# NEW PHOTOCATALYST SYSTEMS FOR INTEGRATED WATER TREATMENT IN TEXTILE FINISHING

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## ABSTRACT

Photocatalysis is widely explored for the decontamination of water polluted mainly by organic compounds. Although a nearly unmanageable amount of articles is published the technology is still not established in commercial waste water treatment.

Within two consecutive projects the German Aerospace Center DLR develops together with its industrial partners Carl Albany Gardinenfabrik, Torey, Knopf´s Sohn, Weskott, Brückner, SETEX, and EnviroTex the technology for integrated application in textile finishing processes.

The problems to be solved are an adaptation of the chemistry to the conditions of textile finishing and the integration of the additional treatment plant into the automated production processes. Therefore as well new photocatalyst system are under development as new water treatment reactors, and a computer based input – output analysis to optimise the whole production process.

In this paper recent work on new catalyst systems and application on textile finishing waters are described.

## INTRODUCTION

Photocatalysis is widely explored for the decontamination of water polluted mainly by organic compounds[i]. Although a nearly unmanageable amount of articles is published the technology is still not established in commercial waste water treatment. Photocatalysis belongs to the so called Advanced Oxidation Processes (AOP) which also include combined treatment of UV/ozone, UV/peroxide and so on. It is more powerful than direct photolysis of the contaminants or degradation by hydroxyl radicals formed by photolysis of hydrogen peroxide. Photocatalysis can be divided into heterogeneous and homogeneous photocatalysis using either catalyst particles, coatings like $TiO_2$ or solved catalysts or redox systems like iron ions or iron complexes. The necessary light energy can either be provided by lamps or by solar radiation[ii]. The advantage of $TiO_2$ is that no additional chemicals are necessary but the absorption of the photocatalyst is limited to 385 nm. Therefore at least UV-A light is necessary and the degradation efficiency is much lower compared to the Photo-Fenton treatment.

## DIRECT PHOTOYSIS VS. HYDROGEN PEROXIDE-PHOTOLYSIS

Direct photolysis means degradation of chemical compounds by the absorption of UV-light. It is the most common photochemical treatment technique. It is used for disinfection but also for bleaching of dyes. Generally the degree of mineralisation of the compounds is low because it is only effective for chromophores that are able to absorb the radiation. Therefore it is less interesting for textile finishing processes since the remaining fragments can have effects on the fabrics produced

More effective is UV-photolysis in combination with hydrogen peroxide. The $H_2O_2$ is activated by the light energy forming hydroxyl radicals:

$$Eq.\ 1 \quad H_2O_2 + h\nu \rightarrow 2\ HO^{\bullet}$$
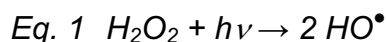
The HO-radicals react fast but not selective with the present compounds. Hydrogen peroxide does not absorb UV-light very efficiently and the radicals are easily recombining. Therefore the efficiency oh hydrogen peroxide photolysis is not very high. Especially expensive light energy is wasted which makes the process less economic.

## SEMI-CONDUCTOR PHOTOCATALYSIS

Semiconductors like $TiO_2$ are excited by UV-Light (< 380nm) forming relatively long-lasting electrons and electron holes. These are highly active reductives and oxidatives adsorbing chemical compounds and degrading them or activating them like oxygen for secondary reactions.
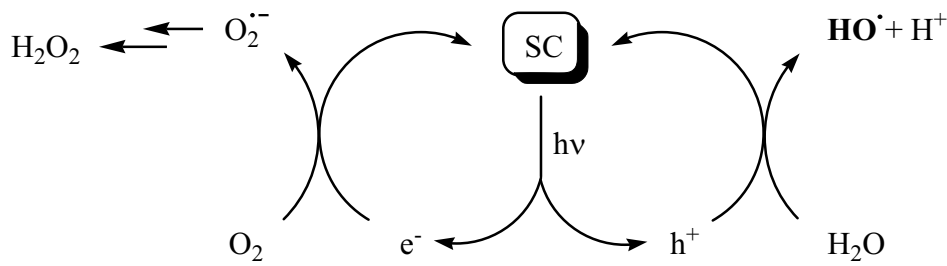
Figure 1: Principle of semi-conductor photocatalysis

