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ORIGINAL PAPER

Fenton-like photocatalyzed degradation of dibutyl phthalate with goethite and carboxylic acids

S. Hejda[1,2] · D. Buzek[1] · P. Kluson[2] · O. Bajt[3,4]

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Abstract

Detailed investigation of photocatalyzed degradation of dibutyl phthalate (DBP), an endocrine disrupter, in the presence of α-FeOOH (goethite) and different carboxylic acids is the focus of this study. To get a better insight into the efficiency of the degradation, the influence of different parameters, such as concentration of total Fe and Fe(II), dissolved oxygen, DBP concentration, pH and salinity is investigated. The reaction mechanism consists of several interrelationship steps. The first step is the chemical reaction of carboxylic acid groups of the organic acids with hydroxyl groups of the α-FeOOH and a charge transfer upon illumination generating Fe(II). The second step is the release of Fe(II) into the solution followed by H_2O_2 oxidation to form highly photoactive hydroxyl complex of iron(III) and $^{\cdot}OH$. Simultaneously, the superoxide radical $O_2^{\cdot -}$ and hydroperoxyl radical is formed in acidic solutions in presence of carboxylic acids as well. This mechanism explains the genesis of different reactive species oxidizing DBP. From the variety of the studied carboxylic acids (oxalic, citric, salicylic, pyruvic, maleic, and fumaric), oxalic acid is the best Fe-ligand for the photoreductive dissolution of goethite. Concentrations of the total amount of Fe and its dissociated forms Fe(II) as well as oxygen and hydroxyl radicals play a fundamental role in efficiency of DBP degradation. The photodegradation of DBP with goethite and the use of suitable carboxylic acids under optimized reaction conditions could be an efficient process for decontamination of polluted waters.

Keywords Photocatalysis · Goethite · Dibutyl phthalate · Carboxylic acid · Water treatment

Introduction

Iron is one of the most abundant element in the environment. It is also an essential micronutrient for most known aquatic organisms. It forms different minerals in the natural environment, for example, magnetite, hematite, goethite, or siderite. Goethite, the most thermodynamically stable oxyhydroxide (Goldberg et al. 1993), is also the most abundant iron oxide in the natural marine environment (Arcon et al. 1999). Considering its low solubility in water, goethite can generally be dissolved by photoreductive processes. Photoreductive dissolution of goethite is a process, where Fe(III), placed in crystal lattice, is transformed into Fe(II) water-soluble form. This process represents an important mechanism for the source of Fe(II) in natural waters (Wu and Deng 2000; Mazellier and Sulzberger 2001). Different mechanisms of the photochemically enhanced reduction of Fe(III) have been proposed. In systems without organic ligands, photoredox reactions may occur in which hydroxide ion donates an electron to a photoexcited Fe(III) surface atoms resulting in Fe(II)-ion formation (Sulzberger et al. 1989). A semiconductor-like mechanism has also been proposed (Borer et al. 2009), involving light-induced electron/hole pair generation in the iron oxide lattice. The latter process is usually less effective due to efficient recombination of photoexcited electrons and holes (Borer et al. 2009).

Higher efficiency of photochemical reduction of Fe(III) with carboxylic acids was observed by (Goldberg et al. 1993). Carboxylic acids are natural products from microbial decomposition of organic matter, and they can also be detected in water

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✉ S. Hejda
stanislav.hejda@ujep.cz

[1] Faculty of Environment, J. E. Purkyne University in Usti nad Labem, Pasteurova 3632/15, 400 96 Usti nad Labem, Czech Republic

[2] Institute of Chemical Process Fundamentals, The Czech Academy of Sciences, Rozvojova 135/2, 165 02 Prague, Czech Republic

[3] Marine Biology Station Piran, National Institute of Biology, Fornace 41, 6330 Piran, Slovenia

[4] Faculty for Maritime Studies and Transport, University of Ljubljana, Pot pomorščakov 4, 6320 Portorož, Slovenia

environments (Lin et al. 2017). The presence of natural carboxylic acids can be beneficial for photodissolution of goethite and degradation of organic pollutants in natural waters. A beneficial effect of the presence of dicarboxylic acids, such as oxalic, salicylic, malonic, citric or phthalic, to the photodissolution of goethite has been observed (Goldberg et al. 1993; Reichard et al. 2007).

Massive contamination of water environment by toxic pollutants occurs because of the human activities. Phthalates have been detected in natural waters, marine sediments, and biota (Preston and Al-Omran 1986; Rice et al. 1993). Phthalate concentrations in natural freshwater, saltwater, or industrial water are at levels ranging from 0.29 to 1.24 μg L^{-1} (Hannon and Flaws 2015). The concentration of phthalates can be much higher near chemical industry sites which produce such compounds, e.g., dialkyl phthalate concentration around 100 mg L^{-1} was measured in wastewaters in the Slovenian coastal area (Bajt et al. 2001). Dialkyl phthalates are used as plasticizers in different resins. They are considered to be toxic for different organisms (Staples et al. 1997) and they are classified as important endocrine disrupting compounds as well. Dibutyl phthalate (DBP) belongs to the five highest production volumes among phthalates (Lyche 2017). Due to the toxic character of DBP, extensive restrictions on its applications have been imposed over the last decade. The replacement of DBP with less toxic long-alkyl phthalates is in progress. Nevertheless, according to the U.S. EPA database (European Chemicals Agency 2021) DBP still belongs to a high-production volume commodity.

