



**PHOTOCATALYTIC OXIDATION OF BIOLOGICALLY TREATED
GREYWATER IN THE PRESENCE OF POWDERED ACTIVATED CARBON**

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ABSTRACT

In this study, the effluent of a constructed wetlands for treatment of separately collected greywater was subdued to photocatalytic oxidation using TiO₂ "P25" in the absence and in the presence of powdered activated carbon (PAC). TiO₂ suspensions in the saline matrix of biologically treated greywater absorbed only about 10 % of UV light compared to suspensions in deionised water due to enhanced agglomeration of TiO₂ nanoparticles. As PAC particles did not severely shade photocatalyst particles in the UV range, PAC addition to photocatalytic oxidation can be looked at as a measure to compensate photocatalytic efficiency impairment by inorganic wastewater constituents. While photocatalytic oxidation of biologically pretreated greywater with UV fluences of 9 Wh/l was not able to reduce its TOC safely below 2 mg/l (which is looked at as a prerequisite for high-quality reuse purposes), the addition of PAC to the photocatalytic oxidation process resulted reliably in TOC concentrations of less than 2 mg/l. PAC/TiO₂ mixtures (1 g/l PAC, 5 g/l TiO₂) could be reused at least 7 times for photocatalytic oxidation reducing TOC from about 6 mg/l to below 2 mg/l. In another series of experiments with a UV fluence of 11 Wh/l and reusing the TiO₂/PAC mixture 13 times, it could be shown that a TOC concentration of ≤ 2 mg/l was achieved until the 10th TiO₂/PAC reuse cycle although the initial TOC was nearly 10 mg/l in these experiments. Adsorption to recycled PAC (in the absence of photocatalyst and without UV irradiation) was not able to reduce TOC to this level. In the TiO₂/UV/PAC combination process, TOC concentrations after irradiation showed an increasing trend with progressive reuse of TiO₂/PAC, indicating that the *in situ* regeneration of PAC was not complete with the applied UV fluences.

KEYWORDS: activated carbon, ecological sanitation, greywater, photocatalyst agglomeration, photocatalytic oxidation

INTRODUCTION

Greywater not mixed with toilet wastewater represents a high quality "nonconventional" water resource, because it represents the largest of the three domestic wastewater streams, but contains the lowest amount of nutrients (Otterpohl, 2001). Moreover, its content of microbiological pathogens is by far lower than that of brown water and it is safely segregated from industrial wastewaters. Greywater is mainly polluted with organic



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substances. TOC concentrations of greywater separately collected in the German eco-settlement Luebeck-Flintenbreite were determined to be between 80 and 94 mg/l and are simply, but efficiently reduced by constructed wetlands treatment to below 15 mg/l (Li et al. 2003).

For many purposes waters have to be disinfected by chlorination before use. Chlorination studies with raw waters in East Germany have shown that trihalomethanes are formed in concentrations above 10 µg/l if the TOC concentration of the raw water exceeds 2 mg/l (Kuehn and Wricke 1995). Therefore, greywater treated in constructed wetlands should be purified in an additional stage for further TOC reduction before chlorination. Another reason for advanced treatment of biologically pre-treated greywater is its content of trace organics, among them endocrine disrupting chemicals (Gulyas et al. 2007). Suitable processes for removing low levels of organics are the so-called advanced oxidation processes (AOPs) as well as ozonation (Gulyas 1997), which are usually highly energy-consuming.

An AOP with low energy consumption is solar heterogeneous photocatalytic oxidation, i.e. solar irradiation of photo-semiconductor particles like TiO₂ either suspended in wastewater or immobilized on support materials like glass panes which are in contact with the wastewater. This process utilises the UV portion of sunlight (about 5 %). Photocatalytic oxidation has been shown to mineralize organics contained in biologically pretreated greywater (Li et al. 2003), but laboratory-generated design data for technical-scale solar reactors led to the conclusion that area demand is large. Required areas do not only depend on initial wastewater TOC and purification target, but also on wastewater alkalinity (Gulyas et al. 2005).

As the combination of activated carbon adsorption with photocatalytic oxidation has been shown to be synergistic (Matos et al. 2001), the aim of this study was to investigate possible advantages of the combination process with mixtures of powdered activated carbon and TiO₂ compared to the non-combined processes.