## FENTON/PHOTO-FENTON-PROCESS

The Fenton/Photo-Fenton Process is based on the redox cycle between $Fe^{II}$ and $Fe^{III}$. This system is able to absorb light up to 580 nm and therefore is able to be used efficiently with solar radiation. The net reaction is also the splitting of hydrogen peroxide into OH-radicals but the radicals are formed in different steps, therefore the recombination is less likely. For an efficient Fenton/Photo-Fenton reaction the pH 3 must be kept because then the most photo-active iron-complexes are formed. An addition of hydrogen peroxide is necessary to run the process which causes higher cost. The degradation is faster compared to semi-conductor photocatalysis, the Fenton part of the process (left cycle in Figure 2) is a thermal reaction which takes place also without irradiation and the kinetic of the process is enhanced by higher temperature (Thermo-Fenton). Especially in textile finishing water temperatures are often between 60°C and 95°C.
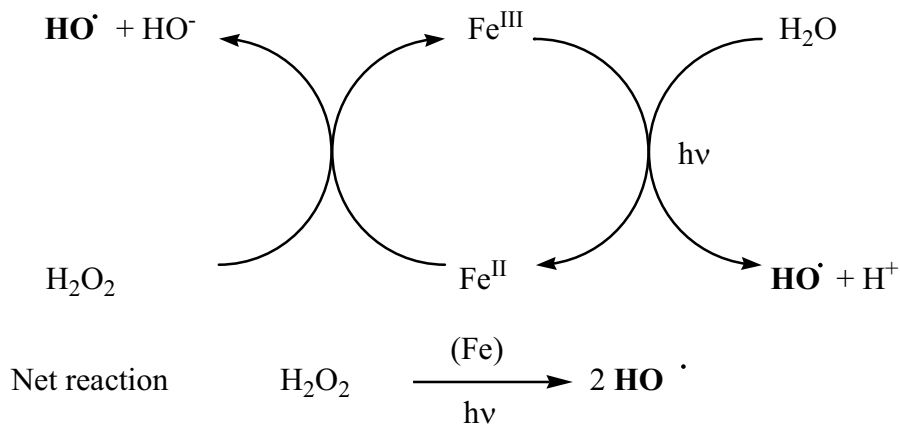


Figure 2: Principle of the Fenton/Photo-Fenton-Process

*Table 1: Comparison of photochemical water treatment processes*

|  | UV-Photolysis | $H_2O_2$-Photolysis | Semiconductor Photocatalysis | Fenton/Photo-Fenton System |
|---|---|---|---|---|
| Absorbtion | < 300 nm | < 300 nm | < 380 nm | < 580 nm |
| Oxidative to be added | - | $H_2O_2$ | - | $H_2O_2$ |
| pH | - | - | 1 – 10 | ~ 3 |
| Reaction rate | Very Low | Low | High | Very High |
| Mineralisation | Very Low | Low | Very High | High |
| Catalyst separation |  |  | Difficult | Moderate |

## NEW PHOTOCATALYST-SYSTEMS

To optimise photocatalysis for textile finishing the abilities of the different process for the most common problems are checked. In general the processes are working like expected but textile finishing has some circumstances that forbid the use of the pure techniques. To guarantee a colour neutral water the separation of the iron ions of the Fenton/Photo-Fenton treatment must be complete and reliable. Also pH 3 is not in every textile finishing process possible. Therefore enhanced Fenton/Photo-Fenton Systems must be easily separated as well as pH tolerant.

The separation of semiconductor photocatalysts is also challenging. The most common are used as powders with a particle size of few microns. Therefore an energy intensive filtration is necessary. If the catalyst shall be reused it must not adsorb the contaminants what would cause also possible effects on the fabrics and reduce the efficiency of the catalyst. To enhance the catalysts a broader light absorption especially in the visible range would be necessary. Doped catalysts showed promising activities[iii],[iv].

The newly synthesised dye doped photocatalysts need to be improved to make them more durable under real treatment conditions.

