Photooxidation of cyanide in mining effluents

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Abstract. The photooxidation process using polychromatic UV xenon lamp and persulfate was studied for the destruction of cyanide in mining effluents, for example, potassium hexacyanoferrate. The kinetic regularities of a photooxidation process of hexacyanoferrates were studied (dependence on process parameters such as pH, temperature and concentration of the oxidant). The optimal molar ratio of oxidant to pollutant \( \left[ \text{S}_2\text{O}_8^{2-} \right] / \left[ \text{Fe(CN)}_6^{3-} \right] \) was found to be 20÷1. Comparative destruction hexacyanoferrate experiments showed that the efficiency of the destruction process in the selected oxidative systems can be changed in the following order: of \( \{ \text{UV} - \text{VIS} / \text{PS} \} > \{ \text{PS} \} > \{ \text{UV} - \text{VIS} \} \). High treatment efficiency of hexacyanoferrates using an oxidative system \( \{ \text{UV} - \text{VIS} \} / \text{PS} \) is due to both \textit{in situ} generation of ROS - hydroxyl and sulfate anion radicals and the disproportionation persulfate by \( \text{Fe}^{2+} / \text{Fe}^{3+} \) ions produced during the destruction of hexacyanoferrate complex.

1. Introduction

Each year it produces about one million tons of cyanide in the world [1,2] due to its global use in many industrial activities such as mining (mining, extraction of gold and silver from ores and flotation concentrate), metalworking (steel hardening, metal products, electroplating), dyeing and textile (nylon production), automotive and other industries [3-5].

Cyanides are priority ecotoxins of wastewater of gold mining. The waste and circulating waters of mine are multicomponent and contain cyanide compounds, both in the form of weakly dissociated very toxic hydrocyanic acid (HCN), and in the form of stable complex cyanides.

Typically, treatment of waste water containing \( \text{CN}^- \), performed using both biological and chemical methods. As much biological treatment depends on the climatic conditions of the surrounding environment, its use for most wastewaters difficult [4-6]. At the same time, chemical methods such as alkaline chlorination using an “active chlorine” (NaOCl, HOCl and Cl_2) which is the most widely used, leading to oxidation of cyanides to CO_2 and N_2, has significant limitations. Method limitations are the formation of a large amount of sludge (sediments), in the case of wastewater with a high COD possibility of not less harmful chlorinated organic compounds, the release during the process of a toxic by-product - cyanogen chloride. In addition, complex cyanides - hexacyanoferrates (HCF) \( \left[ \text{Fe(CN)}_6^{3-} \right] / \left[ \text{Fe(CN)}_6^{2+} \right] \) being one of the most stable (\( K=1\cdot10^{-35}, 1\cdot10^{-42} \), respectively), are difficult to oxidation with ozone, potassium permanganate, and even chlorination. Thus, while in
the process solutions in high concentrations, they have a disturbing effect when implementing the preliminary purification technologies acidification solutions form insoluble colored compounds mixed ferrocyanides for example, when implementing AVR («acidification-volatilization-reneutralization») processes [7].

Stringent requirements of environmental and economic considerations strongly dictate the need for new low-waste / waste-free and energy-efficient technologies that provide the greatest environmental benefits.

Advanced Oxidation Processes - (AOPs) are becoming a real alternative for the wastewater treatment from compounds which cannot readily be oxidized by conventional methods [8-11]. Functional principle of AOPs based on using as oxidizing agents for toxincats effective destruction in conditions in situ of highly reactive oxygen species (ROS) (primarily hydroxyl \( \cdot \)OH \( (E_o = 2.7 \text{ B}) \) radicals) [8].

In the past decade, there is a tendency of growing interest of researchers to use persulfates in Sulfate Radical-based Advanced Oxidation Processes (SR-AOPs) based on the use of \( \text{SO}_4^- \) - sulfate anion radicals for treatment of natural and waste waters [12].

Persulfates (PS) can be directly reacted with the pollutants or are precursors for forming a secondary reactive oxidants - both sulfate \( \text{SO}_4^- \), and \( \cdot \)OH hydroxyl radicals under ultraviolet, high temperature, ultrasound activation, etc. [13,14].

Ultraviolet radiation is also widely used to generate sulphate radical anions [15]. In practice, mercury discharge lamps are widely used. Currently, in the world literature has accumulated enough material for extensive use of polychromatic natural solar radiation (Solar) for intensification oxidative destruction of bioreistant organic pollutants and inactivation of pathogenic microorganisms by photoactivated SR-AOPs [16]. However, there are only few publications on neutralization of toxic inorganic pollutants, in particular cyanide containing wastewater [17-19].