MATERIALS AND METHODS

Samples of the effluent of a constructed wetlands (vertical flow, intermittent loading ensuring aerobic conditions) for treatment of separately collected greywater (Otterpohl, 2001) in the eco-settlement Luebeck-Flintenbreite, Germany, were shipped to the laboratory in glass bottles prior to the experiments.

PAC (1 g/l) and/or TiO₂ P25 (1 or 5 g/l) were suspended in the constructed wetlands' effluent. A volume of 1 l of these suspensions was placed in a slim 2-l beaker (inner diameter 10.8 cm) without any reflectors or other types of enclosure below a face tanner (HD 172, Philips) emitting mainly UV-A light (emission maximum: 352 nm). UV-A intensity on the liquid surface was 25 W/m². Suspensions were agitated by magnetic stirring.

Samples for TOC analyses were only withdrawn after mixing the greywater with the TiO₂/PAC mixture and at the end of the irradiation period (40 hours equivalent to a UV fluence of about 9 Wh/l). The initial sample was centrifuged immediately (40 min, 2800 x g), the pellet resuspended in 50 ml of fresh constructed wetlands' effluent and added again to the bulk suspension in order not to lose solids by sampling. Then the reactor was weighed and irradiation was started subsequently. After irradiation, the reactor was weighed again, the complete suspension was centrifuged (40 min, 2800 x g) and the supernatant decanted for TOC analysis. Evaporation losses during the experiments were calculated from the weights before and after irradiation. Concentration factors (ratio of initial to final net weight) were between 1.12 and 1.24. The pellet recovered at the end of an irradiation experiment was resuspended in fresh greywater for the next irradiation cycle and processed as described above within the next cycle. Besides the photocatalyst/PAC mixture (5 g TiO₂/l, 1 g PAC/l), the pure photocatalyst (5 g/l) was also reused under the same experimental conditions. Moreover, results of these experiments were compared to stirring of PAC (1 g/l) without photocatalyst and without UV irradiation in closed bottles (evaporation was assumed to be negligible and was not quantified).

UV absorbance at 352 of mixtures of PAC (0, 0.1, 0.5, 1, 2, and 5 g/l) and photocatalyst (0, 1, and 5 g/l) suspensions in deionised water or in the constructed wetlands' effluent was measured in a UV/VIS photometer in 1 cm quartz cuvettes subsequent to vigorous stirring with a small spatule. Non-purgeable TOC was measured according to German standard methods using a TOC analyser. For correcting the measured TOC concentrations for evaporation losses, they were divided by the enrichment factor determined by weighing the reactor before and after irradiation.

RESULTS AND DISCUSSION

Unfortunately, biologically treated greywater is not very susceptible toward photocatalytic oxidation (Gulyas et al. 2005). This is referred to the fact that the photocatalyst P25 originally consisting of nano-particles apparently agglomerates in biologically treated greywater. The flocculation of the TiO_2 nano-particles to larger agglomerates also explains why UV absorbance of TiO_2 suspensions in biologically treated greywater is only about 10 % of the absorbance of the photocatalyst suspensions in deionised water (data not shown). Very fine TiO_2 particles with diameters below 100 nm are reported to present high transparency to visible light, but high UV absorbance (Ellsworth et al. 2003) which is a prerequisite for the photocatalytic oxidation process. The absorption measurements also revealed that the addition of PAC in concentrations of up to 5 g/l did not severely shade the TiO_2 particles (data not shown). Therefore, PAC addition might be beneficial for the photocatalytic oxidation of biologically treated greywater.

