

# Treatment of tannery wastewater for reuse by physico-chemical processes and a membrane bioreactor

J. Fettig, V. Pick, M. Oldenburg and N. V. Phuoc

## ABSTRACT

Treatment of wastewater from a tannery in Greater Ho Chi Minh City (Vietnam) was investigated on a pilot scale. After pre-treatment by the tannery that included batch-coagulation and sedimentation, the wastewater was treated by dissolved air flotation, a membrane bioreactor (MBR) and granular activated carbon (GAC) for polishing the MBR effluent. The average removal efficiency for organic substances in the MBR was 81% while total nitrogen could only be removed by 36%. The performance of the GAC column could be successfully predicted using adsorption parameters determined in laboratory experiments. A larger proportion of the organics in the MBR effluent was only weakly adsorbable, therefore the usable carbon capacity was limited as confirmed by the modelling approach. The results were used to outline the size of a technical plant with a volumetric loading rate of 3 kg COD/(m<sup>3</sup>\*d) for the MBR and a specific carbon demand of about 1.8 kg/m<sup>3</sup>.

**Key words** | activated carbon, dissolved air flotation, membrane bioreactor, reuse, tannery wastewater

**J. Fettig** (corresponding author)

**V. Pick**

**M. Oldenburg**

University of Applied Sciences Ostwestfalen-Lippe,

Hoexter 37671,

Germany

E-mail: joachim.fettig@hs-owl.de

**N. V. Phuoc**

Institute for Environment and Resources, National

University,

142 To Hien Thanh Street, District 10,

Ho Chi Minh City,

Vietnam

## INTRODUCTION

The leather and footwear industry is an important economic branch in Vietnam. Tanneries, which need up to 40 m<sup>3</sup> of fresh water per tonne of raw hides (EIPPCB 2013), are a part of this branch. Since the tanning industry has been categorized as one of the most polluting industries, Vietnamese environmental regulations require that each company must install wastewater treatment systems (Thanh 2011). However, there is no differentiation between the effluent standards for different industries, thus chemical oxygen demand COD = 150 mg/L, biochemical oxygen demand BOD<sub>5</sub> = 50 mg/L, ammonium-nitrogen NH<sub>4</sub>-N = 10 mg/L, total nitrogen N<sub>tot</sub> = 40 mg/L and total phosphorus P<sub>tot</sub> = 6 mg/L as major parameters are required for all discharges into receiving waters (MONRE 2011). Since data on actual effluent concentrations are not available, it is difficult to evaluate

the current state of industrial wastewater treatment. In 2010, about 65% of the tanneries did officially comply with the regulations. On the other hand, almost all tanneries have been fined for various environmental violations. This indicates that there is still a lack of appropriate and reliable technologies (Thanh & Truong 2013).

The conventional way to treat tannery wastewater is to apply chemical precipitation and aerobic biological treatment in an activated sludge stage (EIPPCB 2013). It has been shown that sequencing batch reactors (SBR) might be better suited for the removal of organic matter measured as COD and nitrogen compounds (Murat *et al.* 2002). As discussed by Lin *et al.* (2012), the application of membrane bioreactors (MBRs) was also proven to be technically feasible in laboratory-scale studies. According to Munz *et al.* (2008), a MBR showed higher COD removal efficiencies (+4%) and provided more stable and complete nitrification than an activated sludge system. Wang & Liu (2011) obtained 88% COD removal using a MBR at a volumetric loading rate of 4.8 kg COD/(m<sup>3</sup>\*d). Ganesan & Muthulakshmi (2015)

This is an Open Access article distributed under the terms of the Creative Commons Attribution Licence (CC BY-NC-ND 4.0), which permits copying and redistribution for non-commercial purposes with no derivatives, provided the original work is properly cited (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

doi: 10.2166/wrd.2016.036

varied the mixed liquor suspended solids concentration in their MBR. They found that COD removal increased from 75% at 8 g/L to 90% at 12 g/L, but did not give a detailed explanation. There is still a lack of studies with large-scale MBRs and tannery wastewater (Fazal *et al.* 2015).

The combination of MBRs with an adsorption process for enhanced removal of refractory organic matter from tannery wastewater has been investigated by adding powdered activated carbon to the bioreactor (Munz *et al.* 2007; Ng *et al.* 2013). In both studies, small improvements in COD removal were observed, although the main purpose was to improve fouling control and achieve a better filtration performance. Another approach to remove refractory organics was suggested by Giacobbo *et al.* (2015), who combined a MBR with a photoelectron-oxidation stage. However, the energy demand for the oxidation process in order to achieve considerable COD removal efficiencies was quite high.

Besides the concentration of organic matter in treated tannery effluents, the high salt content can limit the options for reuse. Both nanofiltration (Galiana-Alexandre *et al.* 2005) and reverse osmosis (Scholz *et al.* 2005; De Gisi *et al.* 2009) have been applied on a small scale in order to produce a permeate that can be reused by the tannery for all process steps.

