



## Near-UV photooxidation of As(III) by iron species in the presence of fulvic acid



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### HIGHLIGHTS

- Photooxidation of As(III) in ternary As(III)–Fe(III)–Fulvic acid system was investigated.
- Quantum yields of Fe(II) production and As(III) photooxidation were obtained.
- At all values of [FA]/[Fe] ratio the main photoactive species is •OH radical.
- Addition of fulvic acid leads to mainly negative effect on As(III) photooxidation.

### ARTICLE INFO

#### Article history:

Received 17 February 2017

Received in revised form

5 April 2017

Accepted 23 April 2017

Available online 24 April 2017

Handling Editor: X. Cao

#### Keywords:

Arsenite

Arsenate

Iron complexes

•OH radical

Photooxidation

Humic substances

Fulvic acid

ICP-AES

Stationary photolysis

### ABSTRACT

Photooxidation of As(III) in ternary As(III) – Fe(III) – Fulvic acid system at pH 4 was investigated by optical spectroscopy, steady-state photolysis (365 nm) and atomic-emission spectrometry with inductively coupled plasma techniques. It was found that at all values of [FA]/[Fe] ratio the main photoactive species is •OH radical formed by photolysis of Fe(III) hydroxocomplexes. Addition of fulvic acid leads to mainly negative effect on As(III) photooxidation due to the following reasons: (i) slow dark reduction of photoactive Fe(III) species with formation of scattering particles and photoinert Fe(II) species; (ii) formation of photoreductive Fe(III)–FA complexes incapable to oxidize As(III), (iii) competition of both FA and Fe(III)–FA complexes for UVA quanta with FeOH<sup>2+</sup> complex and for •OH radicals with As(III). Aging of ternary system is also very important parameter leading to one order decrease of quantum yields of both Fe(II) formation and As(III) photooxidation.

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### 1. Introduction

Due to arsenic mobility, carcinogenicity and toxicity much attention was paid nowadays to (geo)chemistry and transformation of As(III) species in environment (Cheng et al., 2009; Cullen and

Reimer, 1989; Han et al., 2011). In natural waters arsenic exists in two main inorganic forms: arsenite in the form of H<sub>3</sub>As(III)O<sub>3</sub> and arsenate in the form of H<sub>2</sub>As(V)O<sub>4</sub><sup>−</sup> and HAs(V)O<sub>4</sub><sup>2−</sup>. Organic forms of arsenic in environment are monomethylarsonic and dimethylarsinic acids. Average concentration of dissolved arsenic in natural waters is about 1.4 μg L<sup>−1</sup>, however this parameter is varied greatly: 0.1–75 μg L<sup>−1</sup> (Cullen and Reimer, 1989; Sorg et al., 2014). Moreover, acid mine drainage (AMD) and industrial As-contaminated wastewater may contain as high concentrations of arsenic and iron as several tens and hundreds mg L<sup>−1</sup>, accordingly

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(Amirbahman et al., 2006; Bednar et al., 2005; Morin et al., 2003). Arsenite to arsenate ratio is far from thermodynamic equilibrium due to microorganism activity and some abiotic factors and in average about 20% of total arsenic in nature is presented as mobile and toxic As(III) species. In opposite, photochemical reactions under sunlight and artificial UV light accelerate oxidation of arsenite to arsenate leading to formation less toxic and mobile forms of As(V) (Bissen et al., 2001; Hug and Leupin, 2003; Reav and Asher, 1977).

Dissolved ions and (hydr)oxides of transition metals, especially iron, play an important role in arsenic (geo)chemistry as they provide oxidation, coprecipitation/adsorption of arsenic and reduce rate of its species migration in natural waters (Cheng et al., 2009; Cullen and Reimer, 1989; Sadiq et al., 2002; Song et al., 2015). Another important feature of iron compounds is their (photo)catalytic effect on As(III) oxidation by dissolved oxygen and hydrogen peroxide to As(V) species which are usually less toxic and more easily adsorbed on mineral supports (Cheng et al., 2009; Hug et al., 2001; Hug and Leupin, 2003; Emmett and Khoe, 2001; Kocar and Inskeep, 2003). Also arsenic is partially bound by humic (HS) substances (by humic (HA) and fulvic (FA) acids mainly) and this process could compete with coprecipitation with iron (hydr)oxides (Langston, 1980; Thanabalasingam and Pickering, 1986). Formation of mixed As(V)-Fe(III)-HS complexes is also possible and leads to change in mobility, bioavailability and solubility of arsenic species (Mikutta and Kretzschmar, 2011; Liu et al., 2011).