DBP is stable in the natural environment. Studies of its biodegradation in freshwaters, seawater, sediments, and wastewaters revealed a rather low degradation rate taking between days up to a few months (Staples et al. 1997). In general, dialkyl phthalates exhibit weak optical absorption upon illumination at $\lambda \geq 300$ nm. Photocatalyzed degradation is very efficient in the presence of TiO_2 (Yuan et al. 2008; Jing et al. 2011). Photochemical processes in the presence of iron have mostly been investigated in homogeneous systems (Bajt et al. 2001; Mailhot et al. 2002). Limited data about photocatalyzed degradation of phthalate esters in heterogeneous Fe(III) systems are available in the literature (Krysa et al. 2011; Shuai et al. 2019). Therefore, the present work aims to extensively investigate the photodegradation of model compound DBP with carboxylic acids in a heterogeneous Fe(III) system. At first, the comprehensive laboratory simulation of the process taking place in a water environment is performed. DBP is selected as a model compound and as a representant of anthropogenic contaminants in natural waters. Laboratory-prepared goethite is used as iron source. In our previous work, we demonstrated that goethite and light illumination itself have negligible effect on DBP degradation and carboxylic acid had to be used (Krysa et al. 2011). In the present work, oxalic, citric, salicylic, pyruvic, maleic, and fumaric acids, representing carboxylic acids occurring in natural waters, are tested for goethite photodissolution. The influence of different reaction parameters as pH, goethite concentrations, type and concentration of carboxylic acid, concentrations of DBP and NaCl for modelling the conditions in seawater, and other conditions on the photodissolution process are studied in detail. Furthermore, the effect of total Fe, Fe(III) and Fe(II) and dissolved oxygen concentration in solution on the efficiency of DBP degradation is investigated.

The date of the research was in 2019, the research was located in Piran, Slovenia.

Materials and methods

Goethite synthesis

Goethite was prepared according to the method described by Atkinson et al. (1968). 360 g of $Fe(NO_3)_3 \cdot 9H_2O$ were dissolved in 1460 mL of water, and 500 mL of 3 M NaOH was slowly added under vigorous magnetic stirring, and kept to react at room temperature for 2 days under continuous stirring. Then, saturated NaOH was added drop-by-drop until the pH value between 12 and 13 was reached. The stirring was stopped and the formed slurry was heated at 60 °C for 4 days. The solid product was separated from the mixture by centrifugation. Neutralization to pH around 9 was achieved by repeated resuspension of the product in distilled water and centrifugation. Finally, the prepared goethite was dried at 40 °C.

Goethite was characterized in our previous work (Krysa et al. 2011). The average crystals diameter was 17 nm. The specific surface area (BET) of the goethite was 96 m^2 g^{-1}.

Preparation of the reaction mixture

All the used reagents were of analytical grade. Milli Q water was used for the preparation of solutions. Air (19.95–23.6 vol% O_2, 76.4–80.05 vol% N_2) and nitrogen (purity 99.99%) were purchased from Linde.

The reaction mixture was prepared by adding a certain amount (measured volumetrically) of DBP (Merck) to 2 L of water to reach a concentration of 3.0×10^{-5} M. The mixture was stirred overnight at room temperature. 25 mg of goethite was added to exactly 90 mL of the solution contained in a 100 mL volumetric flask. The formed suspension was well-dispersed in an ultrasonic bath for 3 min. Then the different carboxylic acids (oxalic, citric, salicylic, pyruvic, maleic, or fumaric acid, Sigma-Aldrich, final concentration of 2×10^{-3} M) were added and the flask was filled with distilled water. The pH value was adjusted by using 1 M $HClO_4$ or NaOH just before illumination. The same procedure was repeated for all experiments; only the concentrations of individual components were varied.

Photodegradation experiments

Illuminations were performed in a cylindrical batch type photoreactor. A water-jacketed fused-silica Pyrex tube (a diameter of 3 cm) was placed in the centre of 3 Sylvania HPW 125 W lamps ($\lambda = 365 \pm 5$ nm) symmetrically installed in the reactor. Mixing was done by a magnetic stirrer. The reaction temperature was maintained at 20 °C. Constant pH was continuously adjusted with 1 M $HClO_4$ by using an automatic titrator (Buchi). Samples were taken at different time intervals and analyzed after centrifugation.

When air or nitrogen was applied during the experiments for the simulation of degradation processes of DBP at different levels of O_2 concentration, the reaction mixture was purged for 30 min before and continuously during illumination. In the case of nitrogen, the concentration of dissolved oxygen was measured before and during illumination. It was not possible to completely remove all oxygen, even with prolonged purging time. The lowest oxygen concentration was around 0.25 mg L^{-1}. Dissolved oxygen was measured by using the field oxygen probe Multi 350i, WTW Germany.

Analysis of DBP

Analysis was carried out using a Varian 9010 HPLC equipped with an UV absorption detector ($\lambda = 227$ nm). A chromatographic column was an Eclipse XDB C-18, 5 µm, 4.6 × 150 mm, Agilent, USA. The analysis was performed in an isocratic mode with the mobile phase methanol/water (80/20, v/v) at a flow rate of 1 ml min^{-1}. Quantification was made by using external standard solutions.

Reaction with hydroxyl radical scavenger

The reaction mixture was modified by the addition of propane-2-ol (Sigma Aldrich), a scavenger of $^{\cdot}OH$. Before illumination, the reaction mixture was enriched with 15.4 µL and 30.8 µL of propan-2-ol giving 2 mM and 4 mM solutions, respectively.

