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# EVIDENCE OF THE HYDROXYL RADICAL FORMATION UPON THE PHOTOLYSIS OF AN IRON-RICH CLAY IN AQUEOUS SOLUTIONS

**Xu Zhang[a], Feng Wu[a*], Nansheng Deng[a], Ivan P. Pozdnyakov[b], Evgeni M. Glebov[b*], Vjacheslav P. Grivin[b], Victor F. Plyusnin[b] and Nikolai N. Bazhin[b]**

[a]School of Resources and Environmental Science, Wuhan University
Wuhan 430079, P.R. China
[b]Institute of Chemical Kinetics and Combustion SB RAS, Novosibirsk 630090, Russian Federation; Novosibirsk State University, Novosibirsk 630090, Russian Federation

**Abstract**

With the use of laser flash photolysis, the formation of hydroxyl radicals upon the photolysis of an iron-rich clay (montmorillonite KSF) was demonstrated. The $^{\bullet}OH$ radical was shown to be formed by the photolysis of the $Fe(OH)_{aq}^{2+}$ complex that escaped from the clay into the solution bulk.

*Keywords*: Clay, laser flash photolysis, hydroxyl radical, iron

## INTRODUCTION

In many publications, clays are reported as inexpensive raw materials in a large diversity of industrial processes, pharmaceutical industry, cosmetics, organic synthesis and environmental remediation [1, 2]. Among the clays, montmorillonite was found to be one of the most useful as a catalyst for a wide number of organic reactions [3].

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* Corresponding authors. Tel: 86-27-68778511; Fax: 86-27-68778511
  E-mail: fengwu@whu.edu.cn (F. Wu). Tel: 7-383-3332385; Fax: 7-383-3307350
  E-mail: glebov@kinetics.nsc.ru (E.M. Glebov)

Clay-induced photochemistry can play an important role in the self-purification of natural aqueous systems [4, 5]. There are also several reports on the use of clays in the photodegradation and photooxidation of organic compounds. In these publications, the authors studied both a natural clay [6, 7] and the clay modified with different reagents (such as dye and/or metal [8], or cationic surfactant [9]) to enhance both adsorption of organic pollutants and the generation of singlet oxygen. Therefore, clay particles may be used as photocatalysts in organic chemical synthesis as well as in pollutant removal.

Although there are some reports on the photochemical reactions of clays [10], the nature and origin of the reactive oxygen species involved are still unclear. For example, Gournis *et al.* based on the spin trapping experiments, reported the formation of hydroxyl radicals catalyzed by clay surfaces [11]. Unfortunately, the authors provided no quantitative data and did not describe if their experiments were carried out in the dark or under irradiation. Furthermore, the use of spin traps can provide only the detection of final products of a long reaction pathway. Therefore, this method cannot clarify the mechanism of the adduct formation between a spin trap and a radical, because the adduct can be formed either in a direct reaction (radical + trap) or in some other processes. In contrast to this [11], Kong and Ferry believed that only $^1O_2$ was responsible for the enhanced photooxidation of chrysene (a polycyclic aromatic hydrocarbon) in aqueous suspensions of montmorillonite clay [6].

It seems that there is a conflict between the previous publications and there still many issues remain to be clarified. First of all, one must provide a direct experimental evidence of the existence of reactive oxygen species generated on the clay. From this standpoint, the use or development of various probes to trap possible intermediate species is highly desired.

The current study evidences the $^\bullet$OH radical formation by means of laser flash photolysis, which is a direct time-resolved method. The information obtained is complementary to the data of the work by Gournis *et al.* [11], and provides new evidence of hydroxyl radicals produced by iron-rich clays under illumination.

## EXPERIMENTAL

### Reagents and preparation of samples

Montmorillonite KSF (Sigma-Aldrich) and kaolinite (Fluka) were used for the experiments. The chemical compositions of clays are listed in Table 1. Methyl viologen dichloride hydrate, 98% (Aldrich), was used as a source of $MV^{2+}$ dications (Fig. 1a).

