Project no. 018525

REMOVALS

Reduction, modification and valorisation of sludge

Instrument: Specific Targeted Research Or Innovation Project

Thematic Priority: Global change and ecosystems, 1.1.6.3

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(Part III)

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9. **Minimisation of sludge production by utilisation of biological potential in membrane bioreactors.**

9.1. **Summary description of project objectives, work performed and end results, elaborating on the degree to which the objectives were reached.**

Sludge management accounts for about half of the overall wastewater treatment costs. In this context, the reduction of excess sludge production by utilisation of maintenance metabolism in membrane bioreactors (MBR) is an interesting alternative. The potential of elevated SRT operation has not been investigated in detail due to rising viscosities and decreasing oxygen transfer rates at higher MLSS concentrations. A cost model for submerged membrane bioreactors treating municipal wastewater incorporating energy demand for aeration and fouling prevention as well as sludge handling costs subject to local conditions was developed. The cost model is based on easily accessible input parameters like operational and biokinetic parameters and feed conditions. Based on the developed model simulation studies were performed to determine the optimal operational conditions by varying sludge treatment and electricity costs. First results showed that under certain conditions the optimum SRT is higher than currently applied, therefore minimising sludge reduces the overall cost despite higher aeration demand. Due to the lack of data two bench-scale MBRs were continuously operated at different sludge ages varying between 15-100 days to obtain various sludge characteristics like dewaterability, filterability, viscosity etc. and biokinetic parameters.

9.2. **Methodologies and approaches employed.**

**PLANT CONFIGURATION.**

Two submerged MBRs for C- and N-removal equipped with an anoxic and an aerobic tank and an internal recirculation of 400 % of the inflow were used to study the sludge characteristics at different operating conditions (see Table 9.1). They are of different size (10L and 40 L, respectively) and equipped with different membrane modules (plate and frame and hollow fibre, respectively) and are fed with a complex synthetic wastewater representing a municipal wastewater with a targeted COD of 600 mg/L (see Table 9.2, composition adapted from [3]). A nutrients solution adapted according to Smolders et al. (1994) [4] was added to the synthetic wastewater: 450 μg/L FeSO₄·7H₂O, 45 μg/L H₃BO₄, 6 μg/L CuCl₂·2H₂O, 54 μg/L KJ, 30 μg/L MnSO₄·H₂O, 18 μg/L NaMoO₄·2H₂O, 18 μg/L ZnCl₂·2H₂O, 45 μg/L CoCl₂·6H₂O. Both MBRs are operated at room temperature (18-23°C). The plants were inoculated with activated sludge from an MBR treating municipal wastewater. Due to the diverging behaviour of sludge characteristics of both MBRs, they were reinoculated at the beginning of period 2 with activated sludge from an MBR treating municipal wastewater.

**Table 9.1. Operational parameters of the investigated MBRs.**

<table>
<thead>
<tr>
<th></th>
<th>MBR I</th>
<th>MBR II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Period 1</td>
<td>106</td>
<td>106</td>
</tr>
<tr>
<td>Volume [L]</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Time of operation [d]</td>
<td>106</td>
<td>106</td>
</tr>
<tr>
<td>Solid Retention Time [h]</td>
<td>104</td>
<td>104</td>
</tr>
<tr>
<td>Hydraulic Retention Time [h]</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Steady state sludge loading [kg COD/(kgTS d)]</td>
<td>0.130</td>
<td>0.094</td>
</tr>
</tbody>
</table>

**Table 9.2. Composition of the synthetic wastewater.**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>(mg/L)</th>
<th>Ingredient</th>
<th>(mg/L)</th>
<th>Ingredient</th>
<th>(mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peptone</td>
<td>25</td>
<td>Starch</td>
<td>200</td>
<td>MgSO₄·7H₂O</td>
<td>4.2</td>
</tr>
<tr>
<td>Yeast extract</td>
<td>80</td>
<td>Sodium acetate</td>
<td>150</td>
<td>K₃HPO₄</td>
<td>29</td>
</tr>
<tr>
<td>Milk powder</td>
<td>180</td>
<td>NH₄Cl</td>
<td>150</td>
<td>Urea</td>
<td>40</td>
</tr>
</tbody>
</table>
SAMPLING AND ANALYSIS.

The influent synthetic wastewater and the permeate were sampled once a week and analysed for total and volatile suspended solids (TS, VSS), total COD and total N concentration. Dr. Lange cuvette test kits LCK 338 and LCK 238 were used for total nitrogen determination, LCK 114 and LCK 414 were used for total COD determination.

Sludge samples were taken once a week from the aeration tank of both plants and were analysed immediately for total and volatile suspended solids (TS, VSS) concentration, dewaterability (CST), filterability (TTF), rheology and oxygen transfer coefficient (kLa).

TS and VSS concentrations were measured according to German DIN 38414 part 2 and 3. Capillary Suction Time (CST) as a method to characterise sludge dewaterability was measured in duplicate with a standard CST Device (Model 200, Triton Electronics). The measurement of the CST is very inaccurate due to variations in the structure of the filter paper, therefore the producer of the CST device specifies an accuracy of 20%. The filterability was measured by the filterability index time to filter (TTF) to filter a certain volume. Due to the availability of just small sludge samples, TTF was determined by filtering 3 mL of permeate from a 25 mL sludge sample. Sampling larger sludge volumes would disturb targeted SRT.

For the measurement of rheological properties a rotational viscometer type RheolabQC (Anton Paar Germany GmbH) was used. In order to include low viscosities, the viscometer was supplied with a double gap measurement device DG42. Measurements were carried out as double readings at a shear rate between 5 and 3000 1/s with undiluted samples. Furthermore the viscosity is strongly dependent on temperature; therefore all results were corrected to a temperature of 20°C.

Respirometric measurements and oxygen transfer measurements are carried out in a 1 L batch [5]. One litre of sludge was withdrawn once per week for respirometric tests and returned to the bioreactor afterwards. To provide sufficient mixing and oxygen transfer, the 1L batch was equipped with a Rushton turbine and baffles and was kept at a constant temperature of 20± 2°C. Fine bubble aeration was employed through a porous tube. Aeration was set to 40L/h; in order to avoid evaporation, the air was humidified prior to the reactor inlet. Dissolved oxygen (DO) and temperature were measured with an oxygen probe, type CellOx 325, which was calibrated before each measurement and placed close to the stirrer.

9.3. Achievements of the project related to the state of the art.

PLANT PERFORMANCE.

Both bench-scale MBRs showed good results in terms of COD elimination efficiency, which was mostly above 95%. The TN elimination efficiency in MBR II is mainly between 80-85%, whereas in MBR I the TN elimination varied between 70-85% due to stronger fluctuations in oxygen concentration.

BIOMASS ACCUMULATION.

The first period started on the 1st of June 2007 and lasted until the 14th of September 2007. In this period, the plants were initially inoculated with sludge from a decentralised MBR plant treating municipal wastewater. Both plants were operated with a HRT of 10 h at a nearly infinite sludge age. Sludge was only withdrawn for sampling which resulted in an actual sludge age of 140 days. As can be seen, the initial sludge concentration was around 9 g/L (see Figure 9.1). At the beginning a quick sludge growth could be observed in both plants, but then suddenly the sludge growth in MBR I stopped and the biomass concentration kept nearly constant. This occurred simultaneously with the appearance of Tubifex tubifex worms in MBR I, which were eliminated by dosing of 4.2 mg/L CuCl2 over a couple of days.

Due to problems with the high viscosity of the sludge and the oxygen transport into the sludge in MBR II both plants were reinocculated with sludge from an MBR treating municipal wastewater on the 14th of September 2007 (day 106), when the second period started which lasted to the 1st of April 2008 for MBR I and 1st of August 2008 for MBR II, respectively. Both plants were operated at the same conditions as in the period before, i.e. a very high sludge age of 140 days with a HRT of 10 h. In this second period we had a heavy breakdown of the aeration system in both plants for more than two days on day 185 and a failure of the aeration on day 362. The immersed membrane modules were totally blocked and had to be cleaned which caused a sludge loss in the plants and therefore a decrease in Total Solids (TS) concentration.

The third period with changed conditions for MBR I started on the 30th of April whereas MBR II stayed at the same conditions as in period 2. In this period, the SRT has been retained unchanged, but the hydraulic
retention time (HRT) of MBR I was dropped from 10 h to just 5 h to see the influence on sludge production. Due to several breakdowns of the aeration system and strong fouling events in MBR I, membrane cleaning was frequently performed in both plants, which resulted in partly heavy sludge losses of up to a tenth of the reactor volume, but still the SRT was larger than 100 d.

The forth period for both MBR started on day 439. Here, the SRT of both plants was changed to 15 and 75 days, respectively, while the HRT was kept constant at 10 h. A stable biomass concentration of 6.2±0.7 g/L was reached after 90 days in MBR I and of 14.6±0.2 g/L after two sludge ages in MBR II.

For MBR I the SRT was changed to 30 days on day 613. Due to a worm attack biomass concentration decreases and also nitrogen removal dropped dramatically. It was tried to remove the worms by 2mg/L copper dosing every day for one week, but unfortunately the worms came back and the sludge had to be thrown away.

In Table 9.3, the obtained yield coefficients Y for the different periods are shown. The obtained values for high sludge ages (> 75 d) are comparable to those of other MBRs operated at nearly complete sludge retention [2, 6]. They obtained values in the range of 0.06-0.12 gVSS/gCOD.

Table 9.3. Yield coefficients for the different investigated periods.

<table>
<thead>
<tr>
<th>MBR I Period</th>
<th>MBR II Period</th>
</tr>
</thead>
<tbody>
<tr>
<td>Period 1</td>
<td>0.055</td>
</tr>
<tr>
<td>Period 2</td>
<td>0.079</td>
</tr>
<tr>
<td>Period 3</td>
<td>0.061</td>
</tr>
<tr>
<td>Period 4</td>
<td>0.328</td>
</tr>
<tr>
<td>Period 5</td>
<td>0.226</td>
</tr>
</tbody>
</table>

SLUDGE CHARACTERISTICS.

Activated sludge is known to be a non-Newtonian fluid [7]. The apparent viscosity $\mu_\infty$ as a function of TS concentration is shown in Figure 9.2, where $\mu_\infty$ is the viscosity at a nearly infinite shear rate and should be independent of the shear rate. In this study $\mu_\infty$ was evaluated at a shear rate of 2300 s$^{-1}$. Furthermore apparent viscosity is strongly dependent on temperature; therefore all results were corrected to a temperature of 20°C. In agreement with literature (e.g. [6,8]) apparent viscosity increases with increasing TS concentration which influences fluid dynamics in the plant.
The apparent viscosities of MBR II are slightly higher than those of MBR I at the same TS concentration, although both sludges are fed with the same synthetic wastewater. This might be due to fluctuations in the influent COD concentrations, which results in differently loaded wastewater. Tixier et al. (2003) [8] also observed different viscosities at a defined TS concentration for activated sludges with different influent wastewater. The steady state viscosities for the different periods are showing a certain fluctuation, especially for higher TS values.

In comparison to the literature correlations, the obtained apparent viscosities are up to two times higher, especially for higher TS concentrations between 15 and 20 g/L. In literature correlations established by Khongnakorn et al. (2007) [2] and Tixier et al. (2003) [8] just a TS range from 3-17 g/L was used thus extrapolating results obtained for a lower TS range to higher TS values can result in an underestimation of up to 50% of the investigated parameter. This stresses the need for a larger database as a reliable basis for process optimisation and also shows that with the current correlations, e.g., mixing and pumping power requirements would have been underestimated. In this study more than half of the data obtained are valid for TS concentrations higher than 15 g/L.

In Table 9.4, some literature correlations for the viscosity as a function of TS are given and compared with the correlations found in this study. In agreement with most literature also an exponential relationship is found for the investigated MBRs. Especially the correlation including samples from both MBRs (MBR I and MBR II) is quite similar to the correlations found by Khongnakorn et al (2007) [2] and Tixier et al. (2003) [8], just the coefficient is a bit higher with 1.22 compared to 1.17 and 1.03, respectively. Nevertheless, the exact correlation between viscosity and TS concentration is contradictory in literature.

Table 9.4. Correlations for infinite viscosity.

<table>
<thead>
<tr>
<th>Correlation</th>
<th>MBR I only</th>
<th>MBR II only</th>
<th>MBR I + MBR II</th>
<th>Khongnakorn et al. (2007) [7]</th>
<th>Tixier et al. (2003) [5]*</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mu_\infty )</td>
<td>1.24 ( \cdot ) e^{0.098 \cdot \text{TS} }</td>
<td>1.23 ( \cdot ) e^{0.109 \cdot \text{TS} }</td>
<td>1.22 ( \cdot ) e^{0.105 \cdot \text{TS} }</td>
<td>1.03 ( \cdot ) e^{0.106 \cdot \text{TS} }</td>
<td>1.1747 ( \cdot ) e^{0.1023 \cdot \text{TS} }</td>
</tr>
</tbody>
</table>

Tixier et al. (2003) [8] found an exponential relationship between viscosity \( \mu_\infty \) and TS, whereas Pollice et al. (2007) [9] found a correlation where a downward concavity appeared, indicating a decreasing influence of higher solid concentrations on the viscosity \( \mu_\infty \). Obviously, the viscosity of an activated sludge is not only a
function of TS but also a function of other sludge characteristics which have to be identified, and of operating conditions, specific power input and thus plant size.

The dewaterability of an activated sludge, an important factor influencing sludge disposal costs, can be characterized by the CST. Figure 9.3 shows the CST for both plants as a function of TS concentration. The absolute value of CST differs by up to a factor of 5 for both sludges at the same TS concentration. It is evident that below a critical TS concentration of approx. 15 g/L, the biomass concentration has nearly no influence on the dewaterability, because the CST values fluctuate between 10 s and 100 s. Above 15 g/L a dramatic increase in CST and a broad distribution can be observed. Furthermore it can be seen in Figure 3, that the obtained steady state CST values are normally lower or in the same range as the CST values obtained during the unsteady state conditions. Therefore above 15 g/L higher TS values will result in a strongly lower sludge dewatering potential, however at steady state conditions the dewaterability has slightly improved compared to the unsteady state conditions.

Figure 9.3. Capillary suction time versus Total Solids concentration. The values within the circles are obtained for steady state conditions.

In comparison to literature where the CST was determined to be in the range of 5-20 s [2] the obtained CST values in this study are very high, maybe due to higher viscosities $\mu_\infty$ in this study, thus indicating a poor dewaterability for both sludges. Therefore the potential to dewater these sludges is low and sludge treatment cost would increase dramatically. Again, apparently the available data is not sufficient and a detailed study of the parameters influencing the dewaterability is necessary.

The mass transfer efficiency is important for the aeration requirements in a plant. However, the measurement of this parameter is quite complex, because it is dependent on the experimental setup. Therefore it is important to keep the same conditions (experimental set-up, air flow rate, stirrer speed etc.) for each measurement. In Figure 9.4, the relative mass transfer coefficient over TS concentration can be seen. The evolution of $\alpha$ versus TS is in agreement with literature [5, 9], where a decrease of the mass transfer coefficient with increasing TS concentration is shown thus raising the aeration requirements at higher TS concentrations. The $\alpha$-correlations found in literature show an enormous variation of oxygen transfer efficiency at a given TS (see Figure 4), which can result in huge inaccuracy by optimising the total process. Therefore it is essential to identify the additional parameters that influence mass transfer efficiency like aeration device for a reliable optimisation. In this study the obtained $\alpha$ values fluctuate very strongly but considering just the steady state $\alpha$ values they are pretty good reproducible and can be reliable values for the optimisation.
In Table 9.5 the steady state sludge characteristics arising from the different operating conditions with the standard deviation are given. The stationary infinite viscosity for period 2 is not available due to the breakdown of the measurement device. No stationary conditions for MBR II in period 1 due to problems with the sludge characteristics. In general, increasing SRT and decreasing HRT will result in a higher steady state biomass concentration. Along with the TS increase, CST as well as $\mu_\infty$ increases, whereas the oxygen transfer decreases. Just for MBR I the CST values in period 1 and 4 are quite similar, although the SRT is 15 d and 140 d, respectively. But looking at the other sludge characteristics a strong difference between these two periods is noticeable, which meets the expectations.

### Table 9.5. Steady state sludge characteristics.

<table>
<thead>
<tr>
<th></th>
<th>MBR I</th>
<th>MBR II</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TS [g/L]</td>
<td>$\mu_\infty$ [m Pas]</td>
</tr>
<tr>
<td>Period 1</td>
<td>11.6±0.4</td>
<td>3.7±0.1</td>
</tr>
<tr>
<td>Period 2</td>
<td>14.0±2.2</td>
<td>n.a.</td>
</tr>
<tr>
<td>Period 3</td>
<td>25±1.3</td>
<td>16.5±0.3</td>
</tr>
<tr>
<td>Period 4</td>
<td>6.2±0.7</td>
<td>2.53±0.3</td>
</tr>
</tbody>
</table>

**MODEL DEVELOPMENT.**

The idea of this study is to set up a cost model (see Figure 9.5) for MBR users which is based on a few easily accessible input parameters like operational (HRT, SRT) and biokinetic parameters (yield, decay coefficient) and feed conditions.
SLUDGE PRODUCTION MODEL.

