Catalysis Today 161 (2011) 127–132

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Degradation of organic pollutants in aquatic environment photoinduced by Fe(III)Cit complex: Impact of TiO_2

M. Kolář[a,b], J. Jirkovský[a], G. Mailhot[b,*], M. Bolte[b], J. Krýsa[c]

[a] J. Heyrovský Institute of Physical Chemistry AS CR, Dolejškova 2155/3, CZ-182 23, Prague 8, Czech Republic
[b] Laboratoire de Photochimie Moléculaire et Macromoléculaire, Université Blaise Pascal, Aubière, France
[c] Institute of Chemical Technology, Prague, Czech Republic

ARTICLE INFO

Article history:
Received 23 June 2010
Received in revised form
15 November 2010
Accepted 2 December 2010

Keywords:
Ferric citrate
TiO_2
Monuron
Photodegradation

ABSTRACT

Kinetics of photoinduced degradation of monuron (N-(4-chlorophenyl)-N′,N′-dimethylurea) in three different photocatalytic systems (Fe(III)Cit, TiO_2, combined system Fe(III)Cit + TiO_2) were studied and compared. Principal importance of pH on the efficiency of the systems containing ferric citrate was found (optimal pH near 3). Positive effect of TiO_2 addition ($24\ \mathrm{mg\,L^{-1}}$) to Fe(III)Cit ($2.55 \times 10^{-4}\ \mathrm{mol\,L^{-1}}$) was observed at the optimal pH. This effect was emphasized with tenfold lower concentration of Fe(III)Cit ($2.55 \times 10^{-5}\ \mathrm{mol\,L^{-1}}$). On the contrary, the reaction was practically inhibited close to neutral pH.

At acid pH, more active species of both Fe(III)Cit and Fe(III) aquacomplexes are present. During photolysis of the Fe(III)Cit complex, a proton is consumed, restoring hydroxyl group; if the pH approaches the neutral zone, the Fe(III) tends to form aggregates, which are far less photoactive. In presence of TiO_2, Fe(III) is reduced by conduction band electrons of TiO_2, suppressing the recombination at acid pH. At pH close to neutral, the surface of TiO_2 is no longer positively charged, so Fe(II) is not electrostatically repulsed, which leads to a short-cut by Fe(III)/Fe(II) ions and an inhibition of photocatalytical production of hydroxyl radicals.

1. Introduction

Iron is the most abundant transition metal on the Earth. In the aquatic environment, it is often present in a form of Fe(III) complexes, especially with polycarboxylic acids. Citric acid is an example of such a ligand, which is naturally present in the environment. In general, the complexes of Fe(III) are highly photosensitive. After absorption of a photon with sufficient energy, an electron is transferred from ligand to central ferric ion, yielding Fe(II) and oxidized ligand. In case of ferric citrate complex, citrate radical is formed [1].

$$\mathrm{Fe(III)Cit} + \mathrm{H^+} \xrightarrow{h\nu} \mathrm{Fe(II)} + \mathrm{HCit^{\bullet -}} \tag{1}$$

The proton consumed in course of the photoredox process is probably taken by the oxygen atom bound on tertiary carbon atom on citrate to restore the hydroxyl group [2]. The degradation pathway of citrate radical continues by reaction with dissolved oxygen, which can be followed by decarboxylation, forming acetonedicarboxylic acid [3]. With sufficient supply of hydroxyl radicals, it is further fully mineralized. Besides, $O_2^{\bullet -}$, H_2O_2 and $HO_2^{\bullet}$ are produced in course of the pathway.

The Fe(II) can be reoxidized by Fenton reaction (2), by hydroperoxide (3) or hydroxyl radical (4) to Fe(III):

$$\mathrm{Fe(II)} + \mathrm{H_2O_2} + \mathrm{H^+} \rightarrow \mathrm{Fe(III)} + {}^{\bullet}\mathrm{OH} + \mathrm{H_2O} \tag{2}$$

$$\mathrm{Fe(II)} + \mathrm{HO_2}^{\bullet} + \mathrm{H^+} \rightarrow \mathrm{Fe(III)} + \mathrm{H_2O_2} \tag{3}$$

$$\mathrm{Fe(II)} + {}^{\bullet}\mathrm{OH} \rightarrow \mathrm{Fe(III)} + \mathrm{OH^-} \tag{4}$$

The ferric cations form aquacomplexes, which under irradiation lead to the formation of Fe(II) and hydroxyl radicals (5). This process is efficient enough to induce pollutant degradation [4–6]:

$$\mathrm{Fe(III)} + \mathrm{H_2O} \xrightarrow{h\nu} \mathrm{Fe(II)} + {}^{\bullet}\mathrm{OH} + \mathrm{H^+} \tag{5}$$

The Fe(III)/Fe(II) photocatalytic system is capable of continuous production of hydroxyl radicals. Its efficiency strongly depends on the speciation of Fe(III) aquacomplexes [7]. Besides, the photoactivity of Fe(III)Cit system, expressed by quantum yield of Fe(II) formation, is depending on pH, which determines the speciation of the complex. Four acido-basic species of Fe(III)Cit complex were found [2], the most acid and most basic forms are less photoactive; highest values were found at pH = 3, which suggests predomination of two more photoactive intermediate Fe(III)Cit forms.

