Degradation of ferrohexacyanide by advanced oxidation processes

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Degradation of ferrohexacyanide in aqueous solution by advanced oxidation processes was studied. Advanced oxidation processes included ozone and its combination with H2O2 and ultraviolet radiation (UV). Results demonstrated that UV alone was not sufficient to degrade cyanide ion but an oxidant was required for complete degradation. Degradation of 100 mg/L cyanide in aqueous solution was pseudo-first order reaction at pH 11.0. Lower pH was avoided due to formation of HCN gas but higher pH favoured the degradation. A comparison of three systems i.e. O3, O3/H2O2 and UV/O3/H2O2 showed that UV/O3/H2O2 was the best system. The experimental results showed that the optimum conditions for UV/O3/H2O2 process for total cyanide degradation were obtained at λ = 365 nm (400 W medium pressure UV lamp), ozone concentration = 35 mg/L and H2O2 = 88.2 mM.

Keywords: Degradation, ferrohexacyanide, UV-radiation, ozone, hydrogen peroxide

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Advanced oxidation processes use a combination of oxidizing agent such as ozone or hydrogen peroxide, radiation such as UV or ultrasound and catalyst such as metal ions or photocatalyst to generate hydroxyl radicals1. These hydroxyl radicals do not possess any charge and have high affinity for electrons, they can quickly strip weak acid dissociable cyanides such as sodium cyanide as well as strong acid dissociable cyanides like ferricyanide and ferrocyanides, thus causing their oxidation. Biological oxidation processes are very slow and unattractive for the treatment of toxic and refractory pollutants. Electrochemical processes are inefficient after cyanide falls below certain level and require high current. Classical oxidation processes have also been proved inefficient for the destruction of ferrocyanide. These hexacyanides do not undergo chlorination at all. The direct reactions of ozone involving molecular ozone are highly selective and relatively slow as compared with reactions involving free hydroxyl radicals. The free radical is considered to be the principal reactive species involved in the destruction of organic and inorganic toxicants3. Ozone is a powerful oxidizing agent having oxidation-reduction potential of 2.07 V. Ozone in combination with H2O2 generates hydroxyl radicals which are responsible for fast degradation of cyanide. Present study has been focused on using ozone and its combination with UV and H2O2 at higher pH to degrade ferrocyanide.

Experimental Procedure

Experimental set-up used for this study consisted of a reactor, ozone generator and potassium iodide absorbers (Fig. 1). Experiments were carried out in an annular type batch reactor (length = 550 mm, O.D. = 95 mm, wall thickness = 2.5 mm) made up of borosilicate glass. The reactor assembly is shown in Fig. 2. The effective volume of the reactor was 1000 mL. A double walled immersion well (O.D. of 75 mm) made of high purity quartz was placed inside the glass reactor fitted with a standard joint at the top. UV lamp was housed inside the immersion well. Water was circulated through the annular space of the immersion well to remove heat generated by UV lamp. Cyanide solution was taken inside the glass reactor for photodegradation studies. O3 was bubbled into the reactor solution through the bottom inlet. A sintered disc (Grade 2 Borosil, pore dia. 40-90 μm) was provided for producing small bubbles. There was a sampling port at the middle of the reactor, so that periodic samples could be withdrawn for analysis. A teflon coated thermocouple was introduced into the reactor solution through the bottom inlet. A sintered disc (Grade 2 Borosil, pore dia. 40-90 μm) was provided for producing small bubbles. There was a sampling port at the middle of the reactor, so that periodic samples could 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 was covered with a safety hood, so the person working was not affected by harmful UV radiation. UV lamp was removed while working with O3 and O3/H2O2 processes.

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An aqueous solution of potassium ferrocyanide containing CN$^-100$ mg/L was prepared in distilled water. Tests were performed by bubbling ozone at 1.0 LPM at a concentration of 25-40 mg/L through 1000 mL solution for a given period of time. Ozone was produced from pure oxygen by corona discharge process$^4$. Ozone concentration was measured by iodometric method before and after the experiment.

Materials and reagents
A medium pressure lamp of 400 W was used. In medium pressure lamp 31% radiation is emitted at 365 nm. The lamp was obtained from M/s Heber Scientific, Chennai.

Silver nitrate, 4-dimethylaminobenzylidene rhodamine, sodium hydroxide, pyridine, barbituric acid, hydrogen peroxide, potassium titanium oxalate and other reagents of highest purity were obtained from E. Merck Ltd.

