2 and UV can create a very fast and efficient process for water treatment by producing hydroxyl radicals according to the given equation (7):

$$H_2O_2 \xrightarrow{h\nu} 2OH^\bullet \tag{7}$$

Hydroxyl radicals are devoid of any charge and have a high affinity for electrons, they can quickly strip any chemical of electrons including cyanide thus causing their oxidation. Because reaction (7) occurs so quickly that reactions (1)–(3) do not occur at all [22]. Depending upon the amount of H_2O_2

Table 1
Effect of pH on chemical oxidation of CN^- using Cu^{2+} catalyst ($Cu^{2+} = 75$ mg/l and $H_2O_2 = 88.2$ mM)

pH	Time (min)	Initial CN^- concentration (mg/l)	Final CN^- concentration (mg/l)	Degradation (%)	Normalized space velocity, >99% conversion (l/h)
3.0	120	100	<MDL	99.9	0.5
5.0	110	100	<MDL	99.9	0.54
7.0	90	100	<MDL	99.9	0.66
8.0	20	100	<MDL	99.9	3.0
9.0	15	100	<MDL	99.9	6.0
10.0	9	100	<MDL	99.9	6.6

MDL = minimum detection limit (0.2 μg/l).

used, hydroxyl radicals react with cyanide thus causing its oxidation to form cyanate which further oxidizes to bicarbonate and nitrogen. Reaction stochiometry are 1:1 when cyanate forms and it increases further to 1:3 when nitrogen forms [23]:

$$CN^- + 2OH^\bullet \rightarrow OCN^- + H_2O \tag{8}$$

$$OCN^- + 3OH^\bullet \rightarrow HCO_3^- + \tfrac{1}{2}N_2 + H_2O \tag{9}$$
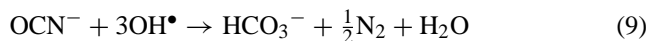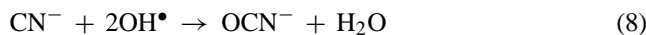
It was found that using 35.3 mM hydrogen peroxide the time taken for complete degradation of 100 ppm cyanide was 40 min.

The kinetics for both reactions (8) and (9) were studied and found to fit in pseudo-first-order rate model. The rate constant for cyanide oxidation for a particular run was found to be $0.099\,min^{-1}$ (for H_2O_2 dose of 35.3 mM) and for cyanate oxidation was $0.0421\,min^{-1}$. It is seen that cyanate oxidation is slower than cyanide oxidation.

3.2.2. Optimisation of H2O2 dose

Experiments were carried out using different concentration of H_2O_2 (8.8, 17.6, 35.3, and 52.9 mM) using 25 W low-pressure Hg lamp and air was bubbled at 1 LPM. It was found that 35.3 mM H_2O_2 was the optimum concentration for the degradation of cyanide. With increasing H_2O_2 concentration, the rate of cyanide oxidation increases, but beyond a certain value of 35.3 mM, the increase of initial H_2O_2 concentration retards the oxidation rate. The results are shown graphically in Fig. 5. It was inferred that 35.3 mM H_2O_2 was the optimum dose in this process. If excess of this dose H_2O_2 is used then less reactive hydroperoxyl radicals are produced and moreover $OH^\bullet$ radicals will readily dimerise to H_2O_2. [24]. These hydroperoxyl radicals are less reactive but attack cyanide ion to break the triple bond thus enhancing the rate of degradation [25]. Hydrogen peroxide has been successfully used for the oxidation of organic and inorganic compounds. Originally, nascent oxygen liberated on decomposition of hydrogen peroxide was considered to be active species for oxidizing action. Later, it was established that perhydroxyl anion (OOH^-) is an active species for the oxidizing property of hydrogen per-
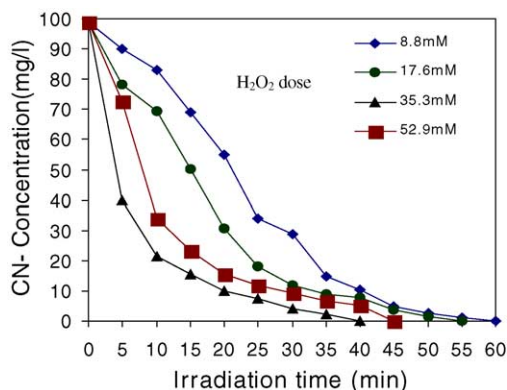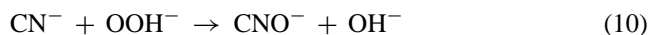
oxide [21]. The perhydroxyl anion attack triple bond present in cyanide ion to oxidize it to cyanate [25]:

$$CN^- + OOH^- \rightarrow CNO^- + OH^- \tag{10}$$

The existence of optimum dose of H_2O_2 has been described by several investigators earlier while working on photodegradation of other organic compounds. Galbriath et al. [26] pointed out that there is an upper limit to the amount of H_2O_2 that can be added, above which peroxide scavenges the hydroxyl radicals.