**Table 1**

Major chemical composition (%) of the clays used in this work[*]

| Clays | $SiO_2$ | $Al_2O_3$ | $SO_3$ | $Fe_2O_3$ | MgO | CaO | $Na_2O$ |
|---|---|---|---|---|---|---|---|
| KSF | 49.1 | 16.3 | 22.3 | 4.76 | 4.3 | 2.3 | 0.06 |
| Kaolinite | 56.1 | 39.1 | 0.03 | 0.6 | 0.15 | 0.11 | 0.04 |

[*] Determined by Wavelength Dispersion X-Ray Fluorescence Spectrometry
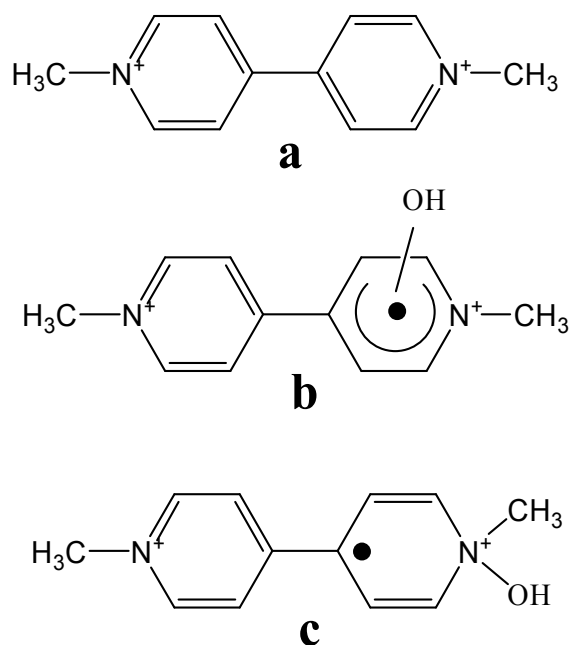
**Fig. 1.** Molecular structure of the methyl viologen dication (**a**) and possible structures of the MV($^\bullet$OH)$^{2+}$ radical (**b**, **c**)

The samples were prepared by using deionized water. Typically, the initial content of clay was 10 g/L. After 60 min sedimentation, the upper fraction of the mixture was taken and used for the experiments. The pH of the solutions was about 3.0, which prevented the Fe(III) hydrolysis. To remove oxygen, the samples were bubbled with argon for 15 min. If necessary, the samples were centrifuged before photolysis (for 10 min with a rotation speed corresponding to 4400 g).

The concentrations of Fe(II), Fe(III) and $SO_4^{2-}$ in solutions were determined by using the following typical analytical procedures. Fe(II) was quantified by the addition of 1,10-phenanthroline and measuring the absorption of the Fe(II)-phenanthroline complex at 510 nm [12]. To measure the concentration of Fe(III), it was reduced to Fe(II) by hydroquinone. When the reduction (monitored by UV spectroscopy) was completed, the concentration of Fe(II) was determined by the 1,10-phenanthroline method. The concentration of $SO_4^{2-}$ was determined by the gravimetric method (with addition of $BaCl_2$) [13]. The concentrations of inorganic species in the solutions were calculated using a visual MINTEQ software [14].

**Laser flash photolysis setup**

Laser flash photolysis was performed with the excitation by a YAG laser (355 nm, 5-6 ns, 40 mJ/pulse) as described elsewhere [15]. All the experiments were carried out in a 1 cm quartz cuvette at 298 K. The oxygen-free condition was ensured by bubbling the solutions with argon for 15 min before flash irradiation and by stirring the solution with argon throughout the experiments. The samples for flash photolysis were used until a 10% decrease in the UV absorption. The UV absorption spectra were recorded using an HP-8453 spectrophotometer (Hewlett Packard).

