Prospects for the using of alternative mercury-free sources of UV radiation in the processes of oxidative destruction of aqua-pollutants

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Abstract. A comparative evaluation of the efficiency of using mercury-free radiation sources – KrCl excilamp (222 nm) and solar radiation to intensify the oxidative processes of pollutants with different chemical nature in ultraviolet-coupled ferrous (ferric)–peroxydisulfate systems was carried out. The oxidation ability of Fenton-like process for persistent target compounds of inorganic nature - on the example of thiocyanate ion, and bisphenol A (BPA) as the organic one, significantly improved under both UV and solar radiation. In this case, excilamps can be used as an independent or standby source of radiation (with low solar activity or adverse weather conditions), which in the future can be an important factor in ensuring reliability under the modular principle of constructing technological treatment schemes.

1. Introduction

In recent years, more and more attention has been paid to advanced oxidation processes (AOPs) for the development of methods for elimination recalcitrant aqua-pollutants. The most widely studied are Fenton and Fenton-like oxidative systems. However, their effective use is possible in an acidic medium (pH ≤ 3), since at higher values the iron hydrolyzes and precipitates. In addition, hydrogen peroxide as a reagent is unstable, explosive and flammable, requires special storage facilities. An alternative oxidizing agent is persulfate. It is a strong non-selective oxidizing agent (E₀ = 2.01 V), relatively stable at room temperature, efficiently operating in a wide pH range. In addition, heating [1,2], ultraviolet irradiation (UV) [3], ultrasonic exposure [4], radiolysis [5] and transition metal ions (Fe²⁺, Cu⁺, etc.) [6,7] are able to activate persulfate ions, which leads to the formation of sulfate anion radicals with an even greater oxidative ability (E₀ = 2.60 V).

In the last decade, there has been a trend for a growing interest of researchers in the use of persulfates in AOPs (Figure 1) [8,9].

Ultraviolet radiation is widely used to generate sulfate radical anions in SR-AOPs (Sulfate Radical-based AOPs), while it has been found that it is most expedient and efficient to use light sources emitting at wavelengths less than 300 nm [10]. In practice, mercury gas discharge lamps of medium and low pressure have become widespread.

Modern mercury-free sources of UV radiation (excimer and exciplex lamps, light-emitting diodes, etc.) are considered as an alternative to traditional mercury lamps, since they have such advantages as a high photon energy (3.5–10 eV), a narrow emission band, a long service life, and the absence of mercury [11,12]. The latter is especially relevant in connection with the ratification of the Global...
Agreement on Mercury - the “Minamata Convention”, which provides for the phasing out of mercury-containing substances and equipment [13].

![Figure 1](image_url). An increase in the number of publications on the use of persulfates in oxidation processes according to the SCOPUS database. The search was conducted for the keywords “(persulfate) and (oxidation)”. Data as of April 17, 2020.

Also, the interest of researchers in using polychromatic natural solar radiation (Solar) to intensify the processes of oxidative destruction of persistent organic pollutants does not decrease [14,15]. The results of studies using inexpensive and renewable sunlight will make photoassisted processes much more attractive in practice [16].

In our opinion, the most attractive for processes of effective oxidation of persistent pollutants are combined photoinitiated systems using environmentally friendly oxidizing agents and catalysts and UV radiation from mercury-free sources.

The presented work is a continuation of studies, which focus on the kinetic fundamentals of oxidative degradation of refractory aqua-contaminants by photoassisted SR –AOPs as a «green technology» for water treatment. The purpose of this study is to evaluate the prospects of using mercury-free radiation sources – KrCl excilamp and solar radiation to intensify the oxidative processes of pollutants with different chemical nature in ultraviolet-coupled ferrous (ferric)–peroxydisulfate systems. Thiocyanate was chosen as the target compound of inorganic nature, and bisphenol A (BPA) as the organic one.

2. Materials and methods

2.1. Materials

As the objects of the study were model solutions of targeted compounds prepared using distilled water ($\chi = 2 \mu S / cm$). The initial concentration of thiocyanate (SCN–) was 1.72 mM, and for Bisphenol A (2,2-bis (4-hydroxyphenol) propane) it was 44 $\mu M$. Potassium persulfate ($K_2S_2O_8$), iron (II) sulfate $Fe_2SO_4 \times 7H_2O$ and iron chloride ($FeCl_3 \times 6H_2O$) were used in experiments. All experiments were performed without introducing any pH regulators into the reaction medium. The experimental series were carried out at a constant molar ratio $[S_2Os^2]: [BPA] = [S_2Os^2]: [CNS^] = 5:1$. 

