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Interaction of adsorption and catalytic reactions in water decontamination processes
Part I. Oxidation of organic contaminants with hydrogen peroxide catalyzed by activated carbon

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Abstract

This series of papers addresses the role of sorption in heterogeneous catalysis aimed at the removal of organic contaminants (OCs) from water. This first part is focused on the oxidative treatment of OCs by H_2O_2 catalyzed by activated carbon (AC). The relative reaction rates of compounds with different hydrophobicities and therefore different sorption tendencies on AC (methyl *tert*-butyl ether, trichloroethene, 2,4,5-trichlorophenol) in the AC/H_2O_2 system differed drastically from those observed in a classical homogeneous Fenton system. Quantitative considerations that take into account the ratio of the reaction rate constants of MTBE and TCE in the AC/H_2O_2 system and the homogeneous Fenton system as well as the ratio of their freely dissolved fractions lead to the conclusion that the predominant pathway for the degradation reaction in the AC/H_2O_2 system is the attack of $OH^\bullet$ radicals on the OC fraction that is freely dissolved in the pore volume of the AC. In contrast, the sorbed fraction is nearly unreactive, i.e. protected against radical attack. Quenching experiments with methanol, a strong competitor for reactions with $OH^\bullet$ radicals in the solution phase, further confirmed this hypothesis. Consequently, sorption on AC has an adverse effect on the oxidation of OCs via $OH^\bullet$ radicals, even though the radicals are formed directly on the AC surface, i.e. in close proximity to the sorbed OCs.

Keywords: Hydrogen peroxide; Activated carbon; Heterogeneous catalysis; Oxidation; Adsorption; Water treatment

1. Introduction

The application of chemical reactions for the treatment of large volumes of contaminated water such as groundwater is often limited by the low concentrations of the contaminants in the water, which may give rise to low reaction rates and over-stoichiometric consumption of reactants. The combination of sorption with destruction of the sorbates by catalytic and other chemical processes may offer several advantages. Generally, adsorption of contaminants to the catalyst leads to an in crease in their residence time within a fixed-bed reactor. Moreover, the preconcentration of contaminants in the vicinity of reactive centres might greatly enhance rates and efficiencies of degradation reactions.

Three modes of operation are possible: (I) a two-step cycle consisting of an adsorption step followed by a regeneration step of the adsorbent, (II) a simultaneous mode where sorption and the destruction reaction take place simultaneously, and (III) a quasi-simultaneous mode with the destruction reaction cyclically performed under intensified conditions for complete regeneration of the adsorbent.

While the simultaneous mode avoids standstill times of the reactor, the cyclic modes offer more freedom in adjusting optimal conditions for the regeneration reaction (e.g. pH of the reaction medium or exclusion of interfering species).

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The extent to which adsorption can positively effect the reactor performance largely depends on the question of whether the sorbed contaminant fraction is still sufficiently available for the applied degradation reaction. Therefore, our aim was to elucidate the role of sorption in different reaction systems, including oxidation and reduction processes of environmentally relevant OCs. The first part of this series is concerned with the effect of sorption on oxidation of OCs with H_2O_2 and AC. The next part will be focused on hydrodehalogenation catalyzed by Pd on various supports.

Adsorption on AC is one of the most widely applied processes for removing organic contaminants from water. However, adsorption is a non-destructive process that transfers contaminants from one phase to another. Frequently, the spent adsorbent has to be treated as hazardous waste that must be disposed of or regenerated expensively. The most commonly used high-temperature thermal regeneration of spent AC cannot be performed in situ in the adsorption reactor but requires shipment of the spent AC to special regeneration units. Matatov-Meytal and Sheintuch proposed an impregnation of AC with Pd [1] or metal oxide catalysts [2] in order to facilitate a cyclical catalytic regeneration of the spent AC by gas-phase oxidation with air [2] or, in the case of chlorophenols, by gas-phase hydrodechlorination with H_2 followed by oxidation with air [1]. These processes could theoretically be performed in situ in the adsorption columns but they require elevated temperatures (200–300 °C).

Advanced oxidation processes (AOPs) using strong oxidants such as $OH^\bullet$ radicals are an emerging technique for the destruction of contaminants in water treatment [3]. $OH^\bullet$ radicals can be produced from H_2O_2 using homogeneous (e.g. Fenton reaction [4–7]) or heterogeneous catalysts (supported metal catalysts, metal oxides, graphite, AC [8–10]). Application of the homogeneous Fenton reaction demands acidification of the water (optimal pH around 3) and involves an additional contamination of the treated water by dissolved iron. This is not the case if heterogeneous catalysts or the combination with O_3 or UV treatment are applied.

It has been investigated in several studies [11,12] whether a preconcentration of the contaminants by introducing AC into Fenton-like reaction systems is favourable. Toledo et al. [11] applied the Fenton reaction (Fe^{2+} and H_2O_2) to regenerate AC loaded with various chlorinated organic compounds (tetrachloroethylene, chloroform, 1,2-dichloropropane and chlorobenzene). They compared the destruction efficiency for treating a certain amount of OCs using the same amounts of Fe^{2+} and H_2O_2 (a) for the homogeneous Fenton reaction in an aqueous solution of the OCs and (b) for the regeneration of AC loaded with the OCs. The authors concluded that, compared to the homogeneous process, the destruction efficiency is higher if the OCs are first adsorbed to AC and the loaded AC is then resuspended in a small solution volume and treated by the Fenton process. However, instead of performing an adsorption step from water, Toledo et al. impregnated their AC directly with the pure OCs resulting in a loading of the AC of 100 wt.% [11]. The adsorbate resulting from this impregnation procedure might not be representative for an adsorption process from aqueous solution. Therefore, it is questionable if these results can be adopted for real treatment systems.

Mourand et al. [12] applied a combination of H_2O_2 and O_3 as well as of H_2O_2 and UV irradiation and compared the consumption of oxidants in the homogeneous AOP with that of a process where the contaminants are firstly adsorbed to AC and the spent AC is afterwards subjected to regeneration by the AOP. The authors came to the conclusion that the adsorption step is not justified, because the quantity of oxidants required in the regeneration step is considerably higher than simply using the homogeneous AOP for the destruction of the OCs. They stated that the reaction takes place in the solution phase and that the slow rate of desorption together with the redox reactions with the adsorbent surface result in a high consumption of oxidants. Consequently, the adsorption step cannot be justified [12].