**RESULTS AND DISCUSSION**

**Content and UV-Vis spectra of iron complexes in the solutions**

Complexes formed by Fe(II), Fe(III) and $SO_4^{2-}$ were expected to be the main species in the clay solutions. The total concentrations of these components in the montmorillonite KSF samples are listed in Table 2. Only 8% of the total amount of iron was extracted to the solution bulk, and the concentration of Fe(II), which is formed during the iron extraction from the clay, was ca. 30% higher than that of Fe(III). The fact that under mildly acidic conditions Fe(II) is preferentially removed from montmorillonite with respect to Fe(III) is known in the literature [16]. The concentration of sulfate anions in the solutions corresponds to complete sulfur removal from the clay particles.

Equilibrium concentrations of these complexes in the montmorillonite KSF solution are listed in Table 3. $Fe_{aq}^{2+}$ and $FeSO_4$ are the main Fe(II) complexes in the solution; $Fe(SO_4)^+$, $Fe(SO_4)_2^-$ and $Fe(OH)_{aq}^{2+}$ are the major complex forms of Fe(III).

**Table 2**

Major chemical composition of the solution bulk in the montmorillonite
KSF suspensions (10 g/L)

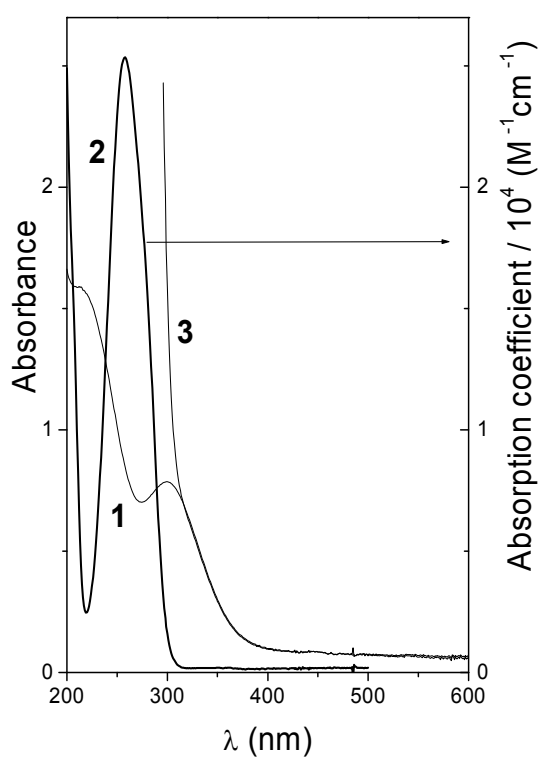| Ions | Fe(II), total | Fe(III), total | $SO_4^{2-}$ |
|---|---|---|---|
| Concentration (M) | $2.8 \times 10^{-4}$ | $2.1 \times 10^{-4}$ | $2.8 \times 10^{-2}$ |
| % of the maximal possible concentration | 4.6 | 3.4 | 100 |



**Fig. 2.** UV absorption spectra of the clay suspension and methyl viologen
dication. Curve 1 (left axis) — montmorillonite KSF, 10 g/L, pH = 3.3, upper
fraction after 60 min of sedimentation in a 1 cm cuvette; curve 2 (right axis) —
the spectrum of $MV^{2+}$; curve 3 (left axis) — the spectrum of sample containing
montmorillonite KSF, 10 g/L, upper fraction after 60 min of sedimentation, and
$10^{-3}$ M of $MV^{2+}$ (pH = 3.3, cuvette 1 cm)

The UV absorption spectrum of the clay sample (montmorillonite KSF) used
in this work is shown in Fig. 2 (curve 1). The optical density of the solutions in

the region of 400-600 nm (curve 1, Fig. 2) is due to the light scattering of the smallest clay particles, for which the sedimentation time exceeds 60 min. The maximum at 300 nm belongs to Fe(III) complexes. The absorption spectra of $Fe(SO_4)^+$ and $Fe(OH)_{aq}^{2+}$ are very similar. UV spectra of both these complexes demonstrate maxima in the region of 300 nm with the absorption coefficient of *ca*. 2000 $M^{-1} cm^{-1}$ [17]. Complexes of Fe(II) do not demonstrate any remarkable absorption at $\lambda < 250$ nm [18, 19].