Determination of iron

Concentrations of Fe(II) and the total Fe in the reaction mixture were measured experimentally by the following procedure. The concentration of Fe(III) was calculated as the difference between those two concentrations.

Determination of Fe(II)

The Fe(II) concentration was determined spectrophotometrically with 1,10-phenanthroline according to an earlier described method (Bajt et al. 2001).

Determination of the total Fe

Concentration of the total iron dissolved in the sample solution was determined after the separation of the solid. 0.5 mL of hydroxylamine chlorohydrate (3 M, Merck) was added into 10 mL volumetric flask, followed by the addition of 0.25 mL of a sample solution. The mixture was kept at room temperature for 15 min, then 0.5 mL of ferrozine (0.02 M, Merck) and 1 mL of ammonium acetate buffer (Merck) were added, and finally, the flask was completed to 10 ml by water. A blank sample was prepared with the same procedure but without the sample solution taken from the reaction mixture. Absorbance was measured at 562 nm.

Results and discussion

Adsorption and experiments under the dark conditions

The adsorption of DBP (3.0×10^{-5} M) on goethite (0.25 g L^{-1}) was measured at pH = 3 without UV irradiation.

The reaction mixture was stirred at room temperature for 8 h. No significant adsorption of DBP on α-FeOOH was detected during the experiment. The experiment was also carried out under the same conditions as the described general experiment, but without irradiation. After 2.5 h, the decrease in DBP concentration was negligible. This indicates the absence of any degradation process in the investigated system, at least for the time scale we were set in photodegradation experiments. The light is essential for the DBP degradation in the presence of goethite by the photoreductive process. Photodegradation of DBP in the presence of goethite, but without carboxylic acid, did not occur as well and also photolysis of DBP was negligible.

Effect of carboxylic acids

Carboxylic acids (e.g. oxalic, citric, malonic) can be helpful for leaching iron from iron oxides and hydroxides. The dissolution process of iron oxides or hydroxides is needed for consecutive reactions, which lead to the formation of reactive $^{\cdot}OH$ by a Fenton-like reaction. Therefore, adding suitable carboxylic acid can be efficient. The effect of the wide range of carboxylic acids (oxalic, citric, maleic, fumaric, salicylic, pyruvic) on DBP degradation was firstly investigated. The photocatalyzed degradation of DBP with goethite at pH = 3 in the presence of used carboxylic acids is presented in Fig. 1. The concentration of all carboxylic acids was 2 mM. It is evident that only oxalic acid and citric acid exhibited an important effect on the photodissolution of goethite and subsequent degradation of DBP. In both cases, about 80% of DBP was degraded, but the reaction rate

$k = 1.59\ h^{-1}$ was significantly higher with oxalic acid in comparison with citric acid ($k = 0.42\ h^{-1}$). All other carboxylic acids showed less efficient (salicylic, pyruvic) or almost no effect on DBP degradation (maleic, fumaric). The kinetic studies revealed that all reactions were of pseudo-first-order kinetics.

In all cases, the complete DBP concentration was not reached, most probably due to the complete consumption of oxygen which is an essential precursor for the formation of the reactive superoxide radical $O_2^{\cdot-}$ (Arcon et al. 1999; Balmer and Sulzberger 1999; Wu and Deng 2000; Shuai et al. 2019). After the complete consumption of O_2, the generation of $O_2^{\cdot-}$ and consequently the $^{\cdot}OH$ was significantly slowed down and only limited degradation of DBP was noticed. This effect is described in "Effect of O_2, N_2, and H_2O_2" section in detail.

To mantain constant pH during the photodegradation of DBP, we continuously added $HClO_4$. The pH of the reaction mixture slightly increased during the degradation of DBP in the presence of oxalic and citric acid, and it had very low or almost negligible difference in the solutions of other acids. The increase in pH during photodegradation could be due to the chemical reaction between carboxylic acid groups of organic molecules with the hydroxyl groups of α-FeOOH and reaction with the formed Fe(II). These results in the degradation of the acid and a further increase in pH could be an indication of the importance of the photoactive Fe(III)/carboxylate complex formation. This complexation and further photoreaction rate depend on different parameters: the structure of carboxylic acid and consequently the reaction of carboxylate anion with the hydroxyl groups of α-FeOOH, acid dissociation and interactions of acids with formed radicals (Staples et al. 1997; Krysa et al. 2011; Zhang et al. 2016; Zhang et al. 2019). It has already been shown that the ability to liberate Fe(II) from the goethite lattice decreases in the following order: oxalate > citrate > maleate > fumarate (Goldberg et al. 1993) which is consistent with our degradation rates of DBP. Filius et al. (1997) reported that the reaction affinity of organic acids depends on the number of reactive groups per bond with oxalic acid showing the highest affinity. Moreover, the $^{\cdot}OH$ production after oxalic acid reaction with the hydroxyl groups of α-FeOOH and irradiation was a few times faster, compared to other carboxylic acids, including citric acid (Zhang et al. 2016; Lin et al. 2017). Goldberg et al. (1993) investigated the effect of photolytic reaction in the case of goethite and organic acids. They assumed, that the presence of α-hydroxyl group and an even number of carbons in the central chain play the most important role. This was explained by the difficulty of both carboxyl groups to undergo redox reaction. In our case, the most effective oxalic acid has no hydroxyl groups and the second citric acid has one hydroxyl group in the α position. The dissimilar effect of different acids can be explained also by the ability to form highly stable iron complexes, which are characteristic for oxalic acid (Rodriguez et al. 2009).

