Application of AOPs for Removal of Stable Cyanide Compounds

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Abstract. The main kinetic regularities of the photochemical oxidation of stable cyanide compounds (exemplified by hexacyanoferrates) by combined treatments involving direct photolysis and persulfate (oxidative system UV/S₂O₈²⁻) and direct photolysis and hydrogen peroxide (oxidative system UV/H₂O₂) were studied. The possibility to perform oxidation processes within a wide pH range was shown. Based on to the energy efficiency, the rate of reaction and duration of the treatment, the considered oxidative systems can be arranged in the following order: {UV/S₂O₈²⁻}>{UV/H₂O₂}>{UV}. The enhanced efficiency of hexacyanoferrates’ degradation by the combined system {UV/S₂O₈²⁻} is due to the high oxidative capacity of sulfate anion radicals SO₄²⁻• formed as a result of persulfate photolysis and its further disproportionation by Fe³⁺ and Fe²⁺ released through the decomposition of [Fe(CN)₆]³⁻. Furthermore, the formation of •OH radicals as a result of SO₄²⁻• reacting with water also contributes to the enhanced oxidation efficiency. The combined method of {UV/S₂O₈²⁻} treatment could be applied for the treatment of cyanide-containing wastewater and recycled water of different industries.

1. Introduction
Cyanides, despite the high toxicity and cost of the sodium cyanide reagent, are still widely used in various industries: annually more than 1 million tons of this substance is used in electroplating, metal processing, production of organic chemicals, plastics, etc. Thus, highly toxic cyanide compounds are present in industrial effluents in a significant number of ore-processing plants, electroplating plants, metallurgical and metal-processing plants, gas and coke plants [1,2]. The methods employing “environmentally unsafe” or “environmentally dirty” oxidants – hypochlorites, chlorinated lime, liquid chlorine, sulfur dioxide, etc. – are still widely used for treatment of these wastewaters [3-6]. In this regard, the priority goal from an environmental standpoint is the development and implementation of low-waste technologies and closed technological cycles, as well as the development and implementation of environmentally safe technologies for treating highly toxic effluents.

The problem of processing liquid technogenic cyanide-containing effluents can be solved using Advanced Oxidation Processes (AOPs), which are based on oxidative degradation reactions initiated by in situ generated reactive oxygen species – highly reactive oxygenated radicals [7-9]. The combinations of environmentally safe oxidants with physical impact (UV, ultrasound) or with catalysts (transition metals, TiO₂) are widely used to generate free radicals [10,11].

During the last decade, the most intensively used AOPs were the photochemical methods employing environmentally safe oxidants and/or catalysts [12-14]. Inorganic peroxocompounds
(hydrogen peroxide, persulfates) are increasingly used as primary oxidants in the AOP processes since they are sources of secondary more powerful and highly reactive oxidants – hydroxyl radicals \( \cdot \text{OH} \) and sulfate anion radicals \( \cdot \text{SO}_4^- \). Different radiation sources (from shortwave UV to infrared) are used for carrying out photochemical processes. Mercury vapor lamps are widely used UV radiation sources. The use of UV radiation for degradation of toxic pollutants of various nature, including cyanide compounds, is becoming increasingly common [15]. Previously, UV radiation has been used in combination with hydrogen peroxide and \( \text{TiO}_2 \) catalyst for degradation of recalcitrant cyanide compounds, including hexacyanoferrates [16-18]. No studies have been carried out previously on the degradation of stable cyanide compounds by a combination of UV radiation and persulfate.

The aim of the present work was to study the photochemical oxidation of stable cyanide compounds, represented here by hexacyanoferrates, by UV radiation in the presence of the environmentally friendly oxidant persulfate, to comparatively evaluate the method with the already known method involving hydrogen peroxide and to develop an energy efficient advanced oxidation method for treatment of highly toxic wastewaters containing stable cyanide compounds.

