Degradation of polyvinyl alcohol (PVA) by homogeneous and heterogeneous photocatalysis applied to the photochemically enhanced Fenton reaction

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Abstract The reaction mechanism of the oxidative degradation of polyvinyl alcohol (PVA) by the photochemically enhanced Fenton reaction was studied using a homogeneous (Fe²⁺aq + H₂O₂) and a heterogeneous reaction system (iron(III)-exchanged zeolite Y + H₂O₂). In the homogeneous Fenton system, efficient degradation was observed in a batch reactor, equipped with a medium pressure mercury arc in a Pyrex envelope and employing 80% of the stoichiometric amount of H₂O₂ required for the total oxidation of PVA and a concentration ratio as low as 1 mole of iron(II) sulfate per 20 moles of PVA sub-units (C₂H₄O). Model PVA polymers of three different molecular weights (15,000, 49,000 and 100,000 g mol⁻¹) were found to follow identical degradation patterns. Strong experimental evidence supports the formation of super-macromolecules (MW: 1 – 5 × 10⁶ g/mol) consisting of oxidized PVA and trapped iron(III) at an early reaction stage. Low molecular weight intermediates, such as oxalic acid, formic acid or formaldehyde were not found during PVA degradation in the homogeneous Fenton system, and we may deduce that the manifold of degradation reactions is mainly taking place within the super-macromolecules from which CO₂ is directly released. However, in the heterogeneous Fenton system, the reaction behavior was found to be distinctly different: a decrease of the molecular weights of all three tested monodisperse PVA samples was observed by the broadening of the GPC-traces during irradiation, and oxalic acid was formed. The results lead to the mechanistic hypothesis that during the heterogeneous Fenton process, the cleavage of the PVA-chains may occur at random positions, the reactive centres being located inside the iron(III)-doped zeolite Y photocatalysts.

Keywords Fenton reaction (photochemically enhanced); heterogeneous photocatalyst; iron(II/III); polyvinyl alcohol (PVA)

Introduction

The uncontrolled release of polyvinyl alcohol (PVA) and structurally related polymers from industrial plants into the environment causes many ecological problems (Lei et al., 1998). An inexpensive and versatile solution, especially for waste water discharged from desizing processes in the textile industry, has not yet been developed. These highly polluted wastewaters contain amounts of dissolved organic carbon (DOC) as high as 10 g/L giving rise to high chemical oxygen demand (COD). The oxidative degradation of PVA in municipal and industrial wastewater treatment facilities is usually limited, provided that specially adapted bacteria strains are employed. Whereas some adapted bacteria showed promising results in biological model plants, high salt contents prevailing in desizing waste waters prohibit their successful application. The use of seawater in industrial processes may help to preserve freshwater resources, and oxidation methods have to be developed which will operate successfully under these conditions. A further environmental problem arises from the enhanced mobilization of heavy metals from the sediments of streams, lakes and oceans by PVA. Therefore, methods for the removal of PVA from wastewater, preferentially by mineralization, have to be developed.

In this study, we have compared the efficiencies as well as the basic reaction mecha-
nisms in a homogeneous and a heterogeneous Fenton reaction system. In 1998, we present-
ed new evidence for the formation of the ferryl ion (Fe$^{4+}_{aq}$) as reactive intermediate of the
thermal as well as of the photochemically enhanced Fenton reaction (Bossmann et al.,

$$[\text{Fe(OH)}(\text{H}_2\text{O})_2]^+ + \text{H}_2\text{O}_2 \leftrightarrow [\text{Fe(OH)}(\text{H}_2\text{O}_2)(\text{H}_2\text{O})_4]^+ + \text{H}_2\text{O} \quad (1)$$

$$[\text{Fe(OH)}(\text{H}_2\text{O}_2)(\text{H}_2\text{O})_4]^+ \rightarrow [\text{Fe(OH)}_3(\text{H}_2\text{O})_4]^+ \quad (2)$$

It is of general interest, whether the formation of the ferryl ion is related to particular model
pollutants, such as 2,4-xylidine, or whether its occurrence is common in AOP processes
involving iron cations. Furthermore, not much is known yet about the reaction mechanisms
proceeding within the framework of a zeolite, when bound iron cations are present.
However, it should be noted that the main perspective of this study is the fast and cost-effi-
cient removal of macromolecular PVA.