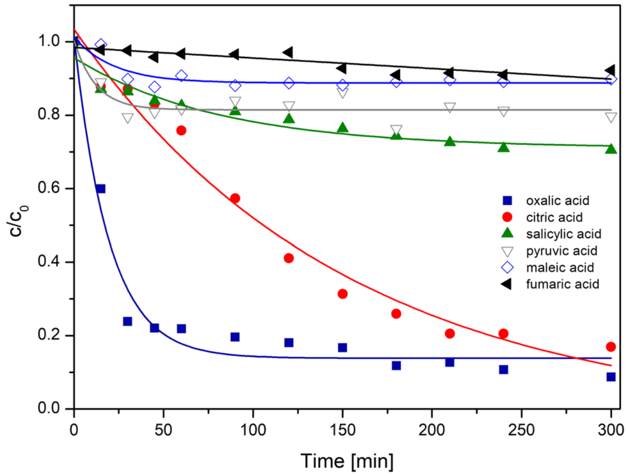


Fig. 1 The influence of different carboxylic acids on the photodegradation of DBP

Finally, perhaps the most important reason for the difference in the reactivity is the different pK_a values. Our experiment was performed at pH = 3. At this pH, the oxalic acid is present in its monodeprotonated form ($pK_{a1} = 1.23$) while citric acid is mostly protonated ($pK_{a1} = 3.13$). Therefore, the reaction of carboxylic acid and subsequent photoreductive dissolution of Fe(II) from goethite determines the kinetics of DBP degradation in the studied heterogeneous system.

Effect of pH

The effect of pH on the photodegradation of DBP was tested at pH = 3, 4, 5, and 6 only in the presence of oxalic acid which was shown as the most efficient compound for leaching Fe ("Effect of carboxylic acids" section). Results, presented in Fig. 2 showed an important effect of pH on the degradation of DBP. The highest degradation rate $k = 1.59\ h^{-1}$ was observed at pH = 3, with about 80% degradation of the substrate. The rate at pH = 4 was slightly lower. At higher pH, a more significant decrease in the degradation rate occurred.

Photodegradation of different organic compounds in Fe(III)/carboxylate systems at different pH was the subject of several studies (Balmer and Sulzberger 1999; Mazellier and Sulzberger 2001). All showed an important relation between the degradation rate and pH. That is, the degradation rate decreased with increasing pH. Filius et al. (1997) investigated the reaction of several weak acids with goethite at different pH. They showed that for pH above the point of zero charges of goethite both the charge of the goethite surface and the charge of the organic acid are negative. Consequently, chemical affinity of carboxylic anions for the goethite surface is relatively small. At pH values below the point of zero charge, where the goethite surface and carboxylate anion are oppositely charged, the reaction increases with decreasing pH. At pH between 3 and 5, two Fe(III) speciations are important in the case of oxalate ligands, $FeC_2O_4^+$ (maximum around pH = 3) and $Fe\left(C_2O_4\right)_2^-$ (maximum at pH = 3–4), which also prevailed at pH = 3 (Balmer and Sulzberger 1999).

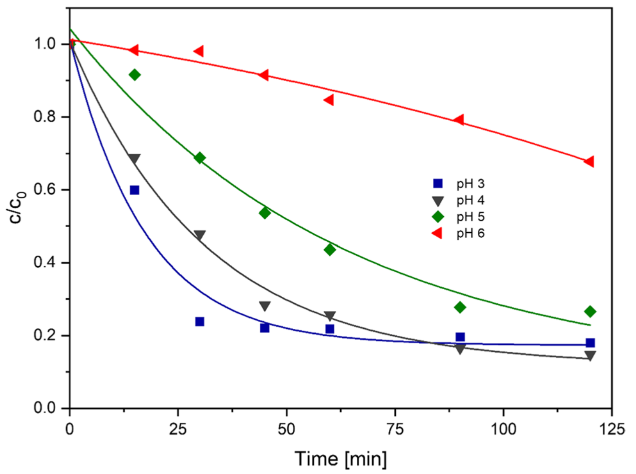


Fig. 2 The influence of pH on DBP photodegradation

At higher values of pH, the Fe(OH)$_2^+$ became the prevailing Fe(III) species. Both oxalate complexes, especially Fe$\left(C_2O_4\right)_2^-$, are much easily photolyzed. This leads to an important consequence-similar rate of DBP degradation at pH = 3–4.

Effect of oxalic acid concentration

For the study, concentrations in the range from 0.5×10^{-3} to 3×10^{-3} M were selected, and results are presented in Fig. 3.

The lowest degradation rate was observed for the lowest concentration of oxalic acid. The degradation rate at three higher concentrations did not differ significantly. However, the degradation in 1 mM oxalic acid was slightly faster compared to those in 2 and 3 mM oxalic acid solutions, at least at longer reaction times. Similar behavior was shown by (Li et al. 2008); the degradation rate of pentachlorophenol increased with increasing oxalic acid concentration from 0.5 to 2 mM, but at higher concentrations, an inhibiting effect appeared. This was attributed to the excessive loss of surface reactive sites, which resulted in the dissolution of goethite with a higher concentration of oxalic acid. The formed polycarboxylic complex with surface-bound Fe(II) can significantly decrease the redox potential of the Fe(III)/Fe(II) redox couple (Li et al. 2008). One of the reasons could also be the competition between different compounds in the reaction mixture for the photogenerated $^{\cdot}$OH (Huang et al. 2012). The importance of Fe(II)-oxalate complexes was investigated in detail with FTIR by Huang et al. (2019).