## TREATMENT OF DYE RINSE WATERS

Introduction

To test the different technologies realistic model waste water for textile dyeing processes were degraded. Regularly they contained 5 g/ dye and 3-10 g/l of other textile finishing agents. The dyeing process was simulated by the following assumptions:

- 60-95% of the dyes are fixed to the fabrics related to the dye class

- The textile finishing agents remain in the wastewater

- Rinse waters are diluted by the factor of 10 to the dyeing solution

The treatment of rinse waters is especially interesting for recycling because there are normally large quantities with low contamination. For the tests a 1000 W photo-reactor was used as shown in Figure 3. It uses a mercury medium pressure lamp with about 80 W of UV radiation and has a batch volume of 5 litres.



| | |
|---|---|
| $P_{el}$ | 1000 W |
| $P_{el}(UV)$ | 80 W |
| $\Phi/P$ | 0,7 Es/kWh |
| I (UV) | 5 kW/m² |
| V | 5 l |
| T | 40°C |

Figure 3: 1000 W photo-reactor for laboratory testing

Degradation of a simulated rinse water from poly-acrylate-dyeing

The contaminants are:
Azo-dye chromium(III)-complex, alkyl amine-ethoxilate, organic buffer

TOC = 110mg/l; CSB = 330mg/l

To evaluate the different treatment methods all are tested under the same conditions: Direct photolysis was carried out with air saturation of the solution. For $H_2O_2$ UV-photolysis 0.5 eq. of $H_2O_2$ based on the COD of the solution was used. Photo-Fenton-process was carried out at pH 3, 40°C, 5-50mg/l Fe(II), and 0.5 eq $H_2O_2$. Photocatalysis was carried out at pH 3-7, 40°C, 100mg/l $TiO_2$ (Degussa P25), 0-1.0 eq $H_2O_2$.

Since the technical treatment of waste water is always adapted to the wanted result which can be decolourisation, degradation of special substances, or total mineralisation different analytical methods were used to compare the methods. For the decolourisation quantitative UV-vis spectroscopy was used at a specific wavelength for the treated substances. For mineralisation TOC was measured.
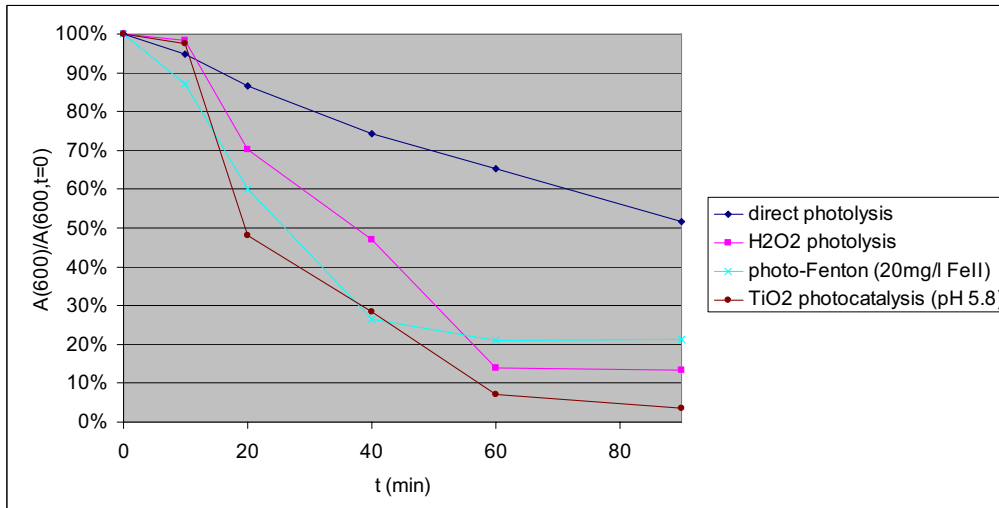
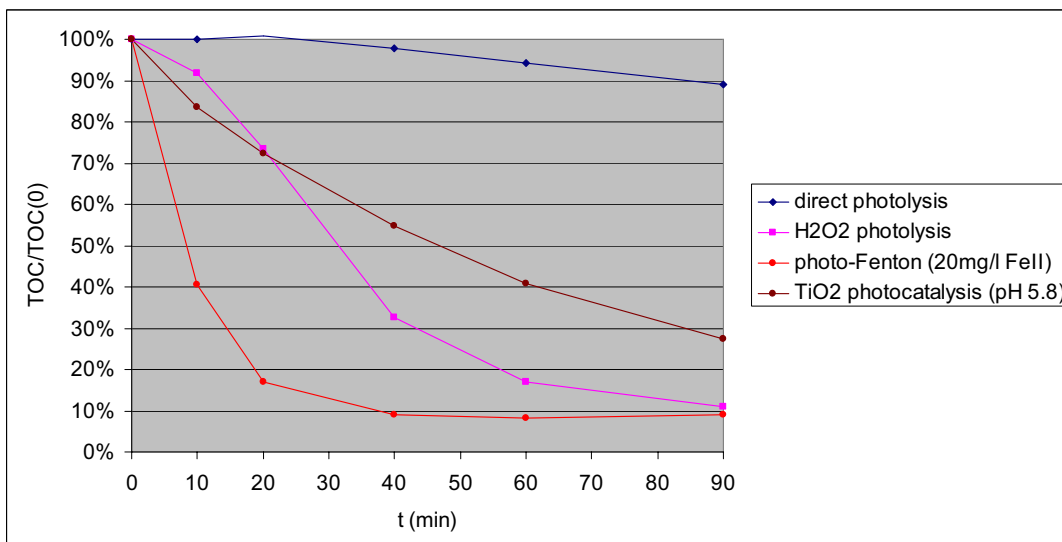Figure 4: UV-vis spectrum at 600 nm, Polyacrylate dyeing



