Photooxidation based on UV/H₂O₂ process for arsenic removal from aqueous solutions

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Abstract. The main regularities of the photochemical oxidation of arsenic (III) were studied using a mercury-free UV source KrCl excilamp (222 nm). Comparative studies of the effectiveness of direct photolysis and combined oxidation of arsenic (III) in the presence of hydrogen peroxide were performed. It was found that the combined treatment of \{UV/H₂O₂\} achieves a significant intensification of the oxidation process. The considered oxidizing systems according to the oxidation state of As(III) can be ranked according to \{UV/H₂O₂\} > \{H₂O₂\} > \{UV\}. The ion-radical mechanism of the photochemical oxidation of arsenic in the combined \{UV/H₂O₂\} oxidation system using the UV radiation of the KrCl excilamp is proposed. The fundamental possibility of using a mercury-free source of quasi-monochromatic radiation of the KrCl excilamp (222 nm) for the photothermal process based on the combined oxidation system \{UV/H₂O₂\} to remove arsenic from aqueous solutions is established.

1. Introduction
In the last decade, the world community is concerned about the problem of toxic substances, including arsenic compounds, entering water bodies [1,2]. The release of this pollutant into the environment is due to both natural (weathering of minerals and geothermal processes) [3-5], and anthropogenic factors (agriculture, electronics, dye production, mining and processing of refractory gold-, arsenic-containing ores).

Nowadays the most widely known methods for the purification of natural, waste water and technological solutions from arsenic are adsorption/coprecipitation methods and oxidative methods [6–8].

As adsorption materials, activated carbons, resins, gels, and Si-based sorbents modified with metal hydroxides (iron II, III), as well as slags, carbons, biosorbents, goethites, etc. are widely used [6, 9-10]. The main disadvantages of these methods are the unsatisfactory cleaning efficiency, due to the limited sorption capacity of the sorbent and the need for its further regeneration.

Of the oxidizing methods for the neutralization of various As-containing solutions, the most commonly used are those in which manganese oxide (MnO₄⁻), compounds of “active” chlorine...
(Cl₂ or OCl⁻) are used as the oxidizing agent, the main disadvantage of which is the toxicity of the reagent itself and the increase salinity of purified water.

In our opinion, safer are methods using environmentally friendly oxidizing agents - atmospheric oxygen and hydrogen peroxide (primarily due to the absence of secondary water pollution with reagent reduction products). Moreover, the methods have a significant drawback, which is the duration of the processing process. Thus, the half-period of the oxidation of As (III) by oxygen reaches from 1 to 3 years [11], and the slow oxidation of arsenic by hydrogen peroxide [12] even with a multiple excess of oxidizing agent indicates the use of combined oxidation processes, the so-called Advanced Oxidation Processes” (AOP) [13-15]. The essence of AOP processes is the liquid-phase chain oxidation of pollutants (pollutants) with highly reactive oxygen species (ROS) generated in situ - hydroxyl radicals, singlet oxygen and others.

Among AOP methods that have been intensively developing recently, the most promising are photoactivated oxidative processes [16]. Water purification and neutralization technologies traditionally use mercury gas-discharge lamps of different pressures as the sources of UV radiation, the main and significant disadvantage of which is the high content of metallic mercury (from 10 mg in low-pressure lamps to 600 mg in high-pressure lamps) [15,16]. At present, a new class of modern mercury-free sources of UV radiation (gas-discharge excimer and exciplex lamps (excilamps), LED lamps, etc.) is becoming more widespread [17]. The main advantage of excilamps is a narrow emission band, in which 80% or more of the total radiation power is concentrated [18], high photon energy (3.5–10 eV), and the absence of mercury. Studies are known on the combined degradation of toxic organochlorine pollutants by UV radiation of KrCl - (222 nm) and XeBr - (283 nm) excilamps in the presence of hydrogen peroxide, indicating a high efficiency of oxidative processes using excilamps compared to similar processes using mercury lamps, due to a significant increase ROS generation intensity [19-21]. Few studies are known on the use of ultraviolet radiation (UV) in combination with oxidizing agents for the neutralization of inorganic pollutants [16, 22], including As-containing solutions [23].

The purpose of this work was to study the laws of photochemical oxidation of arsenic with hydrogen peroxide using UV radiation from an KrCl excilamp.

2. Experimental section
The object of the study was model aqueous solutions of arsenic (III) with a concentration of 2.7 μM (0.2 mg·L⁻¹) prepared in distilled water (χ = 2 μS / cm, pH 5.8). The content of arsenic (III) ions controlled by spectrophotometric method with ammonium molybdate [24]. pH was monitored with a glass electrode/pH meter (model pH-150 M). Na₃AsO₃ used was of analytical grade supplied by “Khimreaktivsnab”. H₂O₂ “Nevareaktive” supplied (38% weight). Initial pH was adjusted by addition of NaOH (0.1 N) or H₂SO₄ (0.1 N).

All experiments (photochemical reactions) for As (III) oxidation were performed in an indigenously designed lab-scale thermostatted 25 ± 2°C photoreactor made up from quarts glass tubes. 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⁻¹.