For lower oxalic acid concentrations, a major part of $^{\cdot}$OH promotes the degradation of DBP. By increasing the oxalic acid concentration, a reaction competition between DBP and oxalic acid for $^{\cdot}$OH results in lower DBP degradation.

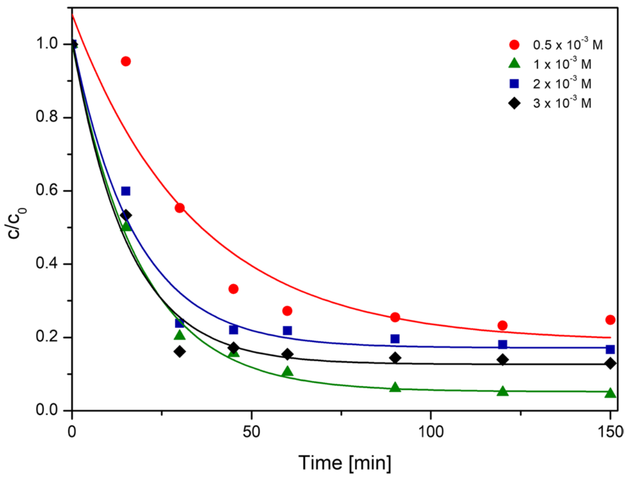


Fig. 3 The influence of oxalic acid concentration on DBP photodegradation

Effect of goethite concentration

Results concerning the effect of goethite concentration on the photodegradation of DBP are presented in Fig. 4. An increase in photodegradation efficiency with increasing goethite concentration is evident up to the concentration of 0.5 g L^{-1}; for higher concentrations, an opposite effect was found. The slowest degradation was obtained at the highest goethite concentration. The reason for this effect could lie in the different light dose. At higher concentrations of goethite particles, the scattering effect of light is more pronounced accompanied by lower penetration deep to the reaction mixture, leading additionally to a lower number of photons available to promote photodegradation.

Very few results regarding such effects are available in the literature. In a homogeneous Fe(III)-carboxylate system, a higher concentration of Fe(III) led to a higher degradation rate of organic compounds (Zhang et al. 2009; Alvarez et al. 2010). But in a heterogeneous system, the effect is more complex. Rodriguez et al. (2009) found an inhibiting effect of increased iron oxide concentration on the amount of leached iron. This may further influence the degradation of different organic substrates. Our results are in agreement with those results, especially for higher concentrations. For lower concentrations, the system seemed to behave more like a homogeneous one, i.e., an increase in goethite concentration led to faster degradation of DBP. The obtained results provide the evidence that above a certain level of goethite concentration the degradation efficiency of DBP decreases and the phototreatment of polluted waters is less effective. This could have some economic impact as well.

Agglomeration of goethite is also a phenomenon, which can affect the reaction kinetics. In this study, the suspension was dispersed in an ultrasonic bath for 3 min for de-agglomeration. The effect of de-aglomeration in time was investigated and confirmed as effective in 3 min of sonification. The pattern

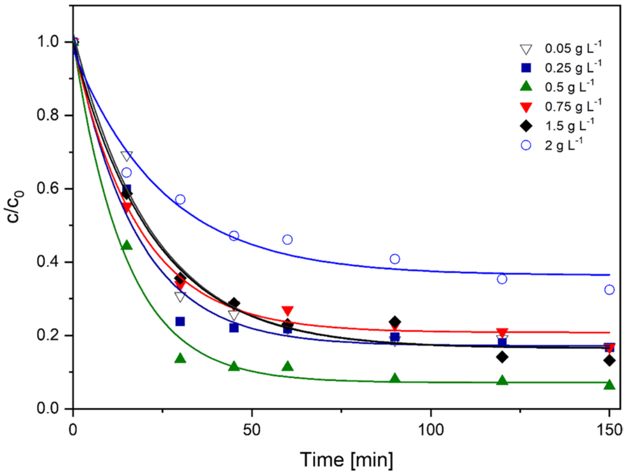


Fig. 4 Photodegradation of DBP in presence of oxalic acid at different goethite concentration

of de-aglomeration was studied and published as independent of power input (Ding and Pacek 2008) and in this study was not investigated. The goethite suspension is at pH 3 stable and no flocculation, which can affect the reaction kinetic, occurs (Blakey and James 2003).

Effect of DBP concentration

One of the parameters we have also included in the study is the concentration of DBP, because different degradation rates could be expected when all other parameters are kept constant. This is especially important when we rescale the process of the decontamination of polluted waters at different DBP concentrations. Unfortunately, we were not able to use a wider concentration range, due to the low solubility of DBP in water. Results showed a decrease in the degradation rate with increasing DBP concentration (Table 1). The data were evaluated by software OriginPro 8.5.

In the studied system, different reactive species formed in different redox reactions. At lower concentrations, the probability for the molecule to react with these reactive species is lower. This can be reflected in a lower degradation rate.