The steady state biomass concentration in the membrane bioreactor is calculated from a mass balance on sludge and substrate in the reactor (ASM1, Xing et al. 2003, Yoon et al. 2004).

\[ \frac{dX}{dt} = \frac{V}{K_s+S} \cdot \frac{\mu_{max}}{S} \cdot X \cdot V - b \cdot X \cdot V - Q_w \cdot X \]  
(1)

\[ \frac{dS}{dt} = \frac{V}{K_s+S} \cdot \frac{\mu_{max}}{S} \cdot X \cdot V - Q \cdot S_0 - Q \cdot S \]  
(2)

Assuming that the bioreactor is completely mixed, the biomass concentration at steady state conditions can be derived by rearranging Eq. (1) and (2) and solving for X.

\[ X = \frac{1}{HRT} \cdot \frac{(S_0 - S)}{Y \cdot SRT} \]  
(3)

I.e., biomass concentration in the MBR is just a function of operating parameters (SRT, HRT), inlet conditions (S_0) and biokinetic parameters (Y, b). Operating parameters and inlet conditions are well known, so only the biokinetic parameters have to be determined experimentally or taken from literature.

Knowing the sludge age SRT and the biomass concentration X, the excess sludge production can be calculated with equation (4):

\[ ESP = \frac{V \cdot X}{SRT} = \frac{Y \cdot Q}{1 + b \cdot SRT} \cdot (S_0 - S) \]  
(4)

AERATION MODEL.

The theoretical aeration demand to maintain the biological process is calculated according to ATV-DVWK-A 131 considering the oxygen requirement for carbon and nitrogen removal. To keep a constant oxygen concentration C_{set} of 2 mg L^{-1} in the reactor, the real aeration demand is then calculated considering the oxygen transfer efficiency \( \alpha \) and the blower efficiency \( \eta \).
The oxygen transfer efficiency $\alpha$ is a function of MLSS concentration and can be calculated according to different correlations found in literature (Krampe and Krauth 2003, Muller et al. 1995, Rosenberger 2003). The blower efficiency can be taken from data sheets. The power demand is then calculated using the correlation established by Krause and Cornel (2004) with $E_{pot} = 5.44 \text{ Wh m}^{-3} \text{m}^{-1}$ and the depth $h$ of the aeration device.

$$P_{\text{biology}} = E_{pot} \cdot Q_{\text{air,real}} \cdot h$$

According to Cornel and Krause (2006) the aeration demand for fouling prevention varies between 0.4 and 1 kWh m$^{-3}$ for immersed membranes. In first approach a linear relationship between power demand for fouling prevention and the viscosity $\mu_\infty$ at a nearly infinite shear rate was assumed in this study.

$$P_{\text{fouling}} = 0.0375 \cdot \mu_\infty + 0.325$$

Furthermore, the coarse bubble aeration already provides a portion (15%) of the dissolved oxygen for the biotreatment.

**SLUDGE HANDLING MODEL.**

The cost models for sludge thickening and transport are specific for each plant, due to different on-site sludge handling availabilities and thus they must be adapted for each case. In a first approach constant sludge treatment cost of 200 - 800 € $t_{DS}^{-1}$ are assumed (Hall 1999). This sub-model has to be refined in the next step.

**SENSITIVITY ANALYSIS.**

In order to evaluate the derived model, simulation studies and sensitivity analyses were carried out in first step a plausibility check with the different sub-models was realised. According to Equation 3 biomass concentration in the MBR can be calculated. Information about operating conditions and the influent parameters are easy accessible for each plant, but information about biokinetic parameters are less precisely known because they are strongly dependent on operating conditions and have to be determined experimentally or taken from literature. Therefore the effect of varying yield coefficient on steady state biomass concentration is shown in Figure 9.6 assuming that the yield coefficient is independent of SRT.

![Figure 9.6](image-url)  

**Figure 9.6.** Biomass concentration in the reactor depending on sludge age assuming a constant yield coefficient ($b=0.009 \text{ d}^{-1}$, HRT=10 h, $S_0=600 \text{ mgCOD L}^{-1}$, $S=30 \text{ mgCOD L}^{-1}$).
Yield coefficients obtained in literature (Spérandio and Espinosa 2008, Wen et al. 1999) vary between 0.38 – 0.13 mgVSS mgCOD\(^{-1}\) for sludge ages from 5–110 days. Own measurements for a sludge age of 75 d resulted in a yield coefficient of 0.228 mgMLSS mgCOD\(^{-1}\). It is obvious that an inaccurate yield coefficient can result in an error of up to 50% in the determination of MLSS. Therefore a correlation for biokinetic parameters as a function of operating conditions needs to be implemented in the model.

According to Eq. (3) MLSS concentration changes linear with yield coefficient and influent substrate concentration (\(S_0\gg S\)) and it is inversely proportional to HRT.

Further simulation studies were performed with the values given in Table 9.6. The operational conditions and the biokinetic parameters are taken from a bench-scale MBR for carbon and nitrogen removal operated at a SRT of 75 days with a complex synthetic wastewater in our laboratory (Schaller et al. 2008). The temperature T as well as \(C_{\text{set}}\) are estimated values. The influent concentration \(S_0\) and TN are average values from the plant and the effluent concentration was calculated assuming 95% removal efficiency.

Table 9.6. Parameters of a bench-scale MBR used for the simulation.

<table>
<thead>
<tr>
<th>Operational parameters</th>
<th></th>
<th>Influent conditions</th>
<th></th>
<th>Biokinetic parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Q [m(^3) d(^{-1})]</td>
<td>0.096</td>
<td>(S_0) [mg L(^{-1})]</td>
<td>600</td>
<td>Yield</td>
<td>0.228</td>
</tr>
<tr>
<td>HRT [h]</td>
<td>10</td>
<td>S [mg L(^{-1})]</td>
<td>30</td>
<td>b [d(^{-1})]</td>
<td>0.009</td>
</tr>
<tr>
<td>F/M [kgCOD d(^{-1})]</td>
<td>0.0576</td>
<td>TN [mg L(^{-1})]</td>
<td>80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T [°C]</td>
<td>14</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C_{\text{set}}) [mg L(^{-1})]</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\rho_{\text{air}}) [kg m(^{-3})]</td>
<td>1.225</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In Figure 9.7 the real aeration demand to maintain the biological process were determined using different \(\alpha\) correlation taken from literature (Krampe and Krauth 2003, Muller et al. 1995, Rosenberger 2003) and assuming a blower efficiency of 50%. With increasing SRT the difference between the aeration demands increases up to 60%. It is obvious that the big differences in the calculated aeration demand especially for high sludge ages results in a significant difference of aeration costs. Therefore oxygen transfer for higher MLSS concentrations should be investigated more intensively to get an improved knowledge of the parameters influencing oxygen transfer.

Figure 9.7. Calculated aeration demand to maintain the biological process with different \(\alpha\) correlation assuming a blower efficiency of 50%.

COST CONSIDERATIONS.
The costs of an MBR process vary strongly depending on local conditions due to differences in the electricity tariff and sludge treatment depending on the method used, on local conditions, like plant size, plant equipment, local regulations, transportation costs and sludge characteristics.

In Figure 9.8 the total aeration costs for the biology and fouling prevention as well as the sludge treatment costs per m³ treated wastewater versus sludge age are shown, assuming different electricity tariffs and sludge treatment cost, respectively. The total aeration costs are calculated with the parameters given in Table 1, the $\alpha$ correlation found by Rosenberger (2003), a blower efficiency of 50% and the assumption that the coarse bubble aeration for fouling prevention provides 15% of the aeration demand to maintain the biological process.

Increasing the sludge cost by 40% from 500 €$^{-1}$DS to 700 €$^{-1}$DS at constant electricity costs of 10€cents kWh$^{-1}$ will result in an increase of the total operation cost of 10-25% depending on sludge age. The strongest increase is observed for lower sludge ages. An increase in the electricity tariff by 25 % at constant sludge treatment cost results in an increase of 10-18% of total operating cost whereas the increase is more pronounced for higher sludge ages. Although the costs per m³ treated wastewater is not very distinct, the lowest cost are obtained with a sludge age of 65 days.

**Figure 9.8.** Calculated costs per m³ treated wastewater for aeration and sludge treatment versus sludge age assuming different electricity tariffs and sludge treatment cost, respectively.

**CONCLUSION.**

Two submerged MBRs for C- and N-removal equipped with an anoxic and an aerobic tank and an internal recirculation of 400 % were used to study the sludge characteristics at different operating conditions (SRT, HRT and MLSS concentration). Both bench-scale MBRs showed good results in terms of COD elimination efficiency, which was mostly above 95%. The TN elimination efficiency in MBR II is mainly between 80-85%, whereas in MBR I the TN elimination varied between 70-85% due to stronger fluctuations in oxygen concentration.

With increasing biomass concentration, apparent viscosity increases, while the viscosity for a given MLSS concentration is slightly different in both plants. The available literature correlations are fitted to a short TS range from 3-17 g/L. Therefore especially for higher TS concentrations between 15 and 20 g/L the obtained apparent viscosities in this study are up to two times higher in comparison to literature correlations. For the first time a correlation for the viscosity as a function of TS using a large TS range from 4 g/L to 27 g/L was established. In agreement with literature also an exponential relationship is found for the investigated MBRs.
It is shown that below a critical TS concentration of approx. 15 g/L, the biomass concentration has nearly no influence on the dewaterability. Above 15 g/L a dramatic increase in CST can be observed. The obtained steady state CST values are normally lower or in the same range as the CST values obtained during the unsteady state conditions. Above 15 g/L higher TS values will result in a strongly lower sludge dewatering potential, however at steady state conditions the dewaterability has slightly improved compared to the unsteady state conditions. In comparison to literature [2] the obtained CST values in this study are very high, thus indicating a poor dewaterability for both sludges. Again, for the first time a large TS range from 4 g/L to 27 g/L was investigated. The potential to dewater these sludges is low and sludge treatment cost would increase dramatically. Additionally, mass transfer efficiency decreases with increasing TS, thus increasing aeration requirements.

It is shown, that all sludge characteristics of an activated sludge are not only a function of MLSS but also a function of other sludge properties which further have to be identified as well as their dependence on operating conditions. The obtained yield coefficients for high sludge ages (> 75 d) varying between 0.055 - 0.12 gVSS/gCOD are comparable to those of other MBRs operated at nearly complete sludge retention [2, 6].

A comparative study of two different MBRs operated under various conditions (SRT= 15-140 d, HRT= 5-10 h) fed with a complex synthetic wastewater to eliminate inlet fluctuations showed that elevated SRT operation is feasible and therefore excess sludge reduction is in a considerable degree attainable. For the first time sludge characteristics like viscosity, dewaterability and oxygen transfer were investigated for a very large TS range and correlations including the whole range could be established. It was shown that extrapolating results obtained for a lower TS range to higher TS values can result in an underestimation of up to 50% of the investigated parameter, e.g. viscosity value. The process demonstrates the same removal efficiency as MBR processes with lower SRT values.

A cost model for immersed membrane bioreactors treating municipal wastewater incorporating energy demand for aeration and fouling prevention as well as the related sludge handling costs subject to local conditions is presented. The model presented is suitable for MBR users and is based on a few easily accessible input parameters like operational (HRT, SRT) and biokinetic parameters (yield, decay coefficient) and feed conditions. Only the information for biokinetic parameters and oxygen transfer efficiency vary strongly in literature, therefore the correct choice of these parameters is essential for an applicable model, otherwise the impact of aeration demand is over- or underestimated.

In first simulation studies the model was found to be appropriate to predict the total costs of an immersed MBR, nevertheless some improvements need to be made to be more universally valid. Especially the information of biokinetic parameters as a function of sludge age is needed to have a reliable prediction of the biomass concentration. Furthermore the sludge treatment costs have to be modelled more in detail splitting them into costs for transport, sludge thickening and dewatering and maybe also other sludge treatment routes like anaerobic digestion.

NOMENCLATURE.

- $b$ decay coefficient [d$^{-1}$]
- $C^*$ oxygen saturation concentration [mg L$^{-1}$]
- $C_{set}$ Oxygen conc. in aerated tank [mg L$^{-1}$]
- $E_{pot}$ Potential energy [Wh]
- $ESP$ Excess sludge production [g h$^{-1}$]
- $h$ Depth of aeration device [m]
- $HRT$ Hydraulic retention time [h]
- $K_s$ Half saturation constant [mg L$^{-1}$]
- $P$ Power demand [kW]
- $Q$ Influent flow rate [m$^3$ h$^{-1}$]
- $Q_w$ sludge flow rate [m$^3$ h$^{-1}$]
- $Q_{air}$ Air flow rate [m$^3$ h$^{-1}$]
- $S$ COD concentration influent [mg L$^{-1}$]
- $S_0$ COD concentration effluent [mg L$^{-1}$]
- $SRT$ Sludge retention time [d]
- $t$ Time [d]
- $V$ Volume [m$^3$]
- $X$ Biomass concentration [mg L$^{-1}$]
- $Y$ Yield coefficient [mgMLSS mgCOD$^{-1}$]
- $\alpha$ Dimensionless oxygen transfer coefficient [-]
- $\eta$ Blower efficiency [-]
- $\mu_{max}$ Maximum specific growth rate [d$^{-1}$]
- $\mu_c$ Infinite viscosity [mPas]

REFERENCES.


### 9.4. Impact of the WP on its industry or research sector.

A comparative study of two different MBRs operated under various conditions (SRT= 15-140 d, HRT= 5-10 h) fed with a complex synthetic wastewater to eliminate inlet fluctuations showed that elevated SRT operation is feasible and therefore excess sludge reduction is in a considerable degree attainable. For the first time sludge characteristics like viscosity, dewaterability and oxygen transfer were investigated for a very large TS range and correlations including the whole range could be established. It was shown that extrapolating results obtained for a lower TS range to higher TS values can result in an underestimation of up to 50% of the investigated parameter, e.g. viscosity value. The process demonstrates the same removal efficiency as MBR processes with lower SRT values.

A cost model for immersed membrane bioreactors treating municipal wastewater incorporating energy demand for aeration and fouling prevention as well as the related sludge handling costs subject to local conditions is presented. The model presented is suitable for MBR users and is based on a few easily accessible input parameters like operational (HRT, SRT) and biokinetic parameters (yield, decay coefficient) and feed conditions. Only the information for biokinetic parameters and oxygen transfer efficiency vary strongly in literature, therefore the correct choice of these parameters is essential for an applicable model, otherwise the impact of aeration demand is over- or underestimated.

In first simulation studies the model was found to be appropriate to predict the total costs of an immersed MBR, nevertheless some improvements need to be made to be more universally valid. Especially the information of biokinetic parameters as a function of sludge age is needed to have a reliable prediction of the biomass concentration. Furthermore the sludge treatment costs have to be modelled more in detail splitting them into costs for transport, sludge thickening and dewatering and maybe also other sludge treatment routes like anaerobic digestion.
10. Destruction of organic compounds in sewage sludges suspensions by ultrasound and catalytic wet air oxidation.

10.1. Summary description of project objectives, work performed and end results, elaborating on the degree to which the objectives were reached.

PROJECT OBJECTIVES.
The objectives of this work-package are to efficiently degrade organic compounds in sewage sludge suspensions using heterogeneous catalysts after a pre-treatment by power ultrasound and (or) thermal oxidation in order to break down macromolecules and solubilize the organic solids.

WORK PERFORMED.
Municipal and industrial sewage sludges containing ca. 3 g L$^{-1}$ TOC were subjected to different treatment sequences:

- Ultrasonication (20 kHz, power 0-210W).
- Ultrasonication + batch Wet Air Oxidation (WAO) or Catalytic Wet Air Oxidation (CWAO) at 190-210°C, 37-51 bar air, 1-8h.
- Batch WAO (210°C, 51 bar air, 4h) + batch CWAO of the supernatant (190°C, 37 bar air).
- Batch WAO + continuous CWAO of the supernatant in a trickle-bed reactor.

Different supported metallic catalysts were prepared, fully characterized and used in the CWAO. Platinum and ruthenium were chosen as the active phase. Titanium dioxide, zirconium dioxide and ZrO$_2$-CeO$_2$ mixed oxides were selected supports because they were shown to be stable under the oxidation process operating conditions.

The final suspensions were analysed in terms of residual TOC concentration in the solid, TOC concentration in the liquid phase and overall TOC abatement.

END RESULTS.
Ultrasonic pre-treatments, using a 20 kHz system led to an increase in the solubilized COD and the solubilized TOC, a very severe decrease of the average diameter of the sludge flocs, a disruption of the bacterial cells with release of proteins into the liquid phase, but no clear reduction of the overall organic content. The effect of sonication strongly depends on the nature of the sludge. The municipal sludge was more sensitive to ultrasound than the industrial one, since it is clearly heterogeneous (fibers) and flocs have higher average size.

WAO experiments carried out with or without a sonication pre-treatment also revealed differences between the municipal and industrial sludge. In the case of the municipal sludge only, the transfer of the solid organic compounds slightly increased with the ultrasonic power applied. As expected, WAO largely increased the solubilization of the solid materials. The effect of the pre-treatment on the overall TOC abatement was limited (32-37% for the municipal sludge, 43-47% for the industrial sludge).