The combination of AC adsorption and oxidation by H_2O_2/UV in a simultaneously operated mode [13] as well as in a two-step simultaneous-mode system where the AC was periodically regenerated under intensified oxidation conditions [14] was studied by Ince et al. The finding that the total operating costs estimated for the simultaneous-mode system were close to that of the AOP operated without AC was considered to be typical for a poorly adsorbing contaminant such as was treated in this study (Everzol Black GSP® dye) [13]. Beside the use of less expensive (e.g. natural) adsorbents it is implicitly suggested that the process should be tested for contaminants with higher sorption tendencies [13].

Very recently, two studies have been published which are close to the topic of this paper: the one dealing with an oxidation, the other with a reduction reaction system. Kwan and Voelker [15] investigated the effect of electrostatic interactions between the catalyst surface (goethite) and various probe molecules (formate, nitrobenzene and 2-chlorophenol) to be oxidized with H_2O_2. They came to the conclusion that the negatively charged formate is significantly enriched at the positively charged iron oxide surface (at pH = 4) where the $OH^\bullet$ radicals are produced. This gave rise to an oxidation rate of formate which was higher by a factor of about 50 than that estimated from the oxidation rate of the neutral probes. The results clearly support the hypothesis that the adsorbed formate is preferentially available for oxidation by $OH^\bullet$ radicals. Although the lifetime and diffusion length of $OH^\bullet$ radicals were estimated to be very short under the experimental conditions (~20 ns and ~6 nm, respectively), $OH^\bullet$ radicals are apparently able to reach the surface-adsorbate to be oxidized.

Dries et al. [16] studied the competition between sorption and reductive degradation of tetrachloroethene (PCE) and trichloroethene (TCE) in zero-valent iron (ZVI) suspensions ($100\ g\ L^{-1}$) in the presence of various reactive and non-reactive organic compounds (chlorinated ethenes, BTX, humic acids). In general, the observed effects on reaction rates are relatively small (<factor of 2) and even smaller for TCE than for the more hydrophobic PCE. The most significant observation was an increase of the PCE reaction rate by 50% in the presence of the non-reactive BTX ($10\ \mathrm{mg\ L^{-1}}$ each). The authors interpret this finding as displacement of PCE from non-reactive sorption sites. They conclude that sorption and reaction sites are fundamentally different entities and that the chemical reaction does not profit from sorption at non-reactive sites. Obviously, an important difference between the reaction systems investigated by Kwan and Voelker [15] and Dries et al. [16] is the mobility of the reactive intermediates: short-lived $OH^{\bullet}$ radicals are mobile, whereas electrons to be transferred in the reductive dechlorination on a ZVI-surface are not.

Most of the studies dealing with AC [11–14] considered heterogeneous processes where the production of reactive species (e.g. $OH^{\bullet}$ from H_2O_2) predominantly takes place in the solution phase (by Fe^{2+}, O_3 or UV, respectively). In contrast, the intention of the present study was to elucidate the question of whether concentrating contaminants on AC is favourable in cases where the reactive species are generated *at the surface* of the adsorbent, i.e. in close proximity to the adsorbed OCs. This situation should offer even better conditions for a positive effect of adsorption on the degradation reaction than the systems described above.

AC is known to decompose H_2O_2. It has been assumed that this process involves the exchange of a surface hydroxyl group with a hydrogen peroxide anion (Eq. (1), according to Bansal et al. [17] as cited in [18]). The formed surface peroxide is regarded as having an increased oxidation potential which enables the decomposition of another H_2O_2 molecule with release of O_2 and regeneration of the carbon surface (Eq. (2))

$$\mathrm{AC{-}OH} + \mathrm{H^{+}OOH^{-}} \rightarrow \mathrm{AC{-}OOH} + \mathrm{H_2O} \qquad (1)$$

$$\mathrm{AC{-}OOH} + \mathrm{H_2O_2} \rightarrow \mathrm{AC{-}OH} + \mathrm{H_2O} + \mathrm{O_2} \qquad (2)$$

Beside this decomposition reaction, H_2O_2 can obviously be activated on the AC surface involving the formation of free radicals. AC is considered to function as an electron-transfer catalyst similar to the Haber–Weiss mechanism known from the Fenton reaction with AC and AC^{+} as the oxidized and reduced catalyst states [19]:

$$\mathrm{AC} + \mathrm{H_2O_2} \rightarrow \mathrm{AC^{+}} + \mathrm{OH^{-}} + \mathrm{OH^{\bullet}} \qquad (3)$$

$$\mathrm{AC^{+}} + \mathrm{H_2O_2} \rightarrow \mathrm{AC} + \mathrm{HO_2{}^{\bullet}} + \mathrm{H^{+}} \qquad (4)$$

Several studies have shown that this process can lead to contaminant decay in aqueous AC suspensions [10,20]. Huang et al. [20] compared several AC samples before and after treatment with oxidizing agents that increased the content of acidic groups on the AC. They found that the decomposition activity of the modified AC sample towards H_2O_2 was lower, whereas the catalytic activity towards the decomposition of 4-chlorophenol was slightly higher than with the original AC. However, since the acid–base properties of the AC also influenced the pH of the reaction suspension, one cannot easily distinguish between the two effects, i.e. the change in the nature of the AC surface and in the pH of the reaction medium. Lücking [21] found an optimum at pH ≈ 3 for the oxidation rate of several OCs with AC/H_2O_2, which he ascribed to the superposition of several effects such as the increase in the rate of the H_2O_2 decomposition (via OOH^{-}) with increasing pH, the increase in the redox potential of H_2O_2 (and the resulting reactive oxygen species) with decreasing pH as well as possible changes in the chemical properties of the AC surface [21].

Table 1
Characteristic properties of the applied organic compounds: octanol-water partition coefficient (K_{OW}), water solubility (S) and rate constant for the reaction with $OH^{\bullet}$ radicals (k_n)

Compound	log K_{OW}[a]	S (25 °C) ($\mathrm{g\ L^{-1}}$)[a]	k_n ($\times 10^8\ \mathrm{L\ mol^{-1}\ s^{-1}}$)
Methanol	−0.77	Miscible	9.7[b]
Methyl *tert*-butyl ether	1.24	51	16[c]
Trichloroethene	2.42	1.47	29–43[c]
2,4,5-Trichlorophenol	3.72	1.2	Not available

[a] Recommended values in [22].
[b] [23].
[c] [24].

The present study is focused on the effect of sorption on the oxidation by AC/H_2O_2, which was studied by conducting batch experiments at the reported optimum value of pH = 3 [21] with various OCs differing in their sorption tendency on AC, i.e. TCE, methyl *tert*-butyl ether (MTBE) and 2,4,5-trichlorophenol (TCP) (Table 1).