As a part of the joint Vietnamese–German research project EWATEC-COAST, a treatment concept comprising improved physico-chemical pre-treatment, a MBR as the central stage, and post-treatment by granular activated carbon (GAC) adsorption has been studied on a pilot scale at the Dang Tu Ky tannery in the Nhon Trạch 1 Industrial Zone (Đồng Nai Province). The treated wastewater should be suitable for reuse purposes in the beamhouse of the factory. Therefore, no salt removal was required whereas a target value of 250 mg COD/L was set for the organic matter. The objective of the study was to demonstrate the feasibility of the three-stage treatment concept in reaching this target.

## MATERIALS AND METHODS

### Pilot plant experiments

The feed to the pilot plant was withdrawn from the supernatant of the sedimentation basin of the tannery's technical-scale plant after straining and batch coagulation.

Sulphuric acid, ferrous sulphate, poly-aluminium chloride and an organic polymer are added for pre-treatment in order to adjust pH, precipitate both chromium and sulphide, and remove particulate matter by flocculation. Mean values of some important parameters of the pre-treated wastewater are given in Table 1.

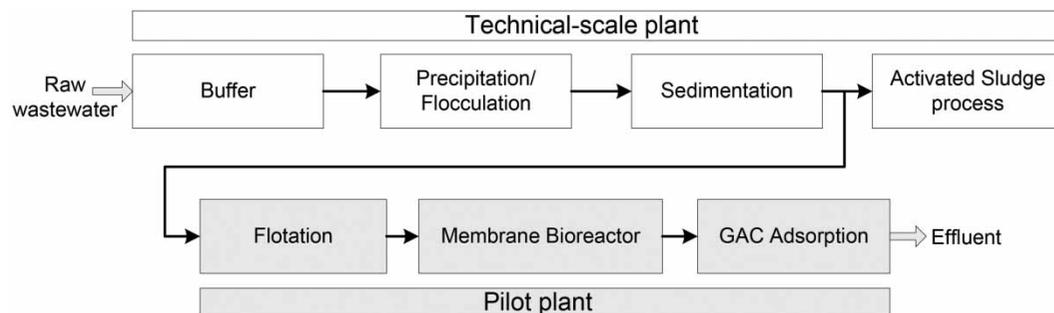
According to the data, the conductivity is quite high because of salts that are both washed out from raw hides and used as process chemicals. Compared with the level of organics in raw wastewater, COD is reduced significantly in the pre-treatment stage due to the removal of particulate organic material. This is in accordance with the findings in European tanneries. Moreover, both chromium and sulphide are removed efficiently. The remaining load of the wastewater is primarily made up of dissolved organic matter and nitrogen compounds.

Due to the field conditions encountered, the parameter BOD could not be measured regularly. Therefore, description of the MBR's performance had to be based on COD data. In the laboratory, both the short-term (5 days) and long-term (20 days) BOD was determined. The ratios obtained were COD/BOD<sub>5</sub> = 4.4 and COD/BOD<sub>20</sub> = 2.8, respectively. These results are in agreement with the literature data (EIPPCB 2013); however, the difference between both ratios indicates that a certain proportion of the organics was not easily biodegradable.

The process scheme of the technical-scale pre-treatment and the pilot plant is shown in Figure 1. It illustrates that the influent to the pilot plant was first treated by dissolved air flotation (DAF) in order to protect the MBR. An Aquatec<sup>®</sup> Microfloat<sup>®</sup> device (Enviplan Company) was applied

**Table 1** | Parameters of the pre-treated wastewater (mean values from 60 samples) and of raw tannery wastewater in Europe

Parameter	This study (inflow to pilot plant)	European tanneries (EIPPCB 2013)
pH	7.6 ± 0.4	
Conductivity	23.0 ± 4.7 mS/cm	
Temperature	30.6 ± 2.0 °C	
Total COD	2,747 ± 728 mg/L	5,200–14,000 mg/L
Ammonium-N	923 ± 282 mg/L	
Total chromium	2.44 ± 2.13 mg/L	6.6–87 mg/L
Sulphide	12.8 ± 10.1 mg/L	47–184 mg/L



**Figure 1** | Process scheme of the technical-scale pre-treatment and of the pilot plant.

for that purpose. Then, the wastewater was fed into the MBR (A3 Water Solutions Company) with a total volume of 40 m<sup>3</sup>. It was equipped with submerged UF flat-sheet membranes (PES, 150 kDa cut-off, supplied by A3) with a total area of 149 m<sup>2</sup>. The reactor was divided into a non-aerated denitrification compartment (12 m<sup>3</sup>) and an aerated volume (28 m<sup>3</sup>) where two membrane modules were located. The latter were each aerated with an air scouring rate of 48 m<sup>3</sup>/h. The average mixed liquor suspended solids concentration was 9.4 g/L. 10 mg/L of phosphate (P) was added in order to prevent growth limitation of the biomass. Influent and effluent samples were regularly analysed for pH, COD, ammonium, nitrite and nitrate.