3.2.3. UV/Cu2+ system

Initial experiments were carried out with different doses of Cu^{2+}, i.e. 25 and 127 mg/l using $CuSO_4 \cdot 5H_2O$ in a photoreactor using low-pressure 25 W Hg lamp. With 127 mg/l of Cu^{2+} dose, rate of CN^- degradation reached up to 85% and with 25 mg/l of Cu^{2+} dose, 33% degradation occurred in 60 min. Results are shown in Fig. 6. Tetracyanocuprate is formed which is difficult to oxidize without an oxidant.

3.2.4. UV/H2O2/Cu2+ system

An investigation using combination of H_2O_2 (35.3 mM) and Cu^{2+} ion concentration, i.e. 10, 12.5, 19 and 25 mg/l showed that complete destruction of CN^- occurred in 9 min with 19 mg/l of Cu^{2+} and 35.3 mM of H_2O_2 using 25 W low-pressure Hg lamp (Fig. 7). With H_2O_2 alone degradation rate was very slow but when Cu^{2+} was added the rate was accelerated as it acted as catalyst. It was observed that as the dose of Cu^{2+} increased, the rate of oxidation increased and 19 mg/l Cu^{2+} was found to be the optimum dose. Further experiments were carried out with 19 mg/l of Cu^{2+} only. More difficult to oxidize pollutants require the H_2O_2 to be activated with catalyst such as iron, copper or other transition metals. These metals have O_2 transfer capabilities which improve the utility of H_2O_2 [27]. Table 2 depicts the various findings during photochemical oxidation and chemical oxidation of cyanide by Cu^{2+}. It was also observed that the presence of Cu^{2+} ions increased the photolytic rates of H_2O_2 in aqueous solution by UV radiation possibly because the quantum yield of H_2O_2 at
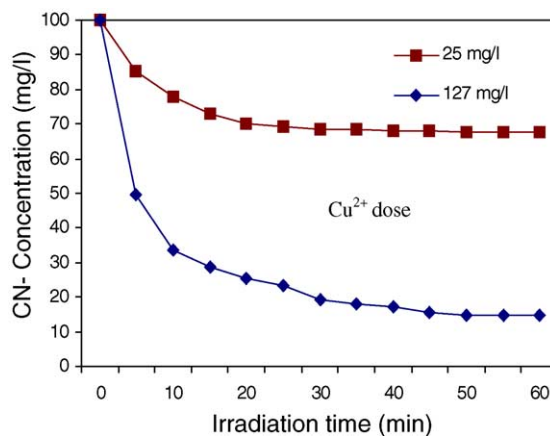

Fig. 5. Optimisation of H_2O_2 dose for photo-oxidation of cyanide (UV/H_2O_2 system).

Fig. 6. Effect of Cu^{2+} concentration (UV/Cu^{2+} system).
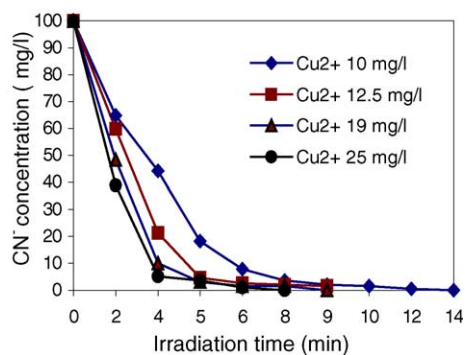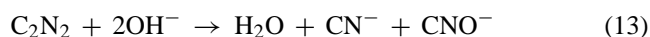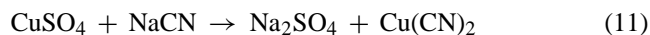
Fig. 7. Effect of Cu^{2+} concentrations for $UV/Cu^{2+}/H_2O_2$ system ($H_2O_2 = 35$ mM).