A comparison of the results of the CWAO of the sludge in the presence of different noble metal supported catalysts, without or with pre-sonication, revealed that the effect of ultrasounds was a disintegration of the flocs and the formation of finer solid particles with even higher ability to adsorb on the catalyst surface. The beneficial effect of the catalyst on the mineralization of the organic compounds in the liquid phase was then annealed. Finally, the overall conversion of TOC was in the same range with or without pre-treatment.

The final strategy we tested was a combination of a thermal oxidation of the sludge, to ensure sufficient solubilization of the organic material followed by a CWAO of the supernatant. Upon batch experiments, this sequence led a final TOC abatement of the industrial sludge of 80-90% when a Ru catalyst was used. The remaining solid phase contained only ca.3 % TOC after the WAO treatment at 210°C and 70 bar total pressure.
CWAO of aqueous supernatants in a continuous trickle-bed reactor confirmed the high activity and stability of the catalyst for TOC abatement. The final effluent contained only acetic acid. In parallel, nitrogen containing compounds were selectively transformed to dinitrogen and nitrates.

Milestones M10.1 and M10.2 (selection of pre-treatments and reaction conditions and of two catalysts following the criteria of residual TOC in the solid < 5% and TOC conversion > 80% in trickle-bed continuous reactor) were reached.

10.2. Methodologies and approaches employed.

METHODOLOGIES.

Wet air oxidation (WAO), based on the oxidation of pollutants in the liquid phase at high temperature and pressure, in the presence of an oxidizing agent (oxygen), is currently gaining interest, in particular for sewage sludges. The main purpose is the destruction of the particulate organic materials and their conversion into biodegradable compounds and inorganic carbon dioxide. Catalysts are often used in Wet Air Oxidation to improve the process, by enhancing the reaction rate and allowing the use of milder operating conditions. Soluble transition metal salts (such as copper and iron salts) have been found efficient. However they require a post-treatment to be separated from the effluent and recycled. With this respect, heterogeneous catalysts are preferred. Catalysts based on noble metals deposited on stable supports under WAO operating conditions are active and stable catalysts even in the treatment of complex industrial effluents. However, the deposition of solid organic matters present in the sludge at the catalyst surface may rapidly deactivate the catalyst.

To overcome this problem, ultrasonication or (and) thermal oxidation were considered as pre-treatment methods to improve the solubilization of the solid fraction before the catalytic wet air oxidation of the liquid in the presence of metallic solid catalysts. High-power ultrasounds at low frequencies generate intensive cavitation and produce hydromechanical shear forces. As a result an effective disintegration of the insoluble particulate matter and cells is observed, leading soluble molecules and a substantial release of the cell intracellular material into the liquid. Studies were conducted with Pt and Ru metal catalysts, since they are resistant towards leaching. TiO₂, ZrO₂ and mixed CeO₂-ZrO₂ oxides were chosen as supports because they remain stable whatever the reaction conditions encountered in CWAO.

APPROACHES.

Approaches followed during the project are presented on scheme 10.1.

![Scheme 10.1. Approaches employed.](image)

At the beginning of the project, batches of industrial and municipal sludges were collected. Since sewage sludges are fermentable and to be sure to perform the experiments on the same initial effluent, the particulate materials were separated from the suspension by centrifugation. The received “pasty sludge” was
then transferred in pillboxes and stored in a freezer. For each experiment, a given amount of sludge was suspended in water to recreate a suspension containing an initial TOC value of ca. 3 g L⁻¹.

The ultrasonic apparatus was an ultrasonic homogenizer Autotune (VibraCell) with a horn diameter of 13 mm. This device operated at 20 kHz and the maximum applied power was 200W. Batch experiments were performed using 300 mL suspension at 25°C. The ultrasonic power input was determined by calorimetric measurements.

Batch WAO and CWAO studies were performed in a 300 mL Hastelloy autoclave equipped with a magnetically driven stirrer and a heating jacket. After a given reaction time, the whole suspension was recovered and filtered. The solid and liquid phases were subsequently analysed separately.

TOC (Total Organic Carbon) analysis on the solid and aqueous phases were performed using a TOC analyser. The liquid phase was also analysed for solubilized COD, using colorimetric tubes and protein content. A few organic acids in the oxidized liquors were analysed by HPLC, in particular acetic acid. The average particle size of the sewage sludge suspension after sonication was measured using a Malvern Laser Diffraction particle Size Analyzer, which measures materials from 0.02 microns to 2000 microns. The protein content was measured using the so-called modified Lowry method.

10.3. Achievements of the project related to the state of the art.

PRELIMINAR.

Upon sewage sludge Catalytic Wet Air Oxidation, the presence of particulates has been identified as an inhibiting parameter [1]. Therefore the pre-treatment of sewage sludge via mechanical or thermal disintegration shall improve the subsequent CWAO. However, no information was available on the impact of different sludge disintegration degrees on further catalytic processes.

Three different sludges have been used for this study. Two were industrial sludges (STVULBAS and SOTREFI), while the third one was from a municipal wastewater treatment plant (TOULOUSE).

Table 10.1. Analysis of the sludges used in this study (na : not analyzed).

<table>
<thead>
<tr>
<th>Sludge</th>
<th>STVULBAS</th>
<th>SOTREFI</th>
<th>TOULOUSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (%)</td>
<td>35.4</td>
<td>32.2</td>
<td>41.1</td>
</tr>
<tr>
<td>H (%)</td>
<td>5.2</td>
<td>4.6</td>
<td>6.15</td>
</tr>
<tr>
<td>N (%)</td>
<td>5.6</td>
<td>4.9</td>
<td>4.2</td>
</tr>
<tr>
<td>S (%)</td>
<td>1.0</td>
<td>0.9</td>
<td>0.6</td>
</tr>
<tr>
<td>Fe (g/L)</td>
<td>7.5</td>
<td>4.4</td>
<td>0.6</td>
</tr>
<tr>
<td>Ca (mg/l)</td>
<td>3.5</td>
<td>15.6</td>
<td>2.5</td>
</tr>
<tr>
<td>P (%)</td>
<td>2.9</td>
<td>3.9</td>
<td>2.0</td>
</tr>
<tr>
<td>Al (%)</td>
<td>0.2</td>
<td>3.8</td>
<td>2.9</td>
</tr>
<tr>
<td>Na (g/l)</td>
<td>0.6</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>Si (%)</td>
<td>1.0</td>
<td>na</td>
<td>2.9</td>
</tr>
<tr>
<td>Cu (%)</td>
<td>&lt;0.1</td>
<td>0.1</td>
<td>na</td>
</tr>
<tr>
<td>K (%)</td>
<td>0.2</td>
<td>0.9</td>
<td>0.3</td>
</tr>
<tr>
<td>Mg (%)</td>
<td>0.1</td>
<td>0.9</td>
<td>0.3</td>
</tr>
<tr>
<td>Ti (%)</td>
<td>0.7</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

INFLUENCE OF POWER ULTRASOUND AS PRE-TREATMENT PROCESS.

The ultrasonic pre-treatment of TOULOUSE and STVULBAS sludges was studied as a function of the ultrasonic power (50W, 100W, 200W) and exposure time. The parameters analysed were the dry solid content, the solubilized COD, the solubilized and non-solubilized TOC, the dp50 and the total protein content.
The nature of sludge has an important effect, because of their physical differences. The municipal sludge was constituted of sediments from the primary settling tank together with the waste activated sludge. It contains a large quantity of fiber particles and the range of particle size is wide with a bimodal distribution at 79 and 1096 microns. The STVULBAS sludge had a more homogeneous structure with mean particle size of 245 microns. After sonication, the particle size gradually changed and decreased to 70 microns and 4.5 microns for the two sludges.

To compare results with those in the literature, the DD\textsubscript{COD} (degree of disintegration based on COD) was calculated according to the formula:

\[
\text{DD}_{\text{COD}} = \frac{\text{COD}\textsubscript{t} - \text{COD}\textsubscript{0}}{\text{COD}\textsubscript{NaOH} - \text{COD}\textsubscript{0}} \cdot 100\% 
\]

where: \text{DD}_{\text{COD}}: degree of disintegration based on COD, \text{COD}\textsubscript{t}: COD soluble at time \( t \) (g \( \text{O}_2 \cdot \text{L}^{-1} \)), \text{COD}\textsubscript{0}: COD soluble at time zero (g\( \text{O}_2 \cdot \text{L}^{-1} \)), \text{COD}\textsubscript{NaOH}: COD soluble in NaOH solution: total estimated disintegration (g \( \text{O}_2 \cdot \text{L}^{-1} \))

The COD\textsubscript{NaOH} is accepted as the maximum possible soluble COD concentration [2]. The evolution of the DD\textsubscript{COD} as a function of time for different powers is given in Figure 10.2 for Toulouse sludge. In 60 min, 56%, 64% and 80% of DD\textsubscript{COD} have been reached, applying 50, 100 and 200 W, respectively.
The power, the time of reaction and the mass of dry solid were varied, keeping the two other parameters constant. Figure 9.3 shows the degree of disintegration as a function of $E_s$ applied.

![Figure 9.3](image)

**Figure 10.3.** Evolution of DD COD in liquid phase of municipal sludge TOULOUSE solution, with respect to specific energy.

The main conclusions can be summarized as “high power-short reaction time” is more effective than “low power-long retention time”, while keeping the volume small and the concentration below a certain level.

The changes in TOC repartition between the solid and liquid phases were analysed after 90 min sonication. Figure 9.4 shows these results. It was shown that ultrasound did not induce any significant mineralization. Soluble matter concentration increased slightly, whereas particulate matter concentration decreased.

![Figure 10.4](image)

**Figure 10.4.** Change of TOC in (a) municipal sludge ($TOC_0 = 3433$ mg L$^{-1}$) and (b) industrial sludge ($TOC_0 = 2977$ mg L$^{-1}$). (■: TOC in the solid phase, □: TOC in the liquid phase) versus ultrasonic power. The process time was 90 min.

The increase of applied power from 50W to 200W had a positive effect on the solubilization of the organic particles. At 200W, while 19% of the solid in the municipal sludge was solubilized, only 7% of the solid was solubilized in the industrial sludge. The evolution of COD in liquid phase followed the same tendency.

**SYNTHESIS AND CHARACTERIZATION OF CATALYSTS.**

**Ultrasonication and subsequent Catalytic Wet Air Oxidation.**

Different Pt and Ru catalysts containing 3wt.% active phase were prepared on commercial oxide supports (TiO$_2$, ZrO$_2$ and Ce$_{x}$Zr$_{1-x}$O$_2$) via a classical incipient-wetness and liquid-phase impregnation methods using aqueous solutions of metallic salts. Catalysts were reduced before use. They were characterized for metallic dispersion. Most catalysts were very well dispersed with average metal particle sizes less than 4 nm (Figure 10.5), as observed by X Ray Diffraction and Transmission Electron Microscopy (TEM).
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Figure 10.5. Particle size distributions obtained from TEM observations of Pt and Ru catalysts.

Sewage sludges (initial TOC content ca. 3000 mg L\(^{-1}\)) were treated in a batch reactor (Figure 10.6) without or with pre-sonication at different power in the presence or in the absence of a catalyst. Based on previous works, the operating conditions were chosen as 190°C and 37 bar air pressure with different reaction times.

Figure 10.6. Lab-scale batch reactor.

Table 10.2 compares the TOC concentrations in the liquid phase, the solid phase and "overall" suspension and the overall TOC conversion, for some experiments performed on the untreated STVULBAS sludge. Figure 10.7 illustrates these results.

Table 10.2. TOC concentration in the liquid phase, the solid phase and the "overall" suspension as a function of reaction time upon CWAO of STVULBAS sludge. (TOC\(_{0}\) = 3000 mg/L, T = 190°C, 37 bar air pressure, catalyst concentration = 6.67 g/L).

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Without catalyst</th>
<th>3%Ru/ZrO(_2)</th>
<th>3%Pt/ZrO(_2)</th>
<th>3%Pt/CeO(_2)-ZrO(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>liq</td>
<td>sol</td>
<td>susp</td>
<td>conv</td>
</tr>
<tr>
<td>&lt;0 (^a)</td>
<td>246</td>
<td>2754</td>
<td>3000</td>
<td>-</td>
</tr>
<tr>
<td>0 (^b)</td>
<td>1199</td>
<td>1773</td>
<td>2972</td>
<td>0</td>
</tr>
<tr>
<td>0.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>1532</td>
<td>682</td>
<td>2214</td>
<td>25</td>
</tr>
<tr>
<td>4</td>
<td>1417</td>
<td>269</td>
<td>1686</td>
<td>43</td>
</tr>
<tr>
<td>8</td>
<td>1396</td>
<td>179</td>
<td>1575</td>
<td>47</td>
</tr>
</tbody>
</table>

\(^a\) the TOC concentration in the liquid phase and in the suspended matter contents were determined in the initial suspension of 10 g of sludge into 150 ml of distilled water.

\(^b\) TOC concentrations determined after heating the suspension to the reaction temperature (190°C) under Ar under stirring. This point was taken as "zero time".
Figure 10.7. Evolution of TOC concentration in the liquid phase (♦), the solid phase(■), and the “overall” suspension (▲) upon WAO or CWAO of non pre-treated STVULBAS sludge in the absence of catalyst (a), or in the presence of 3%Ru/ZrO₂ (b), 3%Pt/ZrO₂ (c), 3%Pt/CeO₂-ZrO₂ (d).

Heating the suspension to the reaction temperature under argon did not change the overall TOC content in the suspension (3000 mg L⁻¹). The result was a transfer of the organic matter from the solid phase to the liquid phase (from 2754 mg L⁻¹ to 1773 mg L⁻¹). Then, after the introduction of air, the TOC content in the solid phase decreased rapidly, the TOC content in the liquid phase continued to increase during the first hour, and significant mineralization occurred (25-32%). Further mineralization occurred (40-48% after 4h) and a plateau at 47-55% was reached after 8 h. Thus, it appears that the hydrothermal oxidation degrades the solid organic matter in two steps: the hydrolysis of the complex polymeric substances and the bacterial cells, and the subsequent oxidation [3].

Finally, the addition of any solid catalyst prepared did not significantly improve the final TOC abatement. Moreover, the Pt catalysts supported on the CeO₂-ZrO₂ supports gave even higher amounts of residual TOC in the solid phase than in the blank experiment (397 and 387 mg L⁻¹ for two supports with different Ce and Zr ratios compared to 281 mg L⁻¹). These mixed supports with high redox properties and high capacities for oxygen storage and mobility appeared to be attractive to promote the oxygen activation step upon oxidation. Indeed, CeₓZr₁₋ₓO₂ used as support for noble metal have shown higher activity in the oxidation of acetic acid [4,5] or 2-chlorophenol [6,7] in the literature. This negative effect in our case on the transfer from the solid to the liquid phase suggested a strong adsorption of the organics on the solid surface, which, indeed, was higher in the case of CeₓZr₁₋ₓO₂ (150-170 m² g⁻¹ compared to 90-100 m² g⁻¹). The retention of the organic material on the catalyst surface may also explain the absence of any significant increase in the overall TOC conversion.

The effect of sonication on the subsequent CWAO treatment was also examined. Three different sludges were sonicated at different power for one hour and then oxidized at 190°C, 37 bar air during 4 h. Selected results are shown in Table 10.3 for the STVULBAS sludge and Table 10.4 for the SOTREFI sludge.
Table 10.3. Effect of ultrasonication (200W, 1 h) on the STVULBAS sludge subsequent CWAO (TOC\(_0\) = 3000 mg L\(^{-1}\), 190°C, 37 bar air, 6.67 g L\(^{-1}\) catalyst, 4 h).