The design flow rate was 500–2,000 l/h, corresponding to a flux of 3.4–13.6 L/m<sup>2</sup>·h. Since it was difficult to build up the activated sludge, the reactor was run solely at the lower limit of that range. During some weeks the plant was operated with only one module, and the flux could be doubled without any problems. Thus, the operation of the membranes had to be optimized further for a full-scale application.

The MBR effluent was used to study further removal of dissolved organics by GAC (Carbsorb 30, Calgon Carbon Corp.). This product is based on bituminous coal; the median particle diameter by weight of the material applied was 1.95 mm. The particle density was 0.704 g/cm<sup>3</sup> and the filter density 0.420 g/cm<sup>3</sup>, corresponding to a bed porosity of 0.40. Altogether, 200 L/h of the MBR effluent were fed into a fixed-bed column with an inner diameter of 0.49 m and a bed depth of 1.26 m. The resulting empty bed contact time (EBCT) was 1.2 hr. Such a high value is not unusual for GAC columns operated with high inlet concentrations and small volumetric flow rates (Fettig et al. 1996).

## Modelling approach

Adsorption of the MBR effluent was also investigated by determining overall isotherms applying the bottle-point method, and by conducting both adsorption rate tests and a rapid small-scale column test (RSSCT). For the isotherm studies, the carbon particles were crushed in a ball mill. The resulting powdered activated carbon had particle diameters below 40 µm. For each test, between 0.01 g and 1.0 g of activated carbon were added to 0.1 L of solution with a pH of 6–7. After 96 hr of contact time on a shaker, samples were filtered through 0.45 µm membranes and analysed for dissolved organic carbon (DOC) and UV absorbance at 254 nm. The solid-phase concentrations were calculated from a mass balance.

The isotherm data were evaluated using the ADSA software (Johannsen et al. 1992). This approach assumes that multi-solute systems can be described as a mixture of a few competing fictive components, based on the IAST model, and a non-adsorbable fraction. Each component is characterized by the parameters  $K_i$  and  $n_i$  of the Freundlich isotherm and its initial concentration  $c_{o,i}$ . For the sake of simplicity, the  $n_i$  values are usually assumed being the same for all adsorbable components (Johannsen et al. 1992).

Granular carbon samples were taken for the rate tests. The short fixed-bed reactor technique was used in order to determine a mean external mass transfer coefficient for the organics' uptake by GAC. Diluted solutions must be applied here, and UV absorbance was used as a surrogate for DOC. For MBR effluent samples a specific UV absorbance of  $2.82 \pm 0.8$  was determined, thus UV data were considered being suitable as surrogates. From the results, an effective diffusivity of the organics as well as mean film transfer

coefficients for other flow rates was derived. Details of this approach are given by Fettig & Sontheimer (1987). A mean intra-particle diffusivity of the organics was determined from a concentration-vs-time curve measured in a 2 L glass beaker. The film-homogeneous diffusion model was fitted to the experimental data assuming the same value of the intra-particle diffusivity for all adsorbable components. The model is described in detail by Sontheimer et al. (1988).

The RSSCT is intended to provide information about the breakthrough in technical-scale adsorbers. For that purpose, a glass column with an inner diameter of 8 mm was filled with 33 cm of  $60 \times 70$  mesh carbon particles which were obtained by crushing and sieving a representative sample of Carbsorb 30. The resulting median particle diameter by weight was 0.23 mm. A peristaltic pump was used to feed the column at constant rate corresponding to a filter velocity of 2.28 m/h and an EBCT of 8.7 min. These operating data were determined according to Crittenden et al. (1991), who proposed to calculate the EBCT for a RSSCT from the EBCT of the large column by multiplying the latter with the ratio of the carbon particle diameters assuming that the intra-particle diffusivity is proportional to particle size. The breakthrough curve was compared with data predicted by the film-homogeneous diffusion model using the isotherm and kinetic parameters determined from batch tests.

## Analytical methods

COD, ammonium ( $\text{NH}_4\text{-N}$ ), nitrite ( $\text{NO}_2\text{-N}$ ) and nitrate ( $\text{NO}_3\text{-N}$ ) were measured on-site with Merck Spectroquant test kits, and total suspended solids were determined according to DIN 38409 H2. DOC concentrations were measured with a Dimatoc 2000 analyser (DIMATEC), and UV absorbance was determined with a UviLine 9400 spectrophotometer (SCHOTT). pH was measured with a pH meter 539 (WTW).

