Efficient photo-assisted Fenton catalysis mediated by Fe ions on Nafion membranes active in the abatement of non-biodegradable azo-dye

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Highly dispersed Fe ions on Nafion membranes are shown to decompose H_2O_2 with similar kinetics as found for homogeneous solutions containing Fe^{3+} ions during the photo-assisted Fenton degradation of Orange II, avoiding the drawbacks of the homogeneous treatment.

Membrane related research has attracted much attention in recent years as a structured medium for a variety of chemical reactions. Nafion perfluorinated membranes have been used during the last decade in a variety of catalytic/electrocatalytical integrated chemical reactions.[1] Polymer membranes have also been used for charge transfer in inorganic and biological systems.[2] Few studies of chemical transformations with CdS or TiO$_2$ loaded membranes using photochemical activation have been reported until now.[3–6] This study is concerned with the degradation of non-biodegradable azo-dye Orange II by Fenton photo-assisted reactions in Fe-free solutions. This dye does not undergo bacterial degradation in a waste-water treatment plant due to the aromatic and sulfo-aromatic group found the ring structure. Azo dyes, which account for more than 22% of industrial dye production, are commonly found in effluents of the textile industry.[7]

Experiments were conducted with Nafion perfluorinated cation transfer membrane (Dupont 117, 0.007 in, Aldrich #7.467-4) containing hydrophilic sulfonate groups immobilized on the fluorocarbon matrix. Exchange with $FeCl_3\cdot6H_2O$ (Fluka) at room temperature was carried out for a few minutes after the Nafion was immersed in HCl. After the ion exchange, the membrane was washed with water followed by immersion in 1 M NaOH to convert Fe^{3+} to its hydrated form. The Fe-ion content of the Nafion was found to be 1.78 mass% after digestion in concentrated HNO_3 (Teflon coated autoclave) under high pressure and temperature. The solution obtained in this way was subsequently diluted and the Fe content measured by AAS (flame detector, Philips 20 M). Photolysis experiments were carried out by means of a Hanau Suntest Lamp with tunable light intensity equipped with an IR filter to remove IR radiation. The short UV radiation ($\lambda \leq 305$ nm) was removed by the Pyrex wall of the reaction vessels. Light irradiation reached the Nafion/Fe membrane which was positioned immediately behind the wall of the reaction vessel (60 ml volume containing 40 ml solution) as the only light absorber in this two phase system. The detection of Orange II in solution was carried out *via* an HPLC (Varian 9065 Diode Array) provided with a Phenomenex C-18 inverse phase column. The azo-dye peak was detected at $\lambda = 486$ nm with a retention time of 11.1 min. The solution gradient during the analysis was regulated with a buffer consisting of ammonium acetate and acetonitrile.

The disappearance of Orange II (pH 2.8) under light irradiation on a Fe-loaded Nafion membrane by a Suntest lamp was recorded as a function of time for different concentrations of H_2O_2 in the solution. With increasing concentration of H_2O_2 the Orange II degradation kinetics was accelerated. At H_2O_2 concentrations > 0.8 mM, no further acceleration was observed. This effect is due to the known scavenging effect when using higher H_2O_2 concentration on the further generation of

hydroxyl radicals in solution.[8] The concomitant total organic carbon (TOC) decrease was observed to be modest changing from 16 to 11 ppm C after 120 min. Within this time of the azo dye was observed to completely disappear from the solution. Concomitant CO_2 evolution was checked by gas chromatography (GC) confirming that mineralization of the dye proceeds with a much slower kinetics than the Orange II disappearance. This reveals the formation of longer lived intermediates in solution. The decoloration shown in Fig. 1 reflects azo-bond breakage in Orange II.[9,10] During dye abatement where H_2O_2 (0.8 mM) is added, the solution pH was seen to increase from 2.8 to ≈ 3.2. This corresponds to about a fourfold increase in the OH^- concentration in the solution and suggests reaction (1) as the main pathway for

$$\text{Nafion/Fe}^{II} + H_2O_2 \rightarrow \text{Nafion/Fe}^{III} + {}^{\cdot}OH + OH^- \quad (1)$$

Orange II degradation rather than reaction (2).

$$\text{Nafion/Fe}^{III} + H_2O_2 \rightarrow \text{Nafion/Fe}^{II} + HO_2{}^{\cdot} + H^+ \quad (2)$$