Analytical method
Reactor was filled with potassium ferrocyanide containing CN$^-100$ mg/L. UV lamp was inserted in the immersion well. Time when the UV lamp was switched on was taken as zero. Samples were taken at different time interval and analyzed immediately to avoid any further reaction. Total cyanide concentration was determined after distillation by colorimetric method. Cyanate concentration was determined by hydrolyzing to ammonia at acidic pH (1.5 to 2.0). Ammonia was measured by Nesslerisation method$^5$. H$_2$O$_2$ concentration was determined colorimetrically using potassium titanium oxalate solution at 398.9 nm.

Results and Discussion
Ozonation
Degradation of ferrohexacyanide by ozonation was studied at pH 7.0 and 11.0. At pH 7.0 only 30% degradation occurred. Oxidation of cyanide was fast at alkaline pH 11.0. Results are presented in Table 1 and Fig. 3. Complete degradation took place in 1 h and 45 min by ozone concentration of 35 mg/L at 1.0 LPM for ferrohexacyanide. After 35 mg/L if the ozone concentration was increased rate of cyanide degradation decreased. This anomaly cropped up probably due to excess of O$_3$ acting as OH radical scavenger. At alkaline pH O$_3$ decomposes into hydroxyl radicals according to Eqs (1-2)$^6$.

$$\text{O}_3 + \text{OH}^- \rightarrow \text{O}_2^- + \text{O}_2 \quad \ldots(1)$$

$$\text{O}_3 + \text{H}_2\text{O} \rightarrow 2 \text{OH} + \text{O}_2 \quad \ldots(2)$$

Hydroxyl radicals are the major oxidation species. Ozonation at alkaline conditions has been classified as advanced oxidation process$^{7,8}$. OH$^-$ ions act as catalyst. Ozone decomposition catalysed by OH$^-$ ions
Fig. 3—Effect of O₃ concentration on oxidation of ferrohexacyanide

Fig. 4—Reaction kinetics of ferrohexacyanide by ozone

Table 1—Oxidation of ferrohexacyanide by ozone

<table>
<thead>
<tr>
<th>Ozone concentration (mg/L)</th>
<th>Reaction time</th>
<th>Initial CN⁻ concentration (mg/L)</th>
<th>Final CN⁻ concentration (mg/L)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>2 h 45 min</td>
<td>100</td>
<td>1.0</td>
<td>99</td>
</tr>
<tr>
<td>30</td>
<td>2 h 30 min</td>
<td>100</td>
<td>1.0</td>
<td>99</td>
</tr>
<tr>
<td>35</td>
<td>1 h 45 min</td>
<td>100</td>
<td>&lt;M.D.L</td>
<td>99.99</td>
</tr>
<tr>
<td>40</td>
<td>2 h 15 min</td>
<td>100</td>
<td>1.0</td>
<td>99</td>
</tr>
</tbody>
</table>

M.D.L (Minimum detection limit) = 0.02 μg/L

favours cyanide to cyanate oxidation as well as hydrolysis of the latter. Kinetics of various ozone concentrations is presented in Fig. 4. Roques² has reported that 1 mole of O₃ converts 1 mole of CN⁻ to CNO⁻. Oxidation of CNO⁻ by O₃ is slow reaction compared to cyanide and, therefore, cyanate accumulates while cyanide is almost oxidized.

Mechanism of ozonation

Ozonation for cyanide destruction has been examined extensively because it is a superior oxidant to oxygen⁹. Ozone reacts rapidly with free and many stable metal cyanide complexes. Ozone reacts according to the following reactions:

\[ \text{CN}^- + \text{O}_3 + \text{H}_2\text{O} \rightarrow \text{OCN}^- + \text{O}_2 + \text{H}_2\text{O} \quad \ldots (3) \]

The oxidative/hydrolytic destruction proceeds slowly upon continuous treatment with ozone.

\[ \text{OCN}^- + \text{OH}^- + \text{H}_2\text{O} \rightarrow \text{CO}_3^{2-} + \text{NH}_3 \quad \ldots (4) \]

Continuous ozone treatment of cyanide containing waste involves consecutive oxidation reactions, the first of which involves direct oxidation of cyanide to cyanate. Ozone reacts with cyanide to produce cyanate. Two mechanisms have been proposed¹⁰:

\[ \text{CN}^- + \text{O}_3 \rightarrow \text{OCN}^- + \text{O}_2 \quad \ldots (5) \]
\[ 3\text{CN}^- + \text{O}_3 \rightarrow 3\text{OCN}^- \quad \ldots (6) \]

which are referred to as simple and catalytic ozonation, respectively. Simple ozonation yields oxygen which can further oxidize cyanide. Catalytic ozonation represents a high efficiency and has been observed at high addition rates. If excess of ozone is used, cyanate can be oxidized to nitrogen and carbonate or bicarbonate depending on the pH according to Eq. (7).