## RESULTS AND DISCUSSION

### Performance of the MBR

Figure 2 illustrates the removal of COD in the MBR during about eight months of operation. While the influent concentrations are between 2,000 mg/L and 3,500 mg/L, the

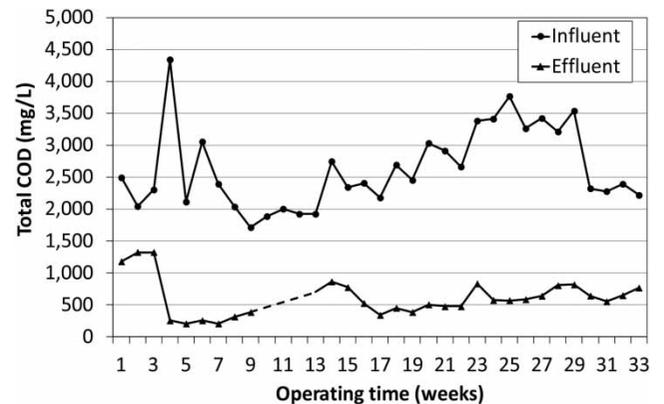


Figure 2 | COD concentrations in MBR influent and effluent samples; volumetric load  $1 \text{ kg COD}/(\text{m}^3 \cdot \text{d})$ .

effluent values are well below 1,000 mg/L. COD removal efficiencies are shown in Figure 3 as a function of sludge loading rate. The data vary between 65% and 95% with an average value of 81%. One must keep in mind that the MBR influent was pre-treated wastewater, that is, particulate organics are not included in the calculation of the removal efficiencies. Since they are not depending on the sludge loading rate in this range, it is concluded that the MBR did not reach its maximum capacity. As pointed out in the previous section, the flow rate was a limiting parameter, therefore the loading of the MBR could not be increased further. The sludge age was estimated to be  $>50$  d. It could not be calculated more accurately because the sludge was withdrawn discontinuously.

The concentrations of different nitrogen compounds are shown in Figure 4. They illustrate that about 74% of

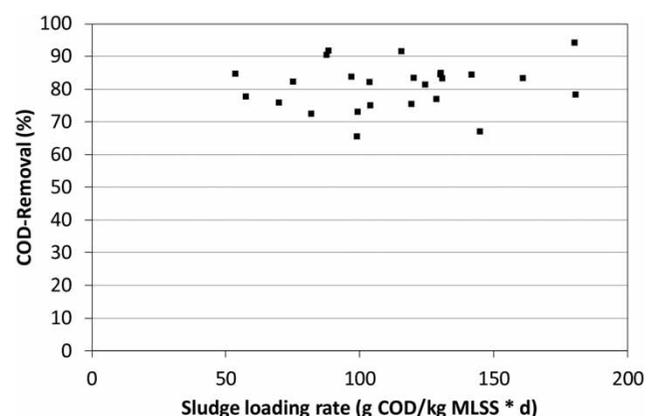
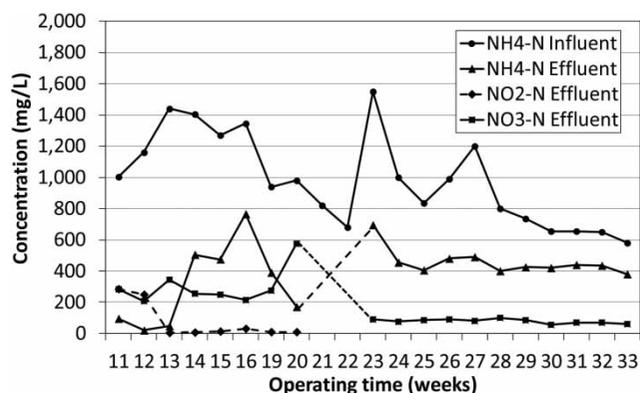


Figure 3 | COD removal as a function of sludge loading rate.

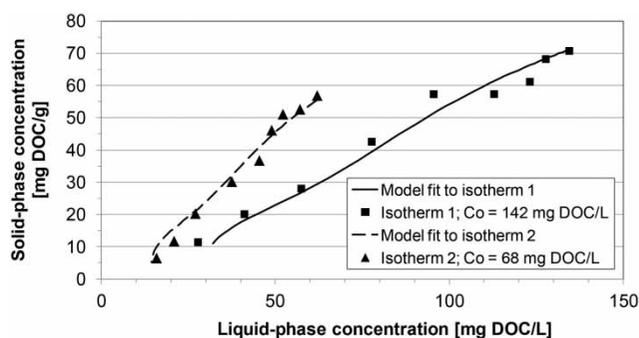


**Figure 4** | Concentrations of ammonium, nitrite and nitrate in MBR influent and effluent samples.

the incoming ammonium could be nitrified after 11 weeks of operation. In the tannery's technical treatment plant, ammonium is not removed at all. However, nitrification in the MBR seemed to be a sensitive process because in the later phase of the investigation ammonium removal decreased to less than 50%. This is in agreement with Ganesh *et al.* (2015), who report that nitrification of tannery wastewater in a SBR was sometimes quite unstable. Orhon *et al.* (2000) also observed a strong inhibitory impact of tannery wastewater on nitrifying bacteria that was primarily attributed to the high chloride content of 7 g/L. In our study, the chloride level was similar (8.7 g/L), thus it could be responsible for an inhibition of nitrifying species. Based on a nitrogen balance it was concluded that some denitrification occurred after several weeks of operation, with the average removal of total nitrogen being 36%. Towards the end of the study period the tannery was not constantly in operation. During the standstill periods, which could last several weeks, the pilot plant was fed with water stored in a basin, however, the composition changed significantly during storage. Therefore a closer investigation of the inhibitory effects was not possible.

