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Competitive adsorption and photodegradation of salicylate and oxalate on goethite

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ABSTRACT

This work deals with the competitive adsorption and photodegradation of salicylate and oxalate on α-FeOOH (goethite) which is a predominant crystalline modification of iron oxide present in sea sediment. pH is a crucial parameter in goethite photodissolution; therefore, by means of a pH stat titration, pH was kept constant during all experiments. For either acidic (pH 3) or neutral (pH 6) pH values oxalate is preferentially adsorbed on the goethite surface. Thus, in the presence of oxalate, adsorption of salicylate is suppressed and for oxalate concentration 2 mM is even negligible. Without oxalate the photodegradation of salicylate on goethite is negligible due to the short circuiting effect of photogenerated h^+ and e^-. When oxalate is present in the system photodissolution of goethite takes place, which results in the formation of OH radicals and photodegradation of salicylate. At pH 3 photodissolution of goethite is faster than at pH 6; oxalate disappears and salicylate photodegradation stops. On the other hand, due to the slower photodissolution of goethite at pH 6, the oxalate concentration decreases more slowly and salicylate photodegradation does not stop and also proceeds at longer irradiation times.

1. Introduction

It is known that Fe(III) aquacomplexes are efficient photocatalysts to induce the complete mineralisation of a variety of pollutants [1–3]. There are several crystalline forms of iron oxide/hydroxide present in soil or marine sediments. It was found that goethite is a dominant crystalline modification as shown by samples of sediments from the Gulf of Triest [4]. Therefore from an environmental perspective it is of great interest to investigate the adsorption properties of goethite as well as its ability to photocatalytically mineralise pollutants present in surface waters. It was reported that carboxylic acids (e.g. oxalic, malonic, citric) are able to "extract" iron from natural iron oxides or hydroxides [5–7]. The photodissolution of hematite and goethite proceeded to a much lower extend than for noncrystalline oxides [5,8]. Salicylic acid was reported to be less active in relation to dicarboxylic acids [5]. However, there are few detailed studies in the literature that explain the mechanism of photo-dissolution of iron oxides. Salicylic acid forms charge transfer complexes on TiO_2 surfaces which partly inhibit photocatalytic degradation of other compounds dissolved in the aqueous phase [9]. It is therefore interesting to investigate whether salicylate influences goethite dissolution photoinduced by oxalate.

Several papers describe the adsorption of oxalate on goethite, often in the presence of other ions [10–16]; adsorption of salicylate on goethite was reported to a lesser extent [17–21]. However, the adsorption of either oxalate or salicylate in the presence of other absorbing anions has been studied only in the case of oxalate (in the presence of benzoate [10], chromate [12] and phosphate (sulphate) [13]). Concerning photodegradation studies, the situation is even worse. Goethite is a material who's photoactivity has been much less studied than TiO_2. This is mainly due to the fact that, for significant photoactivity, another reagent (hydrogen peroxide, oxalate) must be added. There are several studies describing the photodegradation of oxalate [22–24] and other carboxylic acids [23,25] on goethite. For the photodegradation of salicylate on goethite, He [26] found that degradation takes place only in the presence of hydrogen peroxide and that the rate is proportional to sorption ability.

The earliest work describing the preparation of pure goethite (α-FeOOH) was published by Atkinson et al. in 1968 [27]. The majority of further studies on goethite use the same procedure which is based on the addition of NaOH (KOH) solution to $Fe(NO_3)_3$ solution at pH 11–12 and precipitation at elevated temperature for sev-

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eral days [10–18,23–25]. In some studies ferric chloride was used instead of ferric nitrate [26,28]. The specific surface area (determined by the N_2 BET method) was very similar (in the range of 60–90 m^2/g) for all synthesised materials [10–14,17,18]. On the other hand, photodegradation studies on goethite purchased from either Bayer (Bayferrox 910, standard 86) [22] or Aldrich [29,30] report much different values of surface area, 14 and 190 m^2/g, respectively.

No studies of the adsorption or photodegradation of salicylate on goethite in the presence of oxalate have been published. Therefore the aim of the present work is to show the effect of oxalate on salicylate adsorption and photodegradation on goethite at several pH values by means of adsorption probes.