2. Materials and methods

Unless otherwise stated, all chemicals and organic solvents were obtained in 99+ grade from Merck (Germany). The AC applied was Filtrasorb TL830 (Chemviron, Germany). Prior to use, the AC was milled with a mortar and sieved to a size ≤63 μm. The AC has an ash content of 5.4 wt.% and an iron content of about 0.05 wt.%. Using nitrogen adsorption (Gemini-2370, Micromeretics) a BET surface area of $727\ \mathrm{m^2\ g^{-1}}$, a total intra-particle pore volume of $0.46\ \mathrm{cm^3\ g^{-1}}$ and a micropore volume of $0.27\ \mathrm{cm^3\ g^{-1}}$ have been determined for the AC sample.

H_2O_2 content was determined by iodometric titration. Chloride analysis in the reaction solutions was carried out by argentometric titration (TitroLine alpha, Schott). Chloride analysis was not influenced by the presence of powdered AC, as could be confirmed by comparing the results obtained from AC-containing solutions before and after filtration (0.45 μm). All experiments were performed at room temperature (23 ± 2 °C).

The concentration of the OCs in the reaction solutions was determined by GC-MS analysis (QP-5000, Shimadzu) operating in the selected ion monitoring mode. For MTBE and TCE, headspace analysis using gas-tight micro-syringes (100 μL) was applied, whereas in the case of TCP a solvent extraction followed by GC-MS analysis of the extracts was performed. The relative standard deviation of the headspace analysis method was in the range of $\sigma = \pm 3\%$ and in case of the GC-MS analysis of the solvent extracts in the range of $\sigma = \pm 5\%$.

2.1. Sorption kinetics

In order to determine the kinetics of the sorption process, a suspension of AC (1 g L^{-1}) in 220 mL of acidified deionized water (pH = 3, HNO_3) was filled into a 250 mL-flask with a Mininert®-valve and shaken overnight on a horizontal shaker. Afterwards, the sorption experiment was started by the addition of 200 μL of a methanolic stock solution containing MTBE and TCE (resulting concentrations $c_{0,\mathrm{MTBE}} = 0.055$ mM and $c_{0,\mathrm{TCE}} = 0.75$ mM). The samples were vigorously shaken on a horizontal shaker. At several points in time, the concentration of the freely dissolved fraction of the two OCs was determined by headspace analysis.

Furthermore, the kinetics of the desorption process was studied. Samples of the adsorption experiment described above were allowed to equilibrate over a time period of 4 days. Afterwards, the samples were centrifuged and the clear water phase was decanted. The AC was transferred into a 250 mL-flask with a Mininert®-valve. The desorption experiment was started by addition of 220 mL of acidified deionized water (pH = 3, HNO_3). After various time periods, the concentration of the freely dissolved fractions of MTBE and TCE was determined by headspace analysis.

2.2. Homogeneous Fenton reaction

An 240 mL of acidified deionized water (pH = 3, HNO_3) was filled into 250 mL-flasks with Mininert®-valves and purged with nitrogen for at least 15 min. Afterwards, each flask was spiked with a pair of OCs (0.31 mM TCP plus 0.18 mM MTBE and 0.46 mM TCE plus 0.18 mM MTBE, respectively) using aqueous stock solutions of the OCs. An amount of 1 mL of an oxygen-free solution of $FeSO_4{\cdot}7H_2O$ was added, resulting in a concentration of Fe^{2+} of 2 mM. The reaction was started by adding 1 mL of an oxygen-free H_2O_2 solution, resulting in a final concentration of 2 mM. The flasks were vigorously shaken on a horizontal shaker. After 2 min the reaction was stopped by adding 10 mM NaN_3 from an aqueous stock solution. The concentration of the remaining MTBE and TCE was determined by headspace analysis. In order to determine the concentration of TCP, 230 mL-aliquots of the reaction solution were extracted by shaking them for 2 min with 5 mL of *n*-hexane containing chlorobenzene as an internal standard. Afterwards, the extracts were analyzed by GC-MS.

2.3. Oxidation experiments with AC/H_2O_2

The desired amount of AC was filled into a 250 mL-flask with a Mininert®-valve and suspended in 220 mL of an aqueous solution of the OCs. The pH of the suspension was adjusted to pH = 3 by adding HNO_3. Adsorption was allowed to come to equilibrium for at least 48 h, while the samples were shaken on a horizontal shaker. Afterwards, the concentration of the freely dissolved fraction of the organic compounds was determined by headspace analysis for MTBE and TCE. In case of TCP, a 1 mL-aliquot was retained and filtered (0.45 μm) in order to remove the AC. The supernatant was extracted with 0.5 mL of *n*-hexane containing chlorobenzene as an internal standard. The extract was analyzed by GC-MS. The reaction was initiated by adding H_2O_2 solution (30 wt.%) resulting in a starting concentration of 67 mM. The samples were vigorously shaken on a horizontal shaker. During the reaction, the concentration of H_2O_2 was monitored by iodometric titration of 2 mL-aliquots of the suspension. During the first 5–8 h of reaction, the spent amount of H_2O_2 was supplemented in order to maintain an approximately constant H_2O_2 concentration (±15% of the initial concentration). If the reaction was followed over more than one day, H_2O_2 was added discontinuously as denoted in Section 3.

The course of the contaminant decay was monitored by headspace analysis in the case of TCE and MTBE. Residual TCP was determined after solvent extraction, i.e. 1 mL-aliquots of the reaction solution were extracted with 0.5 mL of *n*-hexane containing chlorobenzene as an internal standard by shaking over 24 h. The recovery of TCP was 22 ± 2%. Due to this low recovery, the results for TCP can only be considered as semi-quantitative. However, the trend of the concentration profile should be reflected properly. Chloride was measured by argentometric titration of 5 mL-aliquots of the reaction suspension.

In a control experiment, the reactivity of the aqueous phase of an AC suspension was examined separately. An AC suspension ($c_{\mathrm{AC}} = 1$ g L^{-1}) was prepared as described above but without the addition of OCs and shaken for 3 days. Afterwards, the AC was removed by centrifugation. The clear supernatant was transferred into a 250 mL-flask with a Mininert®-valve and spiked with 1.1 mM MTBE and 67 mM H_2O_2. The concentration of MTBE was monitored by headspace analysis.

