Solar energy efficient – AOP process for treatment of cyanide in mining effluents

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Abstract. Photochemical process using of UV component of natural sunlight (hybrid Solar method) in the presence of an oxidizing agent – persulfates was studied for destruction of cyanides in mining effluents. The kinetic regularities was studied for process of photooxidation of cyanides. Comparative destruction of cyanides experiments have shown that the efficiency of the destruction process in the selected oxidative systems changed in the following order: \{Solar + PS\} > \{Solar\} > \{UV + PS\} > \{UV\}. High treatment efficiency of cyanides using a hybrid system \{Solar + PS\} is due to high intensity of the UV-C component of the sunlight and the rate of generation of hydroxyl radicals \(\cdot \text{OH}\) and sulfate anion radicals \(\text{SO}_4^{\cdot -}\), respectively. The results obtained indicate the high efficiency of the hybrid Solar-induced method for purification of cyanide-containing pollutants, which allows achieving complete destruction of toxic cyanides to non-toxic products.

1. Introduction

It is known that in the process of cyanide leaching of gold and silver from refractory sulfide ores and flotation concentrates in gold processing plants technogenic waters formed containing cyanide compounds, both in the form of slightly dissociated, very toxic hydrocyanic acid (CN\(^-\), HCN free), and in the form toxic complex cyanides (WAD, SAD) \[1,2\]. In this case, the values of cyanide concentrations in these wastewater and circulating solutions are hundreds and thousands of times higher than the legal limits 0.05 mg·L\(^{-1}\) \[3\]. The wastewater and recycling water of the mill are of particular danger to humans and animals, as well as to the environment and must be neutralized before discharge or before reuse.

The mining industry uses technologies based on regeneration methods and chemical oxidation (destruction) methods to neutralize cyanide-containing effluents. Regenerative include: “acidification-volatilization-reneutralization” method (AVR) \[4\], bio-oxidation of cyanides by dissolved oxygen \(\text{O}_2\) and solar photolytic decomposition \[5\]. The main disadvantages of these methods include the need for post-treatment of wastewater due to the high residual concentration of cyanide compounds that do not meet the legal standards, the significant processing time, the need to constantly keeping environmental conditions (oxygen regime, ambient temperature and pH).

Among the methods of oxidation and destruction of toxic cyanide compounds, “environmentally dirty” reagents, for example, chlorine compounds (hypochlorites, bleach, liquid chlorine, etc.) are still widely used as oxidizing agents \[6\]. 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 oxidizing agent over time, and the need for strict pH control to avoid the formation of toxic gas - chlorocyan.

Strict environmental and economic requirements strongly dictate the need to create new low-waste / non-waste and energy-efficient technologies that give the greatest environmental effect.

Currently, much attention of researchers is focused on the development of new combined oxidation processes (AOPs - “advanced oxidation processes”), which consist in the generation in situ by various methods of highly reactive radicals - predominantly reactive oxygen species (ROS) that can induce oxidation and mineralization of dissolved in water pollutants [7-11].

Among the AOPs, the most promising in our opinion are combined photochemical methods. The use of ultraviolet radiation (UV) is becoming increasingly common for the intensification of various oxidative processes. There is evidence that shows the possibility of decomposing complex cyanides of zinc, cadmium, nickel and copper by heterogeneous photocatalysis [12,13]. For carrying out photochemical processes, sources of a wide optical range (from short-wave UV to infrared) are used in combination with various oxidizing agents [14,15].

Among environmentally friendly oxidizing agents (ozone, hydrogen peroxide, Caro acid, ferrates, etc.), persulfates are technologically advanced because they are solids, practically do not lose their activity over time and are easily dosed. Due to inertness, persulfates are low toxic; USEPA normalizes their content in drinking water to 250 mg·L\(^{-1}\) and classifies them as pollutants that worsen only organoleptic properties.

In the world scientific literature, there is a tendency for researchers to increase interest in using persulfates in AOPs [16]. EAAOP-4 (4 European Conference on Environmental Applications of Advanced Oxidation Processes, Athens - Greece, October 21-24, 2015) proposed the inclusion of in situ methods for the generation of in situ sulphate radical anions SR-AOPs (Sulfate Radical-based AOPs) into the modern classification of advanced combined oxidative methods.

An alternative to UV treatment can be the UV component of natural solar radiation. Thus, a group of scientists obtained data on the photochemical oxidation of certain cyanide compounds, including hexacyanoferrates, induced by sunlight in the presence of a photocatalyst TiO\(_2\) [17,18].

The aim of the work was to study the photochemical destruction of cyanides using natural solar radiation (hybrid solar method) in the presence of an oxidizing agent - potassium persulfate.