254 nm UV light could be raised by the addition of Cu^{2+} ions [21].

3.2.5. Mechanism of Cu^{2+} catalysis

Cyanide can be rendered unreactive by the addition of various metals and metal cations to promote the formation of metal cyanide complexes. When copper sulphate is added to cyanide solution, it forms copper cyanide complex which decomposes to form cyanogen. In alkaline solution, cyanogen disproportionates into cyanide and cyanate ions according to Eq. (13) [28]. Cyanate ions can be hydrolysed at pH 1.5–2.0:

$$CuSO_4 + NaCN \rightarrow Na_2SO_4 + Cu(CN)_2 \quad (11)$$

$$2(CuCN)_2 \rightarrow 2CuCN + C_2N_2 \quad (12)$$

$$C_2N_2 + 2OH^- \rightarrow H_2O + CN^- + CNO^- \quad (13)$$

$$2Cu^{2+} + 4CN^- \rightarrow 2CuCN + C_2N_2 \quad (14)$$

$$CuCN + 3CN^- \rightarrow [Cu(CN)_4]^{3-} \quad (15)$$

Tetracyanocuprate $[Cu(CN)_4]^{3-}$ has greater affinity for H_2O_2 hence enhancing the rate of degradation. A very fine precipitate of $Cu(OH)_2$ is formed at the end of this reaction which can act as heterogeneous catalyst for decomposition of excess H_2O_2. Blackish brown precipitate formed in this treatment indicates the end of oxidation reaction. Copper precipitate formed must be removed from the effluent by decantation before discharging the treated water. Alkaline cyanides are paradoxically the most refractory as regards H_2O_2 oxidation in the absence of a catalyser [25].

Table 2
Comparison of chemical and photochemical oxidation of cyanide

UV lamp used	H_2O_2 dose (ml/l)	Cu^{2+} (mg/l)	Initial CN^- concentration (mg/l)	Time of irradiation (min)	Final CN^- concentration (mg/l)	Normalized space velocity, >99% conversion (l/h)
25 W	4.0	10	100	14	<MDL	4.3
25 W	4.0	12.5	100	12	<MDL	5.0
25 W	4.0	19	100	9	<MDL	6.6
25 W	4.0	25	100	8	<MDL	7.5
Without UV	10.0	12.5	100	35	<MDL	1.7
Without UV	10.0	25	100	20	<MDL	3.0
Without UV	10.0	50	100	10	<MDL	6.0
Without UV	10.0	75	100	9	<MDL	6.6
Without UV	10.0	100	100	9	<MDL	6.6

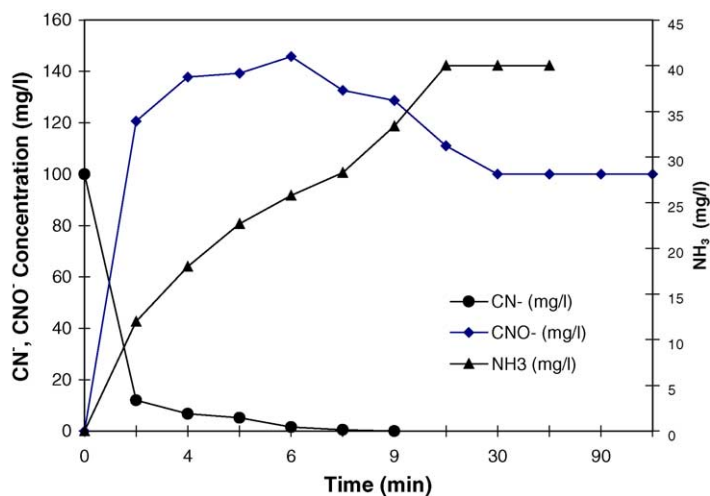MDL = minimum detection limit (0.2 µg/l).

Fig. 8. CN^-, CNO^- and ammonia concentration profile during chemical oxidation of CN^-.