3. Results and discussion

3.1. Homogeneous Fenton reaction

In order to determine relative rate constants of the reaction of different compounds with $OH^{\bullet}$ radicals, a homogeneous Fenton system with stoichiometric concentrations of H_2O_2 and Fe^{2+} was applied (Eqs. (5) and (6))

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-} \quad (5)$$

$$R_n + OH^{\bullet} \xrightarrow{K_n} \text{products} \quad (6)$$

Assuming second order kinetics of two parallel reactions *i* and *j*, the relative rate constant k_i/k_j can be easily derived from Eq. (8)

$$\frac{\mathrm{d}c_n}{\mathrm{d}t} = -k_n c_{\mathrm{OH}^\bullet} c_n \qquad (7)$$

$$\frac{k_i}{k_j} = \frac{\ln c_i/c_{i,0}}{\ln c_j/c_{j,0}} \qquad (8)$$

Under the reaction conditions applied ($c_{0,\mathrm{Fe}^{2+}} = 2$ mM, $c_{0,\mathrm{H_2O_2}} = 2$ mM), the residual fractions c/c_0 in the MTBE/TCE system were 0.16 ± 0.02 of MTBE ($c_{0,\mathrm{MTBE}} = 0.18$ mM) and 0.013 ± 0.003 of TCE ($c_{0,\mathrm{TCE}} = 0.46$ mM) after a reaction time of 2 min. In the MTBE/TCP system (containing the same Fe^{2+} and H_2O_2 concentrations), the residual fractions measured after 5 min were 0.122 ± 0.012 for MTBE ($c_{0,\mathrm{MTBE}} = 0.18$ mM) and 0.045 ± 0.011 for TCP ($c_{0,\mathrm{TCP}} = 0.31$ mM). According to Eq. (8) it follows that $k_{\mathrm{MTBE}}:k_{\mathrm{TCE}}:k_{\mathrm{TCP}}$ = 1:2.4 (±0.1):1.6 (±0.3) with the values in parentheses corresponding to 2σ. In the literature, values of $k_{\mathrm{MTBE}} = 1.6 \times 10^9$ L mol^{-1} s^{-1} [24] and of $k_{\mathrm{TCE}} = 2.9 \times 10^9$ to 4.3×10^9 L mol^{-1} s^{-1} [23,24] were found. The ratio $k_{\mathrm{MTBE}}/k_{\mathrm{TCE}} = 2.4 \pm 0.1$ determined in this work falls within this range ($k_{\mathrm{MTBE}}/k_{\mathrm{TCE}}$ = 1.8–2.7). Rate constants for TCP could not be extracted from the literature.

In the following, the reaction rates of the probe compounds in the presence of AC are compared.

3.2. Decomposition of H_2O_2 on the AC

The decomposition of H_2O_2 on AC follows a first-order kinetics with respect to H_2O_2 with an overall second order rate constant of 6×10^{-3} L g^{-1} min^{-1}. For AC loaded with organic sorbates the decomposition rate of H_2O_2 decreased but still followed a pseudo-first-order kinetics, as Fig. 1 shows exemplarily for AC with an 18% mass loading of TCE. Similar results have also been obtained in other studies [10,20]. The reduction in the decomposition rate due to the loading of AC with organic sorbates has been attributed to the reduction in active surface sites available for the activation of H_2O_2 [10,20].

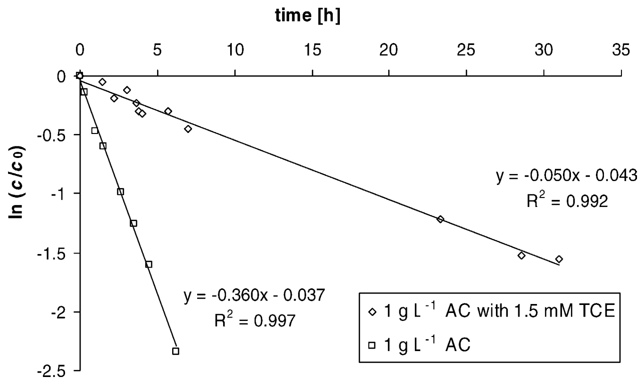

Fig. 1. Decomposition of H_2O_2 ($c_{0,\mathrm{H_2O_2}} = 67$ mM) in AC suspensions ($c_{\mathrm{AC}} = 1$ g L^{-1}) in the absence of organic sorbates and in the presence of 1.5 mM TCE resulting in an 18 wt.% loading of the AC.

3.3. Sorption–desorption kinetics on the AC

In order to make it possible to compare the timescale of reaction with that of sorption and desorption of the model compounds on the powdered AC applied, a simple sorption–desorption experiment was performed (Fig. 2). The sorption process of MTBE on the powdered AC (≤63 μm) closely approached equilibrium within 30 min. In the case of TCE, a slight decrease in the concentration of the freely dissolved fraction was still observed between measurements after 6 and 24 h. No further change was observed between measurements after 24 and 48 h. However, more than 90% of the sorption of TCE already occurred within the first 30 min. The sorbed fractions of MTBE and TCE were about 50 and 94%, respectively. Before starting the desorption stage of the experiment, the remaining freely dissolved fractions were removed. Therefore, it is plausible that the two sorbates reach different concentration levels after reequilibration, which is almost complete within 45 min. More than 80% of this level is achieved within the first 3 min after adding fresh water. These experiments provide clear evidence that sorption and desorption of the probe compounds on AC are fast compared to the timescale of the chemical reaction, as will be shown later in the text. Thus, sorption–desorption processes can be considered to be in nearly complete equilibrium during the course of the reaction.

3.4. Oxidation of the model compounds by H_2O_2 catalyzed by AC – the role of sorption

In order to study the influence of sorption on the reactivity of the substrates in the AC/H_2O_2 system in each

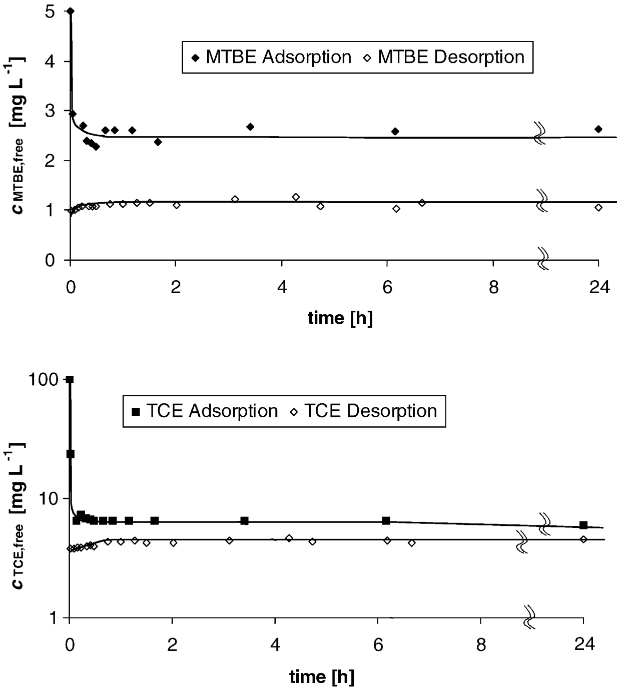

Fig. 2. Kinetics of adsorption and desorption of MTBE and TCE on powdered AC (≤63 μm).