2. Experimental section

1. The hexacyanoferrates \([\text{Fe(CN)}_6]^{4-}\) and \([\text{Fe(CN)}_6]^{3-}\) were chosen as the study’s target compounds as they are among the most stable cyanide compounds (\( K = 1 \times 10^{-35}, 1 \times 10^{-42} \), respectively). The experiments on photochemical transformations of hexacyanoferrates were carried out on model aqueous solutions of \( \text{K}_3[\text{Fe(CN)}_6] \) with an initial concentration of 100 mg/l (0.47 mM) prepared with distilled water (\( \chi = 2 \mu \text{S/cm} \)). Reagents (hexacyanoferrate of potassium, hydrogen peroxide, potassium persulphate) of the grade “chemically pure” were used in the work. The concentration of hexacyanoferrates was controlled by the standard photometric method using the photometer KFK-3 [19]. pH values were monitored using the universal pH 150M ionomer [20]. To adjust pH value of solutions, 0.1 N \( \text{NaOH} \) solution was used.

2. The experiments on the main kinetic regularities of photochemical oxidation of \( \text{K}_3[\text{Fe(CN)}_6] \) by oxidative systems \{UV/S\( \text{O}_8^{2-} \}\) and \{UV/\( \text{H}_2\text{O}_2 \)\} were carried out in a flow-through tube reactor at a thermostatically controlled temperature (25° C). The volume of the treated solution was 300 ml, the circulation rate \( \nu = 0.5-0.6 \) l / min. The source of UV radiation used was a high-pressure mercury gas discharge lamp DRT-400 with a polychromatic emission spectrum with the maximum of the radiant flux at \( \lambda = 365 \text{ nm} \) and the emission intensity of 1.88 mW/cm\(^2\), which was determined by the actinometric method with potassium ferrioxide [21].

3. Results and discussion

At the first stage, comparative experiments were conducted on the kinetics of oxidation of hexacyanoferrates by direct photolysis and the combination of direct photolysis with oxidants \( \{\text{S}_2\text{O}_8^{2-}, \text{H}_2\text{O}_2\} \) (Figure 1).
The oxidation rate of $K_3[Fe(CN)]_6$ by direct photolysis was $W_0 = 3 \cdot 10^{-5}$ M·min$^{-1}$, whereas in the case of the combined treatment UV and $H_2O_2$ (UV/$H_2O_2$ oxidative system) the $W_0$ value increased 1.7 times and was equal to $5.2 \cdot 10^{-5}$ M·min$^{-1}$. The latter was due to the additional formation of OH radicals through the disproportionation of hydrogen peroxide according to the reaction:

$$\text{H-O-O-H} + \text{hv} \rightarrow 2 \cdot \text{OH}$$

When the direct photolysis was combined with $S_2O_8^{2-}$, an almost threefold increase in the initial reaction rate was observed, i.e. up to $8.7 \cdot 10^{-5}$ M·min$^{-1}$, and the total degradation of $K_3[Fe(CN)]_6$ was recorded after 90 min of the treatment. The increase in the efficiency of oxidation of hexacyanoferrates in the presence of persulfate is due to the high oxidizing capacity of the sulfate anion radicals $SO_4^{\cdot-}$ formed according to the reaction:

$$\text{SO}_3^{\cdot-O-O-SO}_3^{\cdot-} + \text{hv} \rightarrow 2\text{SO}_4^{\cdot-}$$

In this case, it is also necessary to take into account the formation of an additional amount of $SO_4^{\cdot-}$ as a result of the disproportionation of persulfate by $Fe^{3+}$ and $Fe^{2+}$ ions formed through degradation of $K_3[Fe(CN)]_6$:

$$Fe^{3+} + S_2O_8^{2-} \rightarrow 2SO_4^{\cdot-} + Fe^{2+}$$

$$Fe^{2+} + S_2O_8^{2-} \rightarrow SO_4^{\cdot-} + SO_4^{2-} + Fe^{3+}$$

Furthermore, OH radicals generated as a result of the interaction of $SO_4^{\cdot-}$ with water also contribute to the increased oxidation efficiency:

$$H_2O + SO_4^{\cdot-} \rightarrow \cdot OH + H^+ + SO_4^{2-}.$$  

In addition, it is known that the oxidative system \{S$_2$O$_8^{2-}$/Fe$^{3+}$\} due to the similarity of the mechanisms is referred to as Fenton-like [8].