### Determination of adsorption parameters

Overall isotherms of MBR effluent for two different initial concentrations are shown in Figure 5. Accordingly, solid-phase concentrations of up to 70 mg DOC/g were obtained while a certain proportion of the organics seems to be non-



**Figure 5** | Adsorption isotherms of MBR effluent and fit of the IAST model.

adsorbable. As demonstrated by Völker *et al.* (1984), the shifting of an overall isotherm with decreasing initial concentration towards higher solid-phase concentrations indicates that species with different affinities to the carbon surface, i.e., different adsorbabilities, are present in the wastewater. This applies also to the MBR effluent.

Therefore, the data were evaluated by selecting one non-adsorbable fraction corresponding to the Freundlich coefficient  $K_1 = 0$ , and three adsorbable fractions corresponding to  $K_2 = 6$ ,  $K_3 = 12$  and  $K_4 = 22$ , respectively, with the Freundlich exponent being  $n = 0.3$ , and fitting the IAST model to both isotherms simultaneously. The resulting fractions of each component ( $c_{o,i}/c_{o,total}$ ) listed in Table 2 reveal that the non-adsorbable fraction is about one-fifth (20.8%) while the major fraction (37.6%) is found for the Freundlich coefficient  $K_4 = 22$ . This means that a significant amount of the organics is fairly well adsorbable.

Kinetic parameters that were determined for the uptake of MBR effluent on granular carbon are given in Table 3. The effective diffusivity  $D_{L,eff}$  was derived from short fixed-bed column test data. The mean molecular weight  $M_W$  for the adsorbable organics was estimated using the following

**Table 2** | Fractions of four fictive components derived from the overall isotherms for MBR effluent

Component	Fraction ( $c_{o,i}/c_{o,total}$ )
1: $K_1 = 0$	20.8%
2: $K_2 = 6$ ; $n = 0.3$	26.2%
3: $K_3 = 12$ ; $n = 0.3$	15.4%
4: $K_4 = 22$ ; $n = 0.3$	37.6%

$K_1$ – $K_4$  and  $n$  are the Freundlich isotherm parameters of each component.

**Table 3** | Effective diffusivity  $D_{L,eff}$ , mean molecular weight  $M_w$ , mean film transfer coefficient  $\beta_L$  for a filter velocity of 2.28 m/h in the RSSCT, and mean intra-particle diffusivity  $D_S$  for the MBR effluent

Parameter	Results
$D_{L,eff}$ (m <sup>2</sup> /s)	$2.3 \cdot 10^{-10}$
$M_w$ (Da)	1,010
$\beta_L$ (m/s)	$1.88 \cdot 10^{-5}$
$D_S$ (m <sup>2</sup> /s)	$0.9 \cdot 10^{-13}$

equation proposed by [Sontheimer et al. \(1988\)](#):

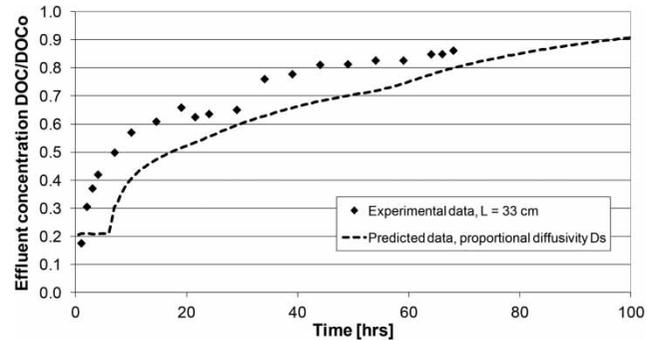
$$D_{L,eff} = 7,3 \cdot 10^{-9} \cdot M_w^{-0,5} \left( \frac{m^2}{s} \right)$$

Accordingly, the mean molecular weight is about 1,000 Da for the adsorbable fraction of the MBR effluent. This can be attributed to the occurrence of humus-type species formed during degradation processes in the MBR, and to refractory organics like tannins in raw wastewater ([Munz et al. 2009](#)). The effective diffusivity was also used to calculate a mean film transfer coefficient for the conditions of the RSSCT test.

The intra-particle diffusivity was derived from concentration-vs-time data of a rate test conducted with a sample of the original GAC particles. The test lasted for 192 hr, and more than 60% of the organics initially present in the water phase were adsorbed. The value of  $0.9 \cdot 10^{-13}$  m<sup>2</sup>/s found for the intra-particle diffusivity is quite small and resembles parameters obtained for humic substances ([Sontheimer et al. 1988](#)).