Three experimental observations substantiate further the mechanism suggested in eqn. (1): (*a*) methanol (0.26 M) precluded the abatement of the azo dye due to its ${}^{\cdot}OH$ radical scavenging properties, (*b*) spectrophotometric results showed that the initial Nafion/Fe^{III} membrane decolored substantially during the photolysis due to the build-up of Nafion/Fe^{II} absorbing at much lower wavelengths. Since the iron has been exchanged at room temperature in aqueous solution the exchanged-hydrated Nafion/Fe^{III} would involve the presence in the Nafion of the Fe-species $Fe(OH)^{2+}$ ($\varepsilon_{366nm} = 275$ dm^3 mol^{-1} cm^{-1}) and $Fe_2(OH)_2^{4+}$ ($\varepsilon_{366nm} = 1000$ dm^3 mol^{-1} cm^{-1}).[18] During the
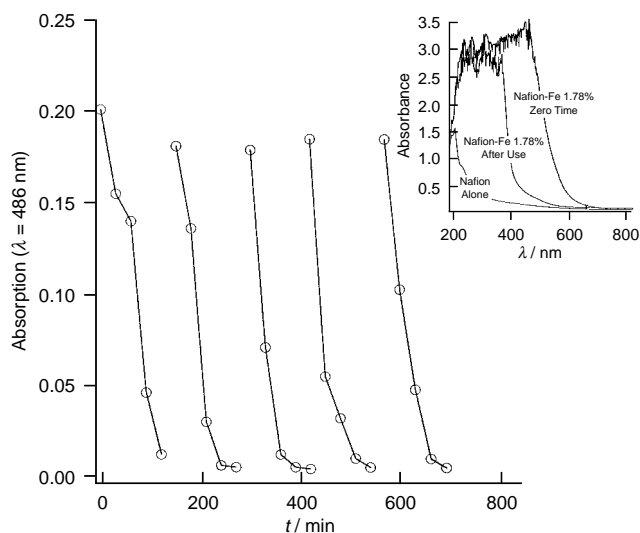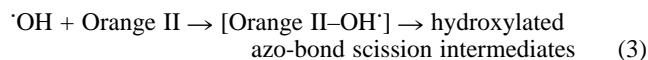

Fig. 1 Nafion/Fe loaded induced degradation of Orange II as a function of time followed by visible spectral observations at the Orange II peak of 486 nm up to the fifth cycle. The inset shows the Fe content in the solution after 26.6 days (1600 min). [Orange II] = 0.05 mM, pH = 2.8, H_2O_2 = 4.85 mM, irradiation intensity = 50 mW cm^{-2}.

dye decoloration (Fig. 1) the orange–brown color of Nafion/Fe^{III} gradually disappears due to the much lower absorption from the charge transfer band of Fe(H$_2$O)$_6^{2+}$ observed below $\lambda = 265$ nm with $\varepsilon_{254nm} = 20$ dm^3 mol^{-1} cm^{-1}.[19] Finally, (c) the superoxide radical HO$_2^\cdot$ (p$K_a = 4.8$) photoproduced according to eqn. (2) has a considerably lower one electron standard reduction potential of $E^\circ = 0.75$ V vs. NHE (HO$_2$/O$_2^{\cdot-}$) than the $^\cdot$OH radical with $E^\circ = 1.90$ V vs. NHE[20] ($^\cdot$OH/OH$^-$) in eqn. (1). The fast oxidation of the Orange II cannot possibly be explained in terms of this kinetically slower and less energetic HO$_2^\cdot$ radical [eqn. (2)].

Fig. 1 shows the repetitive nature of the Orange II photodegradation in the presence of Nafion/Fe-loaded membrane and H$_2$O$_2$. After ca. 25 cycles, the membrane was regenerated by immersion in 1 M NaOH. The timing of this regeneration was determined by two factors: (a) during use, the initial orange–brown coloration with absorption up to $\lambda = 600$ nm slowly changed to gray–yellowish with absorption reaching only an upper limit of ca. 410 nm. This indicated that during the photolysis the Fe^{III} content in the Nafion membrane decreased leading to the formation of colorless Fe^{II} since the total iron content of the membrane was seen to remain constant (see below). The Nafion without any Fe-loading absorbed only below 300 nm; and (b) during the degradation cycles the membrane become more active with time. A faster Orange II degradation of ca. 40% was observed compared to the first degradation run. Highly stable Nafion/Fe^{II} species are probably responsible for the observed acceleration as the reaction progresses.

