ГЕНЕРАЦИЯ РАДИКАЛОВ В ЖЕЛЕЗО-ПЕРСУЛЬФАТНОЙ СИСТЕМЕ С ИСПОЛЬЗОВАНИЕМ KRCL-ЭКСИЛАМПЫ

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Изучена генерация сульфатного анион-радикала ($SO_4^{\bullet-}$) и гидроксильного радикала (•ОН) в железо-персульфатной системе, активированной ультрафиолетовым (УФ) излучением KrCl-эксилампы (222 нм) (УФ/ПС/Fe^{2+}). Для детекции радикалов и оценки уровней их воздействия проведены эксперименты по деструкции соединений-ловушек таргетных радикалов – терефталевой кислоты (ТФК) и п-хлорбензойной кислоты (п-ХБК). Деионизованная вода (ДВ), природная вода (ПВ) и очищенная хозяйственно-бытовая сточная вода (СВ), содержащие соединение-ловушку, последовательно обработаны прямым УФ облучением и в системах УФ/ПС и УФ/ПС/Fe^{2+}. Показано, что для генерации радикалов в одной и той же водной матрице железо-персульфатная система является наиболее эффективной в ряду: УФ/ПС/Fe^{2+} > УФ/ПС > УФ. Сравнительный анализ различных водных матриц показал наиболее низкий уровень генерации радикалов в СВ. Поскольку ТФК и п-ХБК оказались малоподходящими соединениями для оценки вкладов $SO_4^{\bullet-}$ и •ОН путем сравнения степени деструкции без и в присутствии метанола и трет-бутанола, гербицид атразин (АТЗ) взят как модельный органический поллютант, имеющий близкие константы скорости реакции с $SO_4^{\bullet-}$ и •ОН. В результате экспериментов по деструкции АТЗ в присутствии спиртов установлен преобладающий вклад $SO_4^{\bullet-}$ при обработке ДВ (79%) и ПВ (60%) в системе УФ/ПС/Fe^{2+}, тогда как в СВ вклад $SO_4^{\bullet-}$ и •ОН был одинаков. При прямом УФ облучении (без персульфата и Fe^{2+}) выявлена генерация •ОН в СВ, что, возможно, обусловлено высокой фотореакционной активностью растворенного органического вещества (РОВ).

Ключевые слова: очистка воды, радикалы, KrCl-эксилампа, персульфат, фентоноподобный процесс

GENERATION OF RADICALS IN FERROUS-PERSULFATE SYSTEM USING KRCL EXCILAMP

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Generation of sulfate radical anion ($SO_4^{\bullet-}$) and hydroxyl radical (•OH) in the ferrous-persulfate system (UV/PS/Fe^{2+}), activated with KrCl excilamp (222 nm) radiation, was studied. To detect radicals and evaluate levels of their action, degradation experiments were conducted using the probe compounds, which trap the target radicals – terephtalic acid (TPA) and p-chlorobenzoic acid (pCBA). Deionized water (DW), natural water (NW) and wastewater (WW), containing a probe compound, were sequentially treated by direct UV, UV/PS and UV/PS/Fe^{2+} systems. The ferrous-persulfate system was shown to be the most efficient in terms of radical generation within the same water matrix: UV/PS/Fe^{2+} > UV/PS > UV. Comparing different water matrices, the lowest radical generation was observed in WW. Since TPA and pCBA were unsuitable compounds to assess the contributions of $SO_4^{\bullet-}$ and •OH by comparison of degradation degree with and without methanol and tert-buthanol, herbicide atrazine (ATZ) was taken as a model organic pollutant with comparable reaction rate constants with $SO_4^{\bullet-}$ and •OH. Scavenging experiments with ATZ and alcohols

showed a major contribution of SO₄•⁻ during UV/PS/Fe²⁺ treatment of DW (79%) and NW (60%), whereas SO₄•⁻ and •OH contributed equally in WW. Direct UV irradiation (without persulfate and Fe²⁺) indicated the •OH production in WW, presumably, due to high photoreactivity of dissolved organic substance (DOM).