In our recent works (Ding et al., 2016; Pozdnyakov et al., 2016) we studied As(III) photooxidation in binary Fe(III) – As(III) and FA – As(III) systems and demonstrated that both systems provide effective photooxidation of As(III) to As(V). In the first system the oxidation was induced by the formation of  $\cdot\text{OH}$  radicals via photolysis of  $\text{FeOH}^{2+}$  complexes at  $[\text{As}] < 50$  ppm or via charge transfer from coordinated  $\text{H}_2\text{As(III)O}_3^-$  ligand to  $\text{Fe}^{3+}$  ion at  $[\text{As}] > 1000$  ppm (Pozdnyakov et al., 2016). In the second system generation of FA triplet state and reactive oxygen species (ROS) were proposed to explain observed As(III) photooxidation. It should be noted that the experimental conditions in these works were rather far from natural ones (acidic pH, short irradiation wavelengths, high loading of all reagents). Another problem related to simultaneous presence of both Fe(III) ions and HS in natural surface waters which can lead to formation of Fe(III)-HS and As(III)-Fe(III)-HS complexes and partial Fe(III) reduction (Mikutta and Kretzschmar 2011; Liu et al., 2011; Pullin and Cabaniss, 2003a,b). Taking into account these facts the investigation of As(III) evolution in ternary As(III) – Fe(III) – HS system is of high interest.

This work is devoted to determination of As(III) photooxidation efficiency in ternary As(III) – Fe(III) – FA system at concentrations of reagents close to natural ones and pH 4. Main attention was paid to determination of quantum yield of As(III) photooxidation and its dependence on such parameters as  $[\text{FA}]/[\text{Fe(III)}]$  ratio and aging of samples. Influence of the last parameter very rarely discussed in the literature (Pullin and Cabaniss, 2003a) though aging of Fe(III) – FA solutions could greatly modify observed photochemical activity.

## 2. Experimental

$\text{Fe}(\text{ClO}_4)_3$  hydrate (Aldrich), sodium metaarsenite  $\text{NaAsO}_2$  (97%, from Xiya Reagent Center, Sichuang, China), sodium arsenate  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$  (99%, from Alfa Aesar, A Johnson Matthey Co., Tianjin, China) served as sources of Fe(III), As(III) and As(V) respectively. Fulvic acid (Aladdin Industrial Corporation), H108498, CAS: 1415-93-6 (Fulvic acid content  $>90\%$ , moisture  $\leq 2\%$ , chloride (Cl)  $\leq 0.05\%$ , Sulfate ( $\text{SO}_4$ )  $\leq 0.05\%$ , ignition residue  $\leq 0.5\%$ ; C, 39.32%; H, 3.77%; N, 1.03%) was used without additional purification. Trace metal grade hydrochloric acid and nitric acid were

obtained from Reactive (Novosibirsk, Russia). All other chemicals used were of analytical grade or better. Deionized water was prepared using an Ultra Clear (SG, Barsbuttel, Germany) and was used for preparation of reference and samples solutions. pH value was controlled by ion-meter ANION-4100 (LTD Infraspak-Analit, Russia) with combined electrode ESK-10614.

Typical concentrations of total As, iron species and humic substances in surface waters (rivers, lakes and swamps) as well as pH values can vary in rather big range (Table S1). In our work FA concentration was varied from 0 to  $10 \text{ mg L}^{-1}$ , As(III) and Fe(III) concentrations were fixed at  $0.2 \text{ mg L}^{-1}$  and  $1.12 \text{ mg L}^{-1}$  (or  $2 \times 10^{-5} \text{ M}$ ), accordingly, pH of solutions was adjusted at 4. Four systems were investigated with  $[\text{FA}]/[\text{Fe(III)}]$  ratio of 0:1; 1:1; 3:1 and 9:1, accordingly. These conditions roughly correspond to acidic iron-reach surface waters contaminated by As(III) with low to middle content of humic substances.