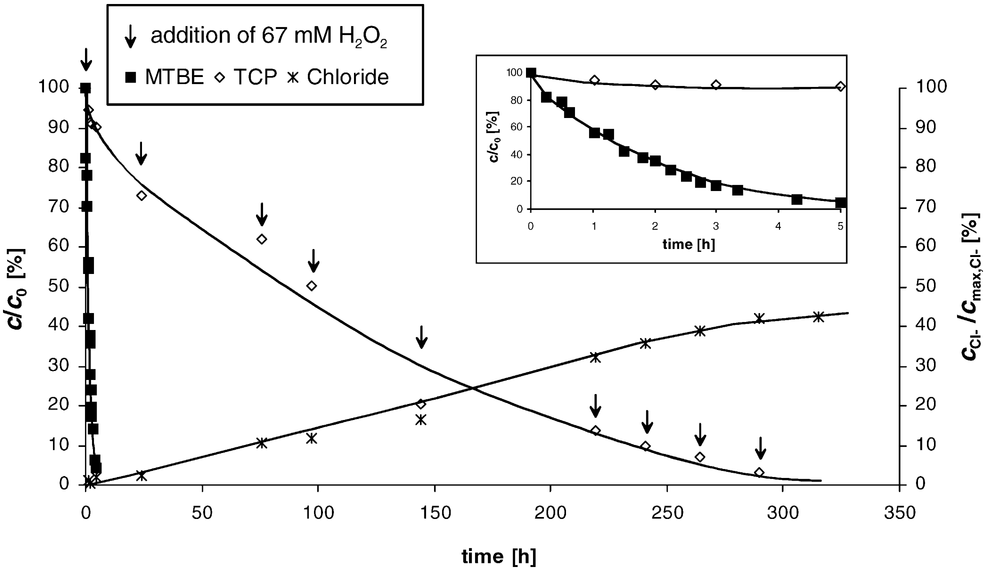

Fig. 3. Reaction of MTBE and TCP in an AC/H_2O_2 suspension (c_{AC} = 1 g L^{-1}, $c_{0,MTBE}$ = 1.1 mM and $c_{0,TCP}$ = 1.0 mM). $c_{Cl^-}/c_{Cl^-,max}$ is the ratio of the amount of chloride formed from TCP relative to the maximum possible amount at 100% TCP mineralization. Concentration of H_2O_2 was kept at 67 ± 10 mM during the first 5 h of reaction. Afterwards, H_2O_2 was added in a concentration of 67 mM after every TCP measurement. The inserted diagram shows the starting period of the reaction.

case, two probe compounds differing markedly in their extent of sorption were applied simultaneously so that both were subjected to identical reaction conditions.

Firstly, the reaction of MTBE and TCP was studied. Before starting the reaction by adding H_2O_2, the AC (1 g L^{-1}) was pre-equilibrated with the aqueous solution of the OCs for 2 days. The fractions of sorbed MTBE and TCP were determined as 0.15 and 0.98 of the total amounts ($c_{0,MTBE}$ = 1.1 mM, $c_{0,TCP}$ = 1 mM), respectively. The corresponding total loading of the AC was 21.1 wt.%. As can be seen from Fig. 3, in the presence of AC the reaction rate of MTBE is much higher than that of TCP, even though the relative rate constant for oxidation in homogeneous solution, k_{TCP}/k_{MTBE}, was found to be 1.6 ± 0.3. After a reaction time of 5 h the residual fraction of MTBE was 0.044 whereas it was 0.90 for TCP (Fig. 3). By means of 10 further additions of H_2O_2, mostly in 1-day intervals, the residual fraction of TCP could be further depleted down to 0.04. At this point the concentration of chloride released in the TCP degradation reaction corresponded to 44% of the maximum stoichiometric amount possible. That means on average only 1.4 of the three Cl-atoms per TCP molecule were released. The slow reaction of TCP, which is for the most part in the sorbed state, indicates that sorption has an adverse effect on the availability for the oxidation reaction.

In order to check a possible contribution of homogeneous oxidation reactions (e.g. by leaching of iron species from AC), a control experiment was performed using the leachate of an AC suspension after the AC had been completely removed. In this experiment, the concentration of MTBE (1.1 mM) remained constant in the presence of 67 mM H_2O_2 over an observation period of 5 h. Obviously, the reactivity in the AC/H_2O_2 system can be attributed exclusively to the heterogeneous catalysis by the AC.

In another experiment, the oxidation of MTBE ($c_{0,MTBE}$ = 1.1 mM) was studied in a mixture with TCE ($c_{0,TCE}$ = 1.5 mM) in an AC/H_2O_2 suspension containing 1 g L^{-1} of AC. The elimination of both compounds followed approximately a first-order kinetics with respect to the concentrations of the OCs (Fig. 4). At the start of the reaction the sorbed fractions of MTBE and TCE were 28 and 90% of the total amounts, resulting in a 20.8 wt.% loading of the AC. TCE showed a significantly lower reaction rate than MTBE. After a reaction time of 7 h, the concentrations of MTBE and TCE decreased to values of 0.06 and 0.38 of the initial concentrations, respectively. The TCE conversion proceeded along with a release of Cl^- corresponding to a 60% mineralization of Cl. The ratio of the pseudo-first-order rate constants is $(k'_{MTBE}/k'_{TCE})_{het}$ = 2.7 ± 0.4 (mean value of two experiments). This is again in contrast to the ratio obtained from the homogeneous oxidation reaction (k_{MTBE}/k_{TCE} = 0.42).

For the interpretation of the experimental findings we use a simple model which is based on the following three assumptions: (1) The reactive species in the AC/H_2O_2 suspension are the same as in the homogeneous Fenton system (i.e. $OH^\bullet$ radicals). (2) The freely dissolved hydrocarbons are reactive and the sorbed hydrocarbons are non-reactive. (3) The sorption equilibrium is established and the ratio of the freely dissolved fractions of MTBE and TCE is constant over the considered reaction period. On this basis, we can formulate the following rate law:

$$\frac{dc_n}{dt} = -k_n c_{OH^\bullet} x_{free,n} c_n = k'_{n,het} c_n \qquad (9)$$