Table 3
Rate constants of chemical and photochemical oxidation of CN⁻

System	Oxidant/catalyst concentration	Rate constant	R^2
H_2O_2	H_2O_2 concentration (mg/l)	h^{-1} (pseudo-first order)	
	35.3	0.6137	0.96
	52.9	0.4209	0.88
	70.5	0.3401	0.92
	88.2	0.7277	0.98
	132.3	1.28	0.97
H_2O_2/Cu^{2+}	Cu^{2+} concentration (mM)	min^{-1} (pseudo-first order)	
	12.5	0.0706	0.97
	25	0.1385	0.87
	50	0.1799	0.99
	75	0.3160	0.99
UV/H_2O_2	H_2O_2 concentration (mM)	min^{-1} (pseudo-first order)	
	8.8	0.086	0.92
	17.6	0.0766	0.96
	35.3	0.099	0.97
	52.9	0.074	0.97
$UV/H_2O_2/Cu^{2+}$ (H_2O_2 concentration = 35.3 mM)	Cu^{2+} concentration (mg/l)	min^{-1} (pseudo-first order)	
	10	0.4654	0.97
	12.7	0.5497	0.95
	19	0.7035	0.98
	25	0.7690	0.97
UV/Cu^{2+}	Cu^{2+} concentration (mg/l)	K, $mol^{-1} min^{-1}$ (second order)	
	25	0.1796	0.99
	127	0.1398	0.99

3.3. Reaction pathways of CN⁻ oxidation

Cyanide and cyanate concentrations were determined quantitatively in both chemical oxidation as well as photochemical oxidation. Results are shown in Figs. 8 and 9. It was seen that cyanate did not completely hydrolysed to bicarbonate and ammonia in case of chemical oxidation. Rate of ammonia formation was slow, only 40% ammonia was formed as shown in Fig. 8. Whereas during photochemical oxidation cyanate formation was faster at the beginning and cyanate is subsequently oxidized to bicarbonate and nitrogen. It was also observed that cyanide concentration was below MDL after distillation in both processes, i.e. photochemical oxidation as well as chemical oxidation in the absence of UV.

3.4. Reaction kinetics of photo-oxidation of cyanide using H_2O_2 and Cu^{2+} catalyst

Rate constants for different systems were calculated and experimental data found to be fit in pseudo-first-order model. A high value of R^2 in each case evidenced its applicability. Reaction kinetics of cyanide oxidation can be calculated from the equation:

$$-\frac{d(CN^-)}{dt} = K_{obs} C_{CN^-} \tag{16}$$

where C_{CN^-} is the cyanide concentration and K_{obs} is the pseudo-first-order rate constant. According to Eq. (16), lin-
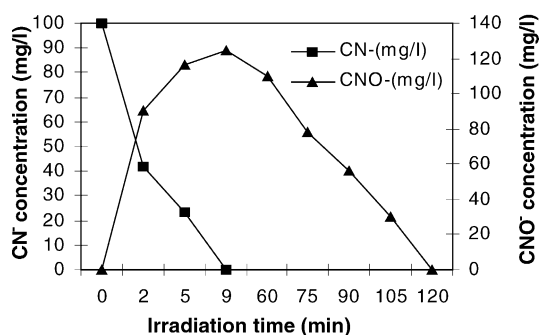

Fig. 9. CN⁻ and CNO⁻ concentration profile during photochemical oxidation of CN⁻.

ear plots of $-\ln C_t/C_0$ versus time are plotted and from slopes K_{obs} can be evaluated.

However, rate constant for UV/Cu^{2+} was found to fit in second-order model. The value of rate constants for different systems are presented in Table 3.

4. Conclusion

Detailed study was carried out for cyanide oxidation by both chemical and photochemical processes. The effect of Cu^{2+} catalysis was also studied. It was observed that chemical oxidation by H_2O_2 was slow but UV/H_2O_2 was much faster and in both cases Cu^{2+} accelerates the oxidation

process and acts as catalyst. CN^- concentration was reduced from 100 mg/l to non-detectable level within 9 min at pH 10.0 using 19 mg/l Cu^{2+} catalyst along with 35.3 mM H_2O_2 and 25 W UV lamp. Chemical oxidation using H_2O_2 and 75 mg Cu^{2+} also occurred in 9 min at pH 10.0 but the dose of H_2O_2 required was 88.2 mM, greater than photochemical oxidation. Moreover, cyanate is subsequently oxidized to bicarbonate and nitrogen in case of photochemical process but in chemical oxidation cyanate was converted to bicarbonate and ammonia. Advantage of photochemical oxidation of CN^- by combination of H_2O_2 and Cu^{2+} is that there is no need of neutralization after treatment. Reaction kinetics of cyanide oxidation was found to be pseudo-first order and the rate constant has been determined for different processes.

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