Key words: water treatment, radicals, KrCl excilamp, persulfate, photo-Fenton-like process

INTRODUCTION

Advanced oxidation processes (AOPs) are known to be effective for degrading bioresistant organic pollutants in water and wastewater via oxidative reactions with generated *in situ* reactive oxygen species (ROS). ROS can be produced upon irradiation with UV light in the presence of dissolved organic matter (DOM), oxidants (hydrogen peroxide, ozone, persulfate) or catalysts (TiO_2, $Fe^{2+/3+,0}$). In recent years, sulfate radical-based AOPs (SR-AOPs) are increas-

ingly gaining attention as a promising strategy to remove organic pollutants from aqueous media and soil. The SR-AOPs utilize peroxysulfo-compounds as oxidants, primarily, peroxydisulfate ($S_2O_8^{2-}$, PS) and peroxymonosulfate (HSO_5^-, PMS or Oxone), which produce sulfate anion radical ($SO_4^{•-}$) and hydroxyl radical (•OH) after activation with various methods, most commonly, with transition metal ions (Fe^{2+}, Co^{2+}) and UV radiation. Basically, the generation of radicals in such photo-Fenton-like systems is described via the following reactions [1]:

$$S_2O_8^{2-} \xrightarrow{h\nu} 2SO_4^{•-} \tag{1}$$

$$SO_4^{•-} + H_2O \rightarrow H^+ + SO_4^{2-} + •OH \qquad k = 6.3 \cdot 10^7 \ M^{-1} \ s^{-1} \tag{2}$$

$$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{•-} + SO_4^{2-} \qquad k = 39\text{-}49 \ M^{-1} \ s^{-1} \tag{3}$$

$$Fe^{2+} + SO_4^{•-} \rightarrow Fe^{3+} + SO_4^{2-} \qquad k = 3.0 \cdot 10^8 \ M^{-1} \ s^{-1} \tag{4}$$

$$SO_4^{2-} + •OH \rightarrow SO_4^{•-} + OH^- \qquad k = 1.5 \cdot 10^8 \ M^{-1} \ s^{-1} \tag{5}$$

$$Fe^{3+} + S_2O_8^{2-} \rightarrow Fe^{2+} + 2SO_4^{•-} \qquad k = 22.5\text{-}33.5 \ M^{-1} \ s^{-1} \tag{6}$$
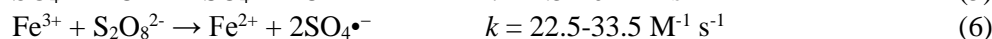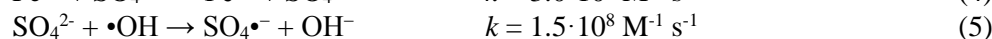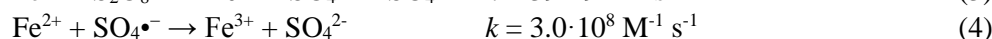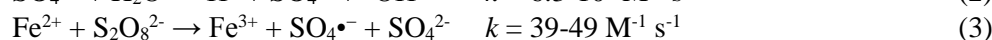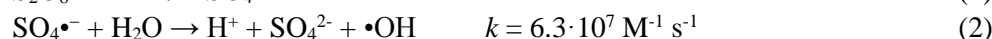
The highly oxidizing $SO_4^{•-}$, which have a comparable redox potential ($E_0 = 2.5\text{-}3.1$ V) with •OH ($E_0 = 1.8\text{-}2.7$ V), has been considered as an alternative to •OH due to its lower pH sensitivity, longer half-time in water and higher oxidative selectivity towards many organic compounds [2]. Moreover, persulfates as salts are advantageous for environmental applications due to their solubility in water, lack of harmful byproducts, safe handling and relatively low cost.

Previous studies reported the generation of •OH and $SO_4^{•-}$ in the oxidative systems such as PS(PMS)/transition metal [3] and UV/PS(PMS) using mercury lamps as UV sources [4-6]. However, the generation of •OH and $SO_4^{•-}$ via photo-Fenton-like processes in real waters remains little investigated. Moreover, in view of the Minamata Convention on Mercury (adopted in 2013, Russian Federation signed in 2014), aimed at providing the gradual phase out of mercury use by 2020, mercury-free UV sources such as excilamps [7] and light-emitting diodes [8] represent

good alternatives for replacement of traditional mercury lamps in AOPs applications.

The objective of this study was to detect and evaluate the radicals exposure in different types of aqueous matrices using the ferrous-persulfate system, activated with KrCl excilamp (222 nm) ($UV/PS/Fe^{2+}$).

MATERIALS AND METHODS

Terephthalic acid (TPA, 98%, Aldrich), *p*-chlorobenzoic acid (*p*CBA, 99%, Acros), atrazine (99.1%, Sigma-Aldrich), iron (II) sulfate heptahydrate (Khimreaktivsnab, Russia), potassium persulfate (Vekton, Russia) were used as received. HPLC grade acetonitrile (ACN) was purchased from Cryochrom (Russia), methanol (MeOH), *tert*-buthanol (*t*-BuOH) and acetic acid from Khimreaktivsnab. Stock solutions of compounds were prepared in deionized water (DW, 18.2 mΩ cm) produced by a Simplicity®UV system from Millipore.