---

[*] Corresponding author at: Laboratoire de Photochimie Moléculaire et Macromoléculaire, Université Blaise Pascal, F-63177 Aubière Cedex, France.
E-mail addresses: kolarm@gmail.com (M. Kolář), gilles.mailhot@univ-bpclermont.fr (G. Mailhot).

0920-5861/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2010.12.004

Heterogeneous photocatalysis on TiO_2 has been widely studied as a method for pollutant removal for last two decades [8–11]. The driving force of mineralization is a production of hydroxyl radicals. The multi-step process is induced by absorption of a photon with sufficient energy, leading to generation of an electron–hole pair (6).

$$TiO_2 \xrightarrow{h\nu} h_{VB}{}^{+} + e_{cB} \tag{6}$$

Certain part of the charge carriers is trapped on the surface, where it can undergo redox reactions with the molecules adsorbed on the particle surface. The holes oxide surface hydroxide groups providing hydroxyl radicals; the electron is reducing dissolved oxygen molecule to peroxyle radical, which further reacts to hydroperoxide radical or hydrogen peroxide. However, major part of the charge carriers recombines, dissipating the excess of energy in a form of heat.

The addition of TiO_2 into Fe(III)Cit photocatalytic system could improve the overall degradation efficiency by mutual complementarity of the systems: the Fe(III) could reduce the recombination on TiO_2 by removing the electron; moreover, the products of electron-induced reduction of oxygen ($HO_2{}^{\bullet}$, H_2O_2) could regenerate photoactive Fe(III) species [12].

Monuron is a herbicide from phenylurea group, the second most abundant pesticide group found in continental surface waters and groundwaters, widely used in Europe. Its degradation pathways were described in different systems of degradation based on hydroxyl radical formation – on TiO_2 [13,14], and photoinduction by iron [12,15]. It does not form a complex with iron and does not undergo redox reaction with ferric cations in the dark, so it was a suitable model pollutant. As monuron does not absorb above 300 nm, its direct photolysis by sunlight is negligible in order of days [16].

Photodegradation of monuron in the combined systems of iron and TiO_2 (suspended or fixed) was studied by Měšt'ánková et al. [12,17]. At low TiO_2 concentration (24 mg L^{-1}), an important positive effect on pollutant degradation was observed due to the iron addition. In the presence of Fe(III) (3×10^{-4} mol L^{-1}), the measured rate constant was similar to that obtained with an amount of TiO_2 more than 20 times higher when the photocatalyst is used alone. The system was optimized for a different role of the catalysts – Fe(III)/Fe(II) system as a primary source of hydroxyl radicals, and TiO_2 as a source of oxidative species for re-oxidation of Fe(II) into Fe(III). The photoproducts of monuron degradation were already studied [15,18].

The goal of this work was to study a natural process, an impact of the ferric citrate complex on an organic molecule. Moreover, the interaction of Fe(III)/Fe(II) ions and TiO_2 could have significant importance for the TiO_2/UV based systems, as the iron is one of the most abundant elements in the environment.

2. Materials and methods

2.1. Chemicals

The chemicals Ferric citrate (Fe(III)Cit, Aldrich, tech. gr.), monuron (Riedel-de-Haën, anal. std.), TiO_2 (P25, Degussa) were used without further purification. The water used was ultra-pure (Millipore MilliQ), whose resistivity was 18.2 MΩ cm. The purity of water and of methanol as solvents for chromatography was HPLC grade (Merck).

2.2. Methods

UV/vis spectra were recorded on Cary 3 double beam spectrophotometer. The pH measurements were performed by pH meter Orion equipped with a combined electrode.

HPLC Waters with autosampler type 717, two pumps type 510 and a diode array UV/vis detector type 996 were used through this work to carry out the analysis. A reversed phase column was a LiChrospher 100 RP-18 (type LiChroCART 125-4, Merck). A mobile phase acetonitrile/water (30/70 v/v) was flowing at the rate of 1 mL min^{-1}. Monuron and its degradation products were detected at 245 nm. The initial concentration of monuron was 1×10^{-4} mol L^{-1}. Sample volume was 1 mL; samples taken at 0 min were injected twice. Standard deviation was below 5%.

The oxygen concentration was adjusted in the following ways: *Deoxygenated solutions* – nitrogen bubbling (1 bar) was used for 20 min before starting the irradiation and during the course of the reaction; *Oxygenated solutions* – oxygen bubbling (1 bar) for 10 min before starting the irradiation and during the course of the reaction.

Fe(II) concentration was determined by 1,10-phenanthroline complexometry, where $\varepsilon_{510} = 1.118 \times 10^4$ L mol^{-1} cm^{-1} was used for [Fe(II)-phenanthroline] complex [18].