Optical spectra were recorded using Agilent 8453 spectrophotometer (Agilent Technologies). All stationary photolysis experiments were carried out in quartz cell with optical path 5 cm and total volume 10 ml at the temperature of 298 K under atmospheric pressure. High-pressure mercury lamp (DRSh-500) with water and glass filters for separating of the 365 nm line of mercury was used as irradiation source. For calculation of As(III) photooxidation quantum yield (mean error 20%) lamp intensity was determined by a ferrioxalate actinometer in the same photochemical cell (Weller et al., 2013). The Fe(II) concentration at various photolysis times was measured by addition of the chelating agent o-phenanthroline to the irradiated solution and subsequent measurement of the absorption of the  $[\text{Fe(II)}(\text{phen})_3]^{2+}$  complex at 510 nm (the molar absorption coefficient of the complex at 510 nm is  $11,000 \text{ M}^{-1}\text{cm}^{-1}$ ) (Weller et al., 2013). In all photochemical studies results of duplicate or triplicate experiments were averaged.

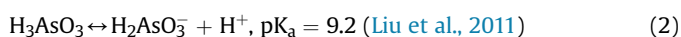
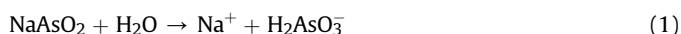
Atomic-emission spectrometry with inductively coupled plasma (ICP-AES) equipped with Opal Mist nebulizer (iCap 6500 Duo, Thermo Scientific, US) and Hydride Generation additive (Thermo Scientific, US) was applied for total arsenic and As(III) determination in solutions. The data processing was provided by iTEVA software (Thermo Scientific, USA).

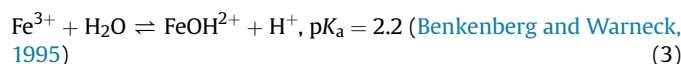
Total arsenic content was determined by ICP-AES using scandium as internal standard at the following working parameters: power supply 1150 W; argon flows,  $\text{L min}^{-1}$ : 0.7 for the nebulizer, auxiliary - 0.5, cooling - 12. For determination of As(III) hydride generation technique in combination with ICP-AES detection was used. A continuous flow hydride generation system is comprised of three units: peristaltic pump for the reagents and sample introduction, a reaction chamber and a gas liquid separator. As a reductant 0.5% sodium borohydride stabilized by 0.05% sodium hydroxide was used. The plasma parameters were optimized to get the best signal to noise ratio: power supply 1350 W; argon flows,  $\text{L min}^{-1}$ : 0.5 for the nebulizer, auxiliary - 0.5, cooling - 12. The calibration was done at the concentration range of  $0.00001\text{--}1 \text{ mg L}^{-1}$ . In all cases the concentration of hydrochloric acid was kept at the level of 10%. ICP-AES method exhibit precision about 10% in region of As(III) concentration used in the study.

## 3. Results and discussion

### 3.1. Optical spectroscopy of As(III) – Fe(III) – FA systems

At pH 4 main forms of As(III) and Fe(III) are  $\text{H}_3\text{AsO}_3$  and  $\text{FeOH}^{2+}$  formed by hydrolysis of corresponding salts:

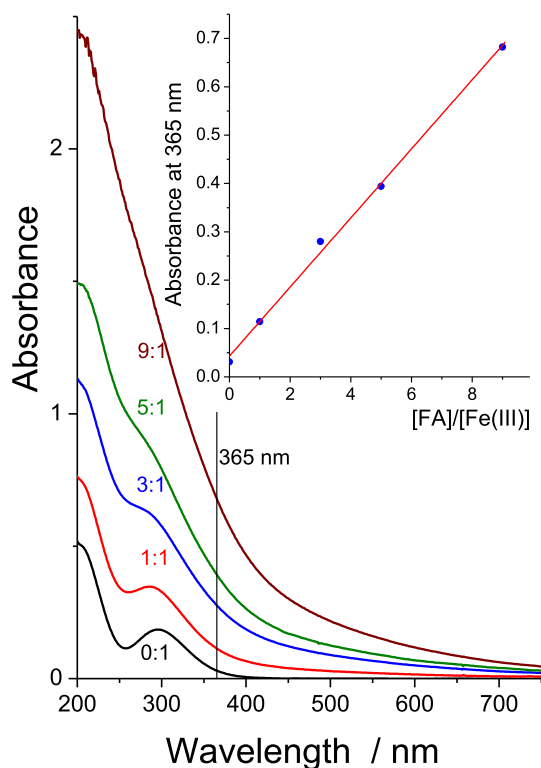




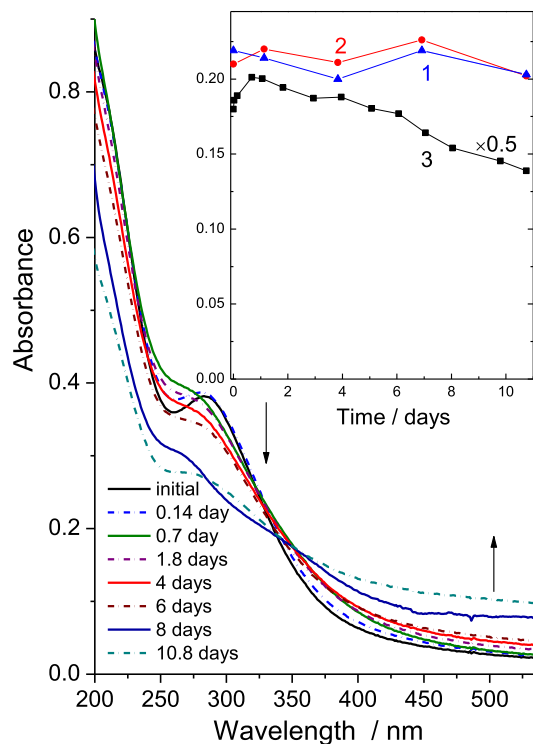
It is worth noting that  $\text{H}_3\text{AsO}_3$  has negligible absorption at  $\lambda > 240$  nm and main near-UV absorbing species are Fe(III) complexes and FA, accordingly (Fig. S1). The UV spectrum of the solution without FA (Fig. 1, black curve) was determined mainly by the absorption of  $\text{FeOH}^{2+}$  complex ( $\lambda_{\text{max}} = 297$  nm,  $\epsilon_{\text{max}} = 1985$   $\text{M}^{-1} \text{cm}^{-1}$ ) (Benkenberg and Warneck, 1995). FA along demonstrates structureless absorption in UV–VIS region (Fig. S1) which is typical behavior of fulvic and humic acids (Nkhili et al., 2014; Twardowski et al., 2004; Yan et al., 2013). Addition of FA to Fe(III)-As(III) system leads to linear increase of optical density at excitation wavelength (365 nm) and disappearance of characteristic band of  $\text{FeOH}^{2+}$  complex due to formation of Fe(III)-FA complexes. Formation of complexes between negatively charged humic substances and  $\text{Fe}^{3+}$  ions were repeatedly demonstrated in literature (Ding et al., 2016; Mikutta and Kretzschmar 2011; Yan et al., 2013). Formation of Fe(III)-FA complexes and competition of FA for the light quanta with photoactive  $\text{FeOH}^{2+}$  complex should lead to decrease of As(III) photooxidation efficiency which was in fact demonstrated in stationary photolysis experiments (see paragraph 3.3 for details).

### 3.2. Stability of As(III) – Fe(III) – FA systems

It was observed that As(III) – Fe(III) – FA systems at all [FA]/[Fe(III)] ratio exhibit good stability of As(III) and total As content in the dark (Fig. 2) indicating the absence of thermal As(III) oxidation and adsorption in conditions used. pH of solutions exhibits small increase (+0.2 in average) during 11 days incubation in the dark at the room temperature with the final value 4.1–4.2. However optical



**Fig. 1.** Absorption spectra of As(III) – Fe(III) – FA system at different [FA]/[Fe(III)] ratio. [Fe(III)] and [As(III)] are 1.12 and 0.2  $\text{mg L}^{-1}$ , accordingly. Insert – dependence of absorbance at 365 nm on [FA]/[Fe(III)] ratio. Optical path length is 5 cm.