**Methods and experiments**

**Chemicals**

All chemicals used were ACS grade. FeSO$_4$ × 7 H$_2$O, (Fe)$_2$(SO$_4$)$_3$ × 11 H$_2$O, H$_2$O$_2$ (30% w/w in H$_2$O), H$_2$SO$_4$, Na$_2$PO$_4$, H$_3$PO$_4$, KMnO$_4$, Na$_2$SO$_3$, Na$_2$SO$_4$, Na$_2$HPO$_4$, TiO(SO$_4$)$_2$, oxalic acid, acetaldehyde, ethanol, formaldehyde (20% w/w in H$_2$O), 1,10-
phenanthroline, acetonitrile and acetic acid were purchased from Merck. Water was of
ultra-pure quality (UHQ II). H$_2$O$_2$ was analyzed by the classic KMnO$_4$-titration. PVA of
defined molecular weight (MW = 15,000, 49,000 and 100,000) was obtained from Sigma.
Four additional PVA standards were purchased from Fluka (MW = 1,000, 2,100, 5,100 and
2,000,000). Stock solutions of PVA in H$_2$O (8.325 × 10$^{-2}$ M of polymer sub-units (C$_2$H$_4$O)
corresponding to 2,000 mg C/L) were prepared by intensive stirring at room temperature
and stored under refrigeration.

The preparation of the iron(III)-doped zeolite Y was performed by ion exchange
(Fe$^{3+}$ vs. Na$^+$) using Linde NaY and (Fe)$_2$(SO$_4$)$_3$ × 11 H$_2$O in H$_2$O (pH = 3.0). The iron(III)-
concentration was determined to be 2.16% by weight. The results are described in detail in
the literature (Shahin, 2000).

**Thermal and photochemically enhanced Fenton reactions**

All photolysis experiments were carried out in a batch reactor (Lei et al., 1998). It consists
of a reservoir (0.60 L) and a flow-through annular photochemical reactor (Pyrex, 0.15 L,
optical path length of 0.7 cm), equipped with a medium pressure mercury lamp (TQ 150,
Heraeus Noblelight). Under our experimental conditions, 5.75 × 10$^{-5}$ M/s of Fe$^{2+}_{aq}$ were
formed, and a value of RP of 45.6 ± 1.2 W was obtained (Bossmann et al., 2000). The solu-
tion was circulated (250 mL/min) by means of a peristaltic pump (Bender & Hobein, mas-
terflex, easy-load 75-118-00).

**Homogeneous Fenton catalysis.** The PVA stock solutions were diluted by a factor of ten
(to 8.325 × 10$^{-3}$ M of polymer sub-units (C$_2$H$_4$O) corresponding to 200 mg C/L) in the
photochemical equipment for a total volume of 0.50 L. Immediately before experiments
were started, iron(II) was added (standard concentration: 4.16 × 10$^{-4}$ M corresponding to a
molar ratio of iron(II) to (C$_2$H$_4$O) units of 1/20). The pH was adjusted to the initial value of
4.0 using diluted H$_2$SO$_4$ (Metrohm pH-analyzer E 512). The reaction mixture was circulat-
ed for 15 minutes. For the same amount of time, the reservoir was purged with compressed
air. A defined amount (1.665 × 10$^{-2}$ to 6.66 × 10$^{-2}$ M) of H$_2$O$_2$ was added at once, and in
cases, where the photochemically enhanced Fenton oxidation of PVA was investigated, the light source was ignited. All experiments were carried out during 120 minutes. The temperature was maintained at 40 ± 2°C, unless otherwise indicated. Samples were taken from the reservoir at various irradiation time intervals and analyzed.