2. Experimental

2.1. Goethite synthesis and characterization

Goethite was prepared using a method similar to that described by Atkinson et al. [27]. 360 g of $Fe(NO_3)_3{\cdot}9H_2O$ was dissolved in 1460 ml of water in a brown 2500 ml bottle. After dissolving, 500 ml of 3 M NaOH was slowly added under vigorous magnetic stirring. The reaction solution was kept under slow stirring at room temperature for 2 days. Then, saturated NaOH was added dropwise until the pH reached a value between 12 and 13. The formed slurry was warmed to 60 °C and kept without stirring. The bottle was shaken twice a day (every 8–12 h) to homogenize the mother liquor. After 4–5 days, the growth of goethite crystals was completed. Then the solid product was separated from the mother liquor by centrifugation. Filtration using a water-jet air pump was found to be totally inefficient. The solid phase was then suspended in distilled water and centrifuged repeatedly until the pH of the liquid phase reached a value below 9. The final product was dried at 40 °C. The resulting goethite particles were identified by X-ray powder diffraction (X'PertPRO powder diffractometer with parafocusing Bragg–Brentano geometry using Co Kα radiation) and FTIR spectroscopy (Nicolet 5700 FTIR spectrometer, range 4000–400 cm^{-1}).

2.2. Adsorption experiments

Adsorption of oxalate on goethite was measured at pH 3 and 6 at constant goethite concentration (2 g/dm^3) and various total sodium oxalate concentrations (0.01–2 mM). Adsorption of salicylate on goethite was studied in two complementary sets of experiments: (1) constant concentration of goethite (2 g/dm^3) and varied concentrations of sodium salicylate (0.01–2 mM) at two different pH values (3 and 6), and (2) constant concentration of sodium salicylate (1 mM) and varied concentrations of goethite (1–25 g/dm^3) at six different pH values (6.7, 6, 5, 4, 3 and 2). The time to achieve adsorption equilibrium was experimentally investigated and it was concluded that 30 min of mixing is sufficient.

Competitive adsorption of salicylate and oxalate on goethite was performed similarly as for single anion adsorption. Solutions of various sodium oxalate and sodium salicylate concentrations (0.1–2 mM) at pH 3 and 6 were mixed with goethite (2 g/dm^3). After centrifugation the clear upper part of solution (1 ml) was taken and analysed.

Salicylate and oxalate were analysed by HPLC: a Waters 540 chromatograph with a Waters 996 Photodiode Array Detector; a Merck column LiChroCART 250-4 filled with a LiChrosphere 100 RP-18 (5 μm); mobile phases H_2O (0.1% H_3PO_4):CH_3CN = 1:1 with detection wavelength of 303 nm in the case of salicylate and H_2O (0.1% H_3PO_4) with wavelength of 210 nm in the case of oxalate were used.

2.3. Photodegradation experiments

Photodegradation experiments were performed in a cylindrical batch type photoreactor. A water-jacketed Pyrex tube (Ø3 cm) was placed in the centre of 3 Philips HPW 125 W lamps, symmetrically installed in the reactor. Mixing was performed by magnetic stirrer. The reaction temperature was held at 20 °C, pH was continuously maintained by pHstat (TIM 856 titration manager, Radiometer analytical) and for pH adjustment 1 M NaOH and $HClO_4$ were used.

Photodegradation experiments were performed at two initial concentrations of salicylate (1 and 0.1 mM), one initial concentration of oxalate (2 mM) and two values of pH kept constant during irradiation. Goethite was added into the solution of oxalate and salicylate, the suspension was homogenised in ultrasound for 5 min and transferred into a Pyrex tube. The pH electrode was inserted into the suspension and the pH was adjusted to the required value. When adsorption equilibrium was reached (after 30 min) the lamps were switched on. The pH electrode was present all the time in the irradiated suspension. Samples were taken frequently by pipette, centrifuged for 15 min at 14,000 rpm and then analysed by HPLC (conditions given above). Due to adsorption, the oxalate concentration when irradiation was started was around 1.6 mM for pH 3 and around 1.7 mM for pH 6. In Figs. 4–6 c_{OX}^0 is, in fact, the concentration of oxalate after adsorption equilibrium when irradiation was started (time = 0).

3. Results

3.1. Characteristics of goethite synthesised

The XRD powder pattern (Fig. 1) shows excellent sharp peaks. Identification was performed using the software package HighScore Plus [31] and a search-match procedure undoubtedly suggested goethite (FeO(OH) – PDF card 81-0462) [32]. The avarage crystalline size of crystallites was measured and the value of 17 nm was calculated. No other crystalline phases were present.

FTIR spectra of goethite (Fig. 2) show 4 main bands. The band between 3600 and 3300 cm^{-1} is assigned to the H···O···H vibration (ν_1). This band is a typical mode of non-stoichiometric hydroxyl units (excess water) in the goethite structure. This type of hydroxyl units can be incorporated into the goethite structure and adsorbed onto the crystal surface during the process of synthesis. Goethite can also adsorb hydroxyl units from the atmosphere. The most intense band at 3300–3000 cm^{-1} is assigned to the O···H stretching vibration (ν_2). The band at ~890 cm^{-1} corresponds to O–H bending vibration [33] and, finally, the band at 620 cm^{-1} to Fe–O stretching vibration.