The source of UV radiation is a KrCl excilamp with excitation by a barrier discharge, emitting in a narrow spectral band with a maximum of 222 nm, with a half-width of the spectral band of 2-15 nm (Excilamps Ltd., Institute of High Current Electronics SB RAS, Tomsk). The absorbed radiation power of the excilamp, determined by the chemical actinometrical method with atrazine [19], was 0.55 mW/ cm². The power consumption of electrical energy of the selected source was controlled by using a Voltcraft EM-3000 meter.
3. Result and discussion

It is known that during direct photolysis, highly active particles with an unpaired electron are generated in the system - radicals involved in secondary processes of oxidation and destruction of pollutants:

\[ \text{H}_2\text{O} + h\nu \rightarrow \text{HO}^- + \text{H}^+ \]  

(1)

It should be noted that the rate of generation of \( \text{HO}^- \) radicals is determined mainly by the properties of the UV radiation source and the presence of reagents - oxidizing agents, which are ROS precursors.

A preliminary assessment of the photochemical activity of As (III) during direct photolysis showed that the nature of the kinetic curve upon irradiation with a KrCl excilamp (222 nm) is significantly different (Figure 2) compared to the same curve obtained under similar conditions, but with a mercury ultraviolet lamp (254 nm) [25]. The oxidation process of As (III) under the influence of an excilamp is almost 20 times faster than the initial reaction rates for mercury UV-C lamp, calculated by the equation \( W_0 = \frac{dC{\text{As}}^{3+}}{dt} \), were 0.80 \( \mu \text{mol} \cdot \text{L}^{-1} \cdot \text{min}^{-1} \) and 0.04 \( \mu \text{mol} \cdot \text{L}^{-1} \cdot \text{min}^{-1} \), and the efficiency of the process after 5 minutes of treatment reaches 36.5% compared with 9%, respectively. Although it is worth noting that after 30 min the efficiency was only 43%, which makes it possible to use the combined oxidizing system in this case.

In this case, it should be noted that oxidation of As (III) in a dark process (“dark”), described by the gross reaction [12]:

Figure 1. Schematic diagram of the experimental setup.

Figure 2. Comparative experiments on the oxidation of As (III) at pH 5.8. Initial [As\(^{3+}\)] 2.7 \( \mu \text{M} \), [H\(_2\)O\(_2\)] = 2.7 \( \mu \text{M} \).
As(OH)$_3$ + H$_2$O$_2$ $\Rightarrow$ HAsO$_4^{2-}$ + 2H$^+$ + H$_2$O

In spite of rather high initial oxidation rate of 1.41 μmol·L$^{-1}$·min$^{-1}$, an inhibition of the reaction was observed due to deactivation of the reaction mixture during the first 15 minutes.

In the presence of hydrogen peroxide in the {UV/H$_2$O$_2$} combined system, after 10 min of exposure, the residual concentration of As (III) in the solution was 0.009 mg·L$^{-1}$, which corresponds to the MPC standards (0.01 mg·L$^{-1}$) [26, 27]. According to the efficiency and speed of the As (III) oxidation process, the considered oxidizing systems can be arranged in order to {UV/H$_2$O$_2$} > {H$_2$O$_2$} > {UV}.

The following is a comparative assessment of the specific energy efficiency of the photochemical oxidation of As (III) in various combined systems using different radiation sources (the results obtained in comparison with literature data) (table 1) by the amount of oxidized substance per unit of consumed electric energy by calculating the specific conversion ($Y$) according to the formula:

$$Y = \frac{[(C_0 - C_f) \times V \times 1000]}{(W \times t \times 60)}, \text{ mkg} / \text{kJ}$$

where $C_0$ is the initial concentration of arsenic (III), μg/l;
$C_f$ is concentration of arsenic (III) after treatment, μg/l;
$V$ is volume of the treated solution, ml;
$W$ is power consumption, W;
$t$ is duration of the process, min.

| Parameter | US / UV $\rightarrow$ 254 | UV $\rightarrow$ Xe / TiO$_2$ | UV $\rightarrow$ Xe / TiO$_2$ / Ag / air | UV $\rightarrow$ 222 / H$_2$O$_2$ $^*$ |
|-----------|----------------|----------------|--------------------------------|-----------------------------------|
| $P$, W    | 48             | 300            | 300                           | 30                               |
| $t$, min  | 60             | 150            | 60                            | 10                               |
| $\psi$, % | 95.5           | 80             | 80                            | 95.5                             |
| $W_0$, mM/L·min | 0.04 | 2.90 | 6.67 | 1.82 |
| $Y$, mkg / kJ | 1.67 | 1.0 | 2.47 | 3.20 |

$^*$- results of this work

The specific conversion ($Y$) for the considered combined oxidizing systems with various UV radiation sources changed in the order UV $\rightarrow$ 222 / H$_2$O$_2$ > UV $\rightarrow$ Xe / TiO$_2$ / Ag / air > US / UV $\rightarrow$ 254 / H$_2$O$_2$ > UV $\rightarrow$ Xe / TiO$_2$.