2. Experimental section

The experiments carried out on sunny days from May to September. The intensity of solar radiation (Solar) in the ultraviolet, visible ranges and general illumination measured using metrologically verified UV - radiometer "TKA-PKM" and Luxmeter - UV-radiometer (A, B) "TKA-PKM -6". The range of values measured during the experiments presented in table 1.

| The intensity of solar radiation in the UV ranges, W·m\(^{-2}\) | Illumination, Lx |
|---------------------------------------------------------------|------------------|
| UV-A (315-400 nm)                                             | 8.0-46.6         |
| UV -B (280-315 nm)                                            | 0.51-3.08        |
| UV -C (200-280 nm)                                            | 0.49-3.42        |
|                                                               | 20500-121000     |

Simple cyanide (\(NaCN\)) as an object was chosen to study the kinetic laws of neutralizing the priority ecotoxicant of gold mining effluents under the photochemical effect of solar radiation. All chemical reagents (sodium cyanide, potassium persulfate) were analytical grade. Distilled water \(\chi_e = 2 mS/cm\) was used for the preparation and dilution of solutions.

The cyanide content in the solution was determined by the photometric method [19]. The concentration of ammonium, nitrites and nitrates was determined by standard photometric methods [20-22].
Studies of the kinetic laws of combined cyanide oxidation in the presence of persulfate were carried out in an experimental setup that included (Figure 1): a composite parabolic cylinder concentrator; peristaltic pump with adjustable flow rate; 1-liter glass averager tank. The flow rate of the treated solution is 1 l/min. The volume of the processed solution is 1 liter. The reactor consisted of 5 quartz tubes connected in series with each other, the length of each tube is 42 cm (inner diameter 1.59 cm). Photoreactor internal volume 0.416 L. The irradiated area of the quartz tubes of the reactor is 1047.51 cm². The reflected area of the parabolic cylinder concentrator is 2100 cm².

![Figure 1. Schematic diagram of an experimental Solar installation.](image)

The installation was equipped with measuring instruments (TKA-PKM, TKA-PKM-6, WTW Multi 3410), which allow on-line monitoring of illumination, the level of ultraviolet radiation, pH, and the temperature of the treated solution. Sampling carried out from the averager tank.

3. Result and discussion
Problem previously, the basic kinetic regularities were established of the process of photochemical oxidation of cyanides in the presence of per sulfate on model aqueous solutions

$$C(\text{CN}^-) = 50 \text{ mg} \cdot \text{L}^{-1}, 1.92 \text{mM}$$

in combined oxidizing systems based on the use of in situ generated reactive oxygen species (ROS) under the influence of a polychromatic UV radiation from a xenon lamp with a quasi-solar spectrum. The results allowed conducting correct modeling of the solar photoreactor operating modes in laboratory conditions.

The influence of key factors (pH, concentration of reactants, exposure time) was studied on the effectiveness of the neutralization process (Figure 2). To avoid the formation of volatile hydrocyanic acid (HCN), experiments were carried out at pH > 9.5. The optimal molar ratio of oxidizing agent to pollutant \([S_2O_8^{2-}]/[\text{CN}^-]\) equal to 2:1 was established.

To study the kinetic laws of combined oxidation using natural solar radiation \{Solar + PS\}, experiments were conducted on model solutions of cyanides under dynamic conditions.

Direct photolysis with the sunlight, unlike the UV radiation of a quasisolar lamp, after 96.1 minutes of exposure allows complete oxidation of the pollutant to be achieved. At the same time, under the combined action of the sunlight and the oxidizer \{Solar + PS\} the time is reduced by about half (to 51.5 min) (Figure 3b). In the combined oxidation system \{Solar + PS\} under optimal conditions (molar ratio of oxidizing agent to pollutant equal to \([PS]/[\text{CN}^-] = 2:1\)) 100% complete destruction is achieved after 51.5 min of exposure. While with UV radiation of a quasisolar lamp, the
process speed gradually decreases, and accordingly the process efficiency (~67% after 240 min), the
nature of the kinetic curve of which reflects a decrease in the probability of effective collisions
between reacting particles, i.e. between $CN^-$ ions and $ROS$ molecules due to their consumption
(Figure 3a).

Figure 2. Effect of pH (a) and the concentration of the oxidizing agent (b) on cyanide photooxidation;
initial $[CN^-]=1.92\text{mM}$.

Figure 3. Comparison of cyanide oxidation in various oxidative systems at pH 10-11; initial $[CN^-]=1.92\text{mM}$, $[S_2O_8^{2-}]=3.84\text{mM}$.

The resulting rate constants under solar exposure are almost 5.3–6 times greater than those for
photolysis by UV radiation from a quasi-solar lamp, but are practically comparable (table 2).