The methyl viologen dication (curve 2 in Fig. 2) has no significant absorption at the excitation wavelength (355 nm), which makes it suitable as an acceptor of radicals. The typical UV spectrum of the samples prepared for the experiment is demonstrated with curve 3 in Fig. 2.

**Laser flash photolysis**

The clay samples were examined by the laser flash photolysis for the photolytic formation of hydroxyl radicals. The methyl viologen dication ($MV^{2+}$) was used to capture the nascent hydroxyl radicals.

The addition reaction of the $^\bullet OH$ radical with the $MV^{2+}$ (eq. 1) results in the formation of an intermediate having an absorption band with the maximum at 470 nm [20, 21]. The rate constant of reaction (1) in aqueous solutions obtained by pulse radiolysis is $k_1 = (2.5 \pm 0.2) \times 10^8$ $M^{-1} s^{-1}$, and the maximum absorption coefficient (at 470 nm) is $(16000 \pm 700)$ $M^{-1} cm^{-1}$ [21].

$$MV^{2+} + {}^\bullet OH \rightarrow MV({}^\bullet OH)^{2+} \tag{1}$$
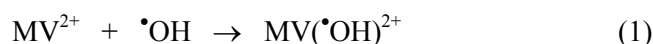
The structure of the $MV({}^\bullet OH)^{2+}$ radical is not really established in the literature. Solar *et al*. [21] proposed the formation of $^\bullet OH$ adducts on a ring carbon atom (Fig. 1b). This idea was also supported by Bahnemann *et al*. [22] after the analysis of the final reaction products. On the other hand, Das *et al*. [23], on the base of quantum chemical calculations, stated that the preferred sites for $^\bullet OH$ radical addition are the N atoms of the $MV^{2+}$ dication. In the latter case, a N-hydroxycyclohexadienyl-type radical is formed (Fig. 1c). However, for the goals of the current study, the structure of the addition radical is not of importance.

The clay samples without $MV^{2+}$ did not demonstrate any intermediate absorption. When $MV^{2+}$ was added, the kinetics of formation and decay of the intermediate were recorded. The typical kinetic curve at 470 nm is shown in Fig. 3. The intermediate absorption spectrum corresponding to the maximum absorption signal (ca. 7 µs) is demonstrated in Fig. 4. The spectrum belongs to the $MV({}^\bullet OH)^{2+}$ radical cation [20, 21] formed in reaction (1). Taking the maximum absorption coefficient of the radical equal to 16000 $M^{-1} cm^{-1}$ [19], one can calculate that the maximum concentration of the radicals is *ca*. $4 \times 10^{-7}$ M.
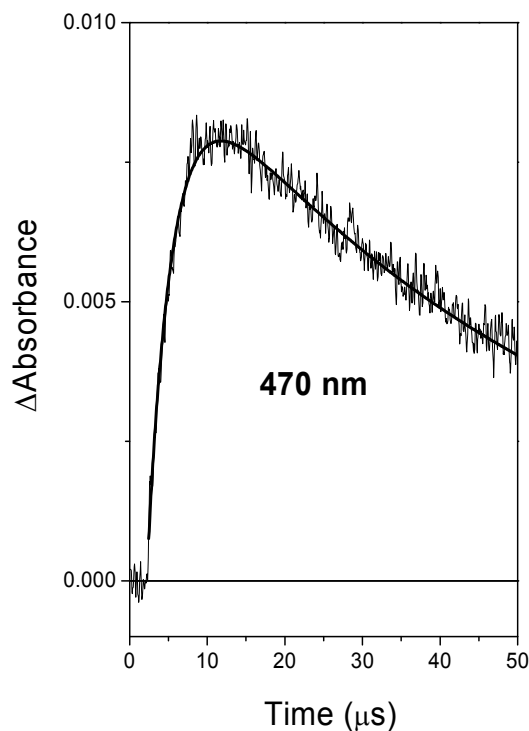
**Fig. 3.** Laser flash photolysis of montmorillonite KSF clay. Noisy line is the kinetics at 470 nm (upper fraction of 10 g/L clay suspension after 60 min of sedimentation and $1 \times 10^{-3}$ M of $MV^{2+}$, pH = 3.3), cuvette 1 cm. Thick line is the approximation with a two-exponential function (see the text)