Figure 5: TOC, Polyacrylate dyeing

Figure 4 shows that the photocatalytic methods are faster decolouring the solution than the photolytic ones. But the best decolourisation can be achieved with the semiconductor-photocatalyst, followed by $H_2O_2$, UV-photolysis, and the Photo-Fenton process.

For mineralization a different result can be observed. By far the fastest and most efficient mineralisation can be achieved with the Photo-Fenton system followed by $H_2O_2$ UV-photolysis and the semi-conductor photocatalysis.

Pure UV-photolysis always shows the least effect, especially its ability to mineralise contaminants is very poor.

Degradation of a simulated rinse water from wool or polyester dyeing

Contaminant classes:
Azo-dyes, anthrachinon-dyes, fibre protection agents, tensides, organic buffers

TOC = 400mg/l; COD = 1100mg/l

To evaluate the different treatment methods all are tested under the same conditions: Direct photolysis was carried out with air saturation of the solution. For $H_2O_2$ UV-photolysis 1.0 eq. of $H_2O_2$ based on the COD of the solution was used. Photo-Fenton-process was carried out at pH 3, 40°C, 5-50mg/l Fe(II), and 1.0 eq $H_2O_2$. Photocatalysis was not carried out.
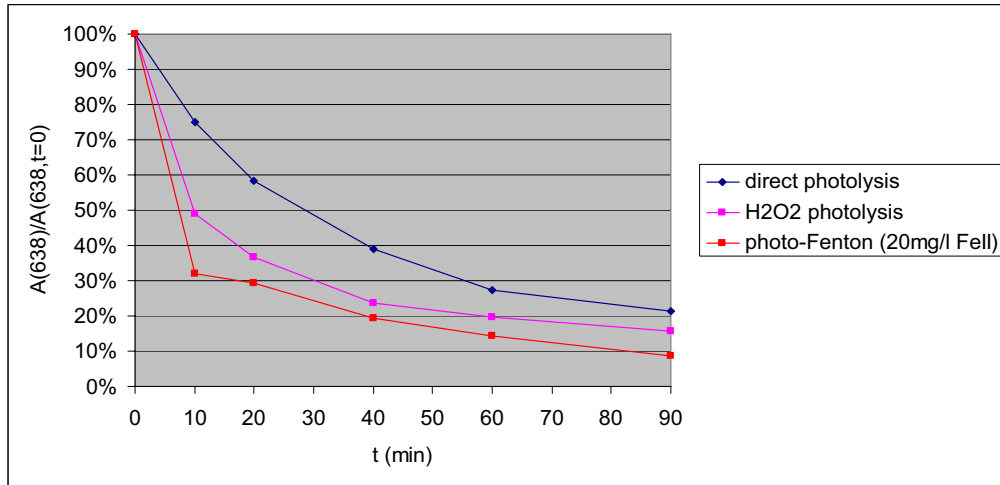