Natural water (NW) was collected from Selenga river (main tributary of Lake Baikal) and urban wastewater (WW) was obtained from the wastewater

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treatment plant in Ulan-Ude (Russia). The samples were delivered and filtered on the same day (0.45 μm RC, Vladisart, Russia) and stored at 4 °C. Dissolved organic carbon (DOC) level in NW and WW was 7.2 and 30.2 mg/L, respectively. Immediately prior to each treatment, water samples were diluted to a DOC value of 5 mg/L in order to elucidate the role of DOM. Water analyses were performed using the standard methods listed in the Environmental normative federal documents (Federal Center of Analysis and Assessment of Technogenic Exposure, Moscow, Russia). DOC was measured by TOC-L CSN (Shimadzu, Japan). Table 1 summarizes the general water quality data after dilution.

Table 1.
Hydro chemical characteristics of aqueous matrices for experiments
Таблица 1. **Гидрохимические характеристики водных матриц для экспериментов**

mg/L*	Natural water	Wastewater
pH	7.2	7.1
NH_4^+	nd	5.1
HCO_3^-	84.7	64.6
CO_3^{2-}	6.3	6.0
NO_3^-	nd	5.4
NO_2^-	nd	2.3
SO_4^{2-}	8.9	11.9
Cl^-	1.3	36.6
PO_4^{3-}	nd	1.8
COD	7.6	4.0

Notes: * except for pH
nd – not detected
Примечания: * кроме pH, nd –не определялось

To detect and evaluate the radical exposure, scavenging experiments were conducted using probe compounds, which trap the target radicals with known second-order rate constants, k_{ROS} (Table 2). Briefly, radicals were detected indirectly via degradation of a probe compound.

Table 2.
Reaction rate constants between probe compounds and radicals (M^{-1} s^{-1})
Таблица 2. **Константы скорости реакции соединения-ловушки и радикалов (M^{-1} c^{-1})**

Radical / Probe compound	•OH	$SO_4^{•-}$
p-chlorobenzoic acid	$5.0 \cdot 10^9$ [9]	$3.6 \cdot 10^8$ [10]
Terephthalic acid	$4.4 \cdot 10^9$ [11]	$1.7 \cdot 10^8$ [10]
Methanol	$9.7 \cdot 10^8$ [10]	$1.1 \cdot 10^7$ [12]
t-buthanol	$6.0 \cdot 10^8$ [10]	$4.0 \cdot 10^5$ [12]

A probe compound (20 μM) was added to each water matrix (50 mL) and sequentially degraded in UV, UV/PS, UV/PS/Fe^{2+} and PS/Fe^{2+} (dark control) systems under magnetic stirring and irradiation in a bench quasi-collimated beam reactor with a KrCl excilamp (Institute for High Current Electronics SB RAS, Russia). The incident irradiance, determined by atrazine actinometry, was 0.08 mW/cm². The molar ratio of Fe^{2+} and PS was 1:3.5 (M/M) and initial pH was 3.5. Samples were withdrawn at desired time intervals, filtered through PTFE filters (0.45 μm, Sartorius) to remove the precipitated iron after pH adjustment to 8.0, and analyzed by HPLC for residual concentrations. Probe compounds were determined using an Agilent 1260 Infinity HPLC system with UV detector equipped with a Zorbax SB-C18 column (4.6×150 mm). The eluents MeOH and 1% CH_3COOH (70:30 – *p*CBA, 30:70 – TPA), ACN and 75 mM CH_3COOH (40:60) were used for *p*CBA (TPA) and ATZ analysis, respectively. The analytes were detected at 220 nm (ATZ), 230 nm (*p*CBA) and 240 nm (TPA) under flow rate of 0.8 mL/min (0.5 mL/min for ATZ). pH measurements were performed using a Metrohm 827 pH meter (Metrohm, Switzerland).

