

Photochemical oxidation of priority ecotoxics of gold mill wastewater

B A Tsybikova, A A Batoeva

Baikal Institute of Nature Management, Siberian Branch of the Russian Academy of Sciences, Sakhyanovoy St. 6, Ulan-Ude, Russia

E-mail: abat@binm.ru

Abstract. The kinetic regularities of the photodestruction process of hexacyanoferrates using sources of mono- and polychromatic UV radiation with different spectral ranges are studied. The comparative experiments on the degradation of hexacyanoferrates in direct photolysis showed that the efficiency of the degradation process changed in the order UV-Vis > UV-222 > UV-Xe > UV-254. It was found that with the UV treatment of hexacyanoferrate-containing solutions in combination with persulfate (oxidation system {UV/S₂O₈²⁻}), the specific conversion of the substance changed in the order UV-222/S₂O₈²⁻ > UV-Xe/S₂O₈²⁻ > UV-254/S₂O₈²⁻ > UV-Vis/S₂O₈²⁻. The high destruction efficiency of hexacyanoferrates with the use of the oxidizing system {UV/S₂O₈²⁻} is due to both generating *in situ* active oxygen species - hydroxyl and sulfate anion radicals, and the disproportionation of persulfate by Fe²⁺ / Fe³⁺ ions, released during the destruction of the hexacyanoferrate complex.

1. Introduction

The Russian Federation, possessing the largest resource base of most types of solid minerals, is one of the world leaders in terms of gold and silver production. A steady trend continues to increase gold mining from indigenous ores, which led to an increase in the consumption of sodium cyanide, which, despite its high toxicity and cost, is the main leaching reagent of precious metals from ores and concentrates.

In the process of cyanide, leaching of gold and silver from persistent sulphide ores and gold-containing flotation concentrates at gold recovery factories, technogenic waters of complex composition are formed that pose a particular danger to the environment. The wastewater and circulating waters of these industries are polycomponent and contain cyanide compounds in their composition, both in the form of weakly dissociated, highly toxic hydrocyanic acid (HCN), and in the form of toxic complex cyanides [1,2]. In addition, sulfur-containing inorganic contaminants (thiocyanates, thiosulphates), as well as heavy metal ions, arsenic, suspended solids, certain organic compounds, may be associated with toxic cyanides in wastewater. In this regard, the last stage of the technological process of processing mineral raw materials - neutralization of harmful substances in waste technological solutions before discharge or reuse is of great importance.

Among the methods of oxidation and destruction of toxic cyanide compounds, "environmentally dirty" reagents, for example, chlorine compounds (hypochlorites, bleach, chlorinated lime, liquid



chlorine, etc.) are widely used as oxidants. The main disadvantages of which are the toxicity of the reagent itself, which poses a real danger when stored in warehouses, a decrease in the activity of the oxidant over time, and the need for strict pH control in order to avoid the formation of a toxic gas – chlorine cyanide [3].

At present, the great attention of researchers is concentrated on the development of new combined oxidation processes (AOPs - “advanced oxidation processes”), which consist in the generation *in situ* of various high reactive radicals, in particular active oxygen species (AOS), which are capable of inducing oxidation and mineralization of dissolved in water pollutants [4-6].

Among the AOPs, the most promising in our opinion are combined photochemical methods in combination with oxidants. Among ecologically pure oxidants (ozone, hydrogen peroxide, Caro acid, ferrates, etc.) persulfates are characterized by technological use, since they are solids, practically do not lose their activity during time and are easily dosed [7-10].

Sulphate anion radicals are a real alternative to hydroxyl radicals, since they, having a high oxidation-reduction potential, have a lower sensitivity to pH, a non-selective high reactivity to most environmental pollutants, and the sources of their formation, salts of persulfates, have high solubility and stability of the resulting solutions at room temperature.

To generate sulfate anion-radicals, ultraviolet radiation is also widely used, and it has been established that it is most expedient and effective to use for this purpose light sources emitting at wavelengths less than 300 nm [11,12]. In practice, mercury discharge lamps have been widely used [13].

Also recently, new mercury-free sources of UV radiation-excimer lamps on excimer Xe_2^* (172 nm) and exciplex KrCl^* (222 nm) [14], XeBr^* (282 nm), XeCl^* (308 nm) molecules, which emit quasi-monochromatic light, sources of polychromatic radiation - LED and xenon lamps, natural solar radiation. There are a few works on the use of UV-LED lamps [15], where comparative results on CN^- photooxidation using different UV-LED lamps and different forms of TiO_2 catalyst (anatase, rutile, Degussa P25) are given. It was established that these lamps economical and effective for photo-oxidation of cyanides.

