Photochemical oxidation of thiocyanates exposed to quasi-solar radiation

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Abstract. The article studies kinetic laws regulating thiocyanate oxidation in direct photolysis and in combined iron-persulfate oxidation systems using quasi-solar (simulated) xenon lamp radiation. The influence of the main factors (pH, reaction medium temperature, characteristics of the catalyst, exposure time) on photochemical thiocyanate oxidation efficiency was identified. A conversion degree and initial thiocyanate oxidation speed in the oxidation systems under study change in the \{ UV/PS/Fe^{3+}\} > \{ UV/PS/Fe^{2+}\} > \{PS/Fe^{3+}\} > \{PS/Fe^{2+}\} > \{UV/PS/Fe^{0}\} > \{PS/Fe^{0}\} > > \{UV/PS\} system.

1. Introduction
Gold-bearing ore extraction and processing enterprises are complex chemical manufacturers with high specific consumption of water and chemical reagents. The result of cyanic leaching of gold and silver from sulphide ores and concentrates is technogenic water which is dangerous for the environment [1]. Waste and circulating water of these plants is multicomponent. It contains cyanides, thiocyanates and other highly toxic compounds - non-ferrous metal ions, flotation reagents, flocculants, thiosulfates, etc. The last stage of mineral raw materials processing (neutralization of harmful substances) is of great importance.

Among the methods of oxidation and destruction of toxic cyanide compounds, “environmentally-unfriendly” reagents are still widely used as oxidizers (e.g., chlorine compounds such as hypochlorite, bleach, liquid chlorine, etc.) [2]. Their main disadvantages are toxicity of the reagent itself which poses a real danger when stored in warehouses, decreasing oxidant activity, and the need for strict pH control to avoid chlorocyanine formation. Strict environmental and economic requirements require creation of new low-waste / waste-free and energy-efficient technologies.

Currently, new advanced oxidation processes (AOPs) involving in situ generation of highly reactive radicals (mainly reactive oxygen species (ROS)) are being developed. The ROS can induce oxidation and mineralization of pollutants dissolved in water [3-4]. In the world researches, there is growing interest in the use of persulfates in AOPs for purification of natural and waste waters [5]. At the EAAOP-4 International Forum (4th European Conference on Environmental Applications of Advanced Oxidation Processes, Athens - Greece, 21-24 October 2015), SR-AOP-based methods were suggested for inclusion in the classification of advanced oxidation processes.

Persulfate can directly interact with pollutants or be a precursor for secondary more reactive oxidizing agents – reactive oxygen intermediates (oxygen-containing radicals — SO₄²⁻, •OH) under ultraviolet, thermal, ultrasound impacts. In the presence of metals with several oxidation states (Men +) (Fe²⁺, Fe³⁺ and Fe⁰), persulfates disproportionate to form sulfate-anion radicals (in Fenton-like oxidative
systems).

Fe⁰ (ZVI- zero-valent iron) is more preferable due to its efficiency, environmental friendliness and universal nature [6].

Fe⁰ persulfate is activated due to generation of Fe²⁺ ions from Fe⁰oxidation in the S2O8²⁻ / Fe⁰ system. Fe²⁺ ions enter the persulfate system continuously which contributes to greater activation and release of sulfate radicals than a single dose of Fe²⁺.

Sulfate anion radicals are a real alternative to hydroxyl radicals. Having high redox potential, they have lower pH sensitivity, non-selective high reactivity to most environmental pollutants. Their sources (persulfates) form solutions which are highly soluble and stable at a room temperature.

Among AOP methods, advanced photochemical ones are the most promising. Currently, the world literature has accumulated extensive material on the use of photoactivated methods for oxidative destruction of bioresistant organic pollutants. Most researchers suggest using UV radiation sources. There is growing interest in the use of polychromatic natural solar radiation to intensify oxidative destruction of persistent organic pollutants, and neutralize pathogenic microflora [7-10]. In terms of energy efficiency and environmental friendliness, these researches seem to be very relevant for neutralization of toxic inorganic pollutants.

The most stable and resistant to oxidation compounds are thiocyanates. Therefore, they are selected as a research object.

The purpose of the article is to study the method of advanced photochemical oxidation (Solar - SR-AOPs) for neutralization of thiocyanates in aqueous solutions.

2. Materials and methods

For the experiments, distilled water-based (χ = 2 μS/cm) model thiocyanate solutions (SCN⁻) with initial concentration [SCN⁻] = 1.72 mmol/l were prepared. For advanced photochemical oxidation system experiments, potassium persulfate (K₂S₂O₈), ferrous chloride (FeCl₂·6H₂O), ferrous sulfate (FeSO₄·5H₂O), and metallic iron (99%, Panreac) were used.

