PHOTOCATALYTIC WATER TREATMENT IN TEXTILE INDUSTRY

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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 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.
Photo-Fenton treatment is a very powerful method to generate hydroxyl radicals to degrade the organic matter in waste water reported for example by Zepp et al. [iii] and Feng et al. [iv]:

$$Fe_{aq}^{3+} \xrightarrow{h*\nu} {}^{*}Fe_{aq}^{3+} \rightarrow Fe^{2+} + {}^{\bullet}OH + H^{+} \quad (1)$$

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

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

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^{+} \quad (4)$$

The “Photo-Fenton reaction” is described by a complex set of individual reactions. The key step comprises the photon induced production of hydroxyl radicals from water by the reduction of iron (III) to iron (II).
The technology is demonstrated as well for solar radiation in the EU FP 5 SOLARDETOX project[v] as for UV lamps in the PhoRTex project. A first commercial solar plant started its operation in 2004 in Andalucía, Spain.

Figure 1: SOLARDETOX pilot plant Arganda del Rey, Spain

Figure 2: PhoRTex lamp driven 500 l by-pass plant Augsburg, Germany and 3 m^3 demonstration plant Gera, Germany

Therefore it is strongly emerging with a high potential for a wide range of industrial waste waters contaminated by organics. The technology has its highest potential in industrial waste water treatment especially for problem waste waters that are non biodegradable or difficult to treat by other conventional treatment technologies.

The technology has the potential to be an alternative for industrial waste water treatment to the established technologies. The feedback from textile industry as well as from the potential producers of the plants is very positive. Nevertheless more demonstrators are necessary to show the industrial feasibility of the technology. Therefore an integration of the photocatalytic water detoxification into the control and monitoring system of textile plants shall be developed and demonstrated by the project InProTex funded by the German Ministry for Education and Research. Positive feedbacks are also given by chipboard producers[vi] and paper industry[vii] as well as chemical industry and waste disposals.

The main advantage of the technique is its applicability to nearly every waste water problem caused by organic pollution. Even toxic substances like hydrazine or polymers like lignin can be treated [viii]. To use the technology most efficiently the wastewater should be of a certain composition to adjust the necessary chemicals like photocatalysts or oxidising agents and the amount of energy. This is crucial to achieve optimised cost effectiveness. The technique can be widely used in textile industry especially for decolourization but also to reduce substances like mineral oils or other textile auxiliaries that can not be treated by biological steps[ix].

In the project PhoRTex funded by the German Ministry of Education and research it could be shown that photocatalytic treatment of waste water from companies finishing knitted goods containing mineral oils can be combined with the biological treatment of the municipal waste water treatment plant. The biological step needs a certain amount of contamination that can be digested by the micro organisms to keep them working efficiently but it is not allowed to discharge more then 20 ppm of hydrocarbons into the receiving water[x].

As a case study for the treatment of waste water from textile finishing an economic evaluation was carried out based on the results of the PhoRTex project [xi]. To evaluate the cost effectiveness of the technology for the implementation in textile industry treatment costs were estimated varying the daily amount of waste water. The basis were the tests in the bypass plant, because a large set of reproducible data was

acquired over a long period and so its stability and handling was proofed. Washing waters like described above are used for this evaluation.
It could be shown how the treatment costs develop from a 50 m^3/d plant to the evaluated 0,5 m^3/d plant [xii].

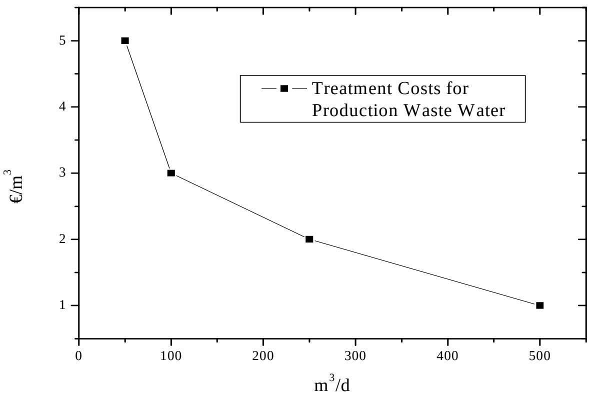

Figure 3 - Treatment cost calculation on basis of the PhoRTex bypass plant

Compared to this calculation the demonstration plant shows the potential for further lowering of the cost by serial production. The investment costs for the 3 m^3 demonstration plant including an advanced control unit were only 1.4 times as high as for the 0,5 m^3 bypass plant.
In the InProTex project the combination of photocatalytic water treatment with an exhaust gas washer will be shown to reduce the amount of water necessary for the aqueous scrubber. This integrative concept has the aim to develop the hardware as well as software systems for the combined control of the production plant with the water treatment plant. Additionally the input and output streams of the processes will be monitored.