3.2. Separate adsorption of salicylate and oxalate

Adsorbed amounts of sodium oxalate are shown in Fig. 3 as a function of equilibrium oxalate concentration. It can be seen that

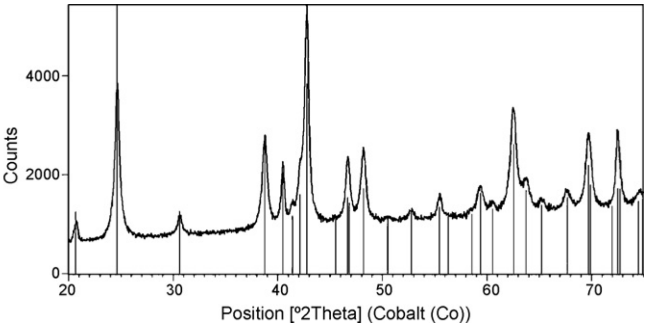


Fig. 1. XRD powder spectra of synthesised goethite.

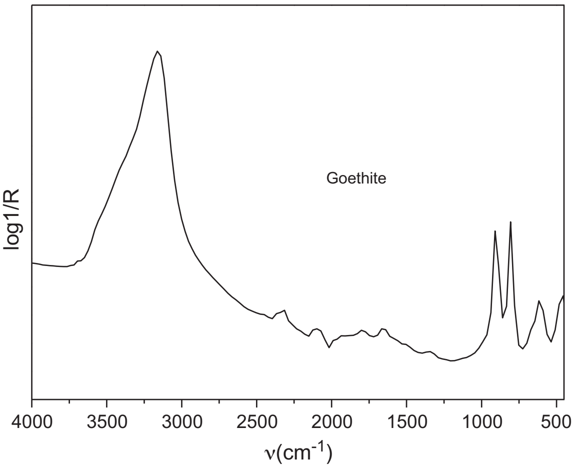


Fig. 2. FTIR spectra of synthesised goethite.

the adsorption is higher at pH 3 than at pH 6. This result corresponds with the maximum adsorption between pH 3.5 and 3.8 reported in the literature [12,13] and can be explained by the acid–base properties of oxalic acid (pK_{a1} = 1.27 and pK_{a2} = 4.28). The possible explanation for the observed difference in limiting adsorbed amounts of oxalate at pH 3 and 6 is the different structure of the surface complexes. At pH 3 the major HCOO–COO$^-$ form is bonded through the deprotonated carboxylic group forming monodental surface complex while at pH 6 the most abundant $(COO)_2{}^{2-}$ form creates bidental surface complex.

Adsorption at varying concentration of sodium salicylate on goethite (2 g/dm^3) at pH 3 and 6 is shown in Fig. 4 as a dependence of adsorbed amounts of salicylate on its equilibrium concentration. Similarly to oxalate, the adsorption of salicylate is higher at pH 3 than 6. In contrast to oxalate, there are no systematic literature data concerning the effect of pH on the adsorption of salicylate. Only data at single pH values and ionic strengths are available in the literature giving the following limiting amounts of adsorbed salicylate: 0.075 mmol/g at pH 4 [17], 0.02 mmol/g at pH 5.6 [18] and 0.08 mmol/g at pH 4.5 [19]. Therefore the following experiments at various pH values were performed.

For each value of pH, the dependence of adsorbed amount of salicylate on equilibrium salicylate concentration was experimentally obtained (as shown in Fig. 4) and using the Langmuir isotherm model and non-linear regression method the maximum adsorbed amount n_{ads}(max) and equilibrium adsorption constant (K_{ads}) were determined. Values of K_{ads} for adsorption of sodium salicylate on goethite at the investigated pH values are shown in Fig. 5. It can be seen that the adsorption of salicylate first increased with decreasing pH to reach a maximum at pH 3. Then the adsorption decreased. This behaviour is in agreement with the recent study of Rusch et al. [21] and relates both to the acid-base properties of salicylic acid (pK_a = 2.97) and to the amphoteric features of the goethite surface (pH$_{zpc}$ ≈ 8).

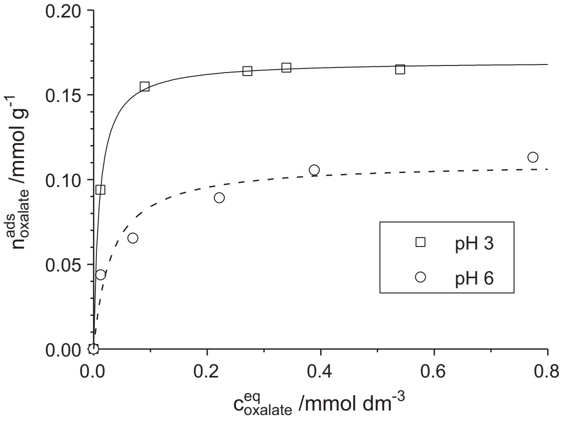


Fig. 3. Adsorption of oxalate on goethite (2 g/dm^3) at pH 3 and 6.