**Heterogeneous Fenton catalysis.** The experimental conditions were exactly identical to above except 0.25 g of iron(III)-exchanged zeolite Y was used instead of the iron(II).

**Treatment of the samples prior to the DOC and HPLC measurements**

2.0 × 10^{-3} L of a reduction and precipitation agent, composed of 0.10 M Na₃PO₄ and 0.10 M Na₂SO₃ were added to a sample of 4.0 × 10^{-3} L taken from the batch reactor. This procedure led to a complete reduction of the residual H₂O₂ as well as to the removal of most of the iron(II/III) by precipitation. The precipitate was removed by filtration using nylon Luer-Lock-membrane filters (Roth, 0.22 × 10^{-6} m).

**Analyses**

The analysis of the dissolved organic carbon (DOC) was carried out using a Dohrmann DC-190 TOC (total organic carbon) analyzer (T = 680°C) from Rosemount Analytical. Calibration was performed using PVA (MW = 15,000, 49,000 and 100,000), oxalic acid and potassium hydrogenphthalate (KHP). The threshold of detection was approximately at 1 mg C/L.

The detection of possible stable low molecular weight intermediates of the PVA degradation, such as oxalic acid, acetic acid, acetaldehyde, formaldehyde or ethanol, was performed using a HP Series II liquid chromatograph, equipped with a diode array detection system (DAD), a LiChrospher-100 RP 18 column (length: 125 mm, diameter: 4 mm, particle size: 5 µm) and an identical pre-column. The pre-column removed higher molecular weight intermediates (MW > 2,000). A mixture of 0.05 M triethylamine/H₃PO₄ (pH = 7.0, 95% v/v) and acetonitrile (Baker) (5% v/v) was chosen as isocratic eluent. However, no low molecular weight intermediates could be detected. Consequently, taking into account the corresponding detection limits, their concentration could not exceed 10^{-7} M.

The gel permeation chromatography (GPC) experiments were carried out using a HP Series II liquid chromatograph and employing a HP TSK-AC/4000 SW column (7.5 mm × 300 mm) equipped with a pre-column of the same type (7.5 mm × 5 mm). An aqueous solution of Na₃SO₄ (0.10 M) and Na₂HPO₄ (0.10 M) was used as eluent. The pH of 7.0 was adjusted using diluted H₃PO₄. The polymers have been detected at a wavelength of 220 nm.

**Results and discussion**

**Homogeneous photoenhanced Fenton oxidation of PVA**

PVA degradation has been assessed by monitoring the dissolved organic carbon (DOC) during the thermal and the photochemically enhanced Fenton oxidation of monodisperse PVA of three different molecular weights (MW = 15,000, 49,000 and 100,000). For comparative purposes, the same concentration of polymer sub-units (C₂H₄O) has been used in all experiments. No molecular weight dependence of the DOC removal has been observed within limits of the experimental error (Figure 1).

A similar trend was observed for the thermal and the light-enhanced degradation of PVA (Figure 1). The DOC/DOC⁰ decreased as a function of reaction time until a residual DOC value was reached, and no further mineralization could be observed by continuing the reaction under the given experimental conditions. However, the residual DOC level was much lower and the time at which it was reached shorter, for the photochemically enhanced Fenton reaction. In the case of the thermal Fenton reaction, mineralization stopped after 50
minutes of reaction time at a residual DOC level of 116 ± 6 mg C/L (corresponding to 42% of DOC removal), whereas in the photochemically enhanced Fenton reaction, 90% of the DOC were mineralized after 30 minutes of irradiation reaching a residual DOC of only 20 ± 6 mg C/L.

The increased PVA degradation efficiency during the photochemically enhanced Fenton reaction is most likely due to the enhanced reduction efficiency of iron(III) to iron(II) under irradiation.