At present, the world literature has accumulated quite extensive material on the use of photoactivated AOPs methods for the oxidative destruction of bioresistant organic pollutants. The interest of researchers to use polychromatic natural solar radiation (Solar) to intensify the oxidative destruction of persistent organic pollutants, inactivation of pathogenic microflora [16, 17] is growing.

From the point of view of energy efficiency and environmental friendliness of processes, this area of research is very relevant for neutralizing toxic inorganic pollutants. In addition, strict environmental and economic requirements strongly dictate the need to create new low waste / non waste and energy-efficient technologies that have the greatest ecological effect.

The object of the study were model solutions of complex cyanide - hexacyanoferrates $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$, since they, being among the most stable ($K = 1 \cdot 10^{-35}$, $1 \cdot 10^{-42}$, respectively), are difficult to oxidize with ozone, potassium permanganate and even chlorination. At the same time, being in technological solutions in high concentrations, they have an interfering effect in the implementation of purification technologies with the preliminary acidification of solutions, forming insoluble colored compounds of mixed ferrocyanides. For example, when implementing AVR (“acidification-volatilization-reneutralization”) – processes [18]. Thus, the aim of the work was to study the oxidative destruction of hexacyanoferrates using various sources of UV radiation and their comparative evaluation.

2. Experimental section

Model aqueous solutions of potassium hexacyanoferrate $\text{K}_3\text{Fe}(\text{CN})_6$ with an initial concentration of 100 mg/L (0.47 mM), prepared on distilled water ($\chi=2 \text{ } \mu\text{S/cm}$). Reagents (hexacyanoferrate of potassium, potassium persulfate) 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]. The pH values were monitored using the universal pH 150M ionomer [20]. To adjust the pH value of solutions, 0.1 N NaOH solution was used.

Investigations of the main kinetic regularities of oxidative destruction of hexacyanoferrates were carried out in a thermostatted (22°C) tube continuous-flow photoreactor. The scheme of the experimental setup is shown in Figure 1. The photoreactor placed in a mirror parabolic-cylindrical reflector casing with an aluminium foil coating to concentrate the light flow. The volume of the treated solution was 500 ml. The circulation rate was 0.5-0.6 l/min.

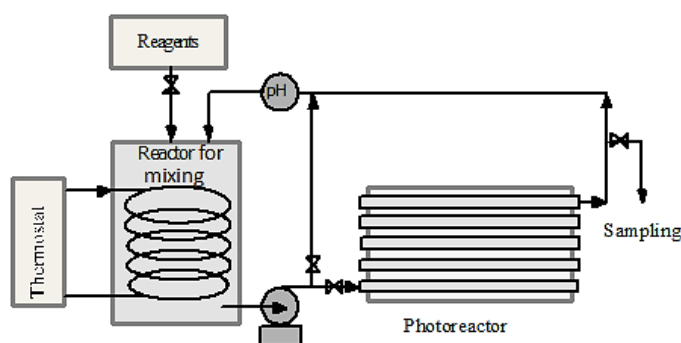


Figure 1. Schematic diagram of the experimental setup.

Sources of mono- and polychromatic UV radiation with different operating spectral ranges were used to study the processes of photodestruction of hexacyanoferrates: low-pressure mercury vapor arc-discharge lamps of the brand DB-30-1 (with emission maximum at 254 nm (UV-254)), DRT-400 high-pressure mercury-vapor lamp (with discrete spectrum in the visible and UV ranges with a maximum radiation at 365 nm (UV-Vis), KrCl barrier-discharge excilamp emitting in a narrow spectral band with a maximum of 222 nm (UV-222), xenon lamp HID 4300KH1 (MaxLight, South Korea) broad spectrum of radiation in the visible region (300 to 800 nm (UV-Xe)). Broadband radiation sources (DRT-400 and UV-Xe) were used to simulate the UV and visible component of natural solar radiation.

3. Result and discussion

It is known that the acidity index of the medium (pH) is a key adjustable parameter in the processes of sewage treatment. At the first stage, experiments were conducted on direct photolysis of model solutions of hexacyanoferrates with varying pH values of the reaction medium (Figure 2). It is obvious that the oxidation of hexacyanoferrates during direct photolysis proceeds slowly enough. However, at a pH of 11, the maximum efficiency of the destruction of the hexacyanoferrates observed and was 72% in 120 min. Therefore, further experiments were carried out at pH 11.