### Modelling of GAC adsorption

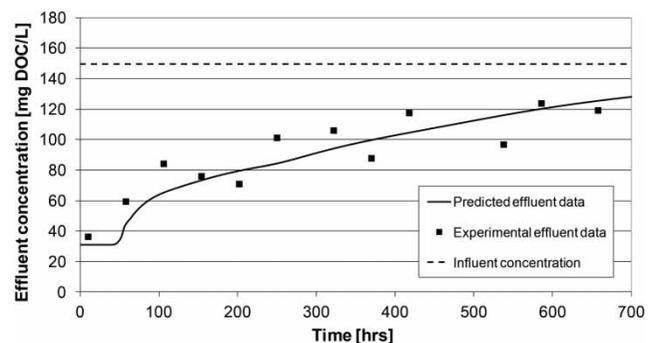
A comparison between experimental and predicted RSSCT breakthrough curves is shown in [Figure 6](#). The prediction is solely based on the equilibrium and kinetic parameters given in [Tables 2](#) and [3](#). The proportional diffusivity approach of the RSSCT was applied, i.e., the mean intra-particle diffusivity given in [Table 3](#) was multiplied by the particle diameter ratio ( $d_{p,SC}/d_{p,LC}$ ) = 0.118. Although the experimental and predicted curves are similar, the breakthrough behaviour is underestimated by the model. As a consequence, the average solid-phase concentration of



**Figure 6** | Experimental and predicted RSSCT breakthrough curves of MBR effluent; influent concentration 142 mg DOC/L.

41.2 mg DOC/g measured after 68 hr of operation, i.e., the experimental carbon capacity, is lower than the predicted value of 57.3 mg DOC/g. A possible reason is that the uptake of the organic substances was slower than predicted. In that case, an even smaller value of the intra-particle diffusivity had to be assumed for the small-sized carbon particles in order to improve the RSSCT modelling approach.

Effluent concentrations of the pilot-scale adsorber are shown in [Figure 7](#) together with predicted data that are again solely based on the equilibrium and kinetic parameters given in [Tables 2](#) and [3](#). Here, the modelling approach is successful in the way that both the breakthrough curve as well as the average solid-phase concentrations can be predicted quite well. After 660 hr of operation the experimental value is 55.4 mg DOC/g while the predicted value is 62.6 mg DOC/g. Thus the film-homogeneous diffusion model in combination with the multi-component approach for the description of the adsorption equilibrium is suited



**Figure 7** | Experimental and predicted breakthrough curves of MBR effluent in the pilot-scale adsorber; influent concentration 149 mg DOC/L.

to predict the performance of a technical-scale GAC column for the post-treatment of MBR effluent.

### Options for water reuse

The adsorption data reveal that activated carbon has a limited potential for polishing the MBR effluent. In a tannery comparable to Dang Tu Ky, the average freshwater water demand is about  $500 \text{ m}^3/\text{d}$ , and the demand for the beam-house processes (soaking and liming) is about  $210 \text{ m}^3/\text{d}$ . Thus the reuse potential can be estimated to 42% of the total freshwater demand. As mentioned earlier, the main reason for this limitation is the requirement for the discharge of salts from the water circuit when reusing water for other process steps in the tannery.

Based on the results from the pilot-plant operation, the size of a technical MBR plant for treating tannery wastewater and of a GAC polishing stage for a part of the total flow were outlined. The process scheme is shown in Figure 8 together with the flow rates and average COD concentrations. According to the pilot-plant results where the volumetric loading rate was  $1 \text{ kg COD}/(\text{m}^3 \cdot \text{d})$ , the volume of the aerated compartment had to be about  $1,350 \text{ m}^3$ . However, according to Scholz et al. (2005), it is possible to operate a MBR with tannery wastewater at a volumetric loading rate of  $3 \text{ kg COD}/(\text{m}^3 \cdot \text{d})$ . If this value was reached after further optimization, the volume of the aerated compartment would be on the order of  $450 \text{ m}^3$ . Chung et al. (2004) found that the optimum ratio of the anoxic denitrification stage to the nitrification tank was 50%, hence a volume of about  $225 \text{ m}^3$  for denitrification had to be added to obtain the MBR's total volume.

For the GAC stage, the operation was simulated with the adsorption model described in the previous section. It was proposed to set up three adsorption columns in series

with 2 m of bed length each. Varying the filter velocity revealed that the carbon capacity could be utilized better when the filter velocity was  $<2 \text{ m/h}$ . Based on the simulation results a value of  $1.8 \text{ m/h}$  was chosen that corresponds to a total EBCT of 3.3 hr. The column diameter will be 2.5 m and the total mass of carbon will be about 12,375 kg. Although the MBR effluent concentration was sometimes as high as  $800 \text{ mg COD/L}$  (Figure 2), an average influent value of  $550 \text{ mg COD/L}$  to the GAC stage was assumed. This number is based on the mean influent concentration to the MBR (Table 1) and the average COD removal efficiency. When the effluent concentration reaches the limit of  $250 \text{ mg COD/L}$ , the first column will receive fresh carbon, then it will be put in the last position. According to the simulation, a usable carbon capacity of at least  $50 \text{ g DOC/kg}$  should be obtained in this way.