Figure 5: Stenter
As a reference plant the exhaust gas washer installed in the off-gas pipe of a stenter will be used to evaluate the feasibility of the technology. Stenters are the main origin

of exhaust gas in textile finishing causing more than 51% of the total amount of mainly hazardous components.

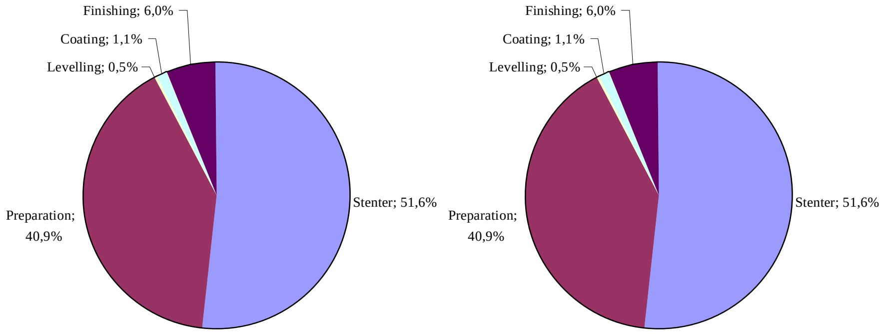

Figure 4: Exhaust gas contaminants in textile finishing, left: Organic-C; right: Textile relevant class 1 substances in the German regulation for Air (TA Luft 5.2.5)

The main compounds in this example which is typical for companies finishing synthetic fibres are caprolactam (ex pPolyamide 6) and formaldehyde. Both are limited in Germany to 20mg/m^3 [xiii]. In this case main Organic-C load (methane) and formaldehyde load is caused by the insufficient incinerastion of the fuel gas of the direct heated stenters.

Today a wide range of processes are used to treat these exhaust gases. These are oxidising processes, (thermal afterburning, catalytic afterburning), condensation, absorption, electro filtration, adsorption, and biological processes[xiv].

Calculated from the water consumption of an exhaust gas washer the possible cost reduction of a closure of the water cycle can be done and the acceptable cost for the treatment technology can be calculated respectively:

The technology will have an economic benefit for the producer if the annuity **a** plus the price for the treatment and the reduced water consumption is lower than the water consumption without treatment and recirculation. Therefore the main factors for the economic evaluation are the prices for energy $\mathbf{p_e}$, chemicals $\mathbf{p_c}$, operation and maintenance $\mathbf{p_l}$, fresh water $\mathbf{p_f}$, and wastewater $\mathbf{p_u}$.

$$1 \leq \frac{\mathbf{a} + \mathbf{v}_2\left(\mathbf{p_e} + \mathbf{p_c} + \mathbf{p_l} + \mathbf{p_f} + \mathbf{p_u}\right)}{\mathbf{v}_1\left(\mathbf{p_f} + \mathbf{p_u}\right)} \tag{5}$$

As a model case a company running an exhaust gas washer with a water consumption $\mathbf{v_1}$ of 5 m^3/h, a daily running time $\mathbf{t_d}$ of 10 h and 250 operation days per year with water costs for $\mathbf{v_1}$ would be

$$\mathbf{p_f} + \mathbf{p_u} = 2 \text{ €/m}^3 \tag{6}$$

amounting to yearly water costs of 25.000 €, if the price is 5 €/m^3 it is 62.500 €. If the water consumption can be reduced by the factor of 4 for in the first case 18.750 € and for the second case 46.875 € are available for the treatment of 12.500 m^3 water in the water cycle. If the treatment cost calculated for the prototype 50 m^3/d plant are compared to this it is very close to be economically feasible.

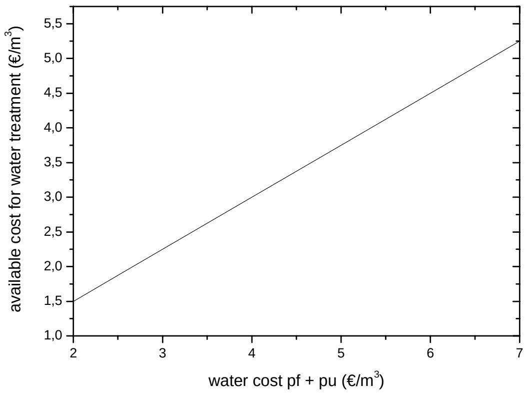

Figure 6: Available cost for water treatment dependent on water cost

In the InProTex project this assumptions will be verified by pilot plant tests as well as by economic analysis.

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