<table>
<thead>
<tr>
<th>Sonication power (W)</th>
<th>Catalyst</th>
<th>TOC liquid (mg/L)</th>
<th>TOC solid (mg/L)</th>
<th>TOC suspension (mg/L)</th>
<th>Overall TOC conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No</td>
<td>No</td>
<td>1419</td>
<td>277</td>
<td>1696</td>
<td>43</td>
</tr>
<tr>
<td>No</td>
<td>3%Pt/ZrO(_2)</td>
<td>1290</td>
<td>281</td>
<td>1571</td>
<td>48</td>
</tr>
<tr>
<td>200</td>
<td>No</td>
<td>1331</td>
<td>254</td>
<td>1585</td>
<td>47</td>
</tr>
<tr>
<td>200</td>
<td>3%Pt/ZrO(_2)</td>
<td>1255</td>
<td>391</td>
<td>1646</td>
<td>45</td>
</tr>
</tbody>
</table>

Table 10.4. Effect of ultrasonication (200W, 1 h) or Ultra-turrax desintegration on the SOTREFI sludge subsequent CWAO (TOC\(_0\) = 2490 mg L\(^{-1}\), 190°C, 37 bar air, 6.67 g L\(^{-1}\) catalyst).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>TOC liquid (mg/L)</th>
<th>TOC solid (mg/L)</th>
<th>TOC suspension (mg/L)</th>
<th>Overall TOC conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No pre-treatment</td>
<td>No catalyst</td>
<td>1393</td>
<td>66</td>
<td>1399</td>
</tr>
<tr>
<td>No pre-treatment</td>
<td>3%Pt/ZrO(_2)</td>
<td>1225</td>
<td>241</td>
<td>1467</td>
</tr>
<tr>
<td>No pre-treatment</td>
<td>3%Ru/ZrO(_2)</td>
<td>1133</td>
<td>202</td>
<td>1335</td>
</tr>
<tr>
<td>Ultrasonication pre-treatment at different power</td>
<td>No catalyst</td>
<td>1125</td>
<td>98</td>
<td>1223</td>
</tr>
<tr>
<td>Ultrasonication pre-treatment at different power</td>
<td>3%Pt/ZrO(_2)</td>
<td>1018</td>
<td>270</td>
<td>1288</td>
</tr>
<tr>
<td>3600 rpm</td>
<td>No catalyst</td>
<td>1445</td>
<td>70</td>
<td>1515</td>
</tr>
<tr>
<td>3600 rpm</td>
<td>3%Pt/ZrO(_2)</td>
<td>1180</td>
<td>180</td>
<td>1360</td>
</tr>
<tr>
<td>3600 rpm</td>
<td>3%Ru/ZrO(_2)</td>
<td>1243</td>
<td>166</td>
<td>1409</td>
</tr>
<tr>
<td>11200 rpm</td>
<td>No catalyst</td>
<td>1330</td>
<td>70</td>
<td>1400</td>
</tr>
<tr>
<td>11200 rpm</td>
<td>3%Pt/ZrO(_2)</td>
<td>1207</td>
<td>180</td>
<td>1387</td>
</tr>
<tr>
<td>11200 rpm</td>
<td>3%Ru/ZrO(_2)</td>
<td>1138</td>
<td>185</td>
<td>1323</td>
</tr>
<tr>
<td>20000 rpm</td>
<td>No catalyst</td>
<td>1307</td>
<td>81</td>
<td>1388</td>
</tr>
<tr>
<td>20000 rpm</td>
<td>3%Pt/ZrO(_2)</td>
<td>1242</td>
<td>170</td>
<td>1412</td>
</tr>
<tr>
<td>20000 rpm</td>
<td>3%Ru/ZrO(_2)</td>
<td>1184</td>
<td>208</td>
<td>1392</td>
</tr>
</tbody>
</table>

After ultrasonication of the STVULBAS sludge and in the absence of a catalyst, the solid TOC concentration remained about constant and the liquid phase mineralization was only slightly decreased after sonication. As a consequence, no clear effect of ultrasonication on the overall TOC conversion was observed after WAO. On the other hand, surprisingly, no increase in the TOC conversion was achieved after CWAO of the pre-sonicated sludge, compared to the CWAO treatment alone. Instead, the use of a catalyst increased the TOC content in the solid. This result suggested again that heterogeneous catalysts behave as adsorbents for the sludge, as it was observed previously with the high surface area CeO\(_2\)-ZrO\(_2\)- supported catalysts.

This effect was also observed upon CWAO of the SOTREFI sludge, performed in the same conditions. The use of a catalyst did not lead any significant increase in the overall TOC abatement. However, it seems that the ability of the catalyst to adsorb the organic matter is more important. Indeed, the concentration of TOC in the solid was 66-98 mg L\(^{-1}\) after WAO, while this value reached 241-270 mg L\(^{-1}\) after CWAO in the presence of platinum catalysts.

This was further observed in the experiments performed after mechanical disintegration of the SOTREFI using an Ultra-turrax apparatus. The results shown in Table 4 as a function of the rotation speed, clearly show that the mechanical pre-treatment did not significantly modify the TOC concentrations in the liquid and solid phases after WAO. Whatever the rotation speed, no improvement in the overall conversion was noted. However, again, in the presence of any heterogeneous catalyst, the TOC content in the solid was significantly higher.

Both after ultrasonication or Ultra-turrax disintegration and even though an efficient disintegration of the sludge was observed, the organic solids were only partly solubilized and the subsequent WAO or CWAO treatments did not give higher TOC abatements. Particulate organic compounds were not sufficiently converted into soluble compounds to avoid the deposition of finely divided solids onto the heterogeneous
catalyst surface and CWAO was not improved. The benefits of the catalyst are significantly annealed by the adsorption of solids.

**Ultrasonication and subsequent Wet Air Oxidation (WAO).**

The effect of the ultrasonication power on the subsequent WAO process was studied in more details, using the STVULBAS and TOULOUSE sludges.

Different behaviours were evidenced for the two sludges. After 90 min, sonication at different powers did not induce mineralization. However, the carbob partition between the liquid and solid phases varied with the specific supplied energy Solubilization occurred and reached 7% maximum for the STVULBAS sludge and 19% maximum for the TOULOUSE sludge. These differences were attributed to the heterogeneous nature of the municipal sludge (fibers) and the higher average size of the flocs.

WAO of the non-sonicated and sonicated sludges also revealed differences between the two sludges (Figure 10.8). While the solid TOC was reduced in the municipal sludge as the sonication power increased, sonication had no effect in the case of the industrial sludge.

![Figure 10.8](image)

**Figure 10.8.** Effect of pre-sonication on the subsequent WAO treatment (190°C, 37 bar air, 4h) of the municipal TOULOUSE sludge (left) and the industrial STVULBAS sludge (right).

**Influence of a thermal WAO pre-treatment on the subsequent CWAO of the supernatant, in a batch reactor.**

To try to solve the inherent difficulties of treating sludges containing solid organic particles, a two step process was tested. The sludge was first pre-oxidized in the absence of any catalyst and the oxidized liquor was then further treated in the presence of a catalyst. The WAO pre-treatment was performed at two different temperatures 190°C, 37 bar air and 210°C, 51 bar air for 4 h. While after WAO treatment at 190°C the residual solid still contained 15% TOC, more severe conditions (210°C) yielded a solid containing less than 5% TOC. CWAO results of the oxidized liquor are given in Figure 10.9 for TOC and TN (Total Nitrogen) abatements.

![Figure 10.9](image)

**Figure 10.9.** TOC and TN abatements upon catalytic oxidation of the supernatant received from a first thermal pre-oxidation of the STVULBAS sludge (210°C, 51 bar air, 4h).

While in the absence of catalyst, no further TOC and TN abatement was observed, the addition of 3%Pt/ZrO₂ or Ru/ZrO₂ led a final TOC conversion higher than 80% and nearly complete TN abatement. These two catalysts were not only able to mineralize the organic carbon, but also to transform the remaining nitrogen selectively into dinitrogen.

The capacity for supported noble metal catalysts to convert nitrogen-containing compounds was previously mentioned in the literature. However, studies usually dealt with model compounds (ammonium salts,
The use of these catalysts for complex effluents was never described. These new results further demonstrate their very promising properties.

Our results showed that with a two step treatment, combining a first WAO of the suspension at T > 210°C (to ensure a sufficient transfer of the solid organics to the liquid phase so that the final solid contains less than 5% TOC) with a CWAO of the supernatant, a 85-90% overall TOC conversion could be attained.

**OPERATION IN A CONTINUOUS TRICKLE BED REACTOR.**

*Stability in the continuous CWAO, following WAO of the sludge suspension.*

Further work was performed to test the catalyst stability upon CWAO in a continuous reactor (trickle-bed reactor, 15 cm length, 1 cm inner diameter), (Figure 10.10). A batch of catalyst was specifically prepared using a TiO₂ shaped support (St Gobain 90 m² g⁻¹) according to procedures developed for powder catalysts.

![Trickle-bed reactor used for the catalytic continuous experimen.](image)

All liquids from WAO batch experiments on the TOULOUSE and STVULBAS sludges were collected separately (2 L each, TOC₀ ca. 1 g L⁻¹) and subsequently treated in a continuous reactor at 190°C, 50 bar air over 1.5 g of 3%Ru/TiO₂. The initial conditions were a liquid flow rate of 0.5 mL min⁻¹, a gas flow rate of 5 NL h⁻¹. Contact time was increased by recirculation of the treated effluent. The results are shown on Figure 10.11 for the TOULOUSE sludge, and in Figure 10.12 for the STVULBAS sludge.

![CWAO in a continuous reactor of the supernatant recovered from the WAO of the municipal sludge (TOULOUSE). TOC₀ = 1030 mg L⁻¹, F_liquid = 30 mL h⁻¹, F_gas = 5 NL h⁻¹, 190°C, 50 bar air, 1.5 g 3%Ru/TiO₂ catalyst.](image)

![CWAO in a continuous reactor of the supernatant recovered from the WAO of the industrial sludge (STVULBAS). TOC₀ = 1013 mg L⁻¹, F_liquid = 30 mL h⁻¹, F_gas = 5 NL h⁻¹, 190°C, 50 bar air, 1.5 g 3%Ru/TiO₂ catalyst.](image)

CWAO of both supernatants led to a large TOC abatement which increased with increasing contact times. The final effluent only contained acetic acid, and nitrogen was transformed to N₂ and nitrates. The catalyst demonstrated a remarkable stability.

These experiments demonstrate that WAO (after pre-sonication or not) can be used as a pre-treatment of the sludge. The residual solid contains less than 5% TOC, which means that the filtered cake from the process could be directly disposed of at landfill sites. The supernatant can then be treated catalytically with high mineralization degrees. TOC in the final effluent mainly consists of acetic acid and the organic and ammonium nitrogen are converted into dinitrogen and nitrates.
To summarize, the work performed in WP10 provided new and valuable scientific data on noble metal catalysts to be used in the CWAO of complex effluents and demonstrated the efficiency of such catalysts in the CWAO of supernatants obtained after a first WAO pre-treatment.

REFERENCES.


10.4. Impact of the WP on its industry or research sector.

Sludge thermal processing attracts more and more attention because of on-going discussions on safe sludge disposal methods according to legal requirements. In this context, Wet Air Oxidation (WAO) has become an economically viable alternative. The process can be defined as the oxidation of substances, which are present either in the liquid or in the suspension, with the use of an oxidant (oxygen or air) at elevated pressure and temperature. The insoluble organic matter is converted into simpler soluble organic compounds that are further oxidized. Currently there are more than 200 plants operated around the world, the majority being dedicated to the treatment of sewage sludge [1]. Some industrial applications were reviewed by Luck et al [2] and Kolaczkowski et al [3].

To achieve optimum results, a catalyst may be added. The objective is then to reduce the operating temperature and pressure and/or to treat pollutants that cannot be destroyed during non-catalytic WAO. Despite, successfull laboratory applications, the absence of stable catalysts has prevented Catalytic WAO (CWAO) from being widely employed at industrial wastewater treatment plants. The main reasons are that soluble catalysts have to be removed from the effluent in a subsequent step, while the heterogeneous catalysts have to maintain their activity for sufficiently long periods. Soluble catalysts such as copper salts were very effective on several organics [4-7]. Such catalysts were used in the Ciba-Geigy (Cu²⁺ separated as copper sulphide) and Loprox (Fe²⁺) processes for industrial effluents. They are presently used in the MINERALIS® and ATHOS® processes dedicated to sewage sludges [8]. Mixtures of metal oxides (Cu, Zn, Co, Mn, Bi) are reported to exhibit good activity, but leaching of these catalysts was detected [4,9,10]. On the contrary, heterogeneous catalysts based on noble metals deposited on stable supports are much less sensitive to leaching [11-15]. Considerable efforts were focused on reducing the unwanted catalyst deactivation. Stable supported catalysts with high activity towards model pollutants as well as industrial effluents (Kraft paper pulp bleaching effluent, olive mill wastewater) have been successfully synthesized and tested at the laboratory scale. Pd, Pt and Ru have received most attention. The Nippon Shokubai-LC and Osaka Gas processes in Japan use monolith reactors with Pt-Pd/TiO₂-ZrO₂ catalyst or mixtures of titania or...
zirconia-titania supported metals (honeycomb or spheres) [1,2]. These catalysts remain, however, relatively expensive materials and to be used, they must demonstrate high stability. In the case of sewage sludges, the presence of solid organic materials has been identified as an inhibiting parameter.

Ultrasonic irradiation might be used to increase solubilization. In the last years, ultrasounds have also gained attention in environmental science and technology as a non-conventional method for improving wastewater and sludge treatment processes. Ultrasounds appeared as a possible technology for the treatment of sludges in the 90's. Ultrasounds have been studied at the laboratory, the pilot and more recently at the industrial scales. Many studies concerning the application of ultrasounds focused on the anaerobic digestion process at biological wastewater treatment plants. Due to micro-scale bubble explosions caused by ultrasonic waves, the structure of sludge flocs was effectively destroyed, cells underwent lysis and, in a subsequent stage, part of the insoluble organic particulates could be transferred to the liquid phase [16-18]. The use of pre-treated sludge significantly improved the COD removal efficiency and the biogas production in anaerobic digesters. Recent developments of high power transducers allowed the treatment of large amounts of sewage sludge. Since a few years, a few firms are commercializing ultrasound homogenizers for the pre-treatment of sewage sludges before anaerobic digestion (Hielsher GmbH, Sonix, Sonotronic GmbH...).

The use of sludge disintegration as a pre-treatment technique may however not be limited to sludge digestion. Sludge disintegration may also be a valuable option before CWAO. Thermal lysis may be another option. Up to now, no reports have been published on possible various pre-treatments before CWAO. Accordingly, the objective of this study was to investigate the effects of various pre-treatments (ultrasonic and/or thermal) on sludge solubilization, the mineralization enhancement upon CWAO and the catalyst stability. This work elucidated experimentally the effects of ultrasonic treatments on the physical and chemical properties of two waste-activated sludges before further catalytic wet air oxidation (CWAO) in the presence of heterogeneous platinum and ruthenium catalysts.

The industry and research sector dealing with the catalytic wet air oxidation of complex effluents will benefit from the knowledge developed in this project. It is likely that these data will be important to decide, whether soluble or solid catalysts shall be preferred. Some drawbacks of the CWAO have been outlined: organic particles in the sludge get deposited on the catalyst surface. The problem of solid deposition is even more stronger after disintegration of the sludge since finer particles are produced. However, it has been shown that CWAO may be a promising technology for abatement of organic pollutants when dissolved. An alternative may be recommended in the case of sewage sludges: the liquid phase might be enriched by performing a thermal WAO treatment before the oxidized liquor will is submitted to CWAO to transform the organic compounds into biodegradable molecules. The use of a monolithic reactor could also allow to overcome this problem. Luck et al., [19] reported for instance the use of a 5%CuO catalyst deposited on a titania monolith with honeycomb structures containing square channels with a width of 3.56 mm and a wall thickness of 0.65 mm for the oxidation of waste streams containing sludges at 235°C, 40 bar. COD removal reached up to 74%, while in the blank noncatalytic tests it was 58%. However, copper was leached from the catalyst. The Nippon Shokubai process (NS-LC) involves a Pt-Pd/TiO2-ZrO2 honeycomb catalyst which is claimed not to be sensitive to the deposition of solids on the catalyst surface [2,20].

11. **Excess sludge reduction by dewaterability.**

11.1. **Summary description of project objectives, work performed and end results, elaborating on the degree to which the objectives were reached.**

**PROJECT OBJECTIVES.**

The upgrade of wastewater treatment plants by filtration and sludge dewatering in order to solve a sludge overload problem in a biological system.

To remove 50-70% of the suspended solids in the influent wastewater and at the same time dewater it.

To reduce drastically the load on the biological process and thus increase the capacity of the WWTP.

**WORK PERFORMED.**

The dewatering unit section was constructed and tested, hereby changing and testing various designs of the dewatering conveyor/screw. Secondly the plant setup was designed, and a test program and scheme was developed by guidelines and advice from Technical Universitaet Berlin. The equipment and consumables for the pilot unit was purchased and the pilot unit, pipes, valves, sample and data collection tools were purchased and finally the plant was built and mounted according to the planned design and the test program.

The full scale test plant was built at an existing primary treatment WWTP, and biological sludge was collected from a small biological wastewater treatment plant. This gave us the opportunity to add various concentrations of bio sludge, and dewatering and hydraulic capacity was tested for 5 different mixtures of raw sewage and biological sludge.

**END RESULTS.**

The dewatering units were tested separately with primary sludge only. By altering the length and the angles of the screw elements, the full scale tests show 30-35% TS or more in the primary sludge. Individual tests showed even 45% TS in the sludge.

The dewatering ability declined from 32% to 28-29,5% TSS when raw sewage and biological sludge was mixed at 1:1, calculated by TSS. For higher concentrations, up 1:8, of biological sludge (8 times more TSS from bio sludge than from raw sewage) there was no significant difference in the dewatering ability.

The hydraulic capacity declined by 1/3 when the concentration of biological sludge TSS exceeded 5 times the normal concentration in raw sewage. This means that the hydraulic capacity will be retained for the actual mixtures of sewage and bio sludge.

When the sludge from the bio reactor/clarifier was fed back to an equalisation tank in front of the filtration, and the mixture of biological/was sludge and raw sewage was fed through the Salsnes Filter fine mesh sieve, the total amount of sludge decreases by 94%. The biological load on the biology process was calculated to be between 34 – 40% compared to the original and traditional design. And the savings and ROI will be considerable, even for very low sludge handling and treatment costs.

11.2. **Methodologies and approaches employed.**

**THE SALSNES FILTER TECHNOLOGY.**

Sketches of a Salsnes Filter sieve unit are shown in Figure 11.1. The wastewater flows through the inlet tube (1), filters through an endless wire cloth and 40 to 80 % of the SS is removed. From the back of the wire cloth filtered water flows out through the outlet tube (3). The wire cloth rotates as the arrows show. The cloth transports the separated SS (sludge) to the air cleaning device (9) where compressed air blows the sludge down into the sludge compartment (8). First stage of dewatering is done by gravity during transport to the screw compartment. The screw conveyor pushes the sludge forward to a compressing cylinder (18) where further dewatering is done. A pressure transmitter (4) measures the level of incoming water and this information is used to vary the speed of the wire mesh cloth to achieve optimum performance at variable flow rates and variable influent SS concentrations.
EXPERIMENTAL INVESTIGATIONS.