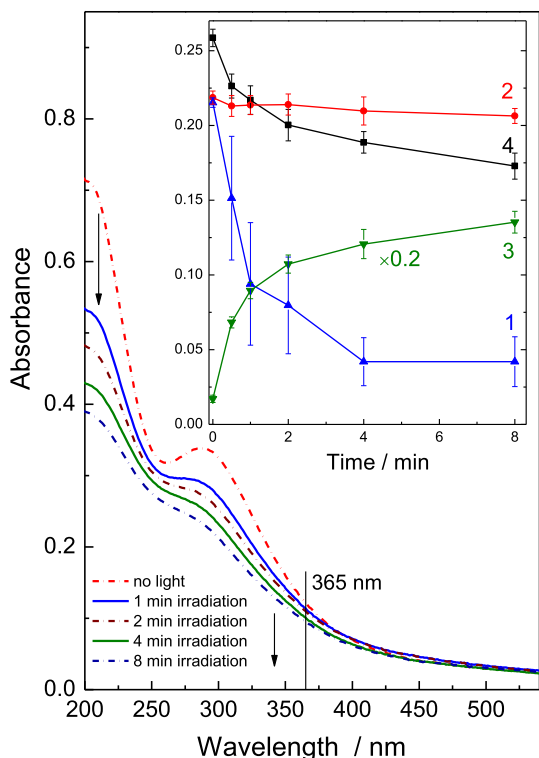
**Fig. 2.** Evolution of absorption spectrum of Fe(III) – As(III) – FA system at [FA]/[Fe(III)] = 1 during staying of the solution in the dark at room temperature. [FA] = [Fe(III)] = 1.12  $\text{mg L}^{-1}$ , [As(III)] = 0.22  $\text{mg L}^{-1}$ , pH 3.9. Insert – changes of As(III) (1) and total As (2) concentrations (in  $\text{mg L}^{-1}$ ) and absorbance at 260 nm (3). Optical path length is 5 cm.

properties of solutions are changed significantly during the incubation (Fig. 2). Accumulation of Fe(II) ions (Fig. S2), decrease of absorbance in the UV region and formation of scattering particles (visible both by eyes and spectrophotometrically) were observed. These facts allow one to conclude that evolution of As(III) – Fe(III) – FA systems is connected with aging of Fe(III) hydroxides (Knight and Sylva, 1975), Fe(III) reduction by reductive groups (amines, phenols) in the body of FA molecules (Pullin and Cabaniss, 2003a) and formation of Fe(III)/Fe(II) – FA colloids (Pullin and Cabaniss, 2003b). The most stable system is the one with the highest [FA]/[Fe(III)] ratio (Fig. S3) indicating stabilization of  $\text{Fe}^{3+}$  ions upon complexation with FA (Pullin and Cabaniss, 2003b).

### 3.3. As(III) photooxidation in As(III) – Fe(III) – FA systems

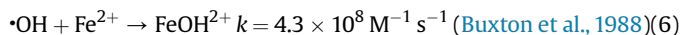
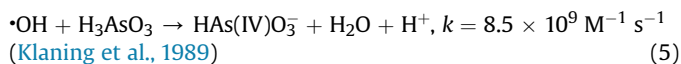
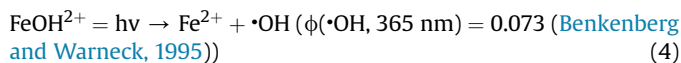
The excitation at 365 nm of As(III) – FA system (0.2  $\text{mg L}^{-1}$  As(III) and 5  $\text{mg L}^{-1}$  FA, pH 4) without addition of Fe(III) ions leads to very ineffective As(III) oxidation (quantum yield less than  $10^{-4}$ ). So transient species formed upon FA excitation by UVA light (triplet states and singlet oxygen (Ding et al., 2016; Makunina et al., 2015; Nkhili et al., 2014) are not effective in As(III) photooxidation. In opposite, the excitation of all the four As(III) – Fe(III) – FA systems at 365 nm leads to the following phenomena: (i) decay of absorption in UV region, (ii) accumulation of Fe(II) ions, (iii) decrease of As(III) concentration. Fig. 3 exhibits results for the system with 1:1 [FA]/[Fe(III)] ratio, similar behavior were observed for other systems too.