The intermediate absorption spectrum (Fig. 4) could be explained with the assumption that Fe(III) complexes are the subject of photolysis in the solution bulk. In the case of montmorillonite KSF suspensions, two species of those listed in Table 3 absorb laser radiation at 355 nm. These are $Fe(SO_4)^+$ and $Fe(OH)_{aq}^{2+}$ complexes. The concentration of the sulfate complex is 7.7 times higher than that of the hydroxocomplex (see Table 3). The absorption coefficients of these two complexes at 355 nm are almost equal [17]. Primary products of the photolysis of $Fe(OH)_{aq}^{2+}$ and $Fe(SO_4)^+$ are the $^{\bullet}OH$ and $SO_4^{\bullet-}$ radicals, respectively [17]. The quantum yields of photolysis at 355 nm are 0.0016 for $Fe(SO_4)^+$ and 0.085 for $Fe(OH)_{aq}^{2+}$ [17]. As a result, the concentration of $SO_4^{\bullet-}$ radicals formed in the solution is estimated as 14% of the $^{\bullet}OH$ radical concentration. The $SO_4^{\bullet-}$ radical anion has a visible absorption band with a maximum at 455 nm, and absorption coefficient 1600 $M^{-1} cm^{-1}$ [24]. In our case, its absorption is too low to be recorded.
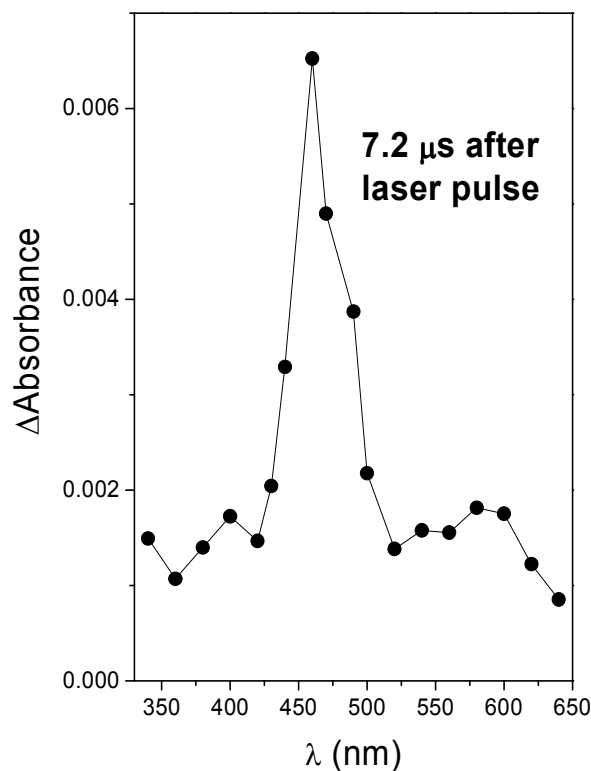
**Fig. 4.** Laser flash photolysis of montmorillonite KSF clay. Intermediate absorption spectrum recorded at 7.2 μs after the laser pulse. Upper fraction of the 10 g/L clay suspension after 60 min of sedimentation and $1 \times 10^{-3}$ M of $MV^{2+}$, pH = 3.3)