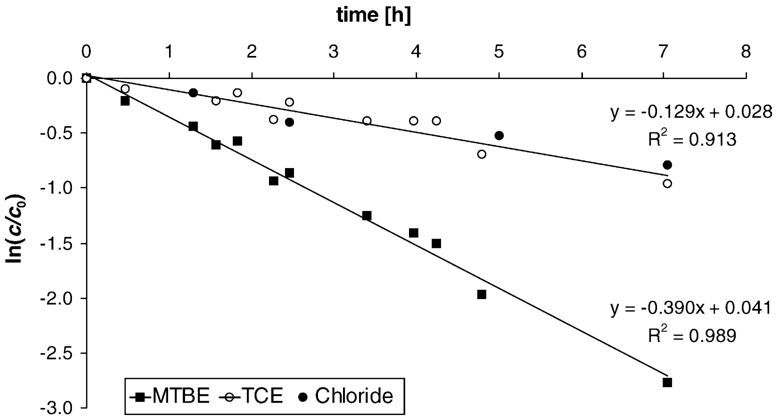

Fig. 4. Reaction of MTBE and TCE in an aqueous AC suspension (c_{AC} = 1 g L^{-1}, c_{t,H_2O_2} = 67 ± 10 mM, $c_{0,MTBE}$ = 1.1 mM and $c_{0,TCE}$ = 1.5 mM). The filled circles represent the TCE conversion according to the detected chloride concentration and assuming the release of 2 mol of chloride per mole of TCE.

Consequently, the ratio of the pseudo-first-order rate constants of the two compounds in the AC system can be calculated according to Eq. (10):

$$\left[\frac{k'_{MTBE}}{k'_{TCE}}\right]_{het} = \frac{k_{MTBE}}{k_{TCE}}\frac{x_{free,MTBE}}{x_{free,TCE}} \qquad (10)$$

with k_{MTBE}/k_{TCE} = 1/(2.4 ± 0.1) being the ratio of the rate constants in homogeneous solution and with $x_{free,MTBE}/x_{free,TCE}$ = 7.2 ± 0.7 being the ratio of the freely dissolved fractions determined after the equilibration period, just before the start of the reaction. On this way we obtain a theoretical value of $(k'_{MTBE}/k'_{TCE})_{het,calc}$ = 3.0 ± 0.4. This is very close to what we observed in the experiment: $(k'_{MTBE}/k'_{TCE})_{het,exp}$ = 2.7 ± 0.4.

In the following we will discuss whether the assumptions made above are reasonable for the applied reaction conditions. Considering the nature of the reactive species in the AC/H_2O_2 suspension, further indications will be given later in the text, which are in accordance with the dominant role of $OH^•$ radicals as discussed in the literature [19]. Time-resolved sorption and desorption experiments confirmed that both processes generally proceed sufficiently fast on powdered AC. It is only at very low residual concentrations that the desorption step can slow down considerably if the sorbed fraction is to be completely removed. However, this is not typical for our reaction system. TCE, for which desorption is most relevant since it is initially nearly completely adsorbed, is degraded to a residual fraction of 38% within the considered reaction period. If we compare the timescales of sorption and desorption observed for the powdered AC with the half-life of the OCs in the AC/H_2O_2 system which is about 2 h for MTBE and 5 h for TCE, we can conclude that it is reasonable to assume that the sorption equilibrium is nearly established at all times during the reaction period considered.

In order to verify that the ratio of the freely dissolved fractions of MTBE and TCE was nearly constant over the time course of the reaction, a separate sorption experiment was conducted with 1 g L^{-1} of AC and with the starting concentrations of MTBE and TCE equal to the residual concentrations observed after a reaction period of 7 h in the oxidation experiments (about 40 and 6% of the initial concentration, respectively). The ratio of the freely dissolved fractions in this experiment was $x_{free,MTBE}/x_{free,TCE}$ = 8.8, which is close to the initial value of 7.2 ± 0.7 found in the oxidation experiment. This means that the ratio of the freely dissolved fraction does not change considerably during the examined reaction period, which is plausible because the concentration of TCE which actually determines the loading of the AC only changes by a factor of 2.5 within the first 7 h of the reaction.

Considering the assumptions (1) and (3) made above as having been sufficiently assured, let us now examine the validity of assumption (2): when the concentration of AC in the system was raised up to 20 g L^{-1}, the fractions of freely dissolved MTBE and TCE decreased to values of 5 and 0.4%, respectively, of the total amount added ($c_{0,MTBE}$ = 15.4 mM, $c_{0,TCE}$ = 21.8 mM). The resulting total loading of the AC was 20.8 wt.%. The oxidation was started by addition of 67 mM H_2O_2. Due to the high concentration of AC in the suspension, H_2O_2 was degraded quickly and 20 additions in total of 6.4 mmol H_2O_2 every 20 min within the reaction time of 7.5 h were necessary in order to keep the H_2O_2 concentration nearly constant. In this system, no significant degradation of MTBE and TCE was observed within a reaction period of 7 h. Obviously, the high degree of sorption of MTBE and TCE on the AC inhibits their reaction with $OH^•$ radicals.

Methanol is known to be a strong quencher of $OH^•$ radicals. The rate constant of the reaction of methanol with $OH^•$ radicals is $k_{MeOH} = 9.7 \times 10^8$ L mol^{-1} s^{-1} [23]. The addition of methanol in concentrations of ≥3 mM to homogeneous Fenton systems exerted a strong inhibiting effect on the reaction of MTBE and TCE (results not shown). Since methanol is a hydrophilic compound it can be assumed not to accumulate on the AC surface to a significant extent. It should rather be a competitor for reactions with $OH^•$ radicals taking place in the solution phase.

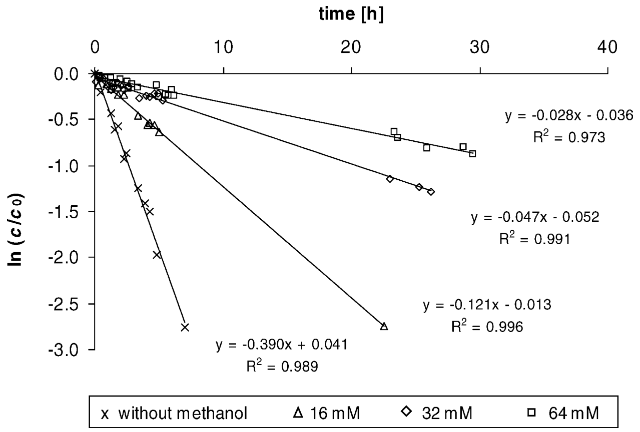

Fig. 5. Reaction of MTBE in the presence of different concentrations of methanol (c_{AC} = 1 g L^{-1}, $c_{0,MTBE}$ = 1.1 mM, $c_{0,TCE}$ = 1.5 mM, c_{MeOH} = 0, 16, 32 and 64 mM, c_{t,H_2O_2} = 67 ± 10 mM).