The reaction between probe compound and ROS is diffusion controlled with the expression of Eq. (7) [13]:

$$-\frac{d[\text{Probe compound}]}{dt} =$$
$$= k_{ROS} [\text{ROS}] [\text{Probe compound}] \quad (7)$$

where k_{ROS} (M^{-1} s^{-1}) is the reaction rate constant between ROS and a probe compound (Table 2). The pseudo-first-order rate constants (k_{obs}, s^{-1}) of degradation of probe compounds were obtained from experimental linear plots of $Ln(C/C_0)$ *vs.* treatment time through Eq. (8):

$$-\frac{d[\text{Probe compound}]}{dt} =$$
$$= k_{obs} [\text{Probe compound}] \quad (8)$$

TPA and *p*CBA, widely used as probe compounds for OH• in hydroxyl radical-based AOPs, also react with $SO_4^{•-}$ (Table 2). Since the difference between $k_{SO4•-}$ and $k_{OH•}$ values is not significant (one order of magnitude), it is difficult to distinguish between •OH and $SO_4^{•-}$ just based on the degradation kinetics of *p*CBA and TPA. Therefore, herbicide atrazine (ATZ) was also taken as a reference compound for scavenging experiments in the presence of MeOH and *t*-BuOH, which quench •OH and $SO_4^{•-}$ with different rate constants. These alcohols have been extensively used previously for •OH and $SO_4^{•-}$ identification [4-6]. Specifically, MeOH readily react with both radicals, the reaction rate with •OH is approximately 88-fold higher than that with $SO_4^{•-}$, while *t*-BuOH mainly react with •OH, the reaction rate with •OH is approximately 10^3-fold higher than that with $SO_4^{•-}$ (Table 2). If $SO_4^{•-}$ is a predominant radical, the addition of *t*-BuOH would not affect a compound degradation as significantly as MeOH.

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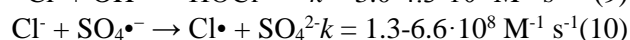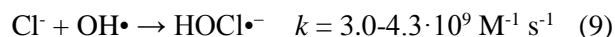
RESULTS AND DISCUSSION

At initial stage, pCBA and TPA were examined as radical probe compounds, based on the monitoring of their degradation. The pseudo-first-order rate constants of pCBA and TPA degradation by direct UV, UV/PS and UV/PS/Fe^{2+} treatment in DW, NW and WW are presented in Table 3. Dark experiments (PS/Fe^{2+}) showed ~50% degradation of pCBA and TPA.

Table 3.

Pseudo-first-order rate constants of pCBA and TPA degradation in different water matrices. [pCBA]$_0$ ([TPA]$_0$) = 20 μM, [Fe^{2+}] : [PS] = 1:3.5 (M/M), pH$_0$ = 3.5
Таблица 3. **Константы скорости псевдо-первого порядка деградации п-ХБК и ТФК в различных водных матрицах. [п-ХБК]$_0$ ([ТФК]$_0$) = 20 мкМ, [Fe^{2+}] : [Персульфат] = 1:3.5 (M/M), pH$_0$ = 3,5**

System	$k_{p\text{CBA}} \cdot 10^{-2}$, s^{-1}	R^2	$k_{\text{TPA}} \cdot 10^{-2}$, s^{-1}	R^2
Deionized water				
UV	0.4	0.99	0.1	0.99
UV/PS	10.1	0.99	7.7	1.00
UV/PS/Fe^{2+}	10.6	0.98	7.6	1.00
Natural water				
UV	0.5	1.00	0.1	0.95
UV/PS	3.1	1.00	2.4	0.99
UV/PS/Fe^{2+}	4.3	1.00	5.0	0.99
Wastewater				
UV	1.0	0.96	1.0	0.95
UV/PS	1.7	0.97	1.5	0.96
UV/PS/Fe^{2+}	3.3	0.96	2.5	0.99

According to pCBA and TPA degradation rates in the selected water matrices, the oxidative systems can be arranged in the following order: UV/PS/Fe^{2+} > UV/PS > UV. This indicates the highest •OH and SO$_4$•$^-$ exposure in UV/PS/Fe^{2+} system in each type of water. However, comparing the k values for both probe compounds obtained by UV/PS/Fe^{2+} treatment of different water matrices, the lowest radical exposure in WW was observed: DW > NW > WW. It is due to •OH and SO$_4$•$^-$ scavenging with common anions and DOM. It is known that NOM (DOM) scavenges ROS, including •OH and SO$_4$•$^-$, with $k_{\text{DOC, OH}•}$ of $2.5 \cdot 10^4$ L mg C^{-1} s^{-1} (on a carbon basis) [14] and $k_{\text{DOC, SO4}•-} = 6.6 \cdot 10^3$ L mg C^{-1} s^{-1} [15]. After dilution of NW and WW to 5 mg/L DOC and acidification, WW contained Cl$^-$ (1 mM) > SO$_4^{2-}$ (0.12 mM) > NO$_3^-$ ≈ NH$_4^+$ > NO$_2^-$ > PO$_4^{3-}$, whereas NW contained mainly SO$_4^{2-}$ (0.09 mM) and Cl$^-$ (0.04 mM). SO$_4^{2-}$ anions do not react with SO$_4$•$^-$, but scavenge •OH. The SO$_4$•$^-$-induced oxidation processes in UV/PS system were previously shown to be largely affected by chloride and bicarbonate [16]. Chlorides react fast with •OH and SO$_4$•$^-$ yielding HOCl•$^-$ and Cl• as primary products (9, 10) [17]:

$$\text{Cl}^- + \text{OH}• \rightarrow \text{HOCl}•^- \quad k = 3.0\text{-}4.3 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1} \quad (9)$$
$$\text{Cl}^- + \text{SO}_4•^- \rightarrow \text{Cl}• + \text{SO}_4^{2-} \quad k = 1.3\text{-}6.6 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1} (10)$$

However, the conversion reactions of SO$_4$•$^-$ into •OH are also probable in WW, increasing the relative contribution of •OH during UV/PS/Fe^{2+} treatment, which was further supported by scavenging experiments with t-BuOH and MeOH. In turn, the higher rate of •OH towards DOC ($k_{\text{DOC, OH}•} > k_{\text{DOC, SO4}•-}$) contributed to lower degradation rate, as compared to that in NW. The scavenging influence and involvement of HCO$_3^-$/CO$_3^{2-}$ to the reactions with •OH and SO$_4$•$^-$ at pH 3.5 can be ruled out.

On the contrary, direct UV irradiation showed the highest rate constants of compounds degradation in WW, indicating the ROS generation in this matrix. It is known that natural organic matter (NOM), a component of real waters, influences photolytic and photocatalytic reactions. The absorption of light by the photoinductive constituents of NOM could generate singlet and triplet excited states of NOM, from which such ROS could be further generated such as •OH, ^{1}O$_2$ [18]. Therefore, alongside the inhibition, NOM is capable of promoting the indirect degradation of organic compounds, depending on the compound and the nature/origin and concentration of NOM. As DOC level in NW and WW was the same, the obtained result suggests a predominance of promoting effect of DOM (as samples were filtered) in WW upon direct irradiation with KrCl excilamp, presumably, due to its higher photochemical activity. Regarding UV/PS system, the degradation rates also decreased moving from DW to WW (Table 2). As TPA reacts with SO$_4$•$^-$ approximately 1.5 times slower than pCBA, the lower degradation rates were observed.

Thus, pCBA and TPA present good trapping agents for total SO$_4$•$^-$ and •OH and can be used as qualitative probe compounds in the persulfate systems. However, the steady-state concentrations of SO$_4$•$^-$ and •OH cannot be calculated from Eq. (8) as a ratio $k_{\text{obs}}/k_{\text{ROS}}$ due to non-selectivity of these compounds towards SO$_4$•$^-$ and •OH and reaction with rates of 10^8-10^9 M^{-1} s^{-1} (Table 2). The contribution •OH and SO$_4$•$^-$ to the compound degradation can be evaluated by comparing the difference between its degradation efficiency in the presence of MeOH and t-BuOH [6, 19]. To identify •OH and SO$_4$•$^-$ in the ferrous-persulfate system, pCBA and TPA were tested by adding MeOH and t-BuOH. As expected, comparison of degradation kinetics showed similar degradation rates in the presence of both alcohols, indicating that pCBA and TPA are unsuitable to differentiate SO$_4$•$^-$ and •OH. t-BuOH reacts 10^3 faster with •OH than with SO$_4$•$^-$, but both pCBA and TPA react with excess amount of SO$_4$•$^-$ by