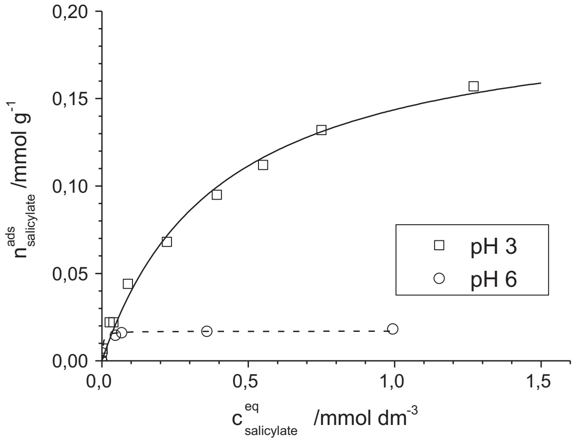


Fig. 4. Adsorption of salicylate on goethite (2 g/dm^3) at pH 3 and 6.

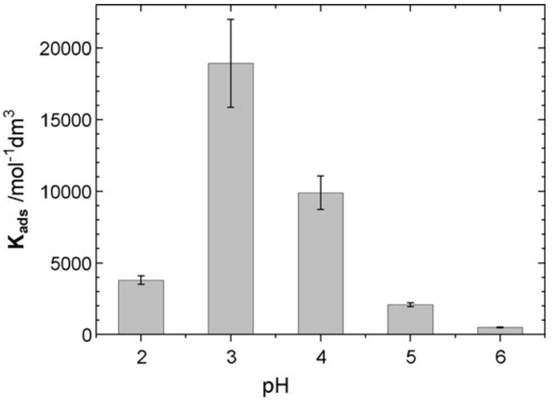


Fig. 5. Adsorption equilibrium constants of salicylate on goethite for pH values in the range of 2–6.

3.3. Co-adsorption of salicylate and oxalate

The results of co-adsorption of oxalate and salicylate at pH 6 and 3 are shown in Tables 1 and 2, respectively. It can be seen that an addition of oxalate resulted in a marked decrease in the adsorp-

Table 1
Co-adsorption of salicylate and oxalate at pH 6.

Total concentration (mM)		$C_{oxalate}/C_{salicylate}$	n^{ads}/m (μmol/g)	
Salicylate	Oxalate		Salicylate	Oxalate
1	0		48.4	
2	0		61.1	
0	1			87.7
1 mM total conc. salicylate, addition of oxalate				
1	0		48.4	
1	0.1	0.1	36.3	[a]
1	1	1	7.01	83.5
1	2	2	1.5	91.1
0.1 mM total conc. salicylate, addition of oxalate				
0.1	0	0	16.2	
0.1	0.1	1	15.7	[a]
0.1	2	20	1.34	101

[a] Under the detection limit.

Table 2
Co-adsorption of salicylate and oxalate at pH 3.

Total concentration (mM)		$C_{oxalate}/C_{salicylate}$	n^{ads}/m (μmol/g)	
Salicylate	Oxalate		Salicylate	Oxalate
1	0		112	
2	0		157	
0	1			166
1 mM total conc. salicylate, addition of oxalate				
1	0		112	
1	1	1	15.9	169
1	2	2	0	165
0.1 mM total conc. salicylate, addition of oxalate				
0.1	0	0	21	
0.1	1	10	3.9	165
0.1	2	20	0	149

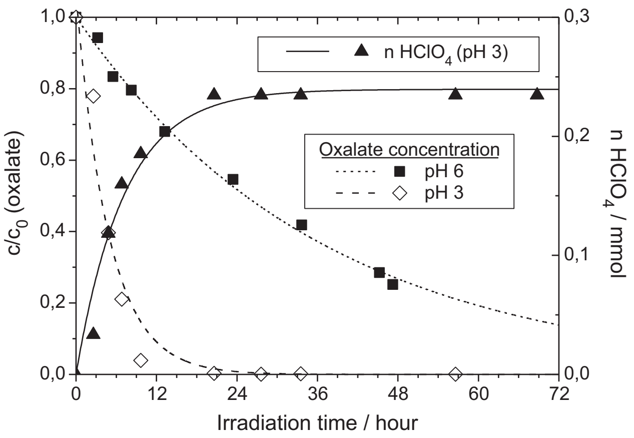


Fig. 6. Dependence of oxalate concentration (for pH 3 and 6) and added molar amount of $HClO_4$ (for pH 3) in the goethite suspension (1 g/dm^3) on irradiation time. Initial oxalate concentration 2 mM, $c^0_{oxalate}$ is concentration of oxalate after adsorption equilibrium (time = 0).