When methanol was added to AC/H_2O_2 suspensions (c_{AC} = 1 g L^{-1}) containing TCE and MTBE ($c_{0,MTBE}$ = 1.1 mM and $c_{0,TCE}$ = 1.5 mM), the reaction of the two compounds slowed down. The inhibiting effect increased with the concentration of methanol (0.5–2 g L^{-1}) added, as shown exemplarily for MTBE in Fig. 5. However, the ratio of the rate constants of MTBE and TCE, as determined from the residual fractions of the educts after a reaction period of 24 h according to Eq. (11), is nearly constant (Table 2), despite the fact that the two compounds are differently distributed between the sorbed and the freely dissolved state (initial freely dissolved fraction: $x_{free,MTBE}$ = 0.72, $x_{free,TCE}$ = 0.10)

$$\left[\frac{k_{MTBE}}{k_{TCE}}\right]_{het} = \frac{\ln c_{MTBE}/c_{MTBE,0}}{\ln c_{TCE}/c_{TCE,0}} \quad (11)$$

This result strongly supports the hypothesis that the predominant degradation pathway is the attack of $OH^{\bullet}$ radicals on the OC fraction freely dissolved in the aqueous pore volume, whereas the direct attack on the sorbed OC fraction seems to be negligible.

The finding that methanol acts as a strong quencher of the contaminant degradation by H_2O_2 in the presence of AC is consistent with a mechanism involving $OH^{\bullet}$ radicals (Eq. (3)). This mechanism is confirmed by the observation that N_3^-, another strong quencher of $OH^{\bullet}$ radicals ($k_{N_3^-}$ = 1.2 × 10^{10} L mol^{-1} s^{-1} [23]), also exerts an inhibiting effect in the AC/H_2O_2 systems. The pseudo-first-order rate constant of the conversion of TCE (c_0 = 1.5 mM) in suspensions containing 1 g L^{-1} AC and 67 mM H_2O_2 decreased by a factor of about 50 when 4.6 mM NaN_3 was added, resulting in 0.1 mM of N_3^- at pH = 3 (pk_{S,HN_3} = 4.6, [25]).

Table 2
Residual fractions of MTBE and TCE in AC/H_2O_2 suspensions containing different concentrations of methanol c_{AC} = 1 g L^{-1}, $c_{H_2O_2}$ = 67 ± 10 mM, $c_{0,MTBE}$ = 1.1 mM, $c_{0,TCE}$ = 1.5 mM, and c_{MeOH} = 0, 16, 32 and 64 mM

	Methanol concentration (mM)			
	0	16	32	64
$c_{MTBE,24\,h}/c_{MTBE,0}$	0.0022	0.0645	0.318	0.497
$c_{TCE,24\,h}/c_{TCE,0}$	0.109	0.401	0.585	0.766
k'_{MTBE}/k'_{TCE}	2.7 ± 0.4	3.0 ± 0.4	2.2 ± 0.5	2.6 ± 0.9

All the results reported so far were obtained from experiments with an initial loading of OCs on the AC of about 20 wt.%. At this mass loading, a considerable portion of the AC pores are filled with a liquid OC phase. For comparison, a 20 wt.% loading of TCE corresponds to a volume of about 0.13 cm^3 g^{-1} of AC. The micropore volume and the total intra-particle pore volume of the AC as determined by N_2 adsorption are 0.27 and 0.46 cm^3 g^{-1}, respectively. It is reasonable to assume that H_2O_2 itself is largely excluded from this organic phase. Consequently, the production of $OH^{\bullet}$ radicals within the filled pores is marginal. This means that the sorbate fraction within the filled pores is only accessible for the attack of $OH^{\bullet}$ radicals via the interface between the two liquid phases, the organic and the aqueous phases inside the pore volume.

In order to diminish this effect, we conducted an experiment with TCE and MTBE at a considerably lower initial loading of the AC (5.5 wt.%). Nevertheless, the reactivity ratio in this experiment was similar to that obtained in the preceding experiments: TCE ($x_{free,TCE}$ = 0.01) reacts slower than MTBE, which is sorbed to a lesser extent ($x_{free,MTBE}$ = 0.22). The concentration of chloride formed during a reaction period of 5 h was below the detection limit, corresponding to a TCE mineralization degree of less than 15% (based on a chloride yield of 100%). This is in accordance with the low degree of TCE conversion observed by headspace analysis (residual fraction of 83% after 5 h). The ratio of the rate constants of MTBE and TCE, as determined from the residual fractions of the educts after a reaction time of 5 h according to Eq. (11), is $(k'_{MTBE}/k'_{TCE})_{het}$ = 8.0 ± 1.5 (Fig. 6).

Applying Eq. (10) to calculate a theoretical value for the ratio of the rate constants of MTBE and TCE with all the assumptions discussed above, we obtained a value of $(k'_{MTBE}/k'_{TCE})_{het,calc}$ = 10.0 ± 1.3. This is again close to the experimentally observed value of 8.0 ± 1.5. This experiment proves that even at a relatively low mass loading of the AC the sorbed fraction of the OCs is hardly available for the oxidation reaction, despite the fact that the $OH^{\bullet}$ radicals are formed at the AC surface, i.e. in close proximity to the sorbed OCs.

3.5. Discussion of possible mechanisms of the adverse effect of sorption

Possible regions of the reaction of the $OH^{\bullet}$ radicals with the OCs are the pore volume of the AC grains and possibly the boundary layer at their outer surface, because the lifetime of $OH^{\bullet}$ radicals is much too short to allow a back-

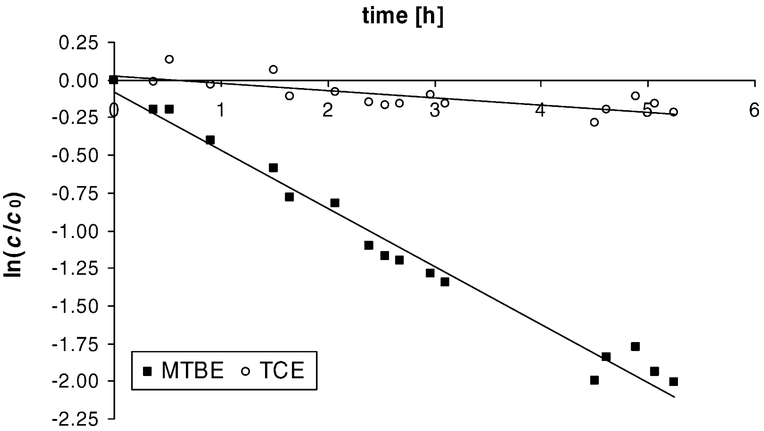

Fig. 6. Oxidation of MTBE and TCE with AC/H_2O_2 with a reduced mass loading of the AC (c_{AC} = 2 g L^{-1}, c_{t,H_2O_2} = 67 ± 10 mM, $c_{0,MTBE}$ = 0.275 mM and $c_{0,TCE}$ = 0.34 mM).

diffusion into the solution bulk phase. There are at least three possible explanations for the finding that sorption has an adverse effect on the degradation in the AC/H_2O_2 system:

(1) H_2O_2 itself might not reach the sorption sites, since it does not effectively partition into pores filled with liquid OCs. However, the negative effect of sorption was also observed at a comparatively low AC loading of 5 wt.%, where pore filling should be of minor importance. Therefore, this effect does not seem to be the predominant reason.