2.3. Irradiation systems

In order to determine the quantum yields, monochromatic irradiations at 365 nm were performed by a high-pressure polychromatic mercury-vapor lamp Osram HBO 200 W provided with monochromator Bausch and Lomb, giving homogenous collinear beam. A cylindrical quartz cell with 2 cm optical path length and 1.85 cm internal diameter was used as a reactor. The photonic flux was determined by the ferrioxalate actinometry [19] (2.6×10^{15} photons s^{-1} cm^{-2} at 365 nm). The quantum yield determinations were performed twice.

For the kinetics studies concerning the iron complexes, an experimental set-up with larger volume (100 mL) and more powerful source ($I_0 \approx 1.5 \times 10^{16}$ photons s^{-1} cm^{-3}) was used. Three middle-pressure mercury vapor lamps Mazda MAW 125 W were placed in the corners of a hypothetical equilateral triangle, while the water-jacketed Pyrex cylindrical reactor ($d = 2.8$ cm) was situated in the centre. The irradiation system was enclosed by a cylindrical aluminum reflexive jacket, whose vertical axis passed through the vertical axis of the reactor. The light was practically monochromatic at 365 nm, which represents about 93% of the emitted light (remaining percents comprised of emission at 313, 334 and 405 nm). The solutions were well stirred all along the irradiation.

3. Results and discussion

The photoinduced degradation of monuron was studied in three various systems producing hydroxyl radicals: aqueous solution of Fe(III)Cit, aqueous suspension of TiO_2 and in the combined system of Fe(III)Cit/TiO_2.

3.1. Fe(III)Cit + monuron

Degradation of monuron photoinduced by Fe(III)Cit followed complex kinetics (Fig. 1). In the course of first fast step, direct photolysis of Fe(III)Cit occurred, producing oxidative radicals, which caused fast degradation of monuron. The citrate completely degraded within first step, which was no longer than 15 min. In the slower second step, the principal source of oxidative radicals was the photoredox cycle of Fe(III)/Fe(II). This cycle is linked at the presence of Fe(III) complexes and more particularly of iron aqua-complexes. The efficiency of the second step is dependent on the pH (see Section 3.1.2).

3.1.1. Impact of oxygen

The saturation by oxygen has a positive effect on both steps of monuron degradation. A relatively higher impact was observed on the second step (total disappearance of monuron in 240 min,

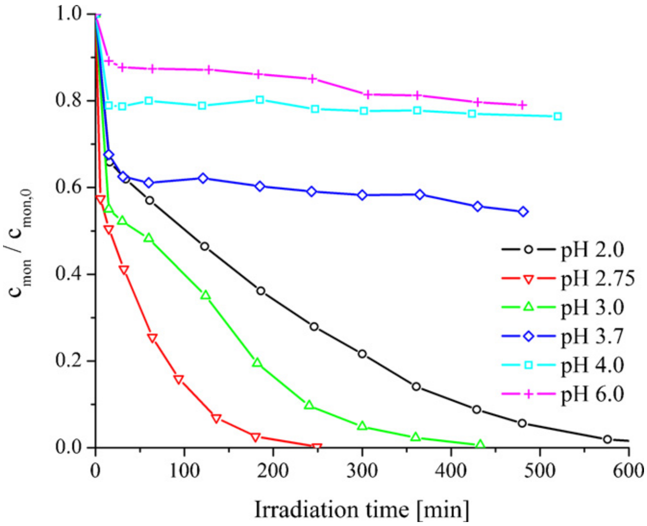

Fig. 1. Kinetics of monuron degradation photoinduced by Fe(III)Cit at various pH; λ_{irr} = 365 nm, $c_{Fe(III)Cit} = 3 \times 10^{-4}$ mol L^{-1}, $c_{monuron} = 1 \times 10^{-4}$ mol L^{-1}.

comparing to 90% disappearance with aerated solution). On the contrary, the absence of oxygen had strong inhibiting effect on the kinetics of monuron degradation. For the system of 3×10^{-4} mol L^{-1} ferric citrate complex, no monuron degradation was observed, possibly due to fast re-oxidation of Fe(II) by citrate radical. The graph is not shown due to limited space.

3.1.2. Impact of pH

The pH is another important parameter in homogenous photocatalysis as one of the determining factors for the speciation of iron complexes. Kinetics of 1×10^{-4} mol L^{-1} monuron degradation in presence of ferric citrate was followed at different initial pH's; the curves of pollutant disappearance kinetics are given in Fig. 1. The kinetics were fitted by a simple model of two formally simultaneous first-order processes:

$$\frac{c_{mon}}{c_{mon,0}} = A_0 e^{-k_a t} + B_0 e^{-k_b t}$$

During the first fast step, the monuron degradation was observed at all pH. When decreasing initial pH, the conversion was increasing until initial pH 2.75; at initial pH = 2, the conversion decreased. The efficiency of monuron degradation in the first step could be also quantified by the value of conversion constant A_0 (see Table 1); the values of monuron degradation rate k_a were fixed. This behavior was caused by different distribution of variously photoactive particular Fe(III)Cit acid–base forms, present at corresponding pH, combining to overall photoactivity [2]. In the course of the second slower step, the degradation kinetics of monuron depended on the speciation of Fe(III) species as well as on the oxidation rate of Fe(II) to Fe(III). The efficiency of the second step could be represented by the value of monuron degradation rate k_b (see Table 1). The B_0 conversion constant corresponds to the amount of monuron transformed in second step. The addition of conversion constants A_0 and B_0 was set to be the total monuron concentration.