In biological wastewater treatment large amount of waste activated sludge is produced which is difficult and expensive to handle and dispose. For sludge volume reduction, thickening and dewatering is usually practised. Methods applied for sludge thickening to a dry solids content of about 6% are gravity, dissolved air flotation and centrifugation. Further sludge dewatering up to a dry solids concentration of 25-30% is normally done by a filter press, an extruder or a centrifuge. However, these processes usually have several disadvantages such as large footprint, low thickening efficiency or high energy cost.

In this study the Salsnes Filter fine mesh sieve unit in the feed line is used for sludge thickening and dewatering (see Figure 11.2). From literature (Berg 2004, Paulsrud 2005, Rusten 2005) it is well known that the Salsnes Filter fine mesh sieve unit with integrated dewatering is a very effective alternative for primary treatment with a BOD removal efficiency of approx. 40-60% and a TSS removal efficiency of approx. 60-70%.
The biological WWTPs that were approached for the full scale trials had all too low inflows to make any significance for the tests. The space for additional equipment at the WWTPs was also limited, and since the trials were to be conducted during wintertime in Norway, all had to be indoors. One large WWTP that was approached did not have the relevant technology for our purpose (biology). The full scale test plant therefore had to be constructed and built at an existing primary WWTP, were the biosludge from a biological WWTP was collected and supplied in significant amounts. A flowsheet of this experimental set-up is shown in Figure 3. The raw sewage had a BOD of 530 mg/L and a TSS concentration of 465 mg/L. The inflow loads to the Salsnes Filter Unit could be controlled by varying the mixing ratio of raw sewage and waste activated sludge. Mixing ratios of TSS raw sewage/ TSS activated sludge from 1:1 up to 1:8 were investigated. The TSS concentration of waste activated sludge was 10500 mg/L.

![Figure 11.2. Basic theory for tests and calculations.](image)

Sampling and analysis was performed using regular industrial size samplers, volume and capacity was measured by timers and volume measurement instruments.

![Figure 11.3. Experimental Setup.](image)

The scope of test parameters for the test points in Figure 11.3 were:

1. TSS and flow.
2. TSS and flow.
3. Mixing ratio and holding time.
4. TSS.
5. DS and weight.
6. TSS and flow.

### 11.3 Achievements of the project related to the state of the art.

**ACHIEVEMENTS.**

In Figure 11.4 the influence of the Salsnes Filter as well as the influence of the Salsnes Filter combined with a sludge recirculation is shown. Simply the Salsnes Filter reduces the BOD and the TSS by 50.9 and 72 %, respectively. Therefore the sludge load for the biological stage is reduced dramatically resulting in a design of a smaller aeration tank compared to the initial BOD. Furthermore, an overload of an existing plant can thus be avoided or minimised by introducing the Salsnes Filter unit in the feed line of a WWTP.
Increasing the sludge recycle certainly results in a higher BOD at the inlet of the Salsnes Filter. Nevertheless up to a specific sludge recycle of 1:1.6 the remaining BOD after the Salsnes Filter is still lower than the initial BOD of the raw sewage. Therefore a large amount of waste activated sludge can be dewatered by the Salsnes Filter unit without changing the load for the biological stage compared with the raw sewage. The TSS removal efficiency with sludge recirculation varies between 60-75% and the BOD removal efficiency between 30-48%.

In Figure 11.5 the Dry Solids Content for the different sludge recirculation ratios is given. After dewatering the raw sewage with the Salsnes Filter unit the dewatered sludge has a dry solid concentration of 32%. This value slightly decreases to 28% by a partial recirculation of waste activated sludge, which is still a very good value for dewatered sludge. A further increase of waste activated sludge recirculation does not change the dry solids content of the dewatered sludge.

**Figure 11.4.** Concentration of BOD and TSS at the inlet and outlet of the Salsnes Filter unit.

**Figure 11.5:** Dry Solids content for the different recirculation ratios.

**CONCLUSIONS.**

Raw sewage pre-treatment somehow is not unusual, but raw sewage pre-treatment combined with WAS dewatering by recycling the secondary sludge from the clarifier has not been tested in full scale operation so
far. The project has documented that the Salsnes technology is capable of dewatering a mixture of raw sewage and biological sludge at high concentrations of TSS from the biology process/clarifier. Using the Salsnes Filter unit the following results were obtained:

(1) The dewaterability of the influent does not deteriorate when a part of the excess sludge is recycled to the Salsnes Filter.

(2) The Salsnes Filter retains about 75%-80% of the recycled sludge. The remaining 20-25% is passing the filter and is entering the biological stage of the wastewater treatment plant. The influence of the increased TSS after the Salsnes Filter on the biological process needs to be further investigated.

(3) The flowrate of dewatered sludge taken out of the Salsnes Filter duplicates when a part of the excess sludge is recycled to the Salsnes Filter.

REFERENCES.


Tiendeholmen WWTP. Aquateam report 00-045, October.


11.4. Impact of the WP on its industry or research sector.

In standard configuration the Salsnes Filter rotary belt sieves are outfitted with an integrated dewatering unit (screw press) that dewater the primary sludge at municipal wastewater treatment plants to typically 30% total solids (TS) (Paulsrud, 2005). This means that Salsnes Filter primary treatment replaces primary sedimentation tanks, sludge thickeners and sludge dewatering in a conventional primary treatment plant. (Rusten 2005)

The traditional impact of the Salsnes Filter alternative is that only 1/10 of the space is required, compared to sedimentation tanks. Furthermore, the investment cost of the Salsnes Filter is expected to be less than half the costs of alternative technology.

The most obvious impacts of our full scale trials and the achievements:
• 60-66% calculated increase of capacity at biological plants will contribute to solving overload problems with practically no additional space required.

• At optimized conditions up to 94% reduced sludge volume will cut transportation and disposal problems. Salsnes Filter has also developed an integrated unit for sludge stabilisation that allows the sludge to be used for fertiliser etc directly. (Not a part of the Removals project)

• The power requirement for aeration will be reduced by 1/3. After the City of Enderby in Canada installed Salsnes Filter rotating belt sieve at their biological wastewater treatment plant the saw a dramatic reduction in aeration demand. The aeration power consumption was calculated based on the experience from Enderby, and the conclusion was 1/3 reduced power requirement. (Rusten 2005)

• The return on investment due to savings in sludge handling, transportation, disposal costs, etc will have significant impact on the industry and contribute to savings in the public sector of wastewater treatment. The figure below indicates the ROI by varying sludge handling costs, from installing Salsnes Filter rotating belt sieves.
12. **Production of activated carbon from sludge.**

12.1. **Summary description of project objectives, work performed and end results, elaborating on the degree to which the objectives were reached.**

**PROJECT OBJECTIVES.**

Produce and characterise sludge-based adsorbents (SBAs)/catalysts under different experimental conditions.

Establish cause-effect relationships between the characteristics of sludge-based adsorbents and the performance in different wastewater treatment applications.

**WORK PERFORMED.**

In order to achieve the first objective, three key activities were undertaken: the collection of an array of different sludge samples; the preparation of SBAs through the use of both established and novel pathways; the characterisation of the SBAs. Sludge samples from a total of eight different wastewater treatment plants (WWTPs) were collected. However, most of the adsorbent preparation work was conducted using two, UK sourced, sludge samples: DRAW (dewatered, raw) and DMAD (dewatered, mesophilic anaerobically digested). Three different techniques were employed to prepare adsorbents from these sludge samples: carbonisation; physical activation; chemical activation. A range of different characterisation techniques were employed, but the fundamental parameter used to evaluate the SBAs was the BET surface area: this is generally regarded as being the principal measure of an activated carbon’s utility.

In order to achieve the second objective, a range of SBAs were sent to the project partners for evaluation in their respective wastewater treatment processes under investigation. Feedback on the SBAs’ performance was then relayed to the leader of this WP (P14 - ICL). The data received was used to ascertain which characteristics were most desirable for each application. Tests conducted by ICL were also used to determine the most promising SBAs’ capacity for adsorbing specific contaminants, notably, phenol, methylene blue and bisphenol A (BP-A - a common endocrine disrupting chemical (EDC)).

**END RESULTS.**

First objective. This objective has been completed. The full range of experimental conditions that may be used to produce SBAs by each of the production techniques have been investigated. The SBAs produced have all been characterised. For carbonisation, it has been ascertained that the optimum carbonisation temperature for maximising the BET surface area is 900-1000 °C. The high variation reflects the fact that this figure is sludge dependent. The maximum BET surface area obtained was ca. 155 m²/g. Carbonisation is the most effective technique for producing highly alkaline SBAs. The maximum BET surface area obtained by physical activation, using steam as the activant, was ca.270 m²/g. The optimum activation temperature is 838 °C and the optimum dwell time is sludge dependent, but is typically 70-80 mins. The maximum BET surface area obtained by chemical activation was 1979 m²/g and the results suggest that surface areas in excess of 2000 m²/g are achievable. The most effective chemical activation reagent is K₂CO₃. The DRAW sludge was the best SBA feedstock of the different sludge samples investigated.

Second objective. This objective was also completed in its entirety. It was found that for applications involving the adsorption of phenol, BP-A and by inference, most common phenolic compounds, SBAs with a high surface area (i.e., > 500 m²/g) were most appropriate; i.e., SBAs produced by chemical activation. However, SBAs produced by physical activation were also suitable if they were washed with hydrochloric acid (HCl). This served to lower their ash (inorganic) content. The porosity is primarily associated with the organic content. Hence, raising the organic to inorganic ratio resulted in a rise in the surface area. For the catalytic wet air oxidation (CWAO) treatment of phenolic compounds (WP13/WP14), the surface area was not such a critical parameter. Thus, the performance of untreated SBAs produced by the physical activation of DRAW sludge was found to be acceptable. However, these SBAs exhibited a low attrition resistance and a high propensity towards leaching. Thus, prior to use, it was necessary to subject these SBAs to a combined hardening and leaching mitigation process. For the use of SBAs as biofilters for the elimination of industrial waste gas (WP16), it was found that only the external surface was of importance: the internal surfaces were not accessible to the micro-organisms. For the adsorption of organic dyes (WP15), the mesoporosity was found to be the critical factor. A key finding was that, due to their high mesoporosity,
SBA produced by the physical activation of the DRAW sludge exhibited a higher adsorption capacity than the reference carbon.

12.2. Methodologies and approaches employed.

SLUDGE PREPARATION.

The two UK sludge samples employed were: Dewatered, RAW filter cake (DRAW), sourced from Little Marlow WWTP, UK and Dewatered, Mesophilic Anaerobically Digested (DMAD) sludge, which was obtained from Ashford WWTP, UK. Both samples were sterilized at 121ºC for 15 minutes (Priorclave direct steam autoclave, London, UK). They were crushed to below 10 mm using a cross beater mill (Glen Creston, London, UK) and stored in air tight containers prior to further use. The non-UK sludge samples employed are as follows: dewatered, aerobically digested, secondary biological sludge with added organic polymer coagulant (DSBS), from Nantes, France; a mixture of primary sludge stabilised by anaerobic fermentation and excess sludge stabilised by aerobic digestion (KAN), from Kalisz, Poland; the limed form of KAN sludge (KAW), mesophilic anaerobically digested sludge (GOS), from Lodz, Poland; thickened, primary, municipal sewage sludge seeded with a mesophilic anaerobic digested sewage sludge and then digested in a laboratory scale, fermentative bio-reactor for hydrogen production (GLAM), from Glamorgan, Wales; sludge obtained from a lab-scale membrane bio-reactor with enhanced phosphorous removal (BERLIN), from Berlin, Germany. All sludge samples were dried to constant weight at 105-110 ºC before utilisation. After drying, the non-UK sludge samples were crushed below 9.5 mm in size using a pestle and mortar prior to use: the relatively small quantities in which these samples were provided discounted the use of the cross beater mill.

SLUDGE CARBONISATION/ACTIVATION.

Carbonisation/physical activation.

The carbonised and physically activated SBAs were prepared using a Carbolite 11/150 laboratory scale rotary furnace (Carbolite, UK). For each run, 210 g of prepared sludge was loaded into a cylindrical quartz reactor, 4.5 litres in capacity, which was set to rotate at 10 rpm. This was heated at a rate of either 5 or 10 ºC/min to the desired temperature, under a nitrogen flow of 500 ml/min. For steam activation, once the desired temperature was reached, water was directly injected into the reactor using a peristaltic pump at a flow rate of 0.7 g/min and isothermal conditions were maintained for the specified activation period. Subsequently, the furnace was automatically cooled down to room temperature.

Chemical activation.

The sludge samples were utilised in three forms: untreated (i.e., wet), dried (105 ºC to constant mass) and carbonised. Two different reagent impregnation methods were employed: wet impregnation and dry impregnation. During dry impregnation, the sludge was mixed directly with the reagent: no water was added. Under wet impregnation, the sludge was mixed with the reagent and water was added to the mixture to aid the dissolution of the reagent. The ratio of reagent to sludge was 1:1 (by dry basis). Before being activated, all of the impregnated samples were dried at 105 ºC for a minimum of 12 hrs (i.e., overnight). After drying the untreated sludge samples were crushed below 2 mm and again dried overnight before being activated: this was necessary because after drying the sludge-reagent mixture was highly agglomerated. The quantity of dried material loaded into the crucible was 30 g: for each activation experiment, one crucible was loaded into the reactor. The crucible and reactor were both made from Alsint (Multi-lab, Newcastle (UK)). The reactor was heated in a Carbolite CTF 12/65 horizontal tube furnace (Carbolite, UK). During activation a constant flow of 500 ml/min of N2 into the reactor was maintained. The recovered SBAs were washed by being placed in a beaker to which was then added, at a ratio of 20 ml/g of SBA, either HCl (concentrations of 2, 4 and 5 M were investigated) or distilled water: the beaker’s contents were subsequently heated for 1 hr at 80-90 ºC or boiling point, before being filtered using Whatman No. 1 paper. The carbon recovered on the paper was rinsed until the filtrate exhibited a constant pH.

SAMPLE CHARACTERISATION.

Prior to characterisation the SBAs were crushed and sieved to a particle size below 150 μm. Their surface area and porosity was characterised using a Coulter Omnisorp® 100 (Beckman-Coulter, UK). Prior to analysis, the SBAs were degassed at 150 ºC (250 ºC was employed for the chemically activated SBAs) for
7-8 hours until a pressure below 10-5 Torr was reached. Their N₂ adsorption adsorption and desorption isotherms were obtained at liquid nitrogen temperature. From the adsorption isotherms the BET surface area (Brunauer et al., 1938) and t-plot surface area (Lippens and deBoer, 1965), which indicates the mesoporosity and macroporosity of the activated carbon, were determined. The micropore surface area was determined by subtracting the t-plot surface area from the BET surface area. The ash content of the carbons was measured using the method prescribed by ASTM standard D 2866-94. The pH of the SBACs was determined using a method derived from Bagreev, et al. (2001), whereby, after being ground and dried for 3 hrs at 150 °C, 0.4 g of the sample was added to 20 ml of deionised water. The mixture was mechanically agitated for 24 hrs and after the removal of the SBACs by filtration, the pH of the recovered solution was measured using a pH meter (Fisherbrand Hydrus 500 (Fisher Scientific, UK)) equipped with a VWR, epoxy, gel, pH electrode (VWR, Lutterworth, Leicestershire, UK). The phenol, bis-phenol A and methylene blue uptakes of the SBAs were all assessed by placing a fixed mass of SBA into a fixed volume of a solution of the compound. After a fixed period of time, the UV absorbance of each sample-solution mixture was measured at a wavelength that corresponded to the compound’s peak absorbance: a UV spectrophotometer (UV 2401, Shimadzu, Japan) was utilised for this analysis. The spectrophotometer was calibrated using a series of solutions of the compound that were prepared using different concentrations: these were chosen to reflect the range of possible concentrations in the sample solutions. Thus, from the absorbance values for the sample solutions it was possible to determine the concentration of the compound remaining in the solution and thus, the amount adsorbed by the SBA. The Ball Pan Hardness method was based upon the ASTM method D 3802-79 (ASTM, 1994) which enables the assessment of a sample’s resistance to particle size degradation under service conditions. The 0.5-2 mm size fraction of the test carbon was used in each test. The carbon, hydrogen and nitrogen content was determined using a Carlo-Erba EA1108-CHNS analyser by MEDAC Ltd, UK.

**HARDED CARBON PREPARATION.**

The hardened carbons were prepared by milling the carbonised (1 hr at 700 °C under N₂) or steam activated DRAW sludge to below 45 μm. This material was then mixed with a binder and an appropriate solvent. Once the mixture exhibited sufficient signs of agglomeration it was then pelletised by means of either a manual extruder or a uni-axial hydraulic press operating at a pressure of 850 kg/cm². The pellets were dried for 4 hrs at 105 °C. Subsequent to drying, some of the pellets were steam activated as described previously.