Table 1 Experimental pseudo-first-order rate constants, k, for DBP degradation and the fit quality, R^2

DBP [$\times 10^{-5}$ M]	k [h^{-1}]	R^2
3.0	1.59	0.89
1.5	1.80	0.91
0.75	3.92	0.98

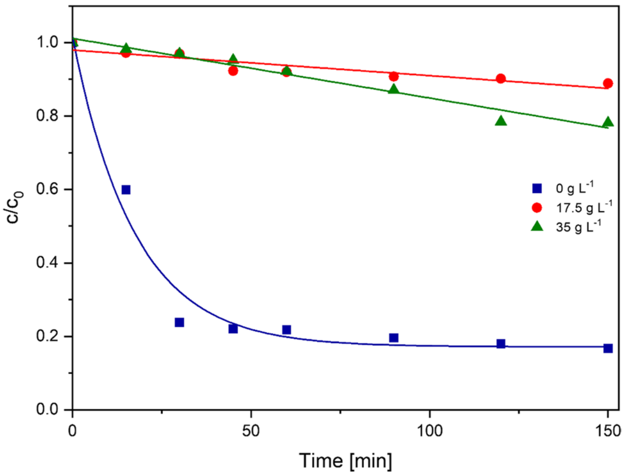


Fig. 5 Inhibition of DBP photodegradation by NaCl

Effect of NaCl

Seawater is a concentrated solution of different salts. The major component is NaCl at concentrations around 35 g L^{-1}. To assess the probability of photodegradation processes with goethite, we also examined the effect of NaCl. Results presented in Fig. 5 show a strong inhibiting effect of NaCl at concentrations significant for seawater.

The inhibition of photodegradation could depend on two factors, complexation and radical scavenging (Lu et al. 2005; Siedlecka and Stepnowski 2006). Both Fe(III) and Fe(II) can form complexes with Cl^- ions, which impedes the $^\cdot OH$ formation. On the other hand, Cl^- can react with $^\cdot OH$ producing less reactive chlorine radicals ($ClOH^{\cdot -}$). If we consider the reaction rates for both processes, 2.9×10^{-3} M^{-1} s^{-1} for complex formation and 4.3×10^{9} M^{-1} s^{-1} for reaction with $^\cdot OH$ (Siedlecka and Stepnowski 2006), the latter effect seems more probable. We observed a significant inhibiting effect of NaCl on DBP degradation.

With longer irradiation Cl radicals may act as oxidants, and at higher NaCl concentration the formation is higher, as published by (Treviño-Reséndez et al. 2022).

However, we can still conclude that even at NaCl concentrations significant for seawater, prolonged irradiation could lead to the photodegradation of organic compounds.

Effect of O_2, N_2, and H_2O_2

Dissolved oxygen usually plays a very important role in photocatalyzed processes. In the case of the heterogeneous Fenton process, it is involved in the redox Fe(III)/Fe(II) process through the formation of superoxide radical after the oxidation of the formed carboxylate radical. In acidic solutions, it also plays an

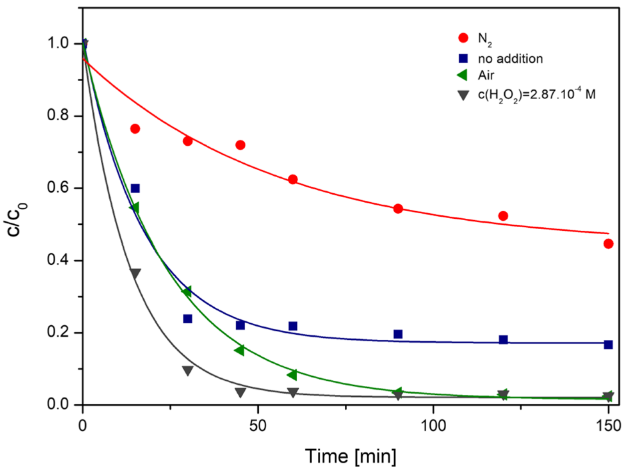


Fig. 6 The influence of nitrogen, air (oxygen) and hydrogen peroxide on DBP photodegradation

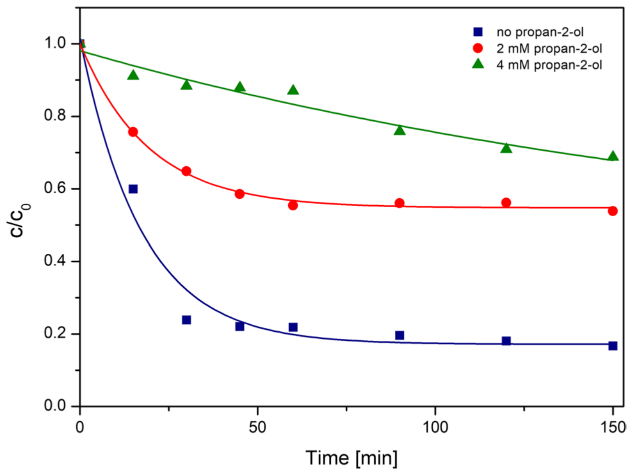


Fig. 7 The influence of propane-2-ol on DBP photodegradation

important role in H_2O_2 formation (Mazellier and Sulzberger 2001; Qourzal et al. 2008; Borer et al. 2009).

To confirm the role of oxygen, we also performed experiments with a purging of nitrogen to eliminate oxygen from the reaction mixture and air and to saturate it with oxygen (30 min before and all the time during the irradiation).

As it can be seen from the results reported in Fig. 6 two main differences were observed. Degradation in anaerobic conditions was significantly slower, but not completely stopped. This is most probably because it was not possible to completely eliminate oxygen from the solution, even by the intensive purging of N_2. The lowest concentration of oxygen [O_2], reached in the solution, was 0.25 mg L^{-1}. Huang et al. reported similar results for a homogeneous photo-Fenton process using Fe(III)-EDDS complexes (Huang et al. 2012).

In the case of the introduction of air to the reaction mixture, the degradation rate was similar to that of the general experiment, but in the end the degradation was more efficient, leading to nearly 100% degradation of DBP. In this case, the oxygen concentration was 7.7 mg L^{-1} in the reaction solution.