Table 1
Quantum yields of monuron degradation for various; conversion constant A_0 and rate constant k_b of monuron degradation for various pH; [Fe(III)Cit] = 2.55×10^{-4} mol L^{-1}, [monuron] = 1×10^{-4} mol L^{-1}.

Initial pH	ϕ (monuron)	A_0	k_b
2.0	0.013 ± 0.002	0.27 ± 0.04	$4.3 \pm 0.3 \times 10^{-3}$
2.5	0.017 ± 0.002	–	–
2.75	0.020 ± 0.002	0.38 ± 0.03	$1.5 \pm 0.1 \times 10^{-2}$
3.0	0.019 ± 0.002	0.35 ± 0.06	$6.7 \pm 0.8 \times 10^{-3}$
3.7	–	0.36 ± 0.02	$3.4 \pm 0.5 \times 10^{-4}$
4.0	0.020 ± 0.002	0.20 ± 0.02	$7.3 \pm 1.8 \times 10^{-5}$
5.0	0.018 ± 0.002	–	–
6.0	0.017 ± 0.002	–	–

The curves of pH change and evolution of Fe(II) concentration during monuron degradation at different initial pH's were followed (Fig. 2). The change of pH seemed to be most significant at the initial pH higher than 3.5. However, calculated real H^+ consumption was highest at initial pH = 3.0. In the first step of degradation kinetics, the pH generally increased. In second step, the pH remained practically unchanged at the value of the plateau reached at the end of first step. The only exception was observed at pH = 6.0, which reflected the carbonation of the solution.

It could be seen that the monuron degradation process was almost stopped when the pH reached the value of 5.0 and more; compare the decrease of k_b rates with increasing pH values of the plateaus. The increase of pH has a major impact on the speciation of the ferric citrate complex and of iron, and results in the formation of less photoactive species. At pH higher than 5.0, the solubility of Fe(III) species is very low and as a consequence the photocatalytic cycle observed at lower pH's is no more present. When Fe(II) is oxidized at pH > 5.0, Fe(III) species precipitate.

The concentration of Fe(II) always rapidly increased to a plateau value in the first step. In the second step it was generally slightly increasing or remained constant. At initial pH = 3.0, the plateau value reached a maximum equal to the concentration of total iron. The highest concentrations of Fe(II) (from 80% to 100% of total iron) were found at low initial pH up to 3.7 (Fig. 2b). At initial pH = 4.0, the concentration of Fe(II) corresponded 55% of total iron. At initial pH = 6.0, the Fe(II) concentration only reached 9% of total iron after 15 min of irradiation, which paralleled the degradation of monuron which almost stopped; as already mentioned, the Fe(II) spontaneously reoxidizes to Fe(III) at this pH. But at such high pH, Fe(III) species precipitated and the concentration of soluble iron decreased. The photocatalytic cycle was no more present.

Quantum yields of monuron degradation in the presence of ferric citrate complex for various initial pH's are shown in (Table 1).

The monuron is degraded in entire studied pH range. The highest quantum yields were found in a wide range of pH between 2.5 and 6. This pH range corresponds to the presence of the most photoactive species generated from ferric citrate complex. However, the difference between the quantum yields is not high-lowest quantum yield at pH = 2 reaches 65% of the highest quantum yields. This indicates existence of photoactive species in the whole range of pH. This result proves that such complexes have a real impact in the natural environment whatever the pH.

3.1.3. Impact of Fe(III)Cit concentration

The kinetics of monuron degradation was studied in the presence of Fe(III)Cit at initial concentrations in the range from 5×10^{-5} to 1×10^{-2} mol L^{-1}. The natural pH of Fe(III)Cit solution depends on its concentration; the initial pH was therefore set to 3 by addition of perchloric acid.

The impact of initial concentration of Fe(III)Cit on the kinetics of monuron degradation was not directly proportional (see Fig. 3a). Surprisingly, the highest degradation efficiency was not observed at highest concentration (see Fig. 3b), but at 3×10^{-4} mol L^{-1}, where 94% of monuron were transformed in 420 min; at the highest ferric citrate concentration (1×10^{-2} mol L^{-1}) only 35% of monuron were degraded after same irradiation time (7 h). On the contrary, 85% of monuron was transformed at the lowest concentration of ferric citrate (5×10^{-5} mol L^{-1}). The low degradation of monuron at a concentration of ferric citrate equal to 1×10^{-2} mol L^{-1} can be due to the presence of high concentration of citric acid, whom the