Comparative experiments on the oxidative destruction of hexacyanoferrates in direct photolysis using various sources of UV radiation were carried out (Figure 3). The minimum efficiency of the process of destruction of hexacyanoferrates observed for UV-254 source and was 5% and maximum for UV-Vis was 93%. On the efficiency of the process of destruction of hexacyanoferrates in direct photolysis, the selected sources can be arranged in a series of UV-Vis > UV-222 > UV-Xe > UV-254.

Obviously, to intensify the process of destruction of hexacyanoferrates, it is necessary to combine direct photolysis with other promising oxidation systems. Thus, experiments were conducted to study the role of the photochemical effect on the destruction efficiency of hexacyanoferrates by persulfate using selected sources of UV radiation. When UV treatment of hexacyanoferrate-containing solutions in combination with persulfate (oxidation system {UV/S₂O₈²⁻}) in all cases, a significant acceleration of the photochemical degradation process leads to a shortening of the treatment time (Figure 4).

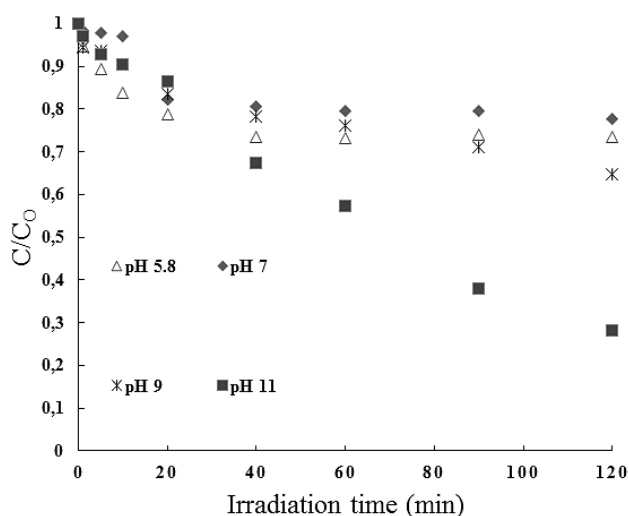


Figure 2. Effect of pH on degradation of hexacyanoferrates; $C_0([\text{Fe}(\text{CN})_6]^{3-}) = 100 \text{ mg/L}$; UV source: UV-222.

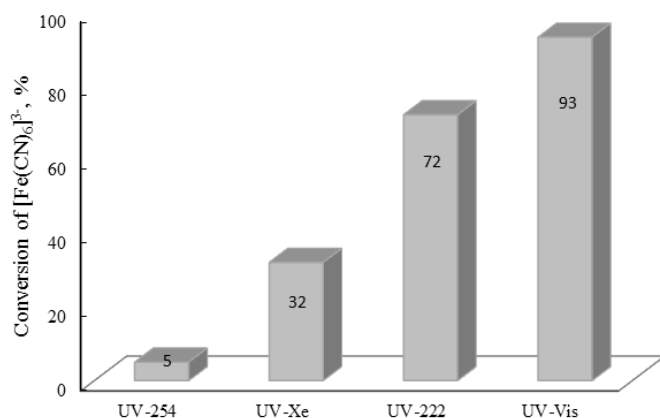
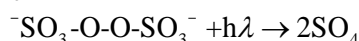
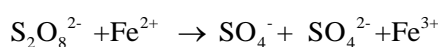
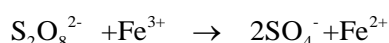
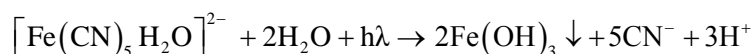
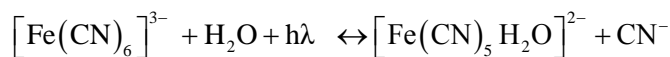


Figure 3. Photolysis of hexacyanoferrates solutions using different light sources; $C_0([\text{Fe}(\text{CN})_6]^{3-}) = 100 \text{ mg/L}$; pH 11; irradiation time 120 min.

The high efficiency of the destruction of hexacyanoferrates in aqueous solutions using the combined oxidation system $\{\text{UV}/\text{S}_2\text{O}_8^{2-}\}$ provided by the generation of *in situ* sulfate anion radicals:



It should be noted that $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions released during the destruction of the hexacyanoferrate complex form an additional amount of sulphate radical anions in the system because of the disproportionation of persulfate. It is known that the oxidative system $\{\text{S}_2\text{O}_8^{2-}/\text{Fe}^{3+}/(\text{Fe}^{2+})\}$ due to similarity of the mechanisms is referred to as Fenton-like [6].