Table 2. Comparative characteristics of the cyanide degradation process in various oxidative systems
at pH 10-11. Initial $[CN^-]=1.92\text{mM}$, $[S_2O_8^{2-}]=3.84\text{mM}$.

| Oxidative system | $W_0$, mM·min$^{-1}$ | k | $t_{\text{comp,destr}}$, min |
|------------------|----------------------|---|-----------------------------|
| $UV$             | 108.8                | 0.0064 L·mM$^{-1}$·min$^{-1}$ | -            |
| $Solar$          | 120.0                | 0.0339 min$^{-1}$            | 96.1         |
| $\{Solar + PS\}$ | 131.0                | 0.0383 min$^{-1}$            | 51.5         |
Obviously, the high efficiency of photodegradation of cyanides in the presence of \{Solar + PS\} persulfate is associated with the simultaneous in situ generation of both \(\cdot OH\) and \(\cdot SO_4\) radicals [23-25]:

\[
\begin{align*}
S_2O_8^{2-} + h_{solar} & \rightarrow 2SO_4^{2-} \\
SO_4^{2-} + SO_4^{2-} & \rightarrow S_2O_8^{2-} \\
H_2O + h_{solar} & \rightarrow \cdot OH + H^+ \\
SO_4^{2-} + OH^- & \rightarrow SO_4^{2-} + \cdot OH
\end{align*}
\]

It is assumed that this effect is caused by the fact that the intensity of the \(UV - C\) component of the sunlight is several times higher, respectively, and the rate of in situ generation of ROS (hydroxyl radicals \(\cdot OH\) and sulfate anion radicals \(\cdot SO_4\)).

On the efficiency of the process of destruction of cyanides, the selected oxidative systems arranged in order to \{Solar + PS\} > \{Solar\} > \{UV + PS\} > \{UV\}.

It was further established that an increase in the concentration of the oxidizing agent – persulfate, respectively, in the molar ratio [PS]:[CN\(^-\)] in the sun leads to a significant reduction in the time of complete destruction of cyanides by 1.5–2 times (Figure 4). It should be noted that local weather conditions, as well as variations in the activity of solar radiation, could cause in the different conversion time of pollutant.

![Figure 4](image)

**Figure 4.** Effect of different concentrations of oxidizing agent on the photooxidation of cyanide at different summer days. Initial [CN\(^-\)] = 1.92 mM, pH 10-11. [S\(_2O_8^{2-}\)] = 3.84 mM: 1 - 22.05.19, 2 – 31.05.19; [S\(_2O_8^{2-}\)] = 5.76 mM: 3 - 31.05.19, 4 – 05.06.19.

It is important to note that during the processing of solutions of pollutants, the pH values vary significantly. Therefore, in direct photolysis, the value decreases slightly to 9.57–9.93. In the combined treatment of \{Solar + PS\} solutions at initial pH values of 10–11, the final values tend to be neutral and lie in the range of 6.3–7.0. It is clear that this behavior indicates that under the selected conditions the oxidation of the cyanide pollutant is quite effective and continues to the end with the formation of neutral salts. It was experimentally found that when using the combined system \{Solar + PS\} toxic cyanides are effectively mineralized to less toxic products (ammonium ions, nitrites, nitrates), which were quantified (table 3). The results obtained are in good agreement with the published data on the heterogeneous photocatalytic oxidation of cyanides using a suspension of titanium dioxide, where it was shown that \(pH > 9\) conditions are necessary for highly efficient mineralization of cyanide ions [26].
Table 3. Changes in end products during photooxidation of cyanide by combined system \{Solar + PS\} at pH 10-11.

| t \(_{\text{row}}\) | Final pH | \(CN^-\), mg·L\(^{-1}\) | \(NO_2^-\), mg·L\(^{-1}\) | \(NO_3^-\), mg·L\(^{-1}\) | \(NH_4^+\), mg·L\(^{-1}\) |
|----------------|----------|----------------|----------------|----------------|----------------|
| 0              | 10.20    | 56.16±14.04   | 0.0           | 0.0            | 0.0            |
| 2.9            | 9.98     | 38.38±9.60    | -             | 7.46±1.64      | -              |
| 8.6            | 9.32     | 34.63±8.66    | -             | 7.27±1.60      | -              |
| 17.3           | 9.03     | 29.00±7.25    | 0.05±0.01     | 5.00±1.10      | 0.02±0.01      |
| 34.5           | 7.07     | 15.91±4.61    | 0.53±0.07     | 3.44±0.76      | 1.66±0.35      |
| 51.5           | 6.87     | 0.0           | 0.57±0.08     | 2.02±0.61      | 2.39±0.50      |

4. Conclusion
The results obtained indicate the high efficiency of the solar-induced method for the purification of cyanide-containing pollutants, which allows to achieve complete destruction of toxic cyanides to non-toxic end products. The developed hybrid method can be used to treat wastewater containing highly toxic cyanide compounds in areas with high solar activity. Thus, it is possible for effectively purify cyanide-containing wastewater using natural sunlight.

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