Figure 6: UV-vis spectrum at 638 nm, wool or polyester dyeing
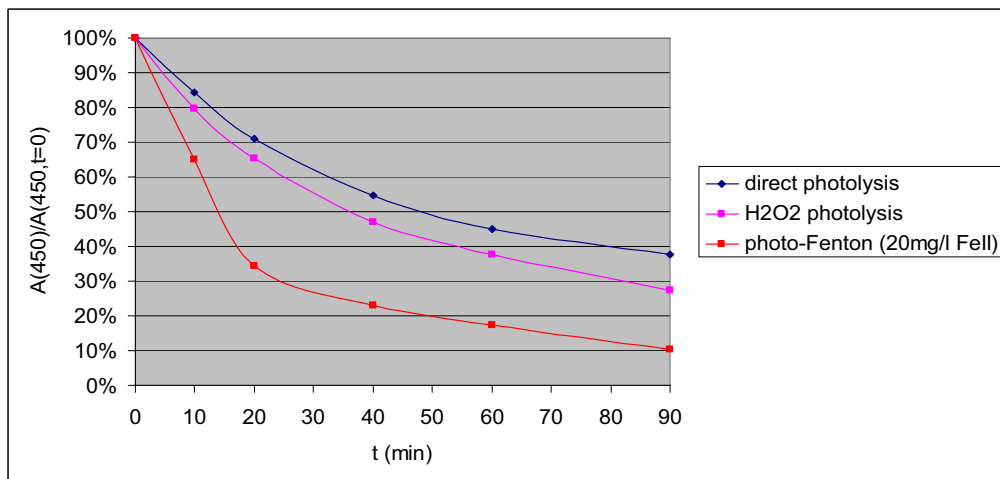


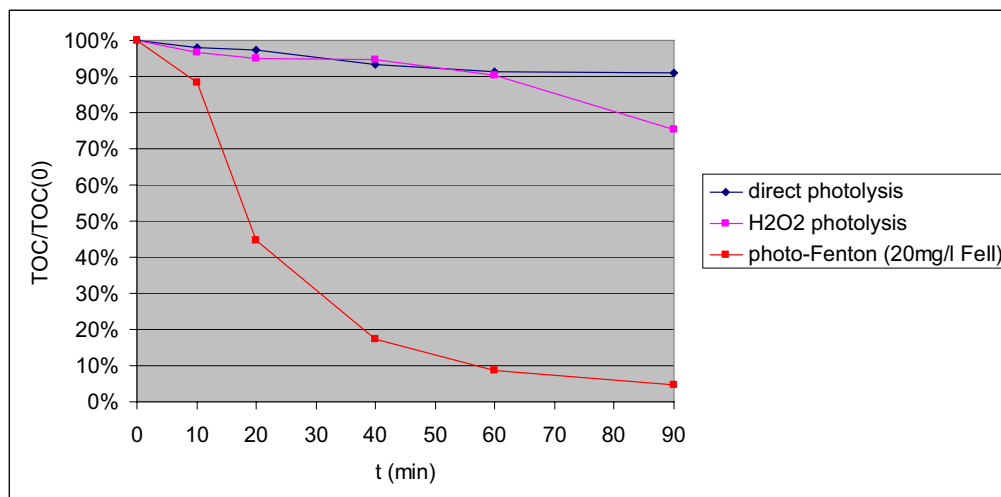Figure 7: UV-vis spectrum at 450 nm, wool or polyester dyeing

Figure 8: TOC, wool or polyester dyeing

For this class of waters the results are comparable. Photo-Fenton is faster decolourising the dyes than the photolysis methods but the final results are comparable, whereas only the Photo-Fenton treatment mineralises the contaminants. The effect of the photolytic technologies on the TOC is very low.

## CONCLUSION

Photocatalytic water treatment technologies showed ones more their abilities to become a useful alternative for industrial water treatment. Although the decolourisation of model rinse waters with sub-stoichiometric amounts of $H_2O_2$ and UV-photolysis is possible photocatalytic treatment showed much better results especially if the contaminants must be mineralised for a reuse of the water.

## ACKNOWLEDGEMENTS

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[iv] Machado A.E.H., de Miranda JA, de Freitas RF, Duarte ETFM, Ferreira LF, Albuquerque YDT, Sattler C, de Oliveira L. „Destruction of the organic matter

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