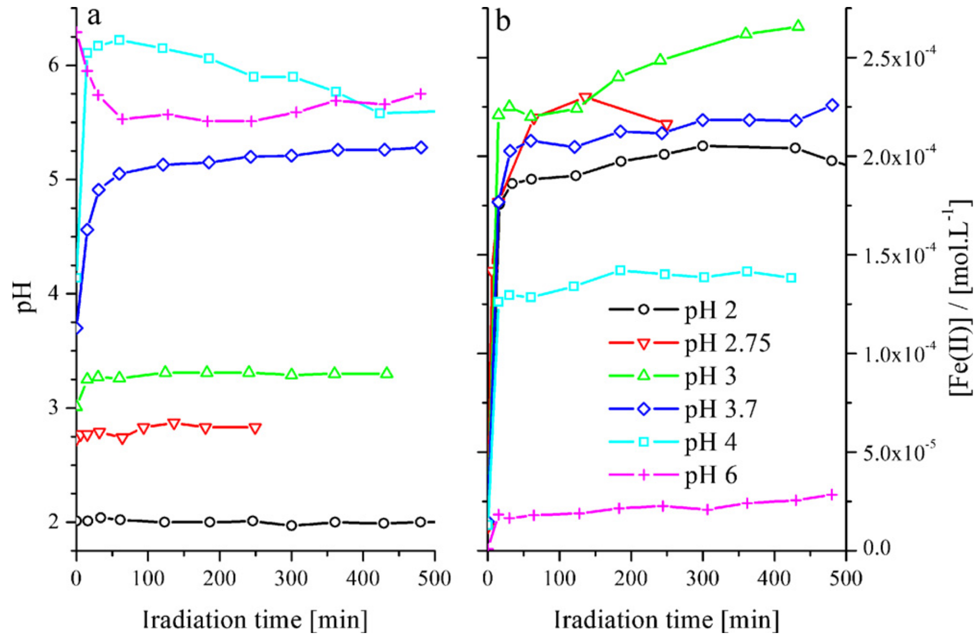

Fig. 2. Evolution of pH (a) and Fe(II) concentration (b) during monuron degradation photoinduced by Fe(III)Cit at difference initial pH; $c_{\mathrm{Fe(III)Cit}} = 3 \times 10^{-4}$ mol L^{-1}, $c_{\mathrm{monuron}} = 1 \times 10^{-4}$ mol L^{-1}.

photogenerated radical species can react with, as there is a competition between monuron and citrate with its intermediates for the reactivity of radical species.

The pH evolution curves observed during the monuron degradation in the presence of the Fe(III)Cit shown that the pH increased with the initial Fe(III)Cit concentration (see Fig. 3b). With higher starting concentration, the pH increased to higher value. This is in an agreement with other work from our lab [2], where we proposed that the increase of pH which occurred during irradiation of ferric citrate complex illustrates the consumption of H$^+$ during the photoredox process of the complex. Thus, the higher the initial Fe(III)Cit concentration was, the higher H$^+$ consumption was.

3.2. Fe(III)Cit + TiO$_2$ + monuron

Photocatalytic degradation of monuron in TiO$_2$ suspension (24 mg L^{-1}) followed formally the first-order kinetics. In the combined system Fe(III)Cit/TiO$_2$, two-step kinetics similar to those of Fe(III)Cit system was observed (Fig. 4).

3.2.1. Impact of pH

The combined system was also dependent on pH, like in the system with Fe(III)Cit complex alone. The range of initial pH's, where the combined systems were most active, was similar to those without TiO$_2$ presence. The most active degradation of monuron was