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one order of magnitude slower than with •OH (Table 2), making the difference between their degradation rates in the presence of MeOH or *t*-BuOH be negligible (data not shown). Therefore, ATZ was further applied as a reference compound with similar rate constants of reaction with OH• and SO$_4$• ($k_{SO4•-} = 1.4 \cdot 10^9$ M^{-1} s^{-1}, $k_{OH•} = 2.2 \cdot 10^9$ M^{-1} s^{-1} [20]).
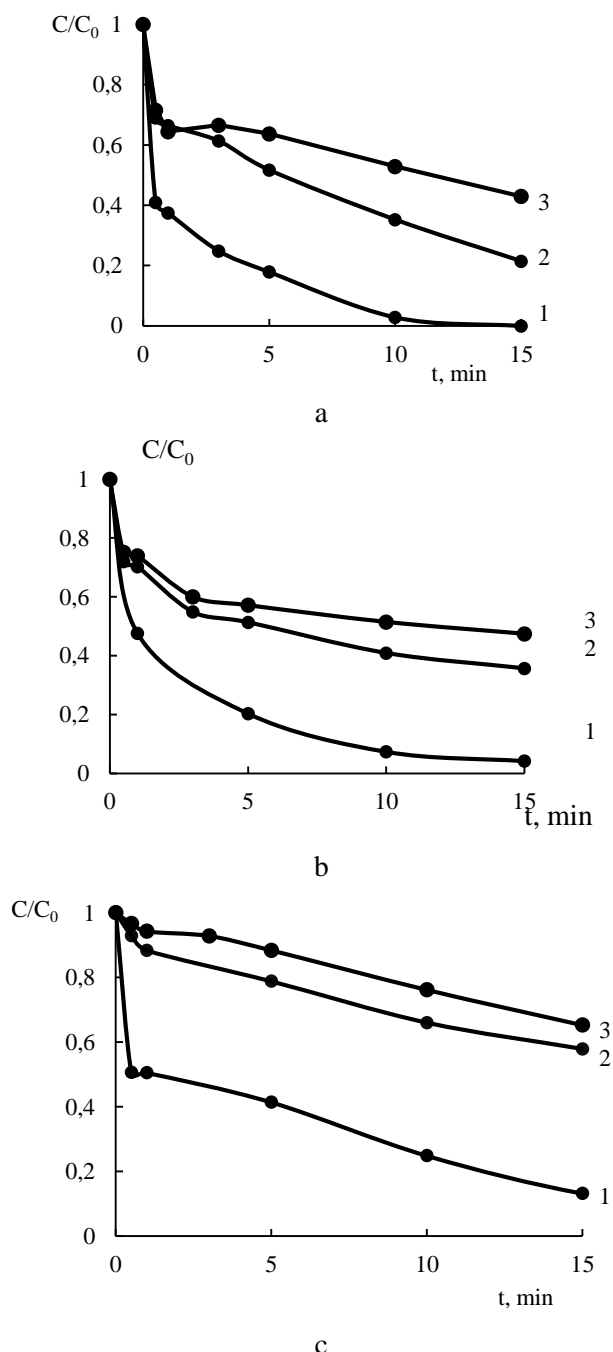

a

b

c

Fig. Kinetic curves of atrazine degradation in the ferrous-persulfate system without (1) and in the presence of t-buthanol (2) and methanol (3) in deionized (a), natural (b) and wastewater (c)

Рис. Кинетические кривые деструкции атразина в железо-персульфатной системе без (1) и в присутствии t-бутанола (2) и метанола (3) в деионизованной (a), природной (b) и сточной воде (c)

ATZ was completely degraded in the absence of alcohols, whereas the degradation in the presence of ferrous-persulfate scavengers was remarkably inhibited, indicating the involvement of both SO$_4$•$^-$ and •OH in the oxidation (Figure). Assuming that ATZ was degraded by SO$_4$•$^-$ in the presence of *t*-BuOH (which faster scavenges •OH), the contribution of •OH can be obtained as the arithmetical difference between the degradation efficiency with *t*-BuOH and without both alcohols [6]. Accordingly, ATZ was 100% degraded after 15 min treatment of DW and NW in the absence of alcohols and SO$_4$•$^-$ appears to be the primary radical formed: 79% SO$_4$•$^-$ and 21% •OH in DW, 60% SO$_4$•$^-$ and 40% •OH in NW). However, in WW, SO$_4$•$^-$ and •OH equally contributed to 87% ATZ degradation in 15 min. This observation was in agreement with previous studies [4-6], where SO$_4$•$^-$ was found to be the primary radical during the persulfate oxidation of organic pollutants.

CONCLUSIONS

Sulfate radical anion and hydroxyl radical are most effectively generated in the ferrous-persulfate system. Though total •OH and SO$_4$•$^-$ exposure in urban wastewater was lower than in natural water, DOM of wastewater demonstrated higher photoreactivity in terms of •OH production in UV system. The estimated contributions of •OH and SO$_4$•$^-$ to the degradation of herbicide atrazine make the UV/PS/Fe^{2+} system with KrCl excilamp be promising for oxidation of bioresistant organic pollutants in water and wastewater.

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