A similar effect was achieved by the addition of hydrogen peroxide in the reaction mixture. During the irradiation, oxygen is consumed leading to incomplete DBP degradation. The continuous saturation of the reaction mixture by oxygen led to the complete elimination of DBP. The addition of H_2O_2 exhibited the same effect.

Presence of hydroxyl radicals

For the study of the influence of $^{\cdot}$OH radicals on photocatalytic degradation, a reaction mixture was prepared via the standard approach, enriched with propane-2-ol, a radical scavanger, giving concentration of 2 mM and 4 mM. The presence of propane-2-ol results in the inhibition of DBP degradation in comparison with the photodegradation experiment without scavenger (Fig. 7). Moreover, the inhibition effect was more significant at higher concentration of propane-2-ol. These results confirm the attack by $^{\cdot}$OH radicals as the main mechanism of DBP degradation. Propane-2-ol has been recognized as a scavenger of hydroxyl radicals in several photocatalyzed degradations of organic pollutants (Gracien et al. 2019; Neto et al. 2021).

Effect of dissolved Fe

For a better understanding of the degradation process in water environment, the concentration of total Fe and Fe(II) in a dissolved phase was determined experimentally. Consequently, the concentration of Fe(III) was calculated as the difference between the total Fe and Fe(II). The release of iron was studied only in a few experiments such as the general setup of the experiment, experiment with N_2 purging, and experiment in the presence of propane-2-ol scavenger.

Figure 8 depicts results for the general setup of the experiment with and without N_2 purging. The results show a significant release of total iron during the reaction regardless of the type of experiment. The concentration of the total iron increased in the course of all reaction time, no decreasing trend was observed. This can be noted as evidence that the α-FeOOH was present all time in the reaction mixture. The effect of α-FeOOH concentration on DBP degradation is described in "Effect of goethite concentration" section in detail.

Analysis of Fe(II) cations for the general experiment showed, that the dominant form of released iron is based on Fe(II) cations which is in good agreement with the data from the literature (Goldberg et al. 1993; Reichard et al. 2007). Interestingly, the release of Fe(II) during the reaction was not constant. During the induction period observed in first 30 min, the presence of released Fe(II) was insignificant; however, the presence of Fe(III) increased simultaneously. These results are consistent

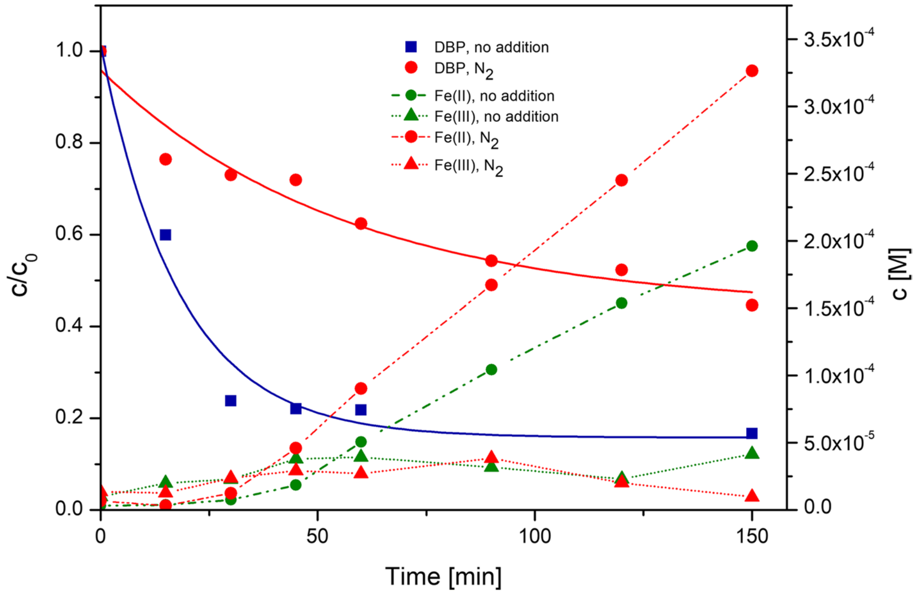


Fig. 8 The influence of dissolved Fe on DBP photodegradation (Left-hand axis: c/c_0 shows DBP concentration; right-hand-axis: c represents the concentration of Fe)

with the course of DBP degradation. In presence of oxalic acid, the DBP was decomposed rapidly in the first 30 min. After this time, the degradation rapidly slowed down. This effect is probably due to the consumption of O_2 present in the reaction mixture. The presence of oxygen in the reaction mixture has a crucial role in goethite dissolution and in the consecutive formation of hydroxyl radicals.