It is also necessary to take into account the formation of OH^\cdot as a result of the interaction of sulfate anion radicals with water:



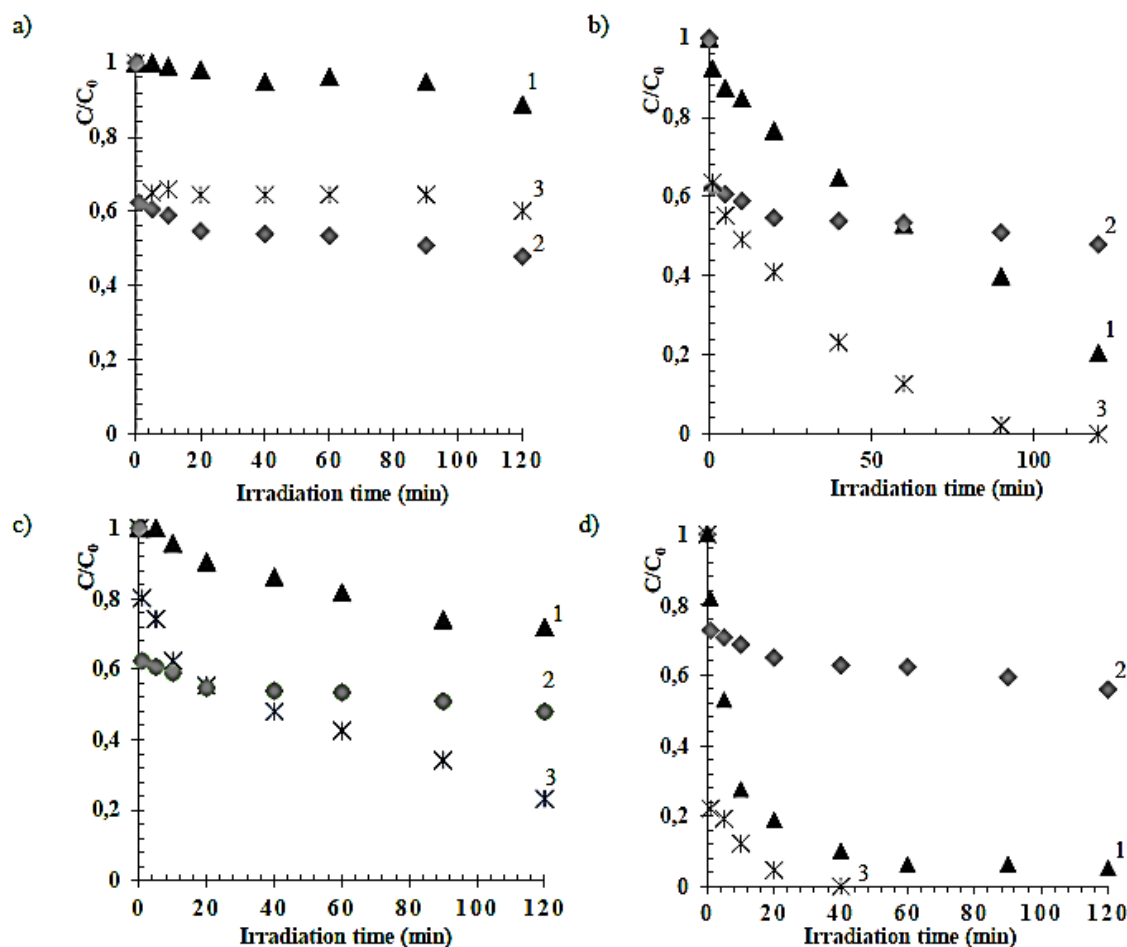


Figure 4. Destruction of hexacyanoferrates using a) UV-254, b) UV-222, c) UV-Xe and d) UV-Vis.

1- UV, 2- $S_2O_8^{2-}$, 3- UV + $S_2O_8^{2-}$. $C_0([Fe(CN)_6]^{3-}) = 100 \text{ mg/L}$; pH 11.

Since the selected sources differed significantly in the characteristics of the consumed electric energy, we used a parameter of specific conversion that was equal to the ratio between the amount of converted compound and the consumed electric energy (Table 1) was introduced to compare the results obtained.