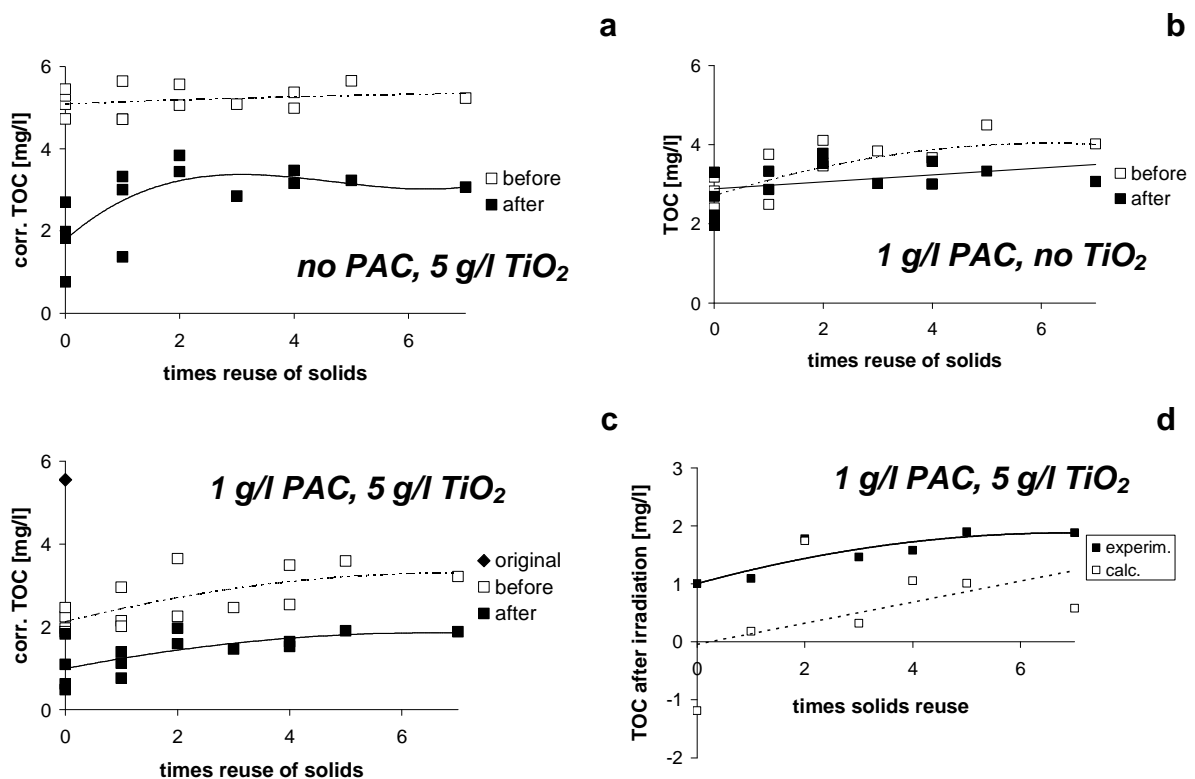


Figure 1 – TOC concentrations (corrected for evaporation losses) before and after photocatalytic oxidation (5 g/l TiO_2 , UV-A fluence 9 Wh/l) of biologically treated greywater in the absence (a) and in the presence of 1 g/l PAC (c) as well as TOC concentrations before and after stirring of greywater with 1 g/l PAC without UV irradiation (b) as a function of number of reuse cycles of solids (TiO_2 and/or PAC); TOC concentration of original biologically pretreated greywater is indicated in (c); (d): experimental (corrected) TOC concentrations for the combination process (means of data given in (c)) and calculated TOC concentrations

When photocatalytic oxidation of biologically pretreated greywater (TOC: 5.5 mg/l) in the absence of PAC with progressive reuse of photocatalyst (fig. 1a) is compared to the same process in the presence of PAC (with reuse of the photocatalyst/adsorbent mixture, fig. 1c), it can be clearly seen that the addition of PAC is beneficial for the process, inasmuch as a UV-A fluence of 9 Wh/l reliably resulted in TOC concentrations ≤ 2 mg/l in the presence of PAC (fig. 1c).

Obviously, the PAC is progressively loaded from cycle to cycle and - if at all - only partially regenerated by the photocatalytic oxidation process, as there is an increasing trend of TOC after photocatalytic oxidation/PAC



adsorption with progressing numbers of solids' reuse (fig. 1c, "after"). This trend is also visible for TOC before irradiation in the combination process (fig. 1c, "before"). TOC elimination in the TiO₂/PAC combination experiment without irradiation was about 40 % and more, while the initial TOC without PAC addition was nearly as large as the original TOC (fig. 1a, "before"), indicating that TiO₂ only adsorbs a minor part of the greywater organics. TOC concentrations after photocatalytic oxidation of the same biologically treated greywater in the absence of PAC were below 4 mg/l with the same UV-A fluences, but only in few experiments below 2 mg/l (fig. 1a, "after"). Moreover, TOC concentrations after photocatalytic oxidation without PAC addition seem to increase within the first two catalyst reuse cycles.