During the operation of the pilot-scale adsorber the mean influent COD and DOC values were  $489 \text{ mg/L}$  and  $149 \text{ mg/L}$ , respectively, resulting in a factor of 3.3 between both parameters. Therefore, the carbon capacity of  $50 \text{ g DOC/kg}$  corresponds to about  $165 \text{ g COD/kg}$ . Under these conditions, the running time of one column after the starting-up phase will be about 33 d and the specific carbon demand on the order of  $1.8 \text{ kg/m}^3$ . This value is quite high, therefore, it might be questioned whether GAC is the best process for polishing MBR effluent. However, there are not many alternatives to remove refractory organics. Advanced oxidation processes have been studied on a laboratory scale for tannery wastewaters (Lofrano et al. 2013), but they require expensive oxidation chemicals and are more complicated to operate than a simple GAC system. Therefore, it will depend on the local conditions whether the approach described herein to produce water for reuse is both economically and ecologically reasonable.

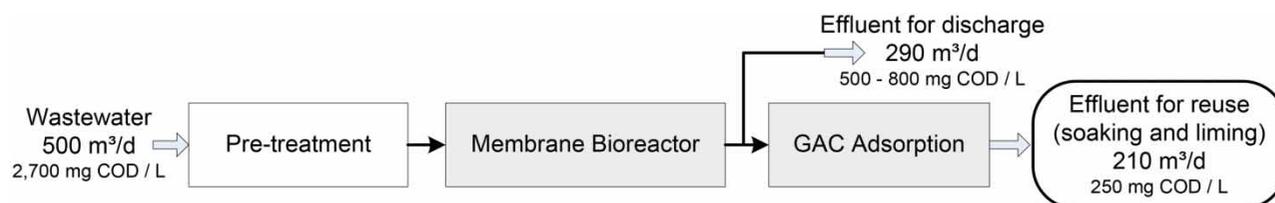


Figure 8 | Process scheme of a technical-scale treatment plant for partial reuse.

## CONCLUSIONS

- (1) In the MBR, dissolved organic matter could be removed from pre-treated tannery wastewater by 81% on average. The reactor did not reach its maximum capacity at a volumetric loading rate of 1 kg COD/(m<sup>3</sup>\*d). Meanwhile, nitrification was obviously an unstable process although more than 70% ammonium removal was obtained during some periods. The average removal of total nitrogen was 36%.
- (2) Adsorption onto activated carbon was suited to remove refractory organic substances from the MBR effluent. Adsorption equilibria could be described by applying the IAST model and a fictive component approach. More than 40% of the organics were either non-adsorbable or weakly adsorbable. The effective diffusivity estimated from short fixed-bed reactor data indicated an average molecular weight of about 1,000 Da. The intra-particle diffusivity was on the same order as kinetic parameters found for humic substances, thus the uptake rate on GAC was rather slow. The breakthrough curve determined for a pilot-scale adsorber could be predicted successfully by the modelling approach based on the film-homogeneous diffusion model while there were some deviations with the RSSCT.
- (3) For the outline of a technical-scale plant, a volumetric loading rate of 3 kg COD/(m<sup>3</sup>\*d) was assumed for the MBR. Three GAC columns in series were to be applied for polishing purposes. However, the usable carbon capacity was estimated to be rather low, and as a result, the specific carbon demand would be about 1.8 kg/m<sup>3</sup>.

## ACKNOWLEDGEMENTS

Project funding by the German Federal Ministry of Education and Research (BMBF) under grant no 02WCL1217B, and by the National University of Ho Chi Minh City is gratefully acknowledged. The authors would like to thank Thomas Lücking, Stefan Nordbruch and Nguyen Thi Thanh Phuong for their support, and Claudia Steinert, Tilman Steinert, Henning Zeich and Nguyen

Cong Vu for their technical assistance and their dedication to the project.

## REFERENCES

- Chung, Y., Choi, H., Lee, S. & Cho, J. 2004 Treatment of tannery wastewater with high nitrogen content using anoxic/oxic membrane bio-reactor. *J. Environ. Sci. Health, Part A* **39** (7), 1881–1890.
- Crittenden, J. C., Reddy, P. S., Arora, H., Trynoski, J., Hand, D. W., Perram, D. L. & Summers, R. S. 1991 Predicting GAC performance with rapid small-scale column tests. *J. Am. Water Works Assoc.* **83** (1), 77–87.
- De Gisi, S., Galasso, M. & De Feo, G. 2009 Treatment of tannery wastewater through the combination of a conventional activated sludge process and reverse osmosis with a plane membrane. *Desalination* **249**, 337–342.
- EIPPCB 2013 *Best Available Techniques (BAT) Reference Document for the Tanning of Hides and Skins*. European Integrated Pollution Prevention and Control Bureau, Seville, Spain.
- Fazal, S., Zhang, B., Zhong, Z., Gao, L. & Chen, X. 2015 Industrial wastewater treatment by using MBR – a review study. *J. Environ. Protection* **6**, 584–598.
- Fettig, J. & Sontheimer, H. 1987 Kinetics of adsorption on activated carbon: III. Natural organic matter. *J. Environ. Eng., ASCE* **113** (4), 795–810.
- Fettig, J., Stapel, H., Steinert, C. & Geiger, M. 1996 Treatment of landfill leachate by preozonation and adsorption in activated carbon columns. *Water Sci. Technol.* **34** (9), 33–40.
- Galiana-Alexandre, M. V., Iborra-Clar, A., Bes-Piä, B., Mendoza-Roca, J. A., Cuartas-Urbe, B. & Iborra-Clar, M. I. 2005 Nanofiltration for sulfate removal and water reuse of the pickling and tanning processes in a tannery. *Desalination* **179** (1–3), 307–313.
- Ganesan, V. & Muthulakshmi, B. 2015 Study on rheology and optimization for treating tannery effluents in submerged aerobic membrane bioreactor. *Int. J. Innovat. Engrg. Technol.* **6** (2), 53–60.
- Ganesh, R., Sousbi, P., Torrijos, M., Bernet, N. & Ramanujam, R. A. 2015 Nitrification and denitrification characteristics in a sequencing batch reactor treating tannery wastewater. *Clean Technol. Environ. Policy* **17** (3), 735–745.
- Giacobbo, A., Feron, G. L., Rodrigues, M., Ferreira, J., Meneguzzi, A. & Bernardes, A. 2015 Integration of membrane bioreactor and advanced oxidation processes for water recovery in leather industry. *Desal. Water Treat.* **56** (7), 1712–1721.
- Johannsen, K., Roggatz, R., Sontheimer, H. & Frimmel, F. H. 1992 Anwendung der Adsorptionsanalyse auf natürliche organische Wasserinhaltsstoffe [Application of adsorption analysis for natural organic substances]. *Vom. Wasser* **79**, 237–248.