**REFERENCES.**


**12.3. Achievements of the project related to the state of the art.**

**PRODUCTION OF HIGH SURFACE AREA SBAs.**

It has been established that it is possible to produce, by chemical activation, SBAs with BET surface areas in excess of 2000 m²/g. The highest BET surface area achieved thus far is 1979 m²/g and the results indicate that higher surface areas are readily achievable. This figure is particularly significant because it was obtained using a reagent:sludge ratio of 1:1: some other studies on the chemical activation of sewage sludge have resorted to ratios of 3:1 or greater (Bagreev et al., (2001), Ros, et al., (2006)). Low ratios are advantageous...
because they make the process more economically attractive through reducing the quantity of reagent required and hence the operating costs.

A key factor in the scale of the BET surface area obtained here has been the use of $K_2CO_3$ as the chemical activation reagent: no precedents for its use in conjunction with sewage sludge exist in the literature. Research conducted for this work package has demonstrated that it is considerably more effective than KOH, which was the key reagent utilised by Lillo-Ródenas et al., 2008. The highest BET surface area reported in the literature for a SBA is 1883 m$^2$/g (Lillo-Ródenas et al., 2008), but this figure was obtained using a synthetic sludge and its validity is questionable.

A major element that contributed to the high degree of success of this achievement was the use of a range of reagents that had not previously been utilised to prepare SBAs. This served to maximise the probability that a breakthrough would be made in the development of a high surface area SBA. In addition to $K_2CO_3$, the other previously untried reagents were: $K_2CO_3$; FeCl$_3$; CaCl$_2$; MgCl$_2$; KCl; K$_3$PO$_4$.H$_2$O.

**OPTIMISATION OF THE CHEMICAL ACTIVATION PROCESS.**

A major discovery has been that when producing SBAs by chemical activation, it is possible and indeed, preferable, to utilise sludge in its as-received (i.e., wet) state. Previously, all published research has utilised only sewage sludge that had been dried and in some cases, carbonised (most notably in the case of Lillo-Ródenas et al., (2008)). The avoidance of the high energy demand and hence, high costs, associated with drying and carbonisation does much to improve the commercial viability of using chemical activation to produce SBAs.

**DEVELOPMENT OF A ONE-STEP PRODUCTION METHOD FOR THE PRODUCTION OF SBAs.**

The physical activation work conducted for this WP constitutes the first major study undertaken on the production of SBAs by a single step physical activation. Previously, all of the large scale studies on steam activation had utilised a two-step method, whereby the sludge was carbonised prior to being activated (Mitchell et al., 1978, Rio et al., 2006a, 2006b, Fitzmorris et al., 2006a, 2006b). The use of a two stage process is, from a commercial perspective, unattractive because of the high energy requirements associated with subjecting the sludge sample to two, distinct, high temperature heating processes and because of the longer production time. However, the single-step process is feasible because the process starts at room temperature and thus the sludge is essentially carbonised as it is heated up to the activation temperature. If the dried sludge was admitted directly to the furnace at temperature, i.e., when the furnace was already at the activation temperature, then the sudden and uncontrolled release of the volatile component of the sludge (i.e., the oils and gases) could adversely affect the operation of the process. Thus, it remains to be seen whether the single-step method could be adopted commercially. An alternative approach would be to improve the commercial viability of the two-step approach through utilising the off-gases arising from the carbonisation process to pre-heat the sludge.

**UTILISATION OF THE RESPONSE SURFACE METHODOLOGY METHOD TO EVALUATE THE EFFECT OF THE SLUDGE TYPE ON THE OPTIMUM STEAM ACTIVATION CONDITIONS.**

The response surface methodology (RSM) is a tool that can be used to reduce the number of experiments required to determine the optimum activation conditions, in relation to the classical, empirical approach (Wächter and Cordery, 1999, Rio et al., 2005), for activating carbonaceous precursors. It uses statistical methods to mathematically express the relationship between two or more variables (Karacan et al., 2007) and thus ascertain the interactions between the examined parameters. The RSM method has previously been utilised to optimise the chemical activation (Rio, et al., 2005) and physical activation (by steam (Rio et al., 2006a, 2006b)) of sewage sludge. However, no attempts have previously been made to investigate how the sludge type may affect the results obtained with the RSM model and thus, the optimum conditions for maximising the surface area. For the investigation undertaken, two sludge types were used: Dewatered, Mesophilic Anaerobically Digested (DMAD) sludge and dewatered raw (DRAW) sludge. From the RSM models developed, it was determined that the optimum activation conditions for these two sludge samples were 838 ºC and 73 mins and 838 ºC and 80 mins respectively. The shared optimum temperature denoted that the nature of the fixed (non-volatile) carbon component did not vary significantly between different sludge types. The disparate dwell times reflected the different fixed carbon content of the sludge samples, which necessitated different dwell times to achieve the optimum degree of carbon burn-off. Under the respective, optimised steam activation conditions for the two sludge samples, the DRAW sludge yielded a
SBA that exhibited a BET surface area that was ca. 100 m$^2$/g greater than the surface area exhibited by the DMAD-derived SBA. This, again, pertained to the fact that the DRAW sludge had a higher organic content: a high ash content was detrimental to the surface area because of the negligible porosity of the ash fraction.

The novelty of this work is reflected by the fact that it has been presented both at a conference (Pullket, et al., 2008) and in a paper published in a peer reviewed journal (Pullket, et al. 2009). Two of the graphs obtained from the RSM models are displayed in Figure 12.1.

![Figure 12.1. a) Mesh response of the SBAs' yield (%) for the steam activated DRAW and DMAD sludges; b) Mesh response of the DMAD sludge with respect to the surface areas of the SBAs generated by steam activation (Pullket, et al. 2009).](image)

DETERMINATION OF THE INFLUENCE OF THE SLUDGE TYPE ON THE PROPERTIES OF THE SBAS PRODUCED BY PHYSICAL ACTIVATION.

The work described in achievement 4 was used as a foundation for undertaking an in-depth study into the effect of the sludge type on its response to steam activation conditions. The optimum steam activation conditions described were applied to six more sludge samples. These were collected with the assistance of the REMOVALS project partners from around Europe. From this research, much of which was published in the aforementioned journal paper (Pullket, et al., 2009), it was established that the treatment/process that the sludge has been subjected to has a fundamental effect on its properties as a SBA feedstock. The optimum sludge type was, due its high organic content, undigested sludge. Sludge that had been stabilised by liming [P9 (TUL) provided a sample], on the other hand, was observed to be a very poor quality activated carbon feedstock. This was predominantly due to the rise in the ash (i.e., non-combustible (inorganic)) content of the sludge. The ash fraction is non-porous and therefore does not contribute to the surface area of the adsorbent. Moreover, the primary component of lime is calcium and this is a noted catalyst of the steam-carbon gasification/oxidation reaction (Cannon et al., 1994). Its presence therefore accelerates the burn-off of the organic fraction during gasification (i.e., physical activation). This therefore makes it harder to control the effects of the activation process.

Another sludge found to be of very poor quality was obtained from University of Glamorgan. This sludge was produced from an anerobically digested, primary sludge that had been fermented in a bio-reactor for the purposes of hydrogen production. The cause of its poor performance was not immediately clear, as prior to activation its ash content, at 25 wt.%, was relatively low. The mass loss it exhibited during carbonisation/devolatilisation was not also not significantly greater than for the other sludge samples tested. However, it was clear that after being activated, the sample exhibited a very high ash content (94.9 wt.%). This indicated either that the fixed carbon content was very reactive, or that the sludge contained a high proportion of catalytically active metals.

PRODUCTION OF HIGH SURFACE AREA SBAS BY PHYSICAL ACTIVATION.

The work conducted on the physical activation of sewage sludge corroborated the findings previously reported in the literature, namely, that because of its high ash content, it was not feasible to produce SBAs with a BET surface area in excess of 300 m$^2$/g from sewage sludge. However, it was determined that
through inducing the partial dissolution and hence removal, of the inorganic fraction, washing the sludge-derived carbons in hydrochloric acid (HCl) was a highly effective technique for raising the surface area of the SBAs. The highest BET surface area achieved in this fashion was 622 m²/g; prior to washing, the SBA exhibited a BET surface area of ca. 125 m²/g. Although there is a precedent in the literature for the HCl washing of SBAs, the highest BET surface previously achieved in this fashion is 428 m²/g (Ros, et al., 2007). However, to obtain a BET surface area of 622 m²/g, it was necessary to heat the SBA in a HCl solution of concentration 4M for 1 hr at a temperature of 80-90 °C. This procedure may not be a commercially attractive proposition. However, P16 (CCC), i.e., the company Chemviron Ltd., currently utilise a HCl process (known as the React process) to wash, prior to thermal regeneration, all spent water treatment activated carbons returned to them. This process entails soaking the carbon in dilute hydrochloric acid (2-3 % w/w) at ambient conditions for ca. 8 hrs. After draining away the acid the carbon is washed with approximately 2 bed volumes of water. It was therefore decided to use a similar process to treat the SBA prepared from DRAW sludge under the optimised steam activation conditions. An extended dwell time of 24 hrs was utilised and the HCl concentration was 3 %. The process resulted in the SBA’s surface area increasing from 255 m²/g to 497 m²/g. Evidently, the use of less severe washing conditions did not significantly compromise the efficacy of the process. Moreover, with respect to its performance in the CWAO process as a catalyst/adsorbent for the destruction and removal of phenolic compounds in water, the SBA performed on a par with the reference commercial carbon.

PRODUCTION OF SBAS WITH A HIGH EDC UPTAKE.

The document of work of the REMOVALS project states in the explanatory text for task “Characterisation of sludge-based adsorbents” that endocrine disrupting chemicals (EDCs), which are described as a class of micro pollutants, are to have their uptake by the SBAs assessed. Bisphenol-A (BP-A) is a common EDC with a relatively high solubility in water and consequently, it was selected as the model EDC compound that would be used for this assessment.

The key finding of this study was that the BP-A uptake of the SBAs was heavily influenced by their surface area. Thus, the SBA that exhibited the highest surface area of those tested - 1979 m²/g – also exhibited the highest BP-A uptake. The BP-A uptake of this SBA was ca. double that of the reference commercial activated carbon, which was consistent with the difference in scale of the surface areas of these two adsorbents. Accordingly, the SBAs produced by physical activation, which all exhibited BET surface areas under 280 m²/g, did not attain high BP-A uptakes.

No other study has been conducted into the analysis of the EDC uptake of SBAs. The finding that it is possible, by chemical activation, to produce SBAs that can attain a BP-A uptake that is ca. double that of a commercial carbon is likely to have huge significance. Chemical activation is generally regarded as being a specialist production process, the use of which is usually only justified when the application specifically demands the use of high grade adsorbents. The research finding reported here may be sufficient to provide the necessary justification to make SBA production by chemical activation a viable enterprise.

DEVELOPMENT OF POST-ACTIVATION TECHNIQUES TO MITIGATE THE HIGH LEACHING PROPENSITY OF SBAS.

A key problem associated with the use of SBAs is their high propensity towards leaching. This issue was studied by Fitzmorris et al., (2006a), who observed that when placed into an aqueous solution with a pH of 1, all of the metals under investigation (As, Cd, Cr, Cu, Ni, Pb, Se and Zn) leached into solution: Cu and Zn leached in the greatest quantities. At a pH of 5 only Zn was leached in significant quantities but prior to testing, the SBA had been washed in both 0.1 M HCl and distilled water. This treatment would therefore have been liable to remove much of the SBA’s readily leachable component.

The SBAs prepared by physical activation were found, when their performance as adsorbents/catalysts in the catalytic wet air oxidation (CWAO) process was tested by Universitat Rovira i Virgili, to exhibit a high propensity towards leaching, most notably with regard to Fe. A range of different post activation leaching mitigation techniques were tested and thermal treatment, which comprised heating the SBA at 950 °C under nitrogen was found to be the most effective. One consequence of this treatment was that the SBA exhibited a greater tendency towards leaching calcium. However, this was not considered to pose a significant problem.
The high propensity towards leaching exhibited by SBAs is well documented. The discovery that it is possible to mitigate this problem through the application of a single-step heating step could therefore provide the impetus necessary to make SBA production a commercial reality.

**PRODUCTION OF LEACHING RESISTANT, HARDENED PELLETS.**

A key problem identified with the SBAs submitted to Universitat Rovira i Virgili – the leader of WP13 – for use in the CWAO process was that they exhibited a low attrition resistance. Under the high pressures and temperatures employed by the CWAO process the SBAs disintegrated. This problem became acute when the SBAs were produced from DRAW sludge. The DRAW-derived SBAs exhibited the best performance of the SBAs tested. Hence, if the specific production, from sewage sludge, of adsorbents for use in the CWAO process was to be realised, then it would be necessary to devise a method of improving the SBAs’ hardness.

Work undertaken to achieve this goal has been successful. Lignosulphonite based binders have been found to be the most effective. Pellets prepared with these binders cannot be prepared by manual extrusion: uniaxial compression was found to be an effective pelletisation method. Moreover, after drying the pellets must be heated to temperatures in excess of 500 ºC in order to attain the necessary hardness and water resistance. However, it was found that subjecting the pellets to the steam activation process was sufficient to cure the pellets. Thus, if the pellets were prepared with carbonised sludge, then the curing and activation steps can be combined in a single step.

No precedents exist in the literature for the production of attrition resistant, activated carbons through the application of a dedicated hardness enhancement procedure. A key factor in this is that conventional activated carbon feedstocks such as, for example, coconut shells, readily yield carbons that exhibit a high attrition resistance. However, it seems likely that many potential activated carbon feedstocks have traditionally been overlooked for the very reason that they would yield carbons with a low attrition resistance. The development of this method may therefore foster a rise in research into the use of feedstocks that have hitherto been discounted.

A further discovery of this work concerns the hardened SBAs that were produced using the lignosulphonite based binders and were then steam activated after being pelleted. When utilised in the CWAO process they were observed by P1 (URV) to exhibit a propensity towards leaching that was lower, even, than the reference commercial carbon. This represents a major advance in this research field and does much to improve the commercial viability of the hardening process. This development could result in the utilisation of feedstocks that, due to their high content of leachable metals, had previously not been considered for use in activated carbon production.

**APPRAISAL OF THE EFFECT OF SEASONAL VARIATION.**

It has been determined that sewage sludge does exhibit some seasonal variation in its fixed carbon and volatile content: hot summers, in particular, were observed to induce a drop in the volatile content of the sludge. However, it was found that the seasonal variation was not of a scale to have adverse effects on the properties of the sludge as an activated carbon feedstock. This finding is highly significant because it will nullify any fears that potential producers of SBAs may have had over the variability of the feedstock.

**REFERENCES.**


12.4. Impact of the WP on its industry or research sector.

RESEARCH IMPACTS.

Review of the literature.

One of the key outputs from this project has been the production and subsequent publication in the journal Water Research of a literature review on the production of SBAs and their utilisation in liquid phase applications (Smith, et al, 2009). This article has drawn attention to the fact that, despite exhibiting low BET surface areas, SBAs are often to exhibit a high uptake of numerous different contaminants. It has also identified areas of research with respect to SBAs that merit further research. Thus, it is anticipated that this paper may stimulate a renewed interest in research into the production and utilisation of SBAs. Furthermore, for researchers already working with SBAs, the review should act as, firstly, a convenient tool for ascertaining what work has already been done and secondly, as an invaluable reference guide to the key works in the field.

This review paper has also highlighted the limitations of SBAs. However, it is hoped that because it has also suggested possible strategies for mitigating these drawbacks, the paper has made a convincing case for the investigation of SBAs and their prospective value. As described in the previous section (2.3) it is, moreover, believed that some of the problems associated with SBAs have been resolved as a direct consequence of the work undertaken for this WP. One paper on the influence of the sludge type has already been published and further papers describing the advances made should be published within a year of the conclusion of this project.
Advancement of knowledge of utilisation of sewage sludge for adsorbent production.

This project has resulted in numerous scientific breakthroughs with respect to the development of SBAs. Some of the key findings include: raw/undigested sludge is the best sludge feedstock for SBA production; the use of chemical activation can result in SBAs with surface areas approaching 2000 m$^2$/g; high surface area SBAs can exhibit a EDC uptake that is double that of commercial activated carbons; the HCl washing of SBAs prepared by physical activation is sufficient to render these materials competitive with commercial carbons. The highest BET surface area attained (1979 m$^2$/g) exceeds all published values for the surface area of SBAs. Thus, it is anticipated that this result will have a galvanising impact on research into SBA production. The finding that chemical activation can produce adsorbents that exhibit not only a high surface area but also a high EDC uptake should bolster research efforts into the use of chemical activation. The discovery that lignosulphonate binders can both improve the attrition resistance and mitigate the propensity towards leaching of SBAs should have major implications not only for research into SBAs, but also for research on the use of waste materials for activated carbon production.

SOCIAL AND ENVIRONMENT IMPACTS.

Introduction.

Sewage sludge production has reached such a scale that if it is not appropriately dealt with, then it will begin to exert a strongly negative effect on the environment and society. In the UK alone, over one million tonnes of sewage are produced every year (dry solids). Although 62% of this sludge is recycled to land (Water UK, 2006) this of course means that the remaining 38% must be disposed of. In 2004, 50% of the sludge not applied to agricultural land was disposed of either by incineration or landfill (Water UK, 2006). Neither approach can be regarded as being sustainable and indeed, both are associated with negative impacts on the environment and, the populations local to the incineration/landfill facilities. Moreover, as the legislation governing the permissible levels of pathogens, heavy metals and other substances in sludge intended for application to agricultural land becomes increasingly stringent, the quantity of sludge requiring disposal is liable only to rise.