2.2. Experimental procedure
The experiments were carried out in laboratory flow-through units with tubular quartz photoreactors. To study the photodestruction processes, mercury-free sources of mono- and polychromatic UV radiation with different spectral ranges were used (Figure 2): a KrCl excilamp of a barrier discharge emitting in a narrow spectral band with a maximum of 222 nm (UV-222) and natural solar radiation (Solar). For comparative experiments, a DB-30-1 low-pressure mercury gas discharge lamp with a maximum radiation in 254 nm (UV-254) was chosen as the radiation source. Experiments with artificial radiation sources were carried out under thermostating conditions (22 ± 2 °C).

Figure 2. Characteristic emission spectra.

“Open-air” experimental series were conducted during summer period in Ulan-Ude city, Russia (N 51°48'47.747'', E 107°7'19.536''). The intensity of solar radiation was measured by portable radiometer “TKA-PKM” (“TKA Scientific instruments”) (Table 1).

Table 1. The intensity of solar radiation during “open-air” experiments.

| UV-A (315-400 nm) | UV-B (280-315 nm) | UV-C (200-280 nm) | Irradiance, Lx |
|-------------------|-------------------|-------------------|----------------|
| 8,0-46,6          | 0,51-3,08         | 0,49-3,42         | 20500-121000   |

2.3. Analytical methods
The concentration of thiocyanate in the solution was controlled by photometric methods: the express method with ferric nitrate [17] and the standard method with pyridine and barbituric acid. BPA concentrations before, during and after treatment were measured by HPLC-FLD on an Agilent 1260 Infinity.

The efficiency of the oxidation process was evaluated by changing the concentration of the target compound in the treated solution according to the formula (1):

\[ E(\%) = (1 - \frac{C_t}{C_0}) \times 100 \]  

where \( C_0 \) and \( C_t \) are initial and after treatment time \( t \) (min) concentrations of CNS or BPA.

3. Results and discussion
Similar to the Fenton system (Fe\(^{2+}/\)H\(_2\)O\(_2\)) in ferrous (ferric)–peroxydisulfate oxidizing systems (so-called Fenton-like systems), first, \textit{in situ} formation of highly reactive oxygen species (ROS) occurs according to the reactions (2)-(4):

\[ S_2O_8^{2-} + Fe^{3+} \rightarrow 2SO_4^{2-} + Fe^{2+} \]  

(2)
It should be noted that thiocyanate and bisphenol A belong to different classes of chemical compounds and, accordingly, the patterns of their oxidation processes also differ. At the same time, the reaction rate constants of these microcontaminants with ROS - hydroxyl (\(\cdot\)OH) and sulfate anionic radicals (SO\(_4\)\(^{•-}\)) are quite high and comparable (Table 2).

Table 2. Second order reaction constants with ROS, M\(^{-1}\)s\(^{-1}\).

| Compound            | \(k_{\text{OH}}\) | \(k_{\text{ROA}}\) |
|---------------------|-------------------|-------------------|
| Bisphenol A         | \(6.9 \times 10^9\) \([18]\) | \(1.37 \times 10^9\) \([19]\) |
| Thiocyanate ion     | \(4.2 \times 10^9\) \([20]\) | \(1.1 \times 10^{10}\) \([21]\) |

Earlier, we proposed an effective method for destruction of thiocyanate using a catalytic system PS/Fe(III) \([22]\). The following optimal conditions for the effective oxidation process were established: \([S_2O_8^{2-}]:[SCN^{-}] = 5:1\) and \([S_2O_8^{2-}]:[Fe^{3+}] = 1:0.2\).

The complete destruction of thiocyanate in the “dark experiment” (without exposure) in the PS/Fe(III) system was achieved after treatment during 120 min (Figure 3a). The initial rate of BPA oxidation under dark conditions was also quite high, but with an insufficient concentration of the oxidizing agent (\([S_2O_8^{2-}]:[BPA] = 5:1\)), the degree of its conversion did not exceed 40\% (Figure 3b).