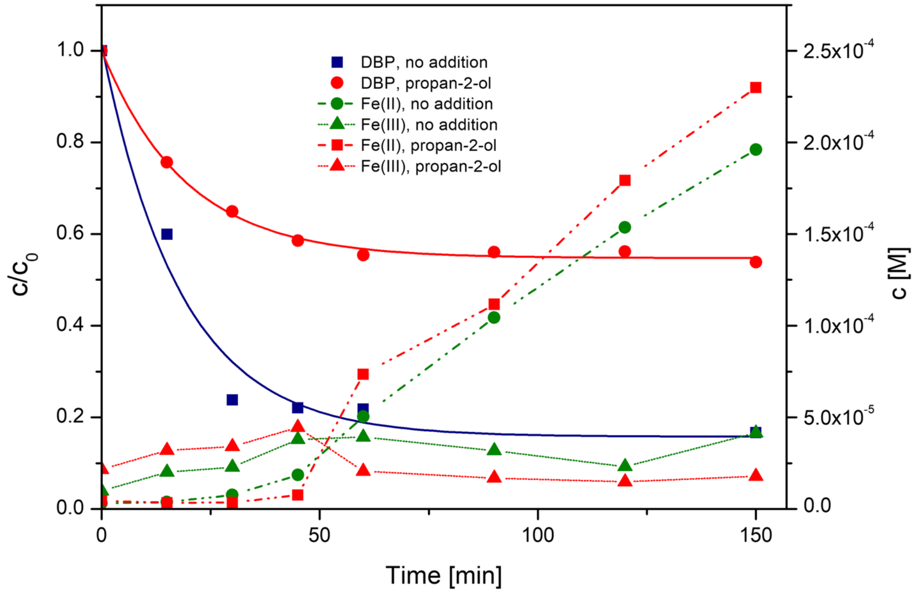
At a low concentration of dissolved oxygen in the reaction mixture, the formation of superoxide radical $O_2^{\cdot -}$ is restricted as well. This leads, in final consequence, to a limited formation of H_2O_2 and $^{\cdot}OH$ needed for the degradation process. The limited formation of H_2O_2 negatively influences also the generation of the highly photoactive hydroxyl complex of iron(III) and hydroxyl radicals in the reaction with Fe(II) and H_2O_2. The photolysis of hydroxyl complex of iron(III) generates Fe(II) and reactive $^{\cdot}OH$, which is due to the low production of H_2O_2 also lacking. In the first 30 min, the O_2 in reaction mixture is consumed and later the degradation of DBP is not effective. The dissolution of atmospheric O_2 into reaction mixture is not sufficient, therefore, the degradation of DBP slowed down after the first 30 min.

As it is obvious from Fig. 8, released Fe(II) was rapidly oxidized by dissolved oxygen and consumed by a Fenton-like reaction. This is the reason, why the dominant form of iron is Fe(III) at the beginning. After 30 min, when the degradation of DBP slowed down, the oxygen was consumed and for this reason, the release of iron is dominantly based on Fe(II) which is accumulating in the reaction mixture and the generation of Fe(III) is suppressed. The photoinduced release of Fe(II) in the solution is necessary for the Fenton process responsible for the degradation of DBP. This process is dependent on the presence of oxygen which leads to two contemporary reactions, the Fe(III) formation and the DBP degradation. After the oxygen is consumed, the oxidation of Fe(II) to Fe(III) and the degradation of DBP became negligible. This was confirmed by the experiment with N_2 purging, where the presence of Fe(II) was the highest and the formation of Fe(III) was suppressed. These results confirmed that the presence of oxygen is responsible for the oxidation of Fe(II) to Fe(III).

For further elucidation of the degradation mechanism, 2 mM propane-2-ol was introduced as the scavenger of hydroxyl radicals. The results, presented in Fig. 9, show that the scavenger in the reaction mixture did not affect the release of total Fe during the experiment because the resulting concentrations are similar to the experiment without the scavenger. Also, the dominant presence of Fe(III) at the beginning, instead of Fe(II), indicates that O_2 is consumed by the oxidation of iron. Similar to the experiment with degradation of DBP, there is a dominant increase of Fe(II) after consuming dissolved oxygen (after 50 min). These results showed that the presence of propane-2-ol is responsible only for scavenging reactive oxygen species; however, the release of total iron during irradiation is not affected. Is evident, that the presence of O_2 plays important role in the photodegradation of DBP with goethite.

Presented results in this work are useful for a better understanding of described degradation process in natural waters. The degradation of DBP and other organic compounds depends on several factors—the presence of carboxylic acid and their concentration, pH, light intensity and its wavelength, presence of other compounds (e.g. NaCl), temperature etc. The other important parameter is the concentration of dissolved oxygen. The concentration of oxygen in water depends on the season, water depth, occurrence of flora oxygen generating by photosynthesis, and other parameters. A low degradation rate of organic

Fig. 9 The influence of dissolved Fe with propane-2-ol (2 mM) on DBP photodegradation (Left c/c_0 shows DBP concentration, right y-axis c [M] depicts concentration of Fe)



pollutants in the presence of goethite and carboxylic acid can be expected in deep water, where no photosynthesis is taking place, no oxygen is present by dissolution from the air and no sunlight is present as well. On the contrary, the best results are expected in well-illuminated water with a high concentration of oxygen in natural waters.

Conclusion

The results presented in this work confirm that the photodegradation of DBP in the presence of goethite-carboxylate complexes is an efficient process for its removal from aqueous media. The triggering mechanism is the reaction of the carboxylate anion with the hydroxyl groups of α-FeOOH on goethite surface and the charge transfer from the carboxylate ligand upon irradiation. The presence of oxalic or citric acids in the reaction mixture showed a highly efficient photodegradation. On the contrary, the presence of salicylic, pyruvic, maleic and fumaric acids had weak or no effect. The degradation of DBP is efficient at lower pH values. Degradation at environmentally significant pH values is low, but not negligible if we consider the timescale of naturally occurring processes. The presence of NaCl inhibits DBP photodegradation to a large extent. The higher efficiency of the reaction is positively influenced by higher concentration of dissolved oxygen. It gives rise to a higher concentration of superoxide radical anion, hydroperoxyl radical and hydrogen peroxide. Released Fe(II) from goethite can afterwards react with a higher amount of hydrogen peroxide and generate hydroxyl radicals by the well-known Fenton reaction. Because of this fact, the higher efficiency of DBP degradation is observed.

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Declarations

conflict of interest The authors declare that they have no conflict of interest.

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