In our view, in terms of energy efficiency and environmental processes, this line of research is very relevant for the neutralization of toxic inorganic pollutants. Thus, the aim of this work was the investigation of photochemical decontamination of cyanide containing effluents (for example stable complex cyanides – hexacyanoferrate) using a mercury-free alternative source of radiation - the natural solar radiation in the presence of an environmentally safe oxidant - persulfate.

2. Experimental section
The studies were conducted on model aqueous solutions of potassium hexacyanoferrate (HCF) with an initial concentration of 50 mg / l (0.235 mM) in a thermostated flow-type photoreactor. All chemical reagents (hexacyanoferrate of potassium, potassium persulfate) were analytical grade. Distilled water \( (\chi = 2\mu S / \text{cm}) \) was used for the preparation and dilution of solutions.

The pH of solutions were adjusted by 0.1 N NaOH.

To simulate solar radiation, as source of optical radiation with a quasi-solar spectrum, a xenon lamp (Xe) (MaxLight, South Korea), was used. The intensity of radiation of the Xe lamp in the bactericidal and visible ranges was measured by UV - radiometer and Luxmeter - UV radiometer (A, B) (32 cm) (Table 1). The emission spectrum of xenon lamp is very wide in the visible region (from 300 to 800 nm) and similar to the solar one (Figure 1). This allowed us to carry out a correct simulation of the operating modes of the solar photoreactor in the laboratory scale.

| Table 1. Characteristics of the radiation source - xenon lamp HID 4300 |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Type of xenon lamp | Color temperature, K | Luminous flux, lm | Illumination, Lk | Radiation intensity of solar lamps in the bactericidal ranges, mW/m² |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| HID 4300        | 4300            | 3200            | 2510            | UV-A (315-400nm) | 200 |
|                 |                 |                 |                 | UV-B (280-315nm) | 15.2 |
|                 |                 |                 |                 | UV-C (200-280nm) | 25.2 |
3. Result and discussion

Preliminary evaluation of photochemical activity of hexacyanoferrates in direct photolysis with varying acidity showed that under the radiation of the Xe lamp HCF decompose slowly. It was found that increasing the alkalinity of the medium in the process of pollutant destruction affects slightly (Figure 2, Table 2). Efficiency destruction irrespective of the pH of the reaction medium (pH range 5.65-11) after 120 minutes of exposure was 33.6-40.0%. Therefore, all subsequent studies were conducted without adjusting the pH (5.65). It is important to bear in mind that one of the important benefits of persulfates compared to other oxidizing agents is less sensitive to changes in the reaction medium.

![Figure 1. The spectral composition of solar radiation and xenon lamp HID 6000KH1.](image)

![Figure 2. Effect of pH on degradation HCF by direct photolysis. [HCF]= 0.235mM.](image)

| pH  | % Destruction |
|-----|---------------|
| 5.65| 33.6%         |
| 9   | 35.0%         |
| 11  | 40.0%         |

Table 2. Comparative characteristics HCF photodestruction process under different pH
When processing solutions HCF in the combined oxidative system \{UV-VIS / PS\} there is a sharp increase (9 times) of the initial pollutant oxidation rate compared to direct photolysis and is $W_0 = 33.42 \, \mu\text{M} \cdot \text{min}^{-1}$. The half-life time and efficiency of photodegradation HCF over 120 minutes of exposure were changed from 151 min to 4.13 min and from 40% to 93%, respectively (Table 3). While the reaction in the dark, in spite of the high initial destruction rate was observed in the deactivation of the reaction mixture within the first 10 minutes and further processing does not lead to a substantial increase in process efficiency (Figure 3). Occurrence synergistic effect was established. A synergistic index calculated on the rate constants of destruction of hexacyanoferrates in different oxidative systems according to the equation:

$$\phi = \frac{k\{UV-VIS/PS\}}{k\{UV-VIS\} + k\{PS\}},$$

is 1.42.

![Graph showing destruction of HCF in different oxidative systems](image)

**Figure 3.** Destruction of HCF in different oxidative systems. $[\text{HCF}] = 0.235 \, \text{mM}$, $[\text{PS}] = 4.7 \, \text{mM}$, pH 5.65.

| pH   | $W_0$, $\mu\text{M} \cdot \text{min}^{-1}$ | $k$, min$^{-1}$ | $t_{1/2}$, min | $\Psi$, % |
|------|------------------------------------------|---------------|---------------|----------|
| 5.65 | 3.76                                     | 0.0046        | 151           | 40       |
| 9.0  | 1.21                                     | 0.0033        | 210           | 34       |
| 11.0 | 2.33                                     | 0.0037        | 187           | 35       |

Treatment time 120 min.