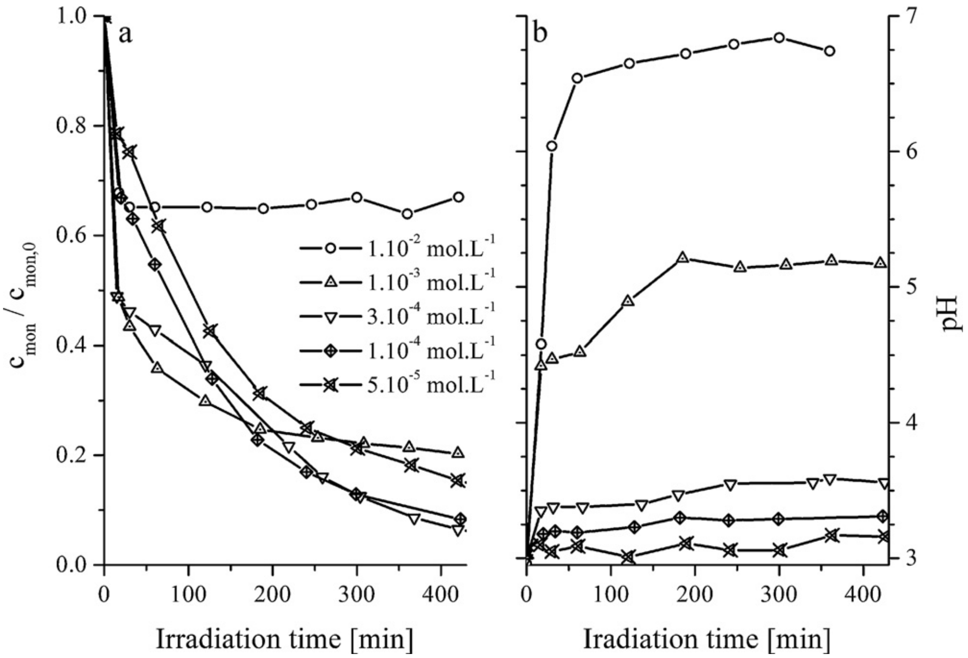

Fig. 3. Kinetics of monuron degradation (a) and evolution of pH (b) during monuron degradation photoinduced by Fe(III)Cit at difference Fe(III)Cit concentrations; initial pH = 3; $c_{\mathrm{monuron}} = 1 \times 10^{-4}$ mol L^{-1}.

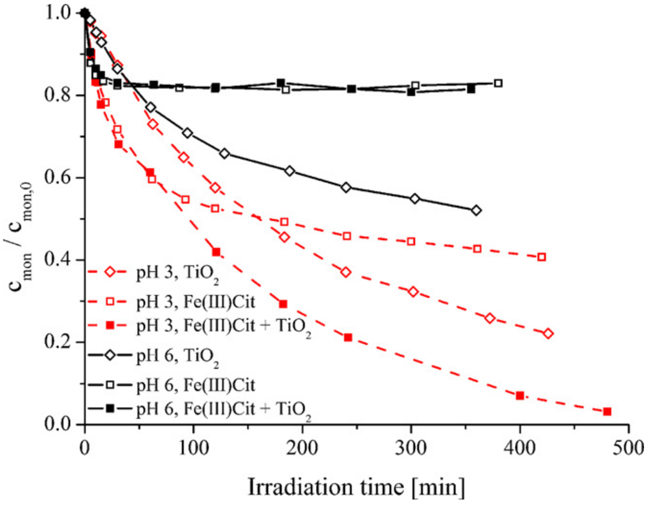

Fig. 4. Degradation kinetics of monuron at various pH for three different phototocatalytic systems: Fe(III)Cit, TiO_2 and Fe(III)Cit/TiO_2 combination irradiated by 1 lamp; pH = 3 and 6, $c_{Fe(III)Cit} = 3 \times 10^{-4}$ mol L^{-1}, $c_{TiO_2} = 24$ mg L^{-1}, $c_{monuron} = 1 \times 10^{-4}$ mol L^{-1}.

observed near pH = 3. The kinetics of the binary systems at pH = 3 was different, the monuron degradation efficiency of ferric citrate system was higher in the first step of the kinetics; subsequently, the degradation slowed down. In the TiO_2 system, the curve of monuron degradation corresponded to first order kinetics. About 60% and 75% of monuron were degraded after 420 min of irradiation with Fe(III)Cit complex and TiO_2 respectively. In the combined system, a strong acceleration was observed after 60 min of irradiation and the degradation continues with the same efficiency than at the beginning; almost 95% of monuron was transformed after 420 min. At pH = 6, no positive effect on pollutant degradation occurred. Moreover, the photodegradation of monuron was inhibited at longer irradiation times. At pH = 6.0, the degradation is much higher with TiO_2 alone.

In the combined system the pH evolution in the first step during monuron degradation shown similar characteristics to the system with ferric citrate alone at both initial pH (Fig. 5). The presence of TiO_2 resulted in a lower pH.

At initial pH = 6, lower concentrations of Fe(II) were found in the combined systems than in the presence of Fe(III)Cit complex alone (Fig. 5), despite lower pH in the combined systems, where the pH plateau value was about 5.5. Normally, the Fe(II) concentration in water increase when the pH decreases. This could be also explained by a re-oxidation of Fe(II) by the holes on the TiO_2 surface. The surface of TiO_2 is positively charged at acid pH; with an increase of pH to the point of zero charge of TiO_2 (6.25) and the TiO_2 particle becomes electroneutral. Thus, at higher pH (e.g. pH = 5.5 was still high enough), the electrostatic repulsion between the Fe(III)/Fe(II) ions and the surface of TiO_2 decreased enough to permit a closer approach of the metal ions to the partially discharged TiO_2 particles. However, the enhanced monuron degradation efficiency was caused by the photocalysis on TiO_2, generating the hydroxyl radicals. At initial pH = 6.0, the degradation of monuron in combined system was practically inhibited in the second step. We can assume that notable part of Fe(II) was reoxidized on the surface of the TiO_2 particles, and that the photocatalysis on TiO_2 was inhibited by this short-cut.

However, addition of TiO_2 has a strong positive effect on the second step of monuron degradation observed with Fe(III)Cit alone in the acidic environment. The second step present in the system with carboxylate ferric complexes, as mentioned above, is attributed to the formation of radical species through the photocatalytic cycle based on the couple Fe(III)/Fe(II). Previous studies performed in the laboratory showed that in the presence of Fe(III) aquacomplexes the limiting step was the reoxydation of Fe(II) into Fe(III). Moreover, Měšťánková et al. [12] showed that the oxidized species photogenerated from TiO_2 increased the oxidation of Fe(II) (reactions (2), (3) and (4)) and then the photocatalytic cycle Fe(III)/Fe(II).