This work-package has demonstrated that the conversion of sewage sludge into an adsorbent is a highly viable alternative to the existing disposal and valorization routes. The primary advantages that it offers are described below.

Reduction in quantity of material.

The reduction in weight typically incurred through the conversion, by physical activation, of dried sludge into activated carbon was 60-80 wt.%. In other words, up to four fifths of the mass of the dried sludge was lost. Although producing SBAs by physical production does result in the production of gases and oils, because they are hydrocarbon-based their utilisation in energy production applications is eminently feasible. Thus, irrespective of the obvious benefits of producing a high value commodity, i.e., activated carbon, the physical activation process is highly advantageous because of the sharp reduction it induces in the quantity of material that needs to be dealt with.

Abrogation of odours.

A common problem associated with WTTPs is their impact on the surrounding area in terms of the highly unpleasant odours that they generate. Consequences include depressed house prices and moreover, harm to the psychological wellbeing of the local residents, which is induced by the discomfort of being perpetually exposed to malodorous smells and the attendant social embarrassment this entails. The odours stem from the release of gases which are produced during microbial decomposition processes. H$_2$S is one such gas and it is released during anaerobic decay (Ansari, et al., 2005). H$_2$S is of particular concern not only because of its strongly odoriferous nature but because it is, firstly, toxic (Bagreev et al., 2005) and secondly, because in the atmosphere it is easily oxidised to SO$_2$. When this comes into contact with atmospheric moisture it can result in the formation of sulphurous (H$_2$SO$_3$) acid and hence, acid rain (Ansari and Bandosz, 2005).

Thus, any process which results in the conversion of the sludge into a decomposition-resistant and therefore, odour-less, form will clearly induce a swift reduction in the noxious and toxic gases associated with WWTPs. Activated carbon is widely recognised as being odourless; hence, the SBA production methodology exhibits this potential in abundance. On the other hand, during the carbonisation process H$_2$S is generated. However,
as this occurs under controlled conditions its release can be safely managed so as not to cause a public or an environmental nuisance.

**Mineralisation/stabilisation of fixed carbon in sludge.**

Biochar is essentially the char arising from the pyrolysis (carbonisation) of biomass. Biochar has long been used as a soil amendment because of its noted effects on plant growth and crop yield (Glaser, et al., 2002, Guant and Lehmann, 2008). However, recently the realisation has occurred that because it results in the biomass becoming degradation resistant, the production of biochar can be a highly effective means of sequestering much of the carbon in biomass. Research has established that the carbon consumed through the consumption of the energy necessary to drive the biochar production process is far exceeded by the carbon sequestered, although this process does assume that the oils and gases released are utilised for energy production (Guant and Lehmann, 2008).

The production of adsorbents from sludge by physical activation is tantamount to the conversion of the sludge into biochar. The issue of whether the SBAs produced are suitable for use as soil amendments remains to be resolved. However, the fact that the SBA production process results in the stabilisation of much of the fixed (i.e., non volatile) carbon is beyond doubt. Due to the fact that some of the fixed carbon is gasified through its reaction with the activant to form either CO or CO₂, it is currently not known whether the SBA production results in a net sequestration or release of carbon (assuming that the furnace is powered with fossil-fuels). However, it is quite feasible that that former scenario applies. Moreover, it is possible to produce SBAs by carbonisation/pyrolysis alone. Researchers have shown that SBAs produced by carbonisation can attain high levels performance in gas phase contaminant capture/immobilisation applications (Bagreev, et al., 2001b). On the other hand, this WP has shown that in their unadulterated state, the adsorbents produced by carbonisation are not suitable for use in aqueous phase applications, but the leader of WP16 has determined that they could act as biofilters for the elimination of waste industrial gases. In this application the SBAs act as supports for microbial populations that are able to digest/consume hazardous gases. Given that the activated carbon used in the activated sludge process fulfils a similar role in the aqueous phase, in that it essentially acts as a support for bacteria, then it is probable that SBAs produced by carbonisation would also be suitable for use in this process.

**Utilisation of adsorbents for decontamination of polluted water and gases.**

A key aim of this WP is to produce adsorbents that can achieve high levels of performance in water treatment applications. Thus far, the SBAs produced have been shown to attain competitive levels of performance in the CWAO process and to exhibit high capacities for organic dyes and EDCs. The results indicate, moreover, that SBAs exhibit great potential for many other gaseous phase pollutants. Hence, the aim, as was comprehensively discussed in the final periodic report, ss considered to have been comprehensively been achieved. The ramifications of this are immense as in essence what has been developed is a low/zero cost feedstock for producing activated carbons. This therefore raises the possibility of the decontamination of polluted water courses and effluents that, previously, had lain untouched due to the prohibitive cost of their treatment. Although, in the developed world, the effects of this discovery perhaps may not be on a seismic scale, in the developing world they could be far reaching. Although there are already many waste streams that can be utilised to produce ACs (Dias et al., 2007, Ioannidou and Zabaniotou, 2007, Pollard et al., 1992), the case for using sewage sludge is particularly strong because, firstly, it is present wherever large urban populations are to be found and secondly, it is a waste that requires disposal. Many other waste materials can be stockpiled, but sewage sludge, because of both its odorous properties and its high content of potentially hazardous pathogens, is not a waste that can be treated in this manner. Moreover, unlike many other activated carbon precursors, for example, agricultural by-products, the availability of sewage sludge is not affected by seasonal variation.

**Development of a low-tech solution to the growing volumes of sludge being produced in the developing world.**

In the long term, the conversion of sewage sludge into adsorbents could represent a leading solution to the problem of how to dispose of the excess sewage sludge in the developing world. Moreover, demand for activated carbon in the developing world is certain to increase as industrialisation and awareness of the primacy of the environment and the importance of having access to clean water, grows apace. The technology required to carbonise and physically activate sewage sludge is not regarded as being
complicated: its use as a purifying agent dates back to 1500 BC, when carbonised wood was used by the Egyptians as a medicinal agent. Furthermore, the ancient Hindus in India utilised charcoal to filter their drinking water (Bansal, et al., 1988). The issue of where to derive the energy necessary to power the plant from could be resolved by making recourse to the carbonisation/pyrolysis hydrocarbon products of the conversion process. The drying stage can be highly energy intensive, but if utilised in countries with warm/hot climates then drying the sludge through prolonged exposure to the air should be feasible. The spent SBAs could be used as biochars or combusted to produce the energy required to drive the production process.

INDUSTRIAL AND ECONOMIC IMPACTS.

Introduction.

The industrial and economic impacts of this work are essentially interchangeable and have therefore been grouped together under a single heading. The approach taken to determining these impacts has been to itemise the different revenue and cost streams that would arise if a plant for commercially producing SBAs by physical activation was built. The outcome of this study is shown in Table 12.1. A description of how the different components of the table were produced is given in the following text.

Table 12.1. Estimated annual costs for producing activated carbon from sewage sludge.

<table>
<thead>
<tr>
<th>Costs</th>
<th>Drying</th>
<th>Pyrolysis</th>
<th>Steam Activation</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA preparation step:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Investments (capital payment) (€)</td>
<td>2,300,000</td>
<td></td>
<td>600,000</td>
</tr>
<tr>
<td>Pyrolyser</td>
<td>NA</td>
<td>1,260,000</td>
<td>NA</td>
</tr>
<tr>
<td>HT Gas treatment</td>
<td></td>
<td>180,000</td>
<td></td>
</tr>
<tr>
<td>Linear depreciation costs (€/year)</td>
<td>153,300</td>
<td>96,000</td>
<td>40,000</td>
</tr>
<tr>
<td>Maintenance costs (€/year)</td>
<td>23,000</td>
<td>14,400</td>
<td>6,000</td>
</tr>
<tr>
<td>Energy consumption (kWh/tonne)</td>
<td>50</td>
<td>630</td>
<td>700</td>
</tr>
<tr>
<td>Daily consumption of sludge (tonnes)</td>
<td>30</td>
<td>6</td>
<td>2.4</td>
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<tr>
<td>Annual electricity consumption</td>
<td>547,500</td>
<td>1,379,700</td>
<td>613,200</td>
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<tr>
<td>Annual electricity cost (€)</td>
<td>41,610</td>
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<td>46,603</td>
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<tr>
<td>Steam consumption (kg/tonne char)</td>
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<td>280</td>
</tr>
<tr>
<td>Annual steam consumption (tonne/year)</td>
<td>N/A</td>
<td>N/A</td>
<td>245.28</td>
</tr>
<tr>
<td>Cost of 1 tonne of steam (€/tonne)</td>
<td></td>
<td></td>
<td>17.8</td>
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<tr>
<td>Steam consumption costs (€/year)</td>
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<td>4365.984</td>
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<tr>
<td>General costs* (€/year)</td>
<td>11,260</td>
<td>23,860</td>
<td>32,300</td>
</tr>
<tr>
<td>Total cost (€/year)</td>
<td>229,170</td>
<td>239,117</td>
<td>89,269</td>
</tr>
<tr>
<td>Total cost (€/tonne)</td>
<td>21</td>
<td>109</td>
<td>102</td>
</tr>
<tr>
<td>Annual cost of running the SBA plant (€/year)</td>
<td></td>
<td></td>
<td>557,556</td>
</tr>
<tr>
<td>Total (average) cost per tonne (€/tonne)</td>
<td></td>
<td></td>
<td>51</td>
</tr>
<tr>
<td>Revenue streams</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Landfill avoidance saving (€/tonne)</td>
<td></td>
<td></td>
<td>83</td>
</tr>
<tr>
<td>SBA retail price (€/tonne)</td>
<td></td>
<td></td>
<td>360</td>
</tr>
<tr>
<td>Total income (€/tonne)</td>
<td></td>
<td></td>
<td>443</td>
</tr>
<tr>
<td>Net profit (€/tonne)</td>
<td></td>
<td></td>
<td>392</td>
</tr>
</tbody>
</table>

*20% of exploitation costs

Costs from the conversion of sludge into activated carbon (SBA preparation).

Only one study has thus far been published on the economics of producing SBAs. The study was undertaken by Rio et al. (2006) and the figures it reports have therefore provided the basis for the figures featured in the
costs section of Table 12.1. Hence, in keeping with the scenario chosen by Rio et al. (2006), the sludge has a solids content of 20 wt.% dry solids by weight and the unit processes 30 tonnes of wet sludge a day (approx 11,000 wet tonnes per annum).

The investment costs refer to all of the capital costs incurred. The depreciation costs are predicated on the assumption that the capital equipment has a lifetime of 15 years. A lifetime of 25 years is perhaps a more realistic figure for major plant such as furnaces/kilns and driers. However, it was decided to maintain the payment period selected by Rio et al. (2006), especially as the choice of a shorter and hence, more severe, payment regime would deflect the charge that generous terms were responsible for the purported profitability of the SBA production facility. The annual depreciation cost is the figure that was used to represent the annual cost of paying the capital costs. Usually, it would be necessary to take a loan to pay for the capital costs. If this loan was paid off over a 15 year period then interest on the loan would also need to be paid. However, at present interest rates are historically low. Moreover, this study was undertaken only in order to obtain an indication of the potential costs of creating and operating a SBA system. Some simplifications have therefore been made in the costing of the proposed scheme.

The drying costs are predicated on the assumption that the sludge is dried for 3 hrs at 105 °C and that the sludge is carbonised at 600 °C for 1 hr. Much of the activation work conducted for this project did not include a dedicated carbonisation step. However, if a single step approach was adopted commercially, then the uncontrolled discharge of the volatile component of the sludge into the activation chamber could result in the fouling of the activation furnace walls and would certainly result in the incursion of significant quantities of water into the pyrolysis products.

It was assumed that the carbonisation step induced a 60 % loss in mass of the dried sludge, which is broadly consistent with the loss in mass exhibited by the DRAW sludge at this carbonisation temperature. The DRAW sludge was selected as the feedstock because the SBAs produced from it exhibited the highest surface areas of those produced from this project. The same steam flow rate that was utilised for the steam activation experiments in the lab (0.7 g H₂O/200 g sludge char) was utilised. It was also assumed that the dwell time for the activation step was 80 minutes.

Revenue from abrogation of landfill costs.

It was assumed that if the sludge was converted into activated carbon then the cost of disposing of the sludge would be obviated. At present, landfill tax in the UK is currently levied at £ 40/tonne waste and this is currently set to rise at a rate of at £ 8/year until at least 2013 (H M Revenue & Customs, 2009). A report by WRAP (2008) estimated that the ‘gate fee’ for disposing of one tonne of waste was £21/tonne. Thus, the total cost of disposing of one tonne of sewage sludge would be £ 61/tonne. However, when the cost of transporting the sludge and other secondary costs are factored in, it is likely that the cost of disposal would total £ 70/tonne. Using an exchange rate of 1 £ = €1.18, this equates to €82.60/tonne. The spent SBAs may also have an associated disposal charge, but it is anticipated that this could be circumvented through their use as biochars (see section “Revenue from retail of SBA”).

Revenue from retail of SBA.

The 2008 edition of what is perhaps the definitive guide to the activated carbon markets, namely, the publication The economics of activated carbon (Roskill Information Services Ltd, 2008) stated that in 2007, coal-based steam-activated granular activated carbon for municipal water treatment retailed in the region of US$1,000/tonne. Using an exchange rate of $ 1 = €0.72, this equates to €720/tonne. The SBAs produced by physical activation are expected to be primarily used in low grade applications. Consequently, it was therefore to reflect this by pricing the SBA at 50 % of the retail price of the commercial carbon: the price quoted in Table 1 is €360/tonne.

Other potential sources of revenue/cost offsetting.

This study assumes that all the energy needed for the process is bought in. There is significant potential to recover energy from the pyrolysis stage of the process and also to utilise waste heat for sludge drying, significantly reducing the need to generate heat for both steps of the process. The calculation of the potential revenue that would be generated by such a scheme was beyond the scope of this project. However, for future work it would constitute an important line of research.
The implementation of a SBA production scheme would obviate the need to have any sludge stabilisation/digestion facilities. The costs saved by this should, at least in part, offset the costs of the SBA production unit.

A further source of income is carbon credits. As previously mentioned, the SBAs generated can potentially also be described as biochars. This therefore makes the process eligible for the accrualment of carbon credits, which may then be sold/redeemed for the market value of these credits. The drive to decarbonise the economy is growing, as is evidenced by the heated negotiations that have surrounded the G8 summit in L’Aquila (Italy), where there have been renewed efforts to agree on a workable cap on greenhouse gas emissions. The potential of the proposed SBA production scheme to sequester carbon can not be overstated and is likely to be a key factor when making the case for the implementation of this scheme.

**The prospective costs of the other options for sludge disposal.**

This study has considered landfill as the only option to SBA production for the disposal/valorization of sewage sludge. Incineration is another alternative, but it is an expensive process, with costs estimated at between €140-300 per tonne of dry solids (Smith, 2004, Rio et al, 2006). Its utilisation is compounded by the fact that it generates residual ash, which can comprise up to 40% of the original volume of the dry sludge, adding to the final disposal charge. Moreover, it could be classified as hazardous waste. The problems associated with incineration are illustrated by the decision, in 2008, of the UK water company Severn Trent Water to close their sludge incineration plant (the Coleshill incinerator). With regards to land application, it was assumed that the proposed system would utilise only sewage sludge that was either ineligible for this use or was surplus to demand.

**CONCLUSIONS.**

The utilisation of sewage sludge as an activated carbon feedstock evidently has the potential to be commercially lucrative, with a prospective profit of 392 €/tonne. This figure is, of course, based on a number of assumptions and would be likely to drop if the application of performance enhancement treatments such as HCl washing or hardening were required. However, despite this the business case for the development of a commercial scale SBA production unit remains strong and it is hoped that the realisation of this concept will constitute the ultimate result of this WP. A schematic of how the proposed SBA production facility would be incorporated into a sludge management scheme that also services the other work-packages associated with this work-package “Production of activated carbon from sludge” is presented on the Figure 12.2.

**REFERENCES.**

Figure 12.2. A schematic of how a SBA production facility would be incorporated into a sludge management solution.


13. **Utilisation of activated carbon as catalyst in wet air oxidation.**

13.1. **Summary description of project objectives, work performed and end results, elaborating on the degree to which the objectives were reached.**

**PROJECT OBJECTIVES.**

The main goal of this workpackage established by former work-package leader, Universidade de Coimbra, was to investigate the utilisation of Wet Oxidation technology for phenolic wastewater remediation employing activated carbons prepared from sewage sludge (SBAC = Sludge Based Activated Carbon) as the catalytic promoter of the reaction process. The study included experiments in laboratory and semi-industrial pilot trickle-bed reactors, and process analysis by means of kinetic modelling and Computational Fluid Dynamics (CFD) simulation.