tion of salicylate on goethite. For example at pH 6, the presence of 0.1 mM oxalate decreased the adsorption of 1 mM salicylate on goethite (2 g/dm^3) by 25%, the presence of 1 mM oxalate by 85% and of 2 mM oxalate by 97%. An analogous effect of oxalate on the adsorption of salicylate was observed for 0.1 mM salicylate. For an equimolar mixture of salicylate to oxalate (0.1 mM), the adsorption of salicylate decreased only by 5%. However, for higher 2 mM concentration of oxalate, the adsorption of 0.1 mM salicylate decreased by 90%. At pH 3, the effect of oxalate on the adsorption of salicylate on goethite was even stronger. For both 0.1 and 1 mM salicylate, the addition of 1 mM oxalate resulted in a decrease in salicylate adsorption by about 80%. In the case of 2 mM oxalate the adsorption of salicylate was negligible.

The presence of salicylate (0.1 or 1 mM) in 2 mM oxalate solution at pH 6 had almost no effect on the adsorption of oxalate. Similar behaviour was observed in the case of pH 3 with the difference that, at pH 6, the amount of absorbed salicylate was about one order of magnitude lower than that of oxalate but, at pH 3, the adsorbed amount of salicylate was negligible. On the other hand a different situation was observed by Mesuere and Fish [12] who studied competitive adsorption of chromate and oxalate on goethite. They found that for equimolar concentrations 0.2 and 0.8 mM the adsorbed amount of chromate is only slightly affected for pH < 7, while the adsorbed amount of oxalate is reduced in the whole pH region by 50% (0.2 mM) and by 75% (0.8 mM) compared to the single solute system.

In 1 mM equimolar oxalate and salicylate solution the effect of pH change from 6 to 3 on adsorption was the same for salicylate and oxalate (increase about 100%) but the amount of adsorbed salicylate was for both pH decreased about 80% (in relation to single salicylate) and about 10 times lower than the adsorbed amount of oxalate. This means that oxalate is preferentially adsorbed on the goethite surface. Similar behaviour was observed by Liu et al. [13] for the case of competitive adsorption of sulphate and oxalate. For an equimolar ratio (total concentrations 0.3 mM) the molar ratio of adsorbed oxalate to sulphate ranged from 2.3 to 3.8 for pH from 3 to 7.5, respectively.

3.4. Photodegradation experiments

3.4.1. Oxalate degradation without salicylate

Fig. 6 shows the dependence of oxalate concentration in the goethite suspension on irradiation time for two values of pH (3 and 6). For both pH 3 and 6 an almost exponential decrease in oxalate concentration was observed (calculated experimental rate constants are shown in Table 3). At pH 3 after 10 h of irradiation the concentration of oxalate reached 5% of the initial value; at pH 6 the degradation rate constant was about 1 order lower than at pH 3 (0.0275 h^{-1}); after 50 h of irradiation the concentration reached about 30% of the initial value. The initial degradation rates of oxalic acid at pH 3 and 6 related to the goethite mass were calculated as 0.248 mol g^{-1} h^{-1} and 0.022 mol g^{-1} h^{-1}, respectively. It is apparent that the degradation rate at pH 3 is about an order higher than that at pH 6 while the limiting adsorbed amount of oxalic acid at pH 3 is only about 50% higher than at pH 6.

The dependence of the added molar amount of $HClO_4$ on irradiation time for the experiment at constant pH 3 is also shown in Fig. 6. It is clear that the course of oxalate disappearance corresponds to the time behaviour of added amount of $HClO_4$ (in fact H^+). When all oxalate is degraded it is not necessary to add H^+ to maintain constant pH.

The presence of Fe^{2+} was found only in the absence of oxygen in the solution as already observed by Sulzberger and Laubscher [22]. This can be explained by the fact that Fe^{2+} formed by photodissolution of goethite is oxidised by hydrogen peroxide or radicals (formed due to oxygen presence) occurring in the course of the photoinduced process. For the purpose of maintaining Fe^{2+} in the solution Goldberg et al. [23] used the addition of bipyridin to keep Fe^{2+} in complexed form and prevent its oxidation. We observed that at pH 3 Fe^{3+} stays dissolved in aqueous solution. However, under the same acidity in the presence of goethite no Fe^{3+} was determined in the liquid phase of the reaction mixture. This implies that Fe^{3+} precipitates on the goethite surface even at relatively acidic pH values.