With additional irradiation, a significant intensification of the processes was observed. At the same time, an increase in the reactions rates and a significant reduction in the duration of the complete destruction of target compounds were achieved for all the systems considered (Figure 3).

![Figure 3](image-url)

Figure 3. Kinetic curves of thiocyanate (a) and BPA (b) oxidation by ferrous (ferric)–peroxydisulfate system under dark conditions and with additional UV irradiation: \([SCN^{-}] = 1.72\) mM, \([S_2O_8^{2-}] = 8.6\) mM, \([Fe^{3+}] = 0.86\) mM, pH 5.2; \([BPA] = 43.8\) \(\mu\)M, \([Fe^{2+}] = 71.4\) \(\mu\)M, \([S_2O_8^{2-}]:[BPA] = 5:1\), pH 5.5.

It is important to note that when implementing the combined oxidation method with additional photoactivation, a synergistic effect was observed (Figure 4), as evidenced by the values of the synergistic indices \((\varphi > 1)\), calculated by the equation (5):

\[
\varphi = \frac{E(Fe / PS / UV)}{E(Fe / PS) + E(UV)}
\]
where $E$ is the oxidation efficiency of target compound in individual or coupled systems after treatment 20 min.

The oxidation of thiocyanates by persulfates in the presence of Fe ions proceeds according to the radical mechanism through the formation of intermediate iron-containing complexes (reactions (6), (7)).

$$
\left[ Fe(\text{SCN})_a (H_2O)_{6-a} \right]^{(3-a)} + S_2O_8^{2-} \rightarrow \left[ Fe(\text{SCN})_a (H_2O)_{6-a} \right]^{(2-a)} + 2SO_4^{2-}
$$

(6)

$$
\left[ Fe(\text{SCN})_a (H_2O)_{6-a} \right]^{(2-a)} + S_2O_8^{2-} \rightarrow \left[ Fe(\text{SCN})_a (H_2O)_{6-a} \right]^{(3-a)} + SO_4^{2-} + SO_4^{2-}
$$

(7)

When BPA is oxidized, a conjugated radical-chain mechanism is realized (reactions (3),(4)).

Figure 4. Comparison of the effectiveness of using various radiation sources in the oxidative destruction of thiocyanate (a) and BPA (b). $[\text{SCN}^-] = 1.72 \text{ mM}$, $[\text{S}_2\text{O}_8^{2-}] = 8.6 \text{ mM}$, $[\text{Fe}^{3+}] = 0.86 \text{ mM}$, pH 5.2; $[\text{BPA}] = 43.8 \mu\text{M}$, $[\text{Fe}^{3+}] = 71.4 \mu\text{M}$, $[\text{S}_2\text{O}_8^{2-}]:[\text{BPA}] = 5: 1$, pH 5.5; $\tau = 20 \text{ min}$.

UV radiation provides additional generation of reactive oxygen species as a result of photoinduced decomposition of persulfate and photoreduction of iron hydroxocomplexes (reactions (8), (9)).

$$
S_2O_8^{2-} \xrightarrow{hv} 2SO_4^{2-}
$$

(8)

$$
FeOH^{2+} \xrightarrow{hv} Fe^{3+} + OH
$$

(9)

Also during the oxidation of BPA, additional photo reduction of $Fe^{3+}$ from organic complexes and the formation of organic radicals occur (reaction (10)).

$$
Fe(OOCR) \xrightarrow{hv} Fe^{3+} + CO_2R^*
$$

(10)

4. Conclusion

A comparative evaluation of the efficiency of using mercury-free radiation sources – KrCl excilamp (222 nm) and solar radiation to intensify the oxidative processes of pollutants with different chemical nature in ultraviolet-coupled ferrous (ferric)–peroxydisulfate systems was carried out. The oxidation ability of Fenton-like process for persistent target compounds of inorganic nature - on the example of thiocyanate ion, and bisphenol A (BPA) as the organic one, significantly improved under both UV and
solar radiation. In this case, excilamps can be used as an independent or standby source of radiation (with low solar activity or adverse weather conditions), which in the future can be an important factor in ensuring reliability under the modular principle of constructing technological treatment schemes.

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