For calculation of TOC concentrations in fig. 1d, TOC decrease by PAC adsorption alone and TOC decrease by photocatalytic oxidation alone were subtracted from TOC of original biologically treated greywater. The combination of photocatalytic oxidation and PAC is less efficient than the addition of the effects of the two separated processes. This can be explained by the fact that photocatalytic oxidation generates more polar transformation products which are adsorbed to PAC to a lower extent than the mother compounds and that the decrease of dissolved organics concentration by PAC adsorption diminishes the reaction rate of photocatalytic oxidation.

Another set of experiments carried out with 13 cycles of reuse of photocatalyst/PAC, a sample of biologically treated greywater with an initial TOC concentration of nearly 10 mg/l and a UV-A fluence of about 11 Wh/l per cycle showed that a TOC concentration of ≤ 2 mg/l after irradiation was ensured within 10 cycles of reuse of the photocatalyst/PAC mixture (data not shown).

CONCLUSIONS

Although there was no synergistic effect of combining PAC adsorption and photocatalytic oxidation, it was possible to achieve lower TOC concentrations during photocatalytic oxidation of biologically treated greywater by the addition of PAC. The PAC/TiO₂ mixtures can be reused 10 times to meet a TOC purification target of ≤ 2 mg/l. With increasing numbers of reuse of the photocatalyst/PAC mixture, the TOC concentrations achieved by photocatalytic oxidation progressively increased. It still has to be clarified which UV fluences are necessary to regenerate the PAC by photocatalytic oxidation in order to ensure TOC concentrations below 2 mg/l in further TiO₂/PAC reuse cycles.

REFERENCES

1. ELLSWORTH, D.K., VERHULST, D., SPITLER, T.M., SABACKY, B.J. Titanium nanoparticles move to the marketplace. *Chemical Innovation*, v. 30, pp. 30-35, 2000.
 2. GULYAS, H. Processes for the removal of recalcitrant organics from industrial wastewaters. *Wat. Sci. Tech.*, v. 36, n. 2-3, pp. 9-16, 1997.
 3. GULYAS, H., JAIN, J.B., SUSANTO, A.L., MALEKPUR, M., HARASIUK, K., KRAWCZYK, I., CHOROMANSKI, P., FURMANSKA, M. Solar photocatalytic oxidation of pretreated wastewaters: Laboratory scale generation of design data for technical-scale double-skin sheet reactors. *Environ. Tech.*, v. 26, pp. 501-514, 2005.
 4. GULYAS, H., REICH, M., OTTERPOHL, R. Qualitative non-target screening of trace organics in greywater treated in vertical-flow constructed wetlands. *International Conference on Sustainable Sanitation – Food and Water Security for Latin America*, November 26-28, 2007, Fortaleza, Ceará, Brasil.
 5. KUEHN, W., WRICKE B. Trinkwasseraufbereitung im mitteldeutschen Raum unter besonderer Berücksichtigung der Haloformbildung. *GWF Wasser/Abwasser*, v. 136, pp. S92-S98, 1995.
 6. LI, Z., GULYAS, H., JAHN, M., GAJUREL, D.R., OTTERPOHL, R. Greywater treatment by constructed wetlands in combination with TiO₂-based photocatalytic oxidation for suburban and rural areas without sewer system. *Wat. Sci. Tech.*, v. 48, n. 11, pp. 101-106, 2003.
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7. MATOS, J., LAINE, J., HERRMANN, J.-M. Effect of the type of activated carbons on the photocatalytic degradation of aqueous organic pollutants by UV-irradiated titania. *J. Catalysis*, v. 200, pp. 10-20, 2001.
8. OTTERPOHL, R. Black, brown, yellow, grey - the new colours of sanitation. *Water21*, October 2001, pp. 37-41, 2001.