Thus, it can be concluded that the photochemical oxidation with the use of oxidizing agents S$_2$O$_8^{2-}$ and $H_2O_2$ leads to a deep conversion of the initial substrate and to a decrease in the treatment duration, which could be useful for application in treatment of sewage and circulating water of various industries. In this case, the oxidative system \{UV/S$_2$O$_8^{2-}$\} is more effective than \{UV/$H_2O_2$\}. Sulphate anion radicals are a viable alternative to hydroxyl radicals, since they have a higher oxidation-reduction potential ($E'_{H_2O_2} = 1.77V$, $E'_{S_2O_8} = 2.5-3.1V$), a high reactivity towards most environmental pollutants, are less sensitive to pH as compared with hydrogen peroxide, and the initial reagents – persulfates – are solids that do not lose their activity for a long time and are easily dosed, which is very convenient when used in wastewater treatment technologies.

The pH of the treated solution is the main variable parameter, which significantly influences the efficiency of the oxidation processes. It is known that the cyanide-containing wastewaters of the galvanic shops are characterized by a fairly wide range of pH values - from 2.8 to 11.5, while wastewater and circulating solutions of gold recovery plants have pH of 10 to 11. Using model aqueous solutions of hexacyanoferrates, the efficiency of direct photolysis and photochemical oxidation employing oxidative systems - \{UV/S$_2$O$_8^{2-}$\} and \{UV/$H_2O_2$\} – was evaluated at higher pH values. Figure 2 shows the photochemical conversion of hexacyanoferrates at pH = 11.

The data obtained confirm the effectiveness of the combined oxidative systems in alkaline medium. Moreover, at the higher pH too the oxidative system \{UV/S$_2$O$_8^{2-}$\} is more efficient than \{UV/$H_2O_2$\}. In addition, due to the increasing residual concentration of the original compound it was established that, in the presence of $H_2O_2$, the photochemical degradation of $K_3[Fe(CN)]_6$ at pH 11 is reversible. This is explained by the formation of intermediates inhibiting further photodegradation or accumulation of free CN$^-$ ions followed by their binding to the initial complex due to a decrease in the concentration of secondary oxidants - OH:

$$[Fe(CN)_6]^{3+} + H_2O \leftrightarrow [Fe(CN)_6(H_2O)]^{2-} + CN^-$$
A comparative assessment of the photochemical degradation of hexacyanoferrates by different oxidative systems, \{UV/S_2O_8^{2-}\} and \{UV/H_2O_2\}, was carried out (Table 1).

| Oxidative system       | Wo·10^{-5}, M·min | \(\tau_{1/2}\), min | \(D^{50}\), mJ/cm^2 | \(D^{90}\), mJ/cm^2 | Wo·10^{-5}, M·min | \(\tau_{1/2}\), min | \(D^{50}\), mJ/cm^2 | \(D^{90}\), mJ/cm^2 |
|------------------------|--------------------|----------------------|---------------------|---------------------|--------------------|----------------------|---------------------|---------------------|
| \(S_2O_8^{2-}\) (dark) | 5.0                | 3.0                  | -                   | -                   | 2.8                | 150                  | -                   | -                   |
| \(H_2O_2\) (dark)      | 0.85               | >150                 | -                   | -                   | 0.52               | >150                 | -                   | -                   |
| \{UV\}                | 3.0                | 27.5                 | 3102                | 13536               | 4.4                | 5.2                  | 586.6               | 4512               |
| \{UV/S_2O_8^{2-}\}    | 8.7                | 1.0                  | 112.8               | 338.4               | 7.6                | 0.64                 | 72.2                | 1241               |
| \{UV/H_2O_2\}         | 5.2                | 6.0                  | 676.8               | 5640                | 6.3                | 2.75                 | 310.2               | 13536              |

\(^a\) The dose of UV radiation required for degradation of 50% of the initial concentration.