\[ 2\text{OCN}^- + \text{H}_2\text{O} + 3\text{O}_3 \rightarrow 2\text{HCO}_3^- + \text{N}_2 + 3\text{O}_2 \quad \ldots (7) \]

Under basic conditions the CNO⁻ hydrolyses to yield ammonia which is then oxidized by ozone to nitrate according to the reaction proposed by Singer and Zilli¹¹.
NH$_3$ + 4O$_3$ → NO$_3^-$ + H$_2$O + 4O$_2$ + 2H$^+$  \hspace{1cm} \ldots (8)

Prolonged ozonation can lead to conversion of nitrate to nitrogen.

Cyanide oxidation is enhanced by O$_3$ oxidation rate. Cyanide ion decreases with time and degradation increases proportionately with O$_3$ addition. However, it was observed that abundance of O$_3$ in this case (40 mg/L) reduced the cyanide degradation probably due to reduction in OH radicals.

**Ozone/H$_2$O$_2$ process**

Experiments were conducted to investigate the effect of combination of ozone and H$_2$O$_2$ with different concentration of hydrogen peroxide. It was observed that 88.2 mM H$_2$O$_2$ was the optimum dose along with ozone concentration of 35 mg/L (Table 2). It has been reported$^{12,13}$, that, H$_2$O$_2$ can initiate the decomposition of O$_3$ by single electron transfer, where the initiating species is the hydroperoxide ion HO$_2^-$.

\[ H_2O_2 = HO_2^- + H^+ \]  \hspace{1cm} \ldots (9)

The hydroperoxide ion reacts with ozone to produce the ozonide ion O$_3^-$ and hydroperoxide radical HO$_2^-$.

\[ HO_2^- + O_3 \rightarrow O_3^- + HO_2^- \]  \hspace{1cm} \ldots (10)

\[ HO_2 = H^+ + O_2^- \]  \hspace{1cm} \ldots (11)

These products can form OH radicals through the following initiation steps,

\[ O_2^- + O_3 \rightarrow O_3^- + O_2 \]  \hspace{1cm} \ldots (12)

Once the hydroxyl radical is formed, the following propagation steps generate hydroxyl radicals by autocatalytic mechanism,

\[ O_3^- + OH \rightarrow O_2 + HO_2^- \]  \hspace{1cm} \ldots (13)

\[ HO_3 \rightarrow OH^- + O_2 \]  \hspace{1cm} \ldots (14)

Cyanide reacts with hydroxyl radicals and cyanate is formed which again reacts with OH radicals to form bicarbonate.

\[ CN^- + 2 OH \rightarrow OCN^- + H_2O \]  \hspace{1cm} \ldots (15)

\[ OCN^- + 3 OH \rightarrow HCO_3^- + 1/2N_2 + H_2O \]  \hspace{1cm} \ldots (16)

**UV process**

Experiments were conducted by medium pressure lamp of 400 W. It was found that 35% degradation took place in 3 h by 400 W medium pressure lamp. Direct photolysis occurs according to Eqs (19-20).

\[ \text{Fe(CN)}_6^{4-} \xrightarrow{hv} \text{Fe(CN)}_6^{3^-} + e^- \]  \hspace{1cm} \ldots (19)

\[ \text{Fe(CN)}_6^{3^-} + H_2O \rightarrow [\text{Fe(CN)}_5H_2O]^{2^-} + CN^- \]  \hspace{1cm} \ldots (20)

**UV/O$_3$/H$_2$O$_2$ process**

Generation of OH radicals by UV/O$_3$/H$_2$O$_2$ process takes place$^{14,15}$ according to Eqs (21-25).

\[ H_2O_2 + H_2O \rightarrow H_2O^+ + HO_2^- \]  \hspace{1cm} \ldots (21)

\[ O_3 + H_2O_2 \rightarrow O_2 + OH + HO_2^- \]  \hspace{1cm} \ldots (22)

\[ O_3 + HO_2^- \rightarrow OH + O_2^- + O_2 \]  \hspace{1cm} \ldots (23)

\[ O_3 + O_2^- \rightarrow O_3^- + O_2 \]  \hspace{1cm} \ldots (24)

\[ O_3^- + H_2O \rightarrow OH^- + O_2 + O_2 \]  \hspace{1cm} \ldots (25)