(2) While diffusing into the inner pore volume of the AC, the concentration of H_2O_2 might be depleted due to its decomposition on the AC surface (Eqs. (1) and (2)). Whether significant concentrations of H_2O_2 reach the entire pore volume or not depends on the ratio of the diffusion rate of H_2O_2 relative to its decomposition rate. According to a sedimentation experiment, 75 wt.% of the AC particles have diameters <40 μm. The characteristic time (τ_{diff}) for the diffusion of an H_2O_2 molecule from the outer sphere of an AC particle into its centre can be approximated from the particle radius (r) and the effective diffusion coefficient of H_2O_2 in the AC pore system (D_{eff,H_2O_2}):

$$\tau_{diff,H_2O_2} = \frac{r^2}{2D_{eff,H_2O_2}} \tag{12}$$

D_{eff,H_2O_2} can be estimated from the diffusion coefficient of H_2O_2 in aqueous solution (D) and the tortuosity factor (f) of the AC: $D_{eff,H_2O_2} = D_{H_2O_2,water}/f$. With $D_{H_2O_2,water}$ estimated as 2×10^{-5} cm^2 s^{-1} (according to the procedures described in [26]), $r \leq 31.5$ μm and assuming a tortuosity factor of about 10 for AC (estimation according to [27]), we obtain a characteristic diffusion time of $\tau \leq 2.5$ s. The half-life of H_2O_2 in the pore volume of the AC grains ($\tau_{1/2,pore}$) can be estimated from the observed half-life ($\tau_{1/2}$) in an AC suspension and the ratio of the intra-particle pore volume (V_{pore}) to the total solution volume of the system (V_{bulk}): $\tau_{1/2,pore} = \tau_{1/2} \cdot V_{pore}/V_{bulk}$. Applying an experimentally determined value for the half-life of H_2O_2 ($\tau_{1/2}$ = 1.9 h) in a system containing 1 g L^{-1} AC with an intra-particle AC pore volume of 0.46 cm^3 g^{-1}, a pore volume half-life of 3.3 s can be calculated. This value is in the same order of magnitude as the characteristic time for the diffusion of H_2O_2 into the centre of the largest AC grains. For an AC loaded with OCs, the pore volume half-life of H_2O_2 will be even higher (cf. Fig. 1). It follows that the concentration of H_2O_2 in the inner pore volume of the AC grains with $d_{particle} \leq 63$ μm may be slightly but not drastically lower than the concentration in the bulk volume. Therefore, the low availability of the sorbed OC fraction for the degradation reaction cannot be explained by an H_2O_2 depletion within the grains.

Another way to check if H_2O_2 is depleted inside the pore volume is to estimate the dimensionless Weisz-modulus Φ [28,29] under the applied reaction conditions:

$$\Phi = L_C^2 k_{eff}/D_e = (6.3 \times 10^{-3}\,\text{cm}/6)^2 \times 0.1\,\text{s}^{-1}/(2 \times 10^{-6}\,\text{cm}^2\,\text{s}^{-1}) \approx 0.05 \tag{13}$$

$L_C = (V/S)_{catalyst\ particle}$ is a characteristic length (the ratio of volume to external surface of the catalyst particle) which characterises the diffusion distance inside the catalyst particle. For spherical particles it is equal to 1/6 of the particle diameter. k_{eff} is the first order rate constant of the H_2O_2 decomposition ($k_{1st\ order} = 10^{-4}$ s^{-1}) in the presence of the catalyst concentration $c_{catalyst} = 10^{-3}$ g cm^{-3}, but related to the catalyst volume, i.e. $k_{eff} \approx 0.1$ s^{-1}. The effective diffusion coefficient of H_2O_2 inside the AC was approximated as 1/10 of its value in water: $D_{eff,H_2O_2} \approx 0.1\ D_{H_2O_2,water} \approx 2 \times 10^{-6}$ cm^2 s^{-1}. The resulting value of the Weisz-modulus Φ = 0.05 indicates that the H_2O_2 concentration inside the pore volume is almost equal to its bulk-phase concentration [28,29].

Even if the assumed value of the effective diffusivity in Eq. (13) were to be lower by an order of magnitude (i.e. $\Phi = 0.5$), the conclusion drawn above remains valid: the depletion of H_2O_2 in the pore volume would be less than 10%. In other words, the mass transfer rate into the pore volume is sufficiently fast in order to compensate for the H_2O_2 consumption.

(3) A third and possibly the most important reason for the adverse effect of sorption on the degradation reaction might lie in the short lifetime of $OH^\bullet$ radicals, which only allows them to react with substrates in direct proximity. In contrast to the estimation of Kwan and Voelker [15], who calculated the mean diffusion distance of surface generated $OH^\bullet$ radicals ($L \sim 6$ nm) nm) into the bulk solution based on the concentration of dissolved species, the consumption of $OH^\bullet$ radicals in the intra-particle pore volume of AC may be additionally controlled by reactions with the carbon surface. Thus, the sphere of oxidation around the catalytic sites will be even more narrow than in iron oxide suspensions.

4. Conclusions

H_2O_2 is activated by AC, forming reactive species that are able to oxidize organic contaminants such as MTBE, TCE and TCP. The inhibition effect of typical radical quenchers such as methanol and N_3^- on the oxidation reactions is in accordance with the commonly accepted opinion in the literature that $OH^\bullet$ radicals are the main reactive species in systems containing AC and H_2O_2. In the AC/H_2O_2 system, the reactive species are formed on the surface of the AC, i.e. in close proximity to the adsorbed OCs. This is a significant difference to other heterogeneous systems containing AC as an adsorbent, where H_2O_2 activators are used in the solution phase (e.g. $Fe^{2+/3+}$, UV or O_3). Nevertheless, our results clearly show that, even in this case, the preconcentration of the substrates to be oxidized on the AC is not advantageous for the degradation reaction. There are strong indications that the predominant degradation pathway is the attack of $OH^\bullet$ radicals on the OC fraction which is freely dissolved in the aqueous pore volume of the AC, whereas the sorbed fraction is nearly unreactive.

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