From the point of view of energy efficiency and environmental safety, the mercury-free KrCl excilamp is the optimal source. It is important to note that the molar extinction coefficient of hydrogen peroxide sharply increases in the short-wavelength region of the spectrum and amounts to 1.12·10$^5$ L·mol$^{-1}$·cm$^{-1}$ at 222 nm, therefore, the rate of formation of hydroxyl radicals will be higher.

The excellent treatment performance by the combined {UV / H$_2$O$_2$} oxidizing system can be explained as follow. Although, H$_2$O$_2$ reacts very slowly with As(III), a significant increase in the rate of As(III) oxidation is a direct consequence of photoactivation by UV radiation of excilamp of hydrogen peroxide with its disproportionation according to the well-known Haber-Weiss radical chain mechanism with the formation of non-selective highly reactive hydroxyl radicals [30, 31]:

$$\text{H}_2\text{O}_2 + \text{hv} \rightarrow 2\text{HO}^*$$ (2)
\[
\begin{align*}
\text{H}_2\text{O}_2 + \text{HO}' & \rightarrow \text{HO}_2 + \text{H}_2\text{O} \quad k = 3 \times 10^7 \text{L} \cdot \text{M}^{-1} \text{s}^{-1} \quad (3) \\
\text{HO}_2^- + \text{H}_2\text{O}_2 & \rightarrow \text{HO}' + \text{H}_2\text{O} + \text{O}_2 \quad k = 9.7 \times 10^7 \text{L} \cdot \text{M}^{-1} \text{s}^{-1} \quad (4) \\
\text{HO}_2'(\text{or} \text{HO}') + \text{HO}_2^- & \rightarrow \text{H}_2\text{O}_2(\text{or} \text{H}_2\text{O}) + \text{O}_2 \quad k = 8.3 \times 10^9 \text{L} \cdot \text{M}^{-1} \text{s}^{-1} \quad (5) \\
\text{HO}' + \text{HO}' & \rightarrow \text{H}_2\text{O}_2 \\
\end{align*}
\]

It is established in the literature that alcohols such as tert-butanol and iso-propanol readily react with hydroxyl radicals. Therefore, tert-butanol and iso-propanol are widely used as the scavengers of HO' radicals. The constant of interaction of tert-butanol with HO' radicals is \(6 \times 10^8\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}\), and of iso-propanol - \(1.9 \times 10^9\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}\). We investigated the effect of these alcohols on the As(III) photooxidation in order to evaluate the reaction mechanism and the species that played role in the \{UV / H_2O_2\} systems (Figure 3). The efficiency of the process of photooxidation decreased by 18.5% after 30 minutes of treatment with iso-propanol and with tert-butanol - by 11%. The results showed that the reaction was inhibited by adding alcohols as an HO' radical scavengers. This clearly indicated that the As(III) photooxidation by combined system \{UV / H_2O_2\} associated with free radicals degradation.

It is also possible in the oxidizing system under consideration, along with OH' radicals, the generation of other ROS, in particular \(\text{HO}_2^\cdot\) and \(\text{O}_2^\cdot\), which can activate hydrogen peroxide (reaction), and also recombine with the formation of additional hydrogen peroxide (reaction), the photoactivation of which increases the yield of hydroxyl radicals. It is known that \(\text{O}_2^\cdot\), superoxide radicals are the most long-lived particles in comparison with hydroxyl radicals [31, 32], and as a result they have a higher degree of dissolution than hydroxyl radicals and in volume react with As(III) with the formation of As(IV) intermediate, oxidation, which is the limiting stage of the process.

Intermediates As(IV) are known, which, depending on the pH of the medium, can take various forms - \(\text{As}^{IV}(OH)_3\), \(\text{As(OH)}_3\text{O}^\cdot\), \(\text{HAs}^{IV}\text{O}_3\), \(\text{As}^{IV}\text{O}_3^2\) [23]. They are further oxidized in an acidic environment - with the formation of two products of both the final As(V) and the starting As(III) (as evidenced by the deactivation of the reaction mixture at pH 3), and in weakly acidic and alkaline media (5.8-9.0) - to the final As(V). The authors of [33] previously confirmed the existence of the As(IV) intermediate by pulsed radiolysis.

Figure 3. Photochemical oxidation of As (III) in the presence of radical scavengers at pH 5.8. Initial [As^{III}]=[H_2O_2]=2.7 μM, [iso-propanol] = 1.35 mM, [tert-butanol] = 1.35 mM.
4. Conclusion
Thus, the obtained results of the photochemical oxidation of As(III) showed the high efficiency of the selected combined oxidation system \{ UV / H_2O_2 \}, based on the use of in situ generated reactive oxygen species.

The results also indicate that it is possible in principle to realize the complete oxidation of As(III) using an energy-efficient source of quasi-monochromatic radiation of an KrCl excilamp (222 nm) for removal of arsenic from As containing natural and wastewaters.

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