All these findings indicate existence of a redox process leading to As(III) photooxidation. It worth noting that rate of photochemical oxidation (minutes) was much faster than the rate of dark degradation of investigated systems (days) so the influence of the last

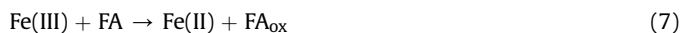


**Fig. 3.** Evolution of absorption spectrum of As(III) – Fe(III) – FA system at [FA]/[Fe(III)] = 1:1 during stationary photolysis (365 nm). [FA] = [Fe(III)] = 1.12 mg L<sup>-1</sup>, [As(III)] = 0.22 mg L<sup>-1</sup>, pH 3.9. Insert – changes of As(III) (1), total As (2) and Fe(II) (3) concentrations (in mg L<sup>-1</sup>) and absorbance at 320 nm (4). Optical path length is 5 cm.

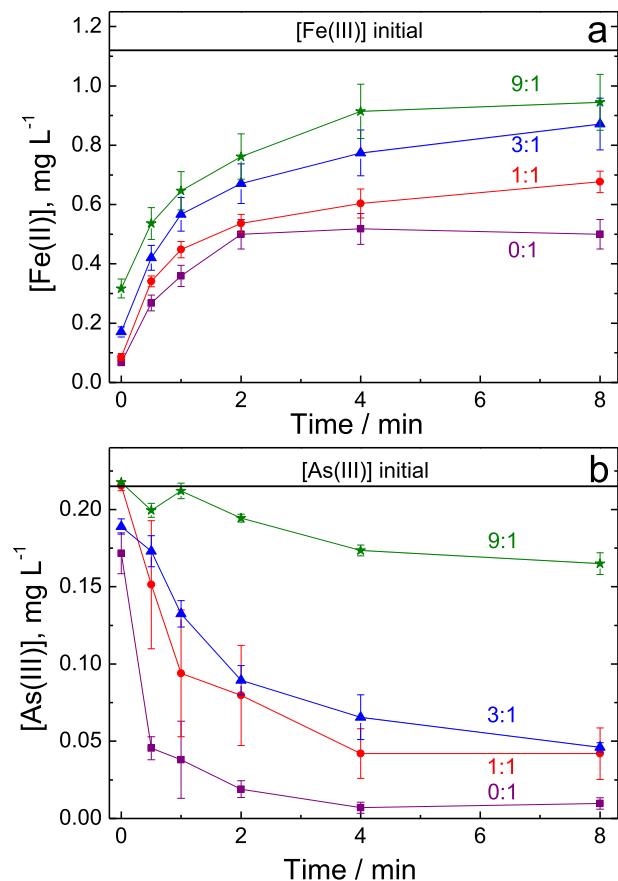
process on photochemical kinetics can be neglected. The fastest As(III) disappearance was observed for the system without FA addition leading to conclusion that  $\cdot\text{OH}$  radical produced in reaction (4) is the main oxidative species in all systems (Fig. 4a and b). This is also in agreement with results of our recent study devoted to As(III) photooxidation in presence of Fe(III) ions (Pozdnyakov et al., 2016). The formation of other oxidative species like Fe(II)-OOH (Varghese et al., 2007) is highly improbable in our conditions. When the main part of As(III) is oxidized the yield of Fe(II) reaches plateau due to back reaction of Fe(II) with  $\cdot\text{OH}$  radical (reaction (6)):



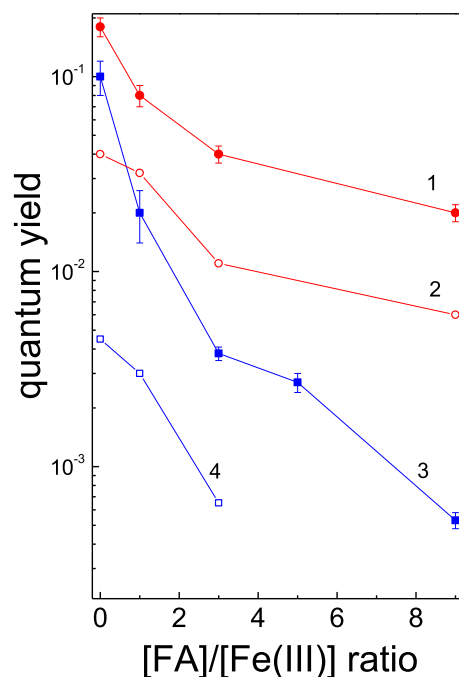
Increase of FA content leads to pronounced Fe(III) reduction without irradiation (reaction (7)) and increase of Fe(II) conversion upon irradiation (Fig. 4a). The last fact could be explained by competition of FA with Fe(II) for  $\cdot\text{OH}$  radical (reaction (8)):