Reaction (2) not only permits the oxidation of Fe(II) but also photogenerates very oxidative species: hydroxyl radicals. Reaction (4) is detrimental in terms of pollutant degradation. But the global balance shows that all these reactions regenerating Fe(III) have a positive influence as evidenced by the degradation curves in the

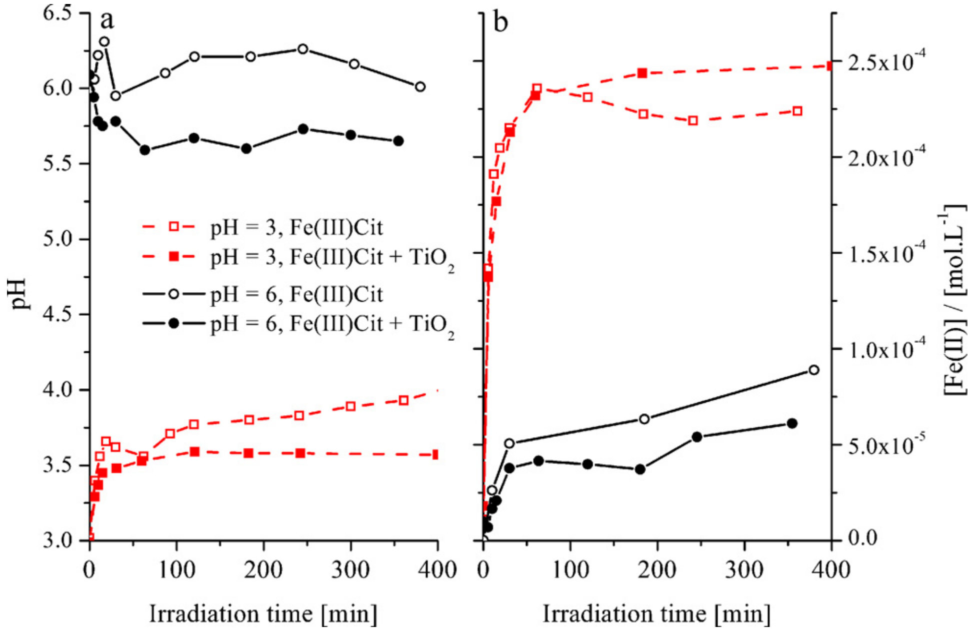

Fig. 5. Evolution of pH and Fe(II) concentration during monuron degradation in Fe(III) system with/without TiO_2 system irradiated by 1 lamp; initial pH = 3 and 6; $c_{Fe(III)Cit} = 3 \times 10^{-4}$ mol L^{-1}, $c_{TiO_2} = 24$ mg L^{-1}, $c_{monuron} = 1 \times 10^{-4}$ mol L^{-1}.

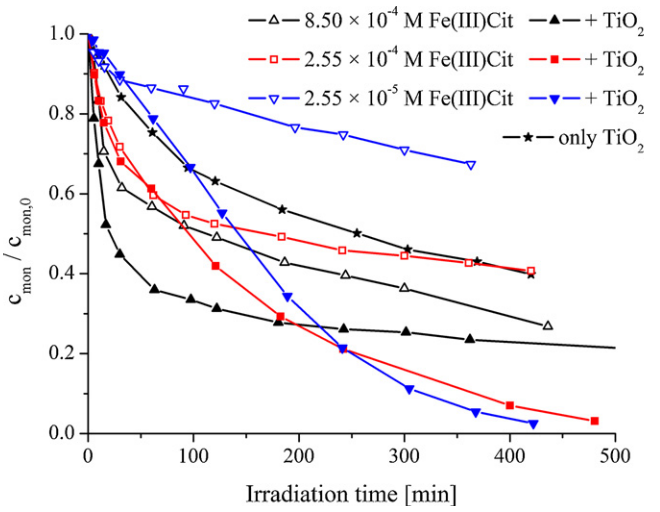

Fig. 6. Impact of Fe(III)Cit concentration on the kinetics of monuron degradation in system of Fe(III)Cit with/without TiO$_2$ (full/empty symbols); c_{TiO_2} = 24 mg L^{-1}, $c_{monuron}$ = 1 × 10^{-4} mol L^{-1}, irradiation by 1 lamp; λ_{irr} = 365 nm, pH = 3.

presence and in the absence of TiO$_2$. Thus, the strong increase of the rate of monuron degradation observed in our system can be attributed to the same effect of the oxidative species photogenerated by TiO$_2$ particles.