The kinetic curves obtained for the clay suspensions (Fig. 3) were satisfactorily fitted with a two-exponential function. The result of the fit is shown in Fig. 3 as a thick curve. The values of the effective rate constants obtained from the fitting are $(3.1 \pm 0.3) \times 10^5\,s^{-1}$ for the increase in the intermediate absorption and $(1.9 \pm 0.2) \times 10^4\,s^{-1}$ for its decay. Assuming that the intermediate is formed in reaction (1) that proceeds in the solution bulk, one can obtain the rate constant $k_1 = (3.1 \pm 0.3) \times 10^8\,M^{-1}\,s^{-1}$. This is close to the value of $(2.5 \pm 0.2) \times 10^8\,M^{-1}\,s^{-1}$ obtained by Solar *et al.* [21]. The proximity of these rate constants indicates that the $MV(^{\bullet}OH)^{2+}$ radical cation is probably formed in the solution bulk.

**Table 3**

Major complexes in the montmorillonite KSF suspensions (10 g/L)[*]

| Iron valence | Complex | Concentration (M) | % of total amount |
|---|---|---|---|
| Fe(II) | $Fe_{aq}^{2+}$ | $1.44 \times 10^{-4}$ | 51.5 |
|  | $FeSO_4$ | $1.36 \times 10^{-4}$ | 48.5 |
| Fe(III) | $Fe_{aq}^{3+}$ | $5.7 \times 10^{-6}$ | 2.7 |
|  | $Fe(OH)_{aq}^{2+}$ | $2.1 \times 10^{-5}$ | 9.9 |
|  | $Fe(OH)_2^{+}$ | $2.4 \times 10^{-6}$ | 1.1 |
|  | $Fe(SO_4)^{+}$ | $1.6 \times 10^{-4}$ | 76.1 |
|  | $Fe(SO_4)_2^{-}$ | $2.1 \times 10^{-5}$ | 9.9 |

[*] Equilibrium data were calculated by Visual MINTEQ software [14] with the initial contents of ions listed in Table 2. Final pH = 3.08

The mechanism of the reactions in heterogeneous systems was proposed to consist of the following stages:
1. The extraction of Fe(III) cations from the clay to the solution bulk with the formation of Fe(III) complexes (see Tables 2, 3).
2. The photolysis of $Fe(OH)_{aq}^{2+}$ in the solution bulk with the formation of $^{\bullet}OH$ radicals [17, 25].
3. Reaction (1), which occurs in the solution bulk.

To check the hypothesis that hydroxyl radicals in the clay samples are formed due to photolysis in the bulk, experiments with centrifuged samples were performed. After centrifuging, the particulate matter was completely removed from the samples. The absorption of the $MV(^{\bullet}OH)^{2+}$ intermediate remained the same as shown in Fig. 3. This evidences that the dissolved Fe(III) (forming $Fe(OH)_{aq}^{2+}$ complexes) is responsible for the formation of the $^{\bullet}OH$ radicals upon the photolysis of the aqueous clay samples.