Cyanide ion is attacked by OH radicals generated from the photolysis of H$_2$O$_2$. The rate of photolysis of H$_2$O$_2$ has been reported to be pH dependent and
increases in alkaline conditions. As the molar ratio of $H_2O_2$ to $CN^-$ increased more $OH$ radicals were available and the rate of degradation was increased. Addition of $H_2O_2$ results in enhancement of dominant production of $OH$ radicals. With $35$ mg/L $O_3$, $88.2$ mM $H_2O_2$ and $400$ W medium pressure lamp $CN^-$ disappeared in $25$ min (Table 3). UV light induced photolysis of $O_3$ and the subsequent production of $OH$ radicals in the degradation of $CN^-$ to $CNO^-$. $H_2O_2$ is also a very strong oxidizing agent. 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 Eq.,

$$H_2O_2 \xrightarrow{hv} 2OH^*$$ \hspace{1cm} \ldots (26)

The decomposition occurred at $365$ nm. The hydroxyl radicals are very reactive free radicals and one of the most powerful oxidizing agents ($E_0 = 2.8V$) second after fluorine ($E_0 = 2.87V$). These radicals have one electron efficiency and due to their excited state they tend to react very fast with other molecules. Initially cyanate was formed which was subsequently oxidized to bicarbonate, water and other non-toxic gaseous products. $CN^-$, $CNO^-$ profile during this process is shown in Fig. 5. Cyanate was completely oxidized in $2$ h and $30$ min.

**Effect of pH**

Since at acidic pH $CN^-$ is released as $HCN$ which is highly toxic so the experiments were carried out at alkaline pH ($11.0$). At alkaline pH hydroperoxyl anion attacks $CN^-$ ion to break the triple bond thereby enhancing the rate of photodegradation.

$$CN^- + OO^- \rightarrow CNO^- + OH^-$$ \hspace{1cm} \ldots (27)

**Reaction kinetics of cyanide oxidation**

Cyanide oxidation is considered to be pseudo-first order reaction. Kinetic equation can be expressed as,

$$-dCN^-/dt = k_{obs}C_{CN^-}$$ \hspace{1cm} \ldots (28)

where $C_{CN^-}$ is the cyanide concentration and $k_{obs}$ is the pseudo first order rate constant. According to Eq. (28) linear plots of $-\ln C_t/C_0$ verses time are plotted from which slopes $k_{obs}$ can be evaluated (Fig. 6). Rate constants for $O_3$, $O_3/H_2O_2$ and $UV/O_3/ H_2O_2$ processes are listed in Table 4. Rate constant for $UV/O_3/ H_2O_2$ process is the maximum as more $OH$ radicals are available to attack $CN^-$ ion as compared to $O_3$ and $O_3/H_2O_2$ process.

![Fig. 5—CN⁻, CNO⁻ profile during UV/O₃/H₂O₂ process](image)

**Table 3—Ferrohexacyanide degradation by UV/O₃/H₂O₂ process**

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>$CN^-$ concentration (mg/L)</th>
<th>% removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>44.5</td>
<td>55.5</td>
</tr>
<tr>
<td>10</td>
<td>24.6</td>
<td>75.4</td>
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<tr>
<td>15</td>
<td>9.8</td>
<td>90.2</td>
</tr>
<tr>
<td>20</td>
<td>2.5</td>
<td>97.5</td>
</tr>
<tr>
<td>25</td>
<td>&lt;M.D.L</td>
<td>99.99</td>
</tr>
</tbody>
</table>

![Fig. 6—Comparison of advanced oxidation processes](image)

**Table 4—Reaction rate constants of the ferrohexacyanide degradation by different advanced oxidation processes**

<table>
<thead>
<tr>
<th>Advanced oxidation process</th>
<th>$k_1 \times 10^{-2}$ (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_3$</td>
<td>$5.2$</td>
</tr>
<tr>
<td>$O_3/H_2O_2$</td>
<td>$5.7$</td>
</tr>
<tr>
<td>$UV/O_3/H_2O_2$</td>
<td>$17.7$</td>
</tr>
</tbody>
</table>
Conclusion
The effect of advanced oxidation processes on the degradation of CN$^-$ ion was studied using potassium ferrocyanide solution at CN$^-$ concentration 100 mg/L. Ozone process is expensive as it requires ozone generator but ensures no secondary by-products formed which are toxic to environment. O$_3$/UV/H$_2$O$_2$ process is safe, as H$_2$O$_2$ does not load any pollutant. Complete degradation of cyanide occurred in 25 min and intermediate cyanate was formed which was subsequently oxidised to bicarbonate and nitrogen.

References