The content of thiocyanates in the solution was controlled by the photometric method using a KFK-3-01 photometer [11]. Iron concentration was determined by the standard o-phenanthroline photometric method. The pH value was controlled with a universal pH-150 MI ionomer.

Continuous-flow studies on kinetic patterns of oxidative thiocyanate destruction were carried out using a laboratory unit which is described in [12]. The volume of the solution was 200 ml, the flow rate was 1.25 l / min. A HID 4300 KN xenon lamp (MaxLight, South Korea) was used as an optical radiation source. The emission spectrum of a xenon lamp is very wide (300–800 nm) and close to the solar one. This allows for correct simulation of operating modes of the solar photoreactor in the laboratory. Lamp radiation intensity in the bactericidal ranges was measured with a TKA-PKMUVRadiometer at a distance of 5 cm in the ranges of 2870 mW / m², 171 mW / m² and 180 mW / m² for UV-A (315-400 nm), UV-B (280-315 nm), UV-C (200-280 nm) respectively.

3. Results and discussion

Rhodonites are resistant to xenon lamp radiation. 2 hours after treatment, their concentration remained unchanged. They do not interact with persulfates. Additional xenon lamp radiation of the persulfate-containing solution can reduce concentration of rhodonites by 9% only. The rhodonite-sulfate radicals interaction rate is rather high (5.2*10⁸ M⁻¹ c⁻¹ [13]), but their concentration is not high. The xenon lamp bulb is made of glass which does not transmit UV-B and UV-C radiation. For persulfate photoactivation, it is necessary to use light sources which emit at less than 300 nm of the wavelength [14].

It is more efficient to activate persulfate with iron compounds. When using Fe³⁺ 120 minutes after treatment, no rhodonites were found in the solution. When using Fe²⁺ and Fe⁰, the oxidative process decelerates. Additional xenon lamp radiation can accelerate rhodonite oxidation. The use of Fe⁰ is less efficient for Fe⁰ activation. Rhodonite oxidation forms intermediate iron-containing systems. When
using Fe⁰, iron is slowly introduced into the solution which negatively affects the efficiency of the whole process.

Figure 1. Destruction of thiocyanates in various oxidation systems 1 – PS; 2 – Fe⁰/PS; 3 – Fe²⁺/PS; 4 – Fe³⁺/PS.

For successful rhodonite oxidation with persulfate, combined activation of Fe³⁺ and xenon lamp radiation is optimal (Figure 1). One of the important advantages of persulfate over hydrogen peroxide is its lower sensitivity to medium reaction changes. It was experimentally identified that this parameter has no effect on the kinetics of rhodonite oxidation with persulfate activated with Fe³⁺ and xenon lamp radiation (Figures 2, 3), in a wide pH range (5.8 - 10).

Figure 2. The influence of the medium reaction on thiocyanide oxidation kinetic sin the system. {Fe³⁺/PS/UV}. [SCN⁻]=1.72 mM, [PS]=8.6 mM, [Fe³⁺]=0.86 mM, 25 °C. 1 – pH 10; 2 – pH 5.8; 3 – pH 7.0.

Figure 3. The influence of temperature on thiocyanide oxidation kinetics in the system. {Fe³⁺/PS/UV}. [SCN⁻]=1.72 mM, [PS]=8.6 mM, [Fe³⁺]=0.86 mM, pH 5.8. 1 – 25°C; 2 – 30°C; 3 – 40°C.
In the Solar processes, solutions are heated up to 40–45 °C. Therefore, it is important to study the effect of temperature on the kinetics of thiocyanide oxidation. It was identified that an increase in the reaction temperature up to 40 °C accelerates thiocyanide oxidation. The duration of their full destruction reduces from 90 to 10 minutes.

4. Conclusion

Thus, kinetic laws regulating thiocyanate oxidation in direct photolysis and in combined iron-persulfate oxidation systems using quasi-solar (simulated) radiation of a xenon lamp were studied. The influence of the main factors (pH, reaction medium temperature, characteristics of the catalyst, exposure time) on photochemical thiocyanate oxidation efficiency was identified. A conversion degree and initial thiocyanate oxidation speed in the oxidation systems under study change in exposure time) on photochemical thiocyanate oxidation efficiency was identified. A conversion degree and initial thiocyanate oxidation speed in the oxidation systems under study change in exposure time.) Variable solution medium reaction in the range of 5.8-10 does not have a significant effect on the kinetics of thiocyanate oxidation in the {Fe3+/PS/UV} system. An increase in solution temperature up to 40 °C reduces the duration of full destruction from 90 to 10 minutes.

There sults proved that solar radiation in the presence of in situ generated environmentally-friendly oxidants is promising for thiocyanate-containing wastewater treatment.

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