The similarity of photochemical processes for the clays and the Fe(III) hydroxocomplex was demonstrated by experiments on the direct photolysis of $Fe(OH)_{aq}^{2+}$ in the presence of methyl viologen. The results are shown in Fig. 5. The initial concentration of Fe(III) was comparable with the total concentration of Fe(III) in the clay samples. Figure 5a shows a typical kinetic curve, and Fig. 5b presents the absorption spectrum of the intermediate attributed to the $MV(^{\bullet}OH)^{2+}$ radical cation. A difference in the maximal absorption between Fig. 2, Fig. 3 and Fig. 5 is explained by a larger concentration of $Fe(OH)_{aq}^{2+}$ in the homogeneous sample.
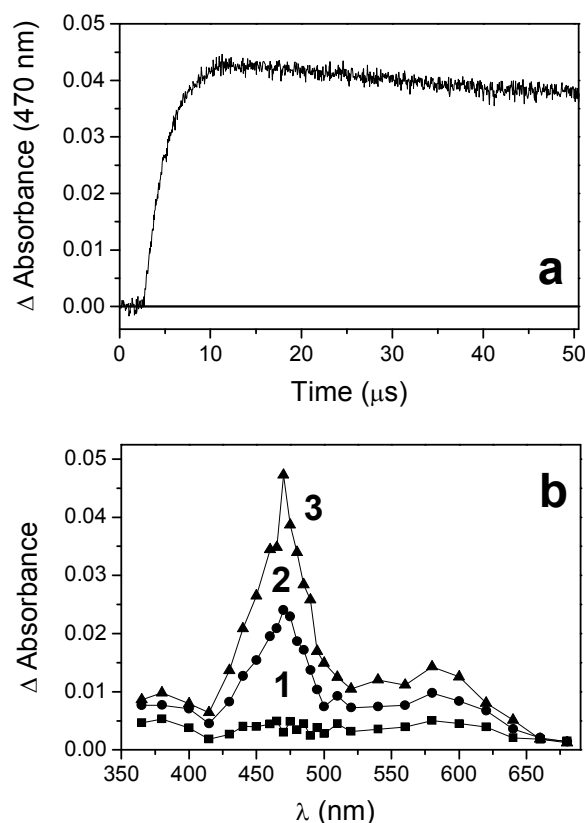
**Fig. 5.** Laser flash photolysis (355 nm) of aqueous solutions (pH = 3.0) of $FeOH_{aq}^{2+}$ ($3.5 \times 10^{-4}$ M) in the presence of $MV^{2+}$ ($1 \times 10^{-3}$ M). Temperature 298 K, cuvette 1 cm, Ar-saturated solutions. **a** — a typical kinetic curve (470 nm), **b** — spectra of an intermediate absorption. Curves 1-3 correspond to 0.4, 2.0, and 10.0 μs after the laser pulse

The last question to be discussed in this paper is the nature of the decay of the $MV(^{\bullet}OH)^{2+}$ radical cation. According to Solar *et al.* [21], the main pathway of its disappearance in aqueous solutions is disproportionation (eq. 2) with the rate constant $2k_2 = (1.3 \pm 0.2) \times 10^8$ $M^{-1}\,s^{-1}$.

$$2\,MV(^{\bullet}OH)^{2+} \quad \rightarrow \quad \text{products} \qquad\qquad (2)$$

Das *et al.* [23] stated that the radical decay is a mixed-order reaction, but did not present any quantitative data; note that both the structure of the $MV(^{\bullet}OH)^{2+}$ radical and its reactions in homogeneous solutions require further research.

Based on the data of [21], the characteristic lifetime of the radical cation due to self-reaction (2) could not be less than 20 ms (the initial concentration of MV($^{\bullet}$OH)$^{2+}$ was estimated as $4 \times 10^{-7}$ M). In our case (Fig. 3), the characteristic time of the MV($^{\bullet}$OH)$^{2+}$ decay was ca. 50 μs. The shorter lifetime of the radical cation in the clay-containing system can probably be explained by the reactions in the solution bulk with the species extracted from the clay (e.g., complexes of bivalent iron). The heterogeneous decay of radical cations on the surface of small clay particles (colloid nanoparticles could remain in the solution even after centrifuging) is also possible. However, as it was already mentioned, the decay of MV($^{\bullet}$OH)$^{2+}$ (even in homogeneous solutions) should be a subject of further investigation.

## CONCLUSION

The current work provides an evidence of the $^{\bullet}$OH radical formation upon the photolysis of an iron-rich clay montmorillonite KSF in aqueous solutions using the direct time-resolved method of laser flash photolysis. The information obtained is complementary to the data in the work by Gournis *et al.* [11]. The most probable mechanism of hydroxyl radical formation is the photolysis of Fe(OH)$_{aq}^{2+}$ complex in the solution bulk.

The $^{\bullet}$OH radical was not observed upon the photolysis of kaolinite suspensions. This is probably because the amount of iron(III) extracted from kaolinite to the solution was too small to provide an observable concentration of $^{\bullet}$OH radicals.

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