On the efficiency of the process of destruction of hexacyanoferrates, the selected oxidative systems arranged in order $\{UV-VIS/PS\} > \{PS\} > \{UV-VIS\}$.

Several sets of experiments were conducted to compare the photodegradation kinetics of hexacyanoferrates for different concentration of oxidant. Final removal efficiencies for each experiment are shown on figure 4. It was established, that the rate of the photodestruction process of HCF increases in proportion to the increase in oxidant concentration at molar ratios of oxidant to pollutant from 1:1 to 20:1 and a result removal efficiency increased with increasing persulfate...
concentration. However, further increasing this ratio is impractical because it does not lead to a considerable increase in process efficiency and leads to excess reagent. Thus, it was found that the optimal ratio of oxidant to pollutants \([\text{S}_2\text{O}_8^{2-}] : [\text{Fe(CN)}_6^{3-}]\) is a ratio of 20:1.

![Figure 4. Comparison HCF photodestruction for different oxidant concentration. \([\text{HCF}] = 0.235 \text{ mM, pH 5.65, treatment time 120 min.}\)](image)

When carry out processes Solar-treatment the treated solutions, as a rule, are generally heated to 40-45° C, so it is important to evaluate the influence of the temperature on the reaction medium on the photodestruction kinetics of hexacyanoferrates. It was found, that the temperature increase in the combined oxidative system \({\text{UV VIS}} / \text{PS}\) influences the process of destruction of hexacyanoferrate slightly (Figure 5).

![Figure 5. Effect of temperature on the photodestruction HCF. \([\text{HCF}] = 0.235 \text{ mM, [PS]} = 4.7 \text{ mM, pH 5.65.}\)](image)

The high efficiency of the destruction of hexacyanoferrates in aqueous solutions using the combined oxidative system \({\text{UV VIS}} / \text{PS}\) provided by the generation of \textit{in situ} sulfate anion radicals:

\[
\text{SO}_3^- - \text{O} - \text{O} - \text{SO}_4^- + \text{hv} \rightarrow 2\text{SO}_4^- \quad (1)
\]

\[
\text{SO}_4^- + \text{SO}_4^- \rightarrow \text{S}_2\text{O}_8^{2-} \quad (2)
\]
It should be noted that in the combined system \( \{ \text{UV−VIS/PS} \} \), sulfate anion radicals are generated not only by photolysis of persulfate \((1)\), but also by disproportionation ions \(Fe^{3+}\) and \(Fe^{2+}\) released by destruction complex \([\text{Fe(CN)}_6]^{3−}\) [21]. It is known that the oxidative system \(\{ S_2O_8^{2−}/Fe^{3+} /\{Fe^{2+}\}\}\) due to similarity of the mechanisms is referred to as Fenton-like [22,23].

\[
[\text{Fe(CN)}_6]^{3−} + H_2O + \text{hv} \leftrightarrow [\text{Fe(CN)}_5H_2O]^2− + \text{CN}− \quad (3)
\]

\[
[\text{Fe(CN)}_5H_2O]^2− + H_2O + \text{hv} \rightarrow 2\text{Fe(OH)}_3 \downarrow + 5\text{CN}− + 3\text{H}^{+} \quad (4)
\]

\[
S_2O_8^{2−} + \text{Fe}^{3+} \rightarrow 2\text{SO}_4^{−} + \text{Fe}^{2+} \quad (5)
\]

\[
S_2O_8^{2−} + \text{Fe}^{2+} \rightarrow \text{SO}_4^{−} + \text{SO}_4^{2−} + \text{Fe}^{3+} \quad (6)
\]

\[
\text{FeOH}^{2+} + \text{hv} \rightarrow \text{Fe}^{2+} + \cdot \text{OH} \quad (7)
\]

It is also necessary to take into account the formation of \(•\text{OH}\) as a result of the interaction of sulfate anion radicals with water:

\[
\text{SO}_4^{2−} + H_2O \rightarrow \cdot \text{OH} + \text{HSO}_4^{−}
\]

4. Conclusion

The obtained results testify to the high efficiency of using the combined oxidative system \(\{ \text{UV−VIS/PS} \}\) in the process of photooxidation hexacyanoferrate-containing wastewaters with the use of polychromatic UV radiation of Xe lamp with quasisolar spectrum. The results of experimental modeling can be scientific basis for development Solar-energy-efficient method for treatment of real mine wastewater.

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