3.4.2. Salicylate degradation without oxalate

Degradation was followed at pH 3 and 6 and in both cases a negligible decrease in salicylate concentration was observed. A similar result for the system containing only goethite, UV and dye Mordant Yellow 10 was reported by He et al. [28]. On the other hand, rather surprising results were reported by He et al. [26] who observed measurable photodegradation of salicylate in the presence of goethite (decrease of 13% after 6 h of irradiation). There are

Table 3
Experimental first order rate constants for salicylate and oxalate degradation.

Total concentration (mM)		pH	k (h^{-1})	
Salicylate	Oxalate		Salicylate	Oxalate
0	2	3		0.2047
1	2	3	0.1607	0.1877
0.1	2	3	0.2728	0.1280
0	2	6		0.0275
1	2	6	0.0454	0.0186
0.1	2	6	0.0737	0.0178

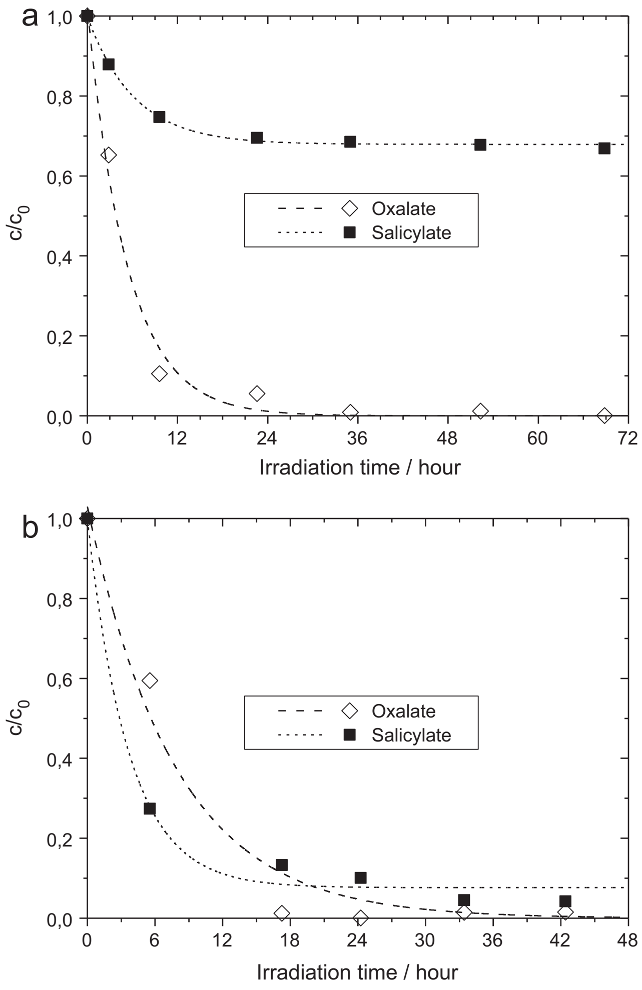


Fig. 7. Photodegradation of salicylate on goethite (1 g/dm^3) in the presence of oxalate at pH 3, initial salicylate concentration 1 mM (a) and 0.1 mM (b), initial oxalate concentration 2 mM, $c^0_{\text{salicylate}}$ and c^0_{oxalate} are concentrations of salicylate and oxalate, respectively, after adsorption equilibrium (time = 0).

two possible reasons for the observed change of salicylate concentration during irradiation: (i) insufficient purity of the goethite used because it was prepared from ferric chloride as a starting material. It is well known that the amorphous part is more soluble in water than crystalline goethite and this results in the release of Fe(III) into the solution, (ii) the initial concentration of salicylate was only 0.05 mM and pH was not constant during irradiation; thus the adsorption equilibrium may change and this may result in a change in concentration of salicylate in the course of irradiation.

3.4.3. Salicylate degradation in the presence of oxalate

The course of oxalate and salicylate concentration (initial concentration 1 mM) during the irradiation of goethite suspension at pH 3 is shown in Fig. 7a. Oxalate concentration decreased rapidly during the first 10 h and then the decrease slowed; but after 35 h the concentration of oxalate became negligible. The decrease in salicylate concentration was proportional to the amount of oxalate in the system. When the oxalate concentration reached zero the salicylate concentration decreased very slowly.