3.2.2. Impact of Fe(III)Cit concentration

The impact of ferric citrate concentration, examined at the most efficient pH (near 3.0), shown that the system was also dependant on this parameter and the results were similar to those obtained with Fe(III)Cit alone. At higher concentration tested (8.5 × 10^{-4} mol L^{-1}) the degradation of monuron after 360 min of irradiation corresponded to 77% and with a concentration of 2.5 × 10^{-4} mol L^{-1} the degradation reached 90% for the same irradiation time (Fig. 6). But with the lowest concentration used in Fe(III)Cit (2.5 × 10^{-5} mol L^{-1}) corresponding to a ratio of Fe/TiO$_2$ equal to 1/12 the degradation of monuron was the most efficient (94%). It was little more efficient than the system with approximately equal ratio and also much more efficient than the system with the ratio of 3 (excess of iron). In the systems with lower Fe(III)Cit concentration, the pH was lower in the combined system, and thus more favourable for more photoactive Fe(III) species.

As the large amount of Fe(II) was formed in the first step, it was reoxidized by TiO$_2$. Fe(II) react with the holes on the surface of the TiO$_2$ and competes with the principal source of hydroxyl radical formation (via reaction of water species with h$^+$). A second explanation can be due to the presence of higher concentration of citrate or degradation products which can react with $^\bullet$OH radicals and as a consequence compete with the reaction of $^\bullet$OH radicals and monuron.

4. Conclusion

Besides oxygen concentration, the key factor for pollutant degradation performance of all systems based on Fe(III)Cit was presence of photoactive species, both initial Fe(III)Cit and Fe(III) aquacomplexes in the later step. The pH determines speciation of both iron species. The best pollutant degradation efficiency was observed near pH = 3.

The addition of TiO$_2$ into the Fe(III)Cit system with active iron species accelerated the degradation. On the other hand, when TiO$_2$ is added to a system of ferric citrate alone with no pollutant degradation, practically no impact of TiO$_2$ is observed. Moreover, the heterogeneous photocatalysis on TiO$_2$ is plagued.

Other factor which impacts on the efficiency of Fe(III)Cit/TiO$_2$ combined system is probably certain ratio of iron/TiO$_2$. At pH = 3, the highest pollutant degradation efficiency was observed with the lowest concentration of Fe(III)Cit. This is an interesting result not only from environmental point of view, but also for the advanced oxidation processes using TiO$_2$ where traces of iron are always present in the waters.

Acknowledgements

The author would like to thank to the Ministry of Education, Sports and Youth of the Czech Republic (project 1M0577). Michal Kolář thanks to the French Embassy in the Czech Republic for financial support of his stay at the Laboratory of Molecular and Macromolecular Photochemistry in Clermont-Ferrand (France).

References

[1] B.C. Faust, R.G. Zepp, Environ. Sci. Technol. 27 (1993) 2517–2522.
[2] M. Kolář, O. Abida, G. Mailhot, J. Jirkovský, M. Bolte, Phototransformation of ferric citrate in aquatic environment (to be published).
[3] H.B. Abrahamson, A.B. Rezvani, J.G. Brushmiller, Inorg. Chim. Acta 226 (1994) 117–127.
[4] H.-J. Benkelberg, P. Warneck, J. Phys. Chem. 99 (1995) 5214–5221.
[5] P. Mazellier, G. Mailhot, M. Bolte, New J. Chem. 21 (1997) 389.
[6] P. Mazellier, J. Jirkovský, M. Bolte, Pestic. Sci. 49 (1997) 259–267.
[7] C.M. Flynn, Chem. Rev. 54 (1984) 31–41.
[8] C.S. Turchi, D.F. Ollis, J. Catal. 122 (1990) 178–192.
[9] D.W. Bahnemann, in: P. Boule (Ed.), Environmental Photochemistry, Springer-Verlag, Berlin, 1999, pp. 285–351.
[10] A. Fujishima, T.N. Rao, D.A. Tryk, J. Photochem. Photobiol. C: Photochem. Rev. 1 (2000) 1–21.
[11] O. Carp, C.L. Huisman, A. Reller, Prog. Solid State Chem. 32 (2004) 33–177.
[12] H. Měšťánková, G. Mailhot, J. Jirkovský, J. Krýsa, M. Bolte, Appl. Catal. B: Environ. 57 (2005) 257–265.
[13] V. Augugliaro, G. Marcí, L. Palmisano, E. Pramauro, A. Bianco-Prevot, Res. Chem. Intermed. 9 (1993) 839–853.
[14] E. Pramauro, M. Vincenti, V. Augugliaro, L. Palmisano, Environ. Sci. Technol. 27 (1993) 1790–1795.
[15] H. Měšťánková, G. Mailhot, J.-F. Pilichowski, J. Krýsa, J. Jirkovský, M. Bolte, Chemosphere 57 (2004) 1307–1315.
[16] G.D. Hill, J.W. MacGahen, H.M. Baker, D.W. Finnerty, C.W. Bingeman, Agronom. J. 47 (1955) 93–104.
[17] H. Měšťánková, J. Krýsa, J. Jirkovský, G. Mailhot, M. Bolte, Appl. Catal. B: Environ. 58 (2005) 185–191.
[18] D.G. Crosby, C.S. Tang, J. Agric. Food Chem. 17 (1969) 1041.
[19] J.G. Calvert, J.N. Pitts Jr., Photochemistry, John Wiley & Sons, New York, 1966, 783.