The assessment of the oxidation state of Fe during the reaction was carried out by XPS in a Leybold–Heraeus instrument. Quantitative evaluation of the Fe^{III} and Fe^{II} species revealed 78% Fe^{III} ($E_b = 710.0$ eV) and 22% Fe^{III}/Fe^{II} ($E_b = 713.8$ eV) at time zero. The former species appeared mainly as Fe$_2$O$_3$ while the latter species consisted mainly of the composite Fe$_3$O$_4$ oxide showing the peaks for the constituent oxides. After reaction, the Nafion membrane showed 16% Fe^{III} and 84% Fe^{III}/Fe^{II} oxidation states. The correction for electrostatic charging of the particles during the measurements was carried out by a polynomial fit of the data with a Shirley-type background subtraction. The XPS experimental result further confirms the spectral change in the Fe-Nafion membrane observed during the photocatalysis. The size of the Fe-clusters on the Nafion was determined by TEM to be 37 ± 4 Å (Philips 20 M instrument). The particles were seen to be uniformly deposited on the Nafion and the size distribution was narrowly centered around the median value.

Membranes were regenerated after 500 h irradiation to attain the same Orange II degradation kinetics as observed during the initial cycle. The highly dispersed Fe^{III} ions could be regenerated in the Nafion. In solution the degradation of Orange II proceeded according to eqn. (3).[3,4]

$$^\cdot\text{OH} + \text{Orange II} \rightarrow [\text{Orange II–OH}^\cdot] \rightarrow \text{hydroxylated} \\ \text{azo-bond scission intermediates} \quad (3)$$

The inset in Fig. 1 shows the change in absorption of the Nafion membranes with time. After 500 h irradiation a substantial change in absorption of the Nafion/Fe^{III} was seen. A decrease in the absorption of Nafion/Fe^{III} is observed along with concomitant growth of the lower absorbing Nafion/Fe^{II}. This change in absorption is consistent with the molar absorption coefficients and the XPS evidence presented above. The optical absorption of Nafion membranes is shown in the left hand side of the inset. The formation of Q-sized Fe^{III}/Fe^{II} clusters in the Nafion upon irradiation has been confirmed by X-ray diffraction. The exchange procedure used to incorporate Fe ions in the membrane is therefore also a method to produce discrete small sized particles of iron oxides embedded in the polymer structure.

Based on the experimental results a simplified scheme of the reaction is presented (Scheme 1). Scheme 1 shows the
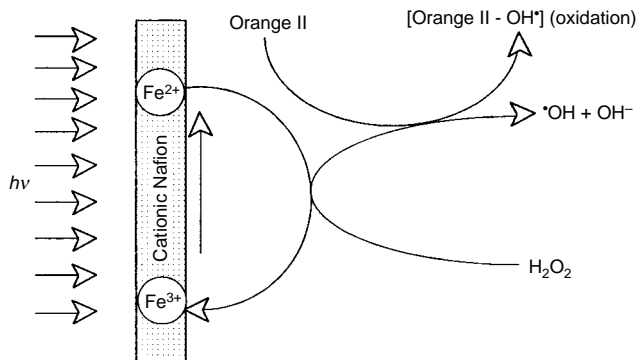
Scheme 1

photocatalytic degradation of Orange II in acidic solutions due to the photoproduction of oxidative radicals in solution and the build up of Nafion/Fe^{III}Fe^{II} species during the degradation process.

The redox processes involving H$_2$O$_2$ decomposition induce Orange II hydroxylation. Less than 60 min pretreatment were necessary to reach a BOD$_5$ value of ca. 100 mg O$_2$ l^{-1}. This is indicative for the presence of biodegradable intermediates in solution since no biodegradation was observed for Orange II in the absence of pretreatment. Azo bonds have been reported not to be susceptible to biological degradation.[13]

In conclusion, we have presented the first evidence for a Fenton-like reaction in a Fe-free solution using Orange II as a model compound. Fig. 1 shows a kinetically significant rate of azo dye disappearance in solution. A similar rate is observed in homogeneous Fe ion–H$_2$O$_2$ solutions containing ≈ 100 times higher concentration of Fe^{3+}. This work demonstrates the possibility of degradation of otherwise recalcitrant azo compounds removing the need to dispose of Fe ions after reaction to meet EU directives.[12]

Notes and References

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