It worth noting that although Fe(II) production rate does not change significantly with [FA]/[Fe(III)] ratio the rate of As(III) photooxidation is decreased sharply with increase of this



**Fig. 4.** Formation of Fe(II) (a) and disappearance of As(III) (b) during stationary (365 nm) photolysis of all four Fe(III) – As(III) – FA systems. [Fe(III)] = 1.12 mg L<sup>-1</sup>, [As(III)] = 0.22 mg L<sup>-1</sup>, pH 3.9–4.0.



**Fig. 5.** Dependence of quantum yield of Fe(II) production (1,2) and As(III) photooxidation (3,4) on [FA]/[Fe(III)] ratio for fresh (1,3) and 11 days old (2,4) systems.



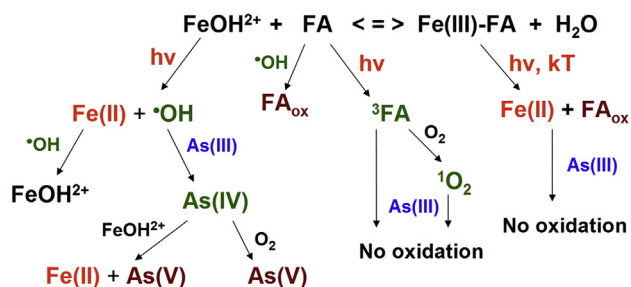


Fig. 6. General scheme of As(III) photooxidation in As(III) - Fe(III) - FA system.

parameter (Fig. 4b). So one can conclude that Fe(III)-FA complexes are photoactive but their photolysis does not produce active species responsible for As(III) photooxidation. Fig. 5 demonstrates the dependence of quantum yields of Fe(II) formation and As(III) photooxidation on  $[FA]/[Fe(III)]$  ratio for fresh and 11 days old samples. About one order decrease of quantum yields was observed for aged systems due to significant thermal reduction of Fe(III) species (about 50% for the system with  $[FA]/[Fe(III)] = 9$ , Fig. S2), the formation of less photoactive Fe(III) hydroxides and scattering Fe(III)/Fe(II) - FA colloids (Fig. 2). Thus aging is very important parameter which should be taken into account in any estimations of impact of photochemical process in Fe(III) and FA containing natural waters on As(III) oxidation.

The general scheme of As(III) photooxidation by Fe(III) species in the presence of FA is shown in Fig. 6. The presence of FA has mainly negative effect on As(III) photooxidation due to the following reasons:

- Dark reduction of photoactive Fe(III) species with formation of scattering particles and photoinert Fe(II) species leading to the great decrease of photochemical activity of aging systems.
- Formation of photoreductive Fe(III)-FA complexes which are incapable of As(III) oxidation.
- Competition of FA and Fe(III)-FA complexes for UVA quanta with photoactive  $FeOH_2^+$  complex.
- Competition of FA for  $\bullet OH$  radicals with As(III).

It is expected that photochemical oxidation of As(III) should be most effective in acidic, Fe(III)-abundant natural waters with low HS content.

#### 4. Conclusions

The UVA excitation of ternary As(III) - Fe(III) - fulvic acid system at pH 4 leads to As(III) photooxidation. Rate of this process depends both on initial  $[FA]/[Fe(III)]$  ratio and aging time of samples. It was found that the main photoactive species was  $\bullet OH$  radical formed by photolysis of Fe(III) hydroxocomplexes and the addition of FA leads to mainly negative effect on As(III) photooxidation. Both aging time and  $[FA]/[Fe]$  ratio seems to be important parameters modifying photochemical As(III) oxidation in Fe(III) and FA containing natural waters.

#### Acknowledgements

The work was financially supported by Russian Foundation for Basic Research (grants N<sup>o</sup> 15-53-53012\_GFEN, 14-03-00692).

#### Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.chemosphere.2017.04.103>.

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