After the change of WP leadership to Universitat Rovira i Virgili occurring at the end of month 18 and according to the recommendation of the European Commission, the objectives of WP13 have been modified as follows. The experimental work initially accorded in task WP13.1 was extended to include a series of phenol oxidation experiments with SBACs. The aim of the batch study was double: 1) to determine the influence that has the method of carbon preparation, i.e. carbonisation, physical and chemical activation and acid washing on the catalytic activity of SBACs and 2) to provide enough active and stable SBACs for subsequent application in continuous operation in Trickle Bed Reactor (TBR). Moreover, the work on the semi-industrial pilot plant corresponding to Tasks WP13.4 and 13.5 was stopped at month 30 following the recommendation of the European Commission.

**WORK PERFORMED.**

In order to select carbons suitable for their use in catalytic wet air oxidation (CWAO) of phenolic contaminants, more than 15 SBACs as well as two commercial carbons were tested in batch and trickle bed reactors. The sludge feedstocks used for carbon preparation were two England sourced samples labelled as DRAW (Dewatered RAW) and DMAD (Dewatered Mesophilic Anaerobically Digested). The experiments were undertaken to ascertain the catalytic activity (compound and TOC removals) and stability (resistance to carbon burn off, metal leaching and mechanical attrition) of the prepared SBACs. Partner 14 from ICL was responsible for the production of carbons; however the final optimisation of carbons was achieved by continuous feedback from Partner 1 (URV) on obtained oxidation results. Due to its industrial relevance, phenol was the model contaminant subjected to CWAO, although other phenolic compounds such as o-cresol, o-chlorophenol and p-nitrophenol were also oxidised in batch and continuous reactors.

The work on CFD was started with the development of Euler-Euler k-fluid and Volume-of-Fluid CFD models to provide a behavior analysis in transient conditions of a pilot scale TBR. CFD codes were used for the purpose of multiphase reacting flow prediction, namely based on Eulerian and Volume-of-Fluid models. Key hydrodynamic parameters such as liquid holdup and pressure drop were previously validated with the exception of catalyst wetting efficiencies under trickle-flow regime. Also, the catalytic wet air oxidation based on manganese-cerium catalysts was modeled with Volume-of-Fluid model under transient conditions. The hydrodynamic prediction of catalyst wetting efficiency by means of interface tracking schemes will be accomplished using level set methods for gas-liquid-solid surface reconstruction. Finally, the integration of sludge based activated carbon kinetics in the computational model will be accomplished towards the successful implementation and deployment of CWAO technology.

**END RESULTS.**

An important outcome of the completed experimental work is the knowledge on how carbon preparation affects the catalytic performance of SBACs. At the conclusion of the project several SBACs are available that demonstrated on laboratory scale to perform acceptable (carbonised and physically activated carbons) or very similar (chemically activated carbons plus acid washing) in CWAO of phenolic contaminants when compared to commercial carbons specially recommended for wastewater treatment. This knowledge should allow establishing guidelines for the production of SBACs with catalytic activity tailored to the specific application needs. Moreover, a range of temperature (140 to 160°C) and partial oxygen pressure (2 to 4 bar) ensuring both carbon activity and stability were assessed using a laboratory scale Trickle Bed Reactor as wastewater treatment on industrial scale has generally to be conducted in continuous mode.
A mayor result of the process analysis is that computational flow modeling techniques can successfully predict gas-liquid distribution and pressure gradient in TBR, mainly with Eulerian codes. Local temperature variation and Total Organic Carbon profiles were evaluated axially and radially providing a more rigorous physical description of the underlying complex two-phase flow. Computational runs exhibited backmixing phenomena, poor radial mixing and revealed the existence of hot spots in the simulated trickle flow regime.

13.2. Methodologies and approaches employed.

INTEGRATED APPROACH EMPLOYED.

To achieve the main goal of workpackage "Utilisation of activated carbon as catalyst in wet air oxidation" that is to obtain stable and active SBACs for the continuous CWAO of phenolic wastewater, a combined experimental-theoretical approach was developed in the workpackage (see figure 13.1). The carbons initially prepared by ICL from recollected municipal wastewater excess sludge were tested by URV and further optimised by a means of continuous feedback between partners on their observed CWAO performance and suggestions for improvement of the preparation methodology. In a parallel design orientated study, Universidade de Coimbra analysed in detail the operation and scale up of larger Trickle Bed Reactor applied to CWAO by using advanced tools of CFD simulation.

![Figure 13.1. Schematic chart of integrated approach employed in workpackage "Utilisation of activated carbon as catalyst in wet air oxidation".]

EXPERIMENTAL METHODOLOGY.

Stirred Batch Reactor.

Figure 2 shows a detailed scheme of the batch reactor used for the oxidation tests. The main element consists in a 316 SS Autoclave (capacity of 300 ml) proved up to 450°C and 345 bar. A jacket-type furnace and a control device allow monitoring and controlling the oven temperature. To this end, a thermocouple is introduced into a thermo well to assess the reaction temperature and to actuate on the furnace power supply. For proper temperature control inside the reactor an internal coil where ambient water circulates at a convenient flow rate is required. Vigorous stirring is ensured by a motor impelling a straight blade turbine-type agitator. Agitation speed can be fixed by means of a speed controller device. The gas stream proceeds from an external high pressurised bottle and the reactor pressure can be adjusted using a pressure reducer placed upstream of the reactor gas inlet. The system can be depressurised with the help of a valve fixed on the vessel top. During experiments, the pressure inside the reactor is monitored through a pressure gauge, while liquid samples are regularly withdrawn through a sample valve assembly.

Typical batch experiments with 1 or 5g/L of contaminant solutions are conducted for 4 h at 160°C and 4 bar of oxygen partial pressure. To start the experiment, 100 mL of solution and 2 g of sludge based carbon are loaded into the reactor vessel, which is then closed. Then, the reactor is pressurised with nitrogen to check for possible leaks. If no leaks are detected, heating and stirring at low speed are started to establish the desired temperature inside the reactor. As soon as the temperature attains the set point, cooling water is fed to the coil at a fixed flow rate to dampen temperature fluctuations caused by the furnace off set. The system needed about 40-50 min to reach stable conditions of temperature. Prior to start the reaction, a first liquid sample is withdrawn to assess the amount of contaminant adsorbed on the carbon and synthetic air is allowed to the vessel to establish a system pressure of 25 bar. The reaction is finally initiated by a sudden
increase of the stirrer speed to 1000 rpm. During the 4h lasting experiment liquid samples are withdrawn at regular time intervals to measure phenol and TOC concentration as well as pH of reaction solution. At the end of each experiment, the reactor is opened to recover both aqueous solution and catalyst for further analysis or reuse.

**Continuous Trickle Bed Reactor.**

A laboratory Trickle Bed Reactor (TBR) was employed for the continuous oxidation tests (figure 13.3). It contains a 5 L stirred feed tank, which is connected to a high precision metering pump that can deliver up to 150 mL/h at a maximum pressure of 350 bar. After dampening the pump pulsation, the liquid flow rate is measured by means of a mass flow meter. The liquid and gas are fed in downflow through a SS tube (20 cm long, 1.1 cm i.d.) normally loaded with 7 g of carbon. A thermocouple is inserted axially to measure the mid temperature inside the bed. The carbon is retained by two sintered metal grids at the bottom and top of the reactor. The reactor with the preheating coil is placed in a temperature-controlled oven. The gas and the liquid streams are mixed and pre-heated before entering the reactor. Downstream of the reactor exit, there are 2 Gas-Liquid separators, a liquid sampling valve, a needle valve and a flow meter to adjust and measure the gas flow rate.

Standard 72 h experiments with 5 g/L of contaminant solutions were conducted in the TBR at a given liquid space time of 0.12h and 120-160°C and 2-8 bar of oxygen partial pressure. Prior to start the experiment, the reactor was carefully loaded with carbon particles crushed down to a diameter of 0.3 to 0.7 mm to obtain a uniform catalyst bed. Then, the reactor was closed and pressurised first under N₂ to check for possible leaks in the system. If no leaks were detected, the oven was heated to the selected reaction temperature, and air pressure was readjusted. As soon as reactor temperature and air pressure reach its operating values, liquid flow is set to the desired rate verified by downstream measurements coming from a liquid mass flow meter. During the runs, outlet liquid samples are periodically withdrawn, measured for pH and then stored at 4 ºC prior to be analysed on phenol, COD or TOC content. At the end of each run, the carbon is dried overnight at 105 °C under nitrogen flow, weighted and stored under inert atmosphere for further analysis. Results obtained in a similar way with the commercial carbon served as a reference to evaluate the CWAO performance of sludge based carbons in terms of activity and stability.
Materials and Analytical Methods.

Analytical grade aromatics were all provided by Aldrich. The commercial carbons tested were from Partner Chemviron (AP4-X) and Merck. All sludge based carbons were provided from partner 14 (ICL). The synthetic air oxidant fed to the reactor has a purity of 99.995%.

Contaminant concentrations of liquid samples were determined by HPLC. To prepare the mobile phase, HPLC grade methanol and ultra-pure-water were mixed in proportion of 35:36 (v/v). The analysis was performed with a C18 reverse phase column (Hypersil ODS) and at a mobile phase flow rate of 1 ml/min and a wavelength in the diode array detector of 254 nm. COD was measured with the standard method 5220D, whereas TOC was quantified following the protocol 5310B.

At the end of the CWAO tests, the used carbons were collected, dried overnight and then weighted. Approx. 0.25 mg of the recovered sample was also subjected to thermogravimetric analysis carried out in a thermobalance heating the sample from 100 to 900°C under nitrogen flow at a heating rate of 10°C/min.

To measure the release of metals from the carbons during CWAO all batch reactor solutions and liquid samples from the continuous TBR were recovered and filtered to allow for detection of metals. Detection and quantification of metals are done by means of Atomic Absorption and standard solution of known metal concentration. Analysis includes the following metals: Fe, Cu, Mn, Mg, Zn, Co and Ca.

CFD SIMULATION OF CWAO IN TRICKLE BED REACTOR.

The development of a TBR model was accomplished using a multiphase CFD approach incorporated in the FLUENT 6 software package by ensemble averaging of the local instantaneous balances for equations for mass, momentum and energy. Momentum transfer between the phases is modelled through an interphase drag term. The methodology consists in dividing the mesh domain in subdomains so that the decomposition of the catalytic bed was unstructured in order to manage with the geometric complexity. The momentum equations are solved with the coupling SIMPLE algorithm and the monotonic upwind discretization scheme. The pressure is computed by means of the PRESTO scheme and model equations were typically solved in a transient fashion with a time step of $10^{-3}$ s. The residuals convergence was accelerated by under-relaxation parameters: 0.4 for pressure and 0.8 for velocity vector field; inlet boundary conditions are assigned at the top distributor and outlet conditions at the free surface.

13.3. Achievements of the project related to the state of the art.

INTRODUCTION.

The main achievements of this workpackage are: the collaboration in the development of original carbons from different sewage sludge feedstock, the assessment of their resulting catalytic activity and stability when
subjected to batch and continuous oxidation of phenolic effluents and CFD simulations of CWAO conducted in a pilot scale trickle bed reactor.

**Pioneering the use of sludge based carbons as a catalytic material in Wet Air Oxidation of phenolic effluents.**

The production of active carbon from sewage sludge feedstock has been patented as early as 3 to 4 decades ago (Kemmer et al., 1971, Nickerson et al., 1975, Lewis, 1978). However, its use as a direct solid catalyst for the treatment of organic waste water effluents has yet not been reported in the recent review literature (Stüber et al., 2005). Most of the studies dedicated to this topic have primarily centred on the production of activated carbons with high surface areas and their applications to liquid phase adsorption of organic pollutants or heavy metals and to adsorption/oxidation of H2S and NO2 from contaminated gaseous effluents (Dias et al., 2007, Smith et al., 2009). Therefore, we can state that our experimental study on CWAO of phenolic effluents using for the first time sludge based carbon as catalyst in a Trickle Bed Reactor is a pioneer work in the field of waste water treatment with sludge based active carbons.

WAO or CWAO are commercially established techniques for the treatment of diverse municipal and industrial waste water streams at large scale (Busca et al., 2008; Levec and Pintar, 2007; Bhargava et al. 2006). Existing WAO processes (ZIMPRO, WETOX, VERTECH, KENOX, OXYJET) use more severe operating conditions of temperature and pressure than do CWAO processes (homogeneous: LOPROX, ATHOS, CIBA-GEIGER, WPO, ORCAM; heterogeneous: NIPPON SHOKUBAI, OSAKA GAS, CALIPHOX), leading to a retail in overall remediation costs per m³ of effluent treated (see also table 13.1 in sub-section “Industrial and economic impacts” of section 13.4. “Impact of the WP on its industry or research sector”). Nevertheless, relatively few works have been published to date on the catalytic liquid phase oxidation of organic compounds in continuous Trickle Bed Reactors and further experimental data, description of mass transfer processes and reactor simulation studies are required for the successful commercial exploitation of continuous CWAO technology (Levec and Pintar, 2007).

**CATALYTIC WET AIR OXIDATION OVER SLUDGE BASED ACTIVE CARBONS IN STIRRED BATCH REACTOR.**

**Effect of sludge origin on active carbon performance in phenol oxidation.**

Batch experiments revealed that the Dewatered RAW sludge is a better carbon feedstock than the Dewatered Mesophilic Anaerobically Digested sludge irrespectively of the preparation method applied (see figures 13.4a and 13.4b). Dewatered undigested sludge has a higher organic content and less mineral ash content and is economically more attractive because it does not require any further pre-treatment. For example, after 4 h of phenol (5 g/L) oxidation at 160°C and 4 bar of oxygen partial pressure, DRAW sludge activated with CO₂ performed conversion of phenol and TOC of 69% and 61%, respectively, compared to 58% and 47% obtained in the case of DMAD sludge activated with CO₂ at the same conditions.

![Figure 13.4. Influence of sludge precursor on a) Phenol and b) TOC removal; batch operating conditions: P_o2=4 bar, T=160°C, C_{Ph,0}=5 g/L, W=2g.](image-url)
It is known that sewage sludge does exhibit some fluctuation in its composition (fixed carbon, volatiles, ash). Nevertheless, tests with carbons prepared from sludge loads that were recollected at different days showed small variation of only ±10% in their catalytic and adsorption performance. This finding is important because it confirms that seasonal variation in the sludge feedstock does not significantly alter the reproducibility of the carbon preparation and their adsorption-oxidation behaviour.

**Effect of carbonisation temperature on active carbon performance in phenol oxidation.**

A mayor discovery has been that the production of stable DRAW carbons requires carbonisation temperatures in the range of 800 to 1000ºC. The so prepared carbons ensure acceptable phenol and TOC conversions (see phenol and TOC conversions reported in figures 13.5a and 13.5b) and at the same time are resistant to metal leaching. Carbons carbonised at temperatures below 500ºC were found to release into the reaction solution considerable amounts of both organic matter (see figure 13.5b) and metals, in particular catalytic active Fe (125 ppm after 4 h of reaction for the carbon carbonised at 250ºC).

![Figure 13.5. Influence of carbonisation temperature on a) Phenol and b) TOC removal; batch operating conditions: PO2=4 bar, T=160ºC, CPh,0=5 g/L, W=2g.](image)

**Effect of physical activation and posterior acid washing on active carbon performance in phenol oxidation.**

The oxidation of phenol over carbons prepared by steam or CO2 activation led to very similar catalytic performance in terms of phenol and TOC conversions, although higher than those obtained for carbonised carbons (see figure 13.6 and figure 13.5). Enhancement of phenol demineralisation achieved by physically activated DRAW carbon is about 50% with a TOC conversion of 62% against 42% obtained with the DRAW carbon carbonised at 1000ºC. A further increase of the catalytic activity can be performed by posterior acid washing of the carbon with HCL solution. In case of the steam activated DRAW carbon, soaked for 24 h in 3% HCL solution, 80% of the TOC fraction corresponding to a 5 g/L solution of phenol were destroyed after 4 h of reaction. Acid washing is thus an efficient post treatment for improving the catalytic activity of SBACs. This result is significant as for a commercial Merck carbon, washed with HCl solution to eliminate the mineral matter of the carbon, a negative effect on conversion (50% decrease compared to the untreated carbon) was reported by Santiago et al. (2005). The mayor drawbacks of acid washing are related to the increasing carbon production costs and the environmental contamination due to the use of HCl solutions.

**Effect of chemical activation and posterior acid washing on active carbon performance in phenol oxidation.**

The work conducted on K2CO3 activated carbons revealed that chemical activation is the most efficient but also the most expensive method to produce active carbons. The use of environmentally friendlier K2CO3 as the chemical activation reagent with subsequent water washing resulted in DMAD carbons (DMK_W) with both high surface areas and phenol and TOC removals of 87% and 76%, respectively (see figures 13.6a and 13.6b). As for physically activated carbons, the chemically activated DMAD carbon subjected to acid
washing with 3% of HCl solution (DMK_A) exhibited a superior oxidation potential reaching 93% and 82% of phenol and TOC destruction at the same reaction conditions (see figures 13.6a and 13.6b). For comparison, the commercial Chemviron Carbon AP4-X performed similar phenol and TOC removals of 97% and 88%.

Figure 13.6. Influence of physical and chemical activation on a) Phenol and b) TOC removal; batch operating conditions: P\textsubscript{O2}=4 bar, T=160\(^\circ\)C, C\textsubscript{Ph,0}=5 g/L, W=2g.

Quantification of metal leaching from sludge based active carbon during batch oxidation of phenol.

SBACs are known to have a high residual mineral content that attained values of 70% for DRAW carbons and up to 