Table 1. Comparison of various sources of UV radiation during destruction of hexacyanoferrates.

Oxidizing system	P, W	W_0 , mM/(L·min)	Specific conversion of $[Fe(CN)_6]^{3-}$, mkg/kJ
$S_2O_8^{2-}$	-	0.128	-
UV-254/ $S_2O_8^{2-}$	40	0.069	182
UV-Vis/ $S_2O_8^{2-}$	433	0.366	52
UV-222/ $S_2O_8^{2-}$	30	0.172	533
UV-Xe/ $S_2O_8^{2-}$	35	0.094	310

The high specific conversion of $[Fe(CN)_6]^{3-}$ was observed after exposure to the UV-222 lamp. On the degree of specific conversion of hexacyanoferrates, the selected sources under the considered study changed in the order UV-222/ $S_2O_8^{2-}$ > UV- Xe/ $S_2O_8^{2-}$ > UV-254/ $S_2O_8^{2-}$ > UV-Vis/ $S_2O_8^{2-}$.

4. Conclusion

The obtained results testify to the high efficiency of using the combined oxidation system $\{UV/S_2O_8^{2-}\}$ in the process of neutralizing hexacyanoferrate-containing wastewaters with the use of various sources of optical radiation, including the quasisolar spectrum and the need for further research.

References

- [1] Nural K and Ata A 2013 *Minerals Engineering* **50-51** 13–29
- [2] Mudder T and Botz M 2004 *The European Journal of Mineral Processing and Environmental Protection* **4** (1) 62–74
- [3] Botz M, Mudder T, Accil A 2005 *Advanced in Gold Ore Processing*, ed M B Adams (Amsterdam: Elsevier) pp 672–702
- [4] Rodriguez-Narvaez O M, Peralta-Hernandez J M, Goonetilleke A, Bandalaet E R 2017 *Chemical Engineering Journal* **323** (9) 361–380
- [5] Yang Y, Ok Y S, Kim K H, Kwon E E, Tsang Y F 2017 *Science of the Total Environment* **596-597** (10) 303–320
- [6] Yang D and Zhao K 2015 *Curr. Pollution Rep* **1** 167–176
- [7] Dai X, Simons A, Breuer P 2012 *Miner. Eng.* **25** 1–13
- [8] Gould W D, King M, Mohapatra B R, Cameron R A, Koren D W, Kapoor A 2012 *Miner. Eng.* **34** 38–47
- [9] Hanela S, Duran J, Jacobo S 2015 *Journal of Environmental Chemical Engineering* **3** 1794–1801
- [10] Wang Z P, Huang L Z, Su J W et al. 2008 *Fresenius Environmental Bulletin* **17** (8) 1082–1087
- [11] Shih Y J, Putra W N, Huang Y H, Tsai J Ch 2012 *Chemosphere* **89** 1262–1266
- [12] Xiang-Rong S Li, Qing Hao 2012 *International Journal of environmental and bioenergy* **1** (1) 61–81
- [13] Moussavi G, Pourakbar M, Aghayani E, Mahdavianpour M 2016 *Chemical Engineering Journal* **294** 273–280
- [14] Budaev S L, Batoeva A A, Khandarkhaeva M S, Aseev D G 2017 *Russian Journal of Physical Chemistry A.* **91** (3) 604–608
- [15] Kim S H, Lee S W, Lee G M 2016 *Chemosphere* **143** 106–114
- [16] Malato S, Fernandez-Ibanez P, Maldonado M I, Blanco J, Gernjak W 2009 *Catalysis Today* **147** (1) 1–59
- [17] Tsydenova O V, Batoev V B, Batoeva A A 2015 *International Journal of Environmental Research and Public Health* **12** 9542–9561
- [18] Prosyaniikov E D, Tsybikova B A, Batoeva A A, Ryazantsev A A 2009 *Physical and Technical Problems of Mineral Processing* **1** 98–105
- [19] PND F 14.1: 2.164 - 2000 *Quantitative chemical analysis of water: Method for performing measurements of mass concentrations of hexacyanoferrates in samples of natural and wastewater using a photometric method* (Moscow) p 12
- [20] PND F14.1: 2: 3: 4.121 - 97 *Quantitative chemical analysis of water: The procedure for performing pH measurements in waters by the potentiometric method* 2004 (Moscow) p 14

Acknowledgments

The reported research was funded by the Russian Foundation for Basic Research and the Government of the Republic of Buryatia, grant No. 18-48-030005.