- Lin, H., Gao, W., Meng, F., Liao, B., Leung, K., Zhao, L., Chen, J. & Hong, H. 2012 Membrane bioreactors for industrial wastewater treatment: a critical review. *Crit. Rev. Environ. Sci. Technol.* **42**, 677–740.
- Lofrano, G., Meric, S., Zengin, G. E. & Orhon, D. 2013 Chemical and biological treatment technologies for leather tannery chemicals and wastewaters: a review. *Sci. Total Environ.* **461–462**, 265–281.
- MONRE 2011 *National Technical Regulation on Industrial Wastewater – QCVN 40:2011*, Ministry of Natural Resources and Environment, Hanoi, S.R. Vietnam.
- Munz, G., Gori, R., Mori, G. & Lubello, C. 2007 Powdered activated carbon and membrane bioreactors (MBRPAC) for tannery wastewater treatment: long-term effect on biological and filtration process performance. *Desalination* **207** (1–3), 349–360.
- Munz, G., Mori, G., Laura, S., Barberio, C. & Lubello, C. 2008 Process efficiency and microbial monitoring in MBR (membrane bioreactor) and CASP (conventional activated sludge process) treatment of tannery wastewater. *Bioresour. Technol.* **99** (18), 8559–8564.
- Munz, G., De Angelis, D., Gori, R., Mori, G., Casarci, M. & Lubello, C. 2009 The role of tannins in conventional and membrane treatment of tannery wastewater. *J. Hazard. Mater.* **164** (2–3), 733–739.
- Murat, S., Ateş Gencell, E., Taşlı, R., Artan, N. & Orhon, D. 2002 Sequencing batch reactor treatment of tannery wastewater for carbon and nitrogen removal. *Water Sci. Technol.* **46** (9), 219–227.
- Ng, C., Sun, D., Bashir, M., Wai, S., Wong, L., Nisar, H., Wu, B. & Fane, A. 2013 Optimization of membrane bioreactors by the addition of powdered activated carbon. *Bioresour. Technol.* **138**, 38–47.
- Orhon, D., Genceli, A. & Sözen, S. 2000 Experimental evaluation of the nitrification kinetics for tannery wastewaters. *Water SA* **26** (1), 43–50.
- Scholz, W. G., Rougé, P., Bódalo, A. & Leitz, U. 2005 Desalination of mixed tannery effluent with membrane bioreactor and reverse osmosis treatment. *Environ. Sci. Technol.* **39** (21), 8505–8511.
- Sontheimer, H., Crittenden, J. C. & Summers, R. S. 1988 *Activated Carbon for Water Treatment*. DVGW-Forschungsstelle, Karlsruhe, Germany.
- Thanh, L. H. 2011 *Greening the Leather Tanning Industry in Vietnam. Research Report No. 2011-RR8*, Economy and Environment Program for Southeast Asia (EEPSEA), Singapore.
- Thanh, L. H. & Truong, D. D. 2013 Compliance of leather tanning industry with environmental regulations in Vietnam. *J. Econ. Develop.* **15** (2), 54–78.
- Völker, E., Brauch, H.-J. & Sontheimer, H. 1984 Charakterisierung organischer Wasserinhaltsstoffe durch Adsorptionsanalyse [Characterization of organics in water by their adsorption behaviour]. *Vom. Wasser* **62**, 1–10.
- Wang, J. G. & Liu, Y. H. 2011 Study on the treatment of tannery wastewater with the high concentration of ammonia nitrogen by MBR. *Appl. Mech. Mater.* **71–78**, 2186–2189.

First received 2 February 2016; accepted in revised form 30 August 2016. Available online 31 October 2016