\(^b\) The dose of UV radiation required for degradation of 90% of the initial concentration.

A comparison of the initial rates of oxidative degradation of \(K_3[Fe(CN)_6]\) in dark experiments shows a 5-6 fold difference between the processes with different oxidants - \(S_2O_8^{2-}\) and \(H_2O_2\). When UV irradiation was additionally applied, the initial rates increased significantly: 1.7-2.7 times for \(S_2O_8^{2-}\) and 6-12 times for \(H_2O_2\). The degradation of 50% of \(K_3[Fe(CN)_6]\) \((\tau_{1/2})\) is achieved by the action of the combined oxidative system \{UV/S_2O_8^{2-}\} after 1 min at pH 6.2 and after 0.64 min at pH 11. In the oxidative system \{UV/H_2O_2\}, the oxidative degradation of hexacyanoferrates is predominantly due to photolysis since \(\tau_{1/2}\) was 6 min (pH 6.2) and 2.75 min (pH 11), while in dark experiments \(\tau_{1/2}\) > 150 min. In the oxidative system \{UV/S_2O_8^{2-}\}, the effect of UV and the oxidant is additive.

Next we estimated the dose of UV radiation required for decomposition of 50% (\(D^{50}\)) and 90% (\(D^{90}\)) of the initial contaminant concentration with regard to pH of the solution being treated (Figure 3).

The maximum doses \(D^{90}\) (3102 mJ/cm^2) were required for direct photolysis (pH 6.2), whereas in the presence of oxidants the required doses were significantly lower and were 679 mJ/cm^2 for \{UV/H_2O_2\} and 113 mJ/cm^2 for \{UV/S_2O_8^{2-}\}. At higher pH values, substantially lower doses \(D^{90}\) were required - 587 mJ/cm^2 for direct photolysis, 310 mJ/cm^2 in the presence of \(H_2O_2\), and 72 mJ/cm^2 in the presence of \(S_2O_8^{2-}\). The UV doses \(D^{90}\) required for decomposition of 90% of the initial concentration of \(K_3[Fe(CN)_6]\) were much higher for direct photolysis and \{UV/H_2O_2\} system since the limiting stages of the hexacyanoferrates degradation are the oxidation of cyanide ions released from the inner sphere of the complex by secondary oxidants - hydroxyl radicals - to less toxic cyanates, which in turn are hydrolyzed to ammonium ions and carbon dioxide, and the formation of insoluble iron (II, III) hydroxocompounds. In the combined system \{UV/S_2O_8^{2-}\}, the required doses of UV radiation \(D^{90}\)
were much lower since, in addition to hydroxyl radicals, sulfate anion radicals also participate in the oxidation reactions.

**Figure 3.** The doses of UV radiation from a mercury lamp necessary for degradation of 50% and 90% of initial concentration of hexacyanoferrates at different pH. 1 - UV, 2 - {UV/H2O2}, 3 - {UV/S2O82-}. [K3[Fe(CN)6]0=0.47 mM, [S2O82-]0 = [H2O2]0 = 4.7mM.

Based on the specific energy efficiency, rate and duration of the treatment, the examined oxidative systems can be arranged in the following order: {UV/S2O82-} > {UV/H2O2} > {UV}. In addition, it should be noted that the process of photochemical oxidation of K3[Fe(CN)6] is irreversible when S2O82- is used.

Based on the data obtained, we propose an efficient method for removal of stable cyanide compounds, including hexacyanoferrates, using the combined oxidative system {UV/S2O82-}.

### 4. Conclusion

Different AOPs were evaluated for oxidation of stable cyanide compounds, exemplified by hexacyanoferrates. It is established that the combined oxidative system {UV/S2O82-} is more effective than the oxidative system {UV/H2O2} and direct photolysis. The developed method can be recommended for treatment of wastewater containing highly toxic cyanide compounds in areas with high solar activity. Thus it is possible to carry out the treatment of cyanide-containing wastewater with the help of natural factors.

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