In the case of lower initial concentration of salicylate (0.1 mM) (Fig. 7b) the decrease in oxalate concentration with irradiation time was similar to that for 1 mM salicylate, the only difference being that a negligible concentration of oxalate was reached earlier. The concentration of salicylate decreased with time and the decrease

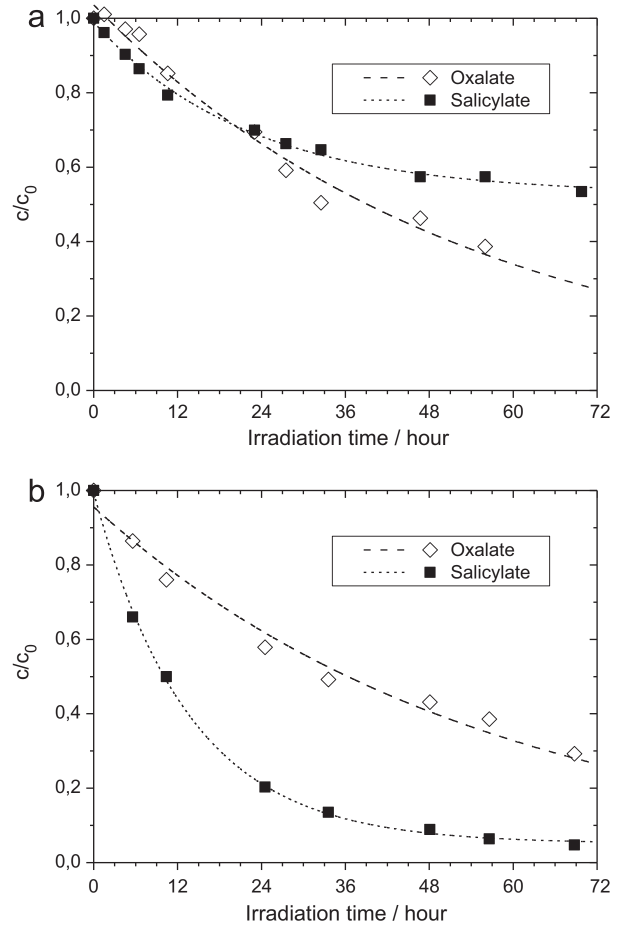


Fig. 8. Photodegradation of salicylate on goethite (1 g/dm^3) in the presence of oxalate at pH 6, initial salicylate concentration 1 mM (a) and 0.1 mM (b), initial oxalate concentration 2 mM, $c^0_{\text{salicylate}}$ and c^0_{oxalate} are concentrations of salicylate and oxalate, respectively, after adsorption equilibrium (time = 0).

was also proportional to the concentration of oxalate. Due to the lower initial concentration the 90% of initial amount of salicylate was degraded until all the oxalate disappeared.

The dependence of oxalate and salicylate concentration (initial concentration 1 mM) during irradiation of goethite suspension at pH 6 is shown in Fig. 8a. Oxalate concentration again decreased with irradiation time but significantly more slowly than at pH 3. Cornell and Schindler [24] followed the decomposition of oxalate via proton consumption and found a similar dependence of reaction rate on pH. They also found that the slow initial stage of photodissolution kinetics could be eliminated by small additions of Fe^{2+}.

Experimental first order rate constants of oxalate and salicylate degradation are shown in Table 3. The decrease in oxalate concentration was for both pH smaller than in the case of oxalic acid alone. One would expect that it was due to the competitive adsorption of both acids resulting in decreased adsorption of oxalate. However, as shown in Table 2, the adsorbed amount of oxalate either at pH 6 or at pH 3 is not influenced by the presence of salicylate.

Salicylate concentration decreased in a similar manner as for oxalate. The degradation rate of salicylate at pH 6 during the first 10 h was comparable to that at pH 3. For longer irradiation times salicylate concentration decreased faster than at pH 3. This can be explained by the presence of oxalic acid in the system at pH 6 at longer irradiation times. In the case of lower initial concentration of salicylate (0.1 mM) (Fig. 8b) the decrease in oxalic concentration with irradiation time was similar as for 1 mM salicylate (Fig. 8a). The concentration of salicylate decreased with time and reached

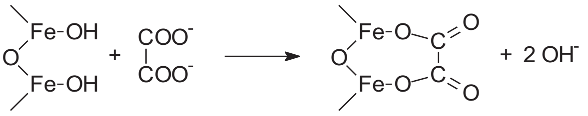
5% of the initial concentration after 70 h irradiation. Similarly as for pH 3 the degradation of salicylate at pH 6 was faster for lower initial salicylate concentration.

Comparison of salicylate degradation rate at pH 3 and 6 depends on the initial concentration of salicylate and is different for long and short irradiation times. At short irradiation times, according to calculated rate constants (Table 3), degradation rate is higher at pH 3 for both initial salicylate concentrations. At long irradiation times (>30 h) the situation is different. For the lower initial concentration (0.1 mM), degradation is faster at pH 3 because oxalate is present in the system until 90% of salicylate is degraded. On the other hand, for 10 times higher initial concentration, degradation is faster at pH 6 because at this pH oxalate remains in the system even after 70 h irradiation (about 40% of initial concentration) while at pH 3 there is only 10% of initial oxalate concentration after 10 h of irradiation and oxalate completely disappears after 35 h.