From gel permeation chromatography, we also obtained experimental evidence for the formation of supermacromolecules consisting of iron(III) and oxidized PVA ($M_w = 15,000, 49,000$ and $100,000$ g/mol) and exhibiting a very high molecular weight ($M_w \sim 1\text{–}5 \times 10^6$ g/mol).

The experimental data supports an advanced oxidation mechanism occurring within the pre-formed iron(III)-PVA-supermolecule. No molecular weight dependence of the DOC removal has been observed within limits of the experimental error (Figure 2).

**Figure 1** Degradation of PVA of different molecular weights (15,000, 49,000 and 100,000) by: (a) the thermal; and (b) the photochemically enhanced Fenton reaction (PVA: $8.33 \times 10^{-3}$ M of $(C_2H_4O)$ units or $200$ mg C/L; $H_2O_2$: $3.33 \times 10^{-2}$ M and $Fe^{2+}$: $4.16 \times 10^{-4}$ M, reaction system purged using compressed air).

**Figure 2** GPC of an aqueous solution of three PVA samples ($MW = 15,000, 49,000$ and $100,000$), and of the reaction mixture during the photochemically enhanced Fenton reaction in the homogeneous reaction system.
The absence of such an effect on the PVA degradation efficiency provides first experimental evidence that a striking similarity of microscopic reaction conditions must exist in all three different PVA systems investigated. In addition, no low molecular weight intermediates, such as oxalic acid, acetic acid, acetaldehyde, ethanol or PVA-oligomers could be detected by HPLC in any of the experiments.

In distinct contrast to the classic paradigm of the Fenton reaction, we do not find evidence for the formation of the hydroxyl radical as a reactive intermediate. However, the Fenton-type oxidation of PVA proceeds via a ferryl-ion (Fe$^{4+}$) formed by a two electron inner-sphere electron transfer reaction within the complex PVA/Fe$^{2+}$/H$_2$O$_2$. We may then conclude that CO$_2$ is released directly from the super-macromolecule.

**Heterogeneous photoenhanced Fenton oxidation of PVA**

For the heterogeneous Fenton oxidation of PVA, an iron(III)-doped zeolite Y was employed. Contrary to the homogeneous reaction mechanism, the heterogeneously photocatalyzed degradation of PVA using the system zeolite Y/Fe(III)/H$_2$O$_2$ generates low molecules weight reaction products (such as oxalic acid, see Figure 3). Note that the DOC-removal remains incomplete after 120 minutes of photolysis.

Another very interesting experimental result is the consecutive disruption of individual PVA chains during the heterogeneous photocatalysis (Figure 4). This mechanistic behavior is clearly discernible from the broadening and shifting towards larger retention times of the PVA-peaks occurring in the GPC chromatograms. This finding shows that no formation of super-macromolecules takes place in the heterogeneous reaction system. This experimental result confirms that iron(III) does not form complexes with PVA and its oxidation products. Most likely, it remains bound inside the zeolite Y framework.

**Conclusion**

DOC-degradation of a homogeneous and a heterogeneous (photochemically enhanced) Fenton reaction system was investigated. The homogeneous system proved advantageous in comparison to the heterogeneous Fenton system, which consisted of an iron(III)-exchanged zeolite Y.

The formation of super-macromolecules formed from iron(III) and oxidized PVA (GPC) could only be detected in the homogenous system. The very complex Fenton oxidation chemistry proceeds within these super-macromolecules and leads eventually to the release of carbon dioxide as main oxidation product.

In sharp contrast to the homogeneous reaction system, a step-by-step decrease of the
molecular weights of three monodisperse PVA samples was observed in the heterogeneous reaction system. This result demonstrates that under these conditions iron(III) is most likely bound within the faujasites framework (zeolite Y).

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References


Figure 4  GPC-analysis of the macromolecular degradation products formed from PVA ($M_w = 100,000$).