3.4.4. *Mechanism of goethite photodissolution*

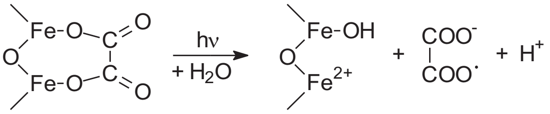
Cunningham et al. [25] reported that photolysis of adsorbed benzoate and oxalate on goethite leads to the formation of OH radicals. They proposed that most of the OH formed derives indirectly from the thermal oxidation of Fe(II) (aq.) rather than from photoredox reactions involving the surface sites >FeIII(:OH−).

The detailed steps in goethite photodissolution can be described as follows. Surface complexation of goethite is a necessary condition for photodissolution. At higher pH, both carboxylic groups of oxalic acid are deprotonated. Thus their condensation with two surface hydroxyl groups is possible leading to the formation of a corresponding bidental surface complex under release of two hydroxyl anions at the same time (Eq. (1)).



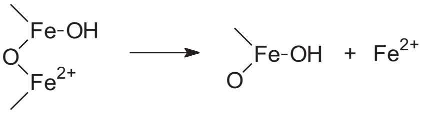
(1)

Photoexcitation of this complex leads to metal–ligand charge-tranfer causing its dissociation (Eq. (2)).



(2)

While the reduced iron releases the goethite surface as Fe^{2+} cation (Eq. (3)), the oxidised oxalate radical anion decomposes to carbon dioxide and CO_2^- radicals (Eq. (4)).



(3)

$$\begin{matrix}\text{COO}^- \\ | \\ \text{COO}^\bullet\end{matrix} \longrightarrow CO_2 + CO_2^{-\bullet}$$

(4)

The CO_2^- radical reacts rapidly with molecular oxygen to form carbon dioxide and superoxide radical anions (Eq. (5)).

$$CO_2{\cdot}^- + O_2 \rightarrow CO_2 + O_2{\cdot}^- \tag{5}$$

The superoxide radical anion is in an acid–base equilibrium with the hydroperoxyl radical (Eq. (6)), which can disproportionate to hydrogen peroxide and molecular oxygen (Eq. (7)).

$$O_2{}^{\bullet-} + H^+ \rightleftharpoons O_2H^\bullet \tag{6}$$

$$2O_2H^\bullet \rightarrow H_2O_2 + O_2 \tag{7}$$

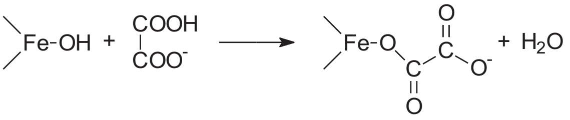
The dissolved Fe^{2+} and hydrogen peroxide undergo a Fenton reaction producing a hydroxy complex of iron(III) and hydroxyl radicals (Eq. (8)).

$$Fe^{2+} + H_2O_2 \rightarrow FeOH^{2+} + OH^\bullet \tag{8}$$

The complex $FeOH^{2+}$ is highly photoactive generating Fe^{2+} upon UV irradiation and also hydroxyl radicals (Eq. (9)).

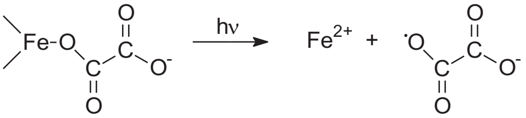
$$FeOH^{2+} \xrightarrow{h\nu} Fe^{2+} + OH^\bullet \tag{9}$$

At lower pH only one of the carboxylic groups of oxalic acid is deprotonated and its condensation with one surface hydroxyl group leads to the formation of a corresponding monodental surface complex (Eq. (10)). This is in agreement with the fact that the maximum adsorbed amount of oxalate at pH 3 was about two times higher than at pH 6 (see Fig. 2). This may be connected with different mono and bidentate structures of oxalate surface complexes proposed in Eqs. (1) and (10).



(10)

Excitation leads to metal–ligand charge transfer with subsequent dissociation (Eq. (11)) as in the previous case of the bidental surface complex (Eq. (2)).



(11)

4. Conclusions

It can be concluded that for both pH values oxalate is preferentially adsorbed on the goethite surface provided that the total concentration is at least 1 mM. The effect of oxalate is stronger at pH 3 where, at an oxalate concentration 2 mM, the adsorption of salicylate is negligible.

Photodegradation of salicylate on goethite proceeds only in the presence of oxalate. This is due to the photodissolution of goethite resulting in the formation of OH radicals. Surprisingly, at pH 3, salicylate photodegradation stops due to total oxalate consumption. On the other hand at pH 6 photodissolution of goethite is slower and the oxalate concentration during irradiation decreases more slowly. As a result, salicylate degradation is slower than at pH 3 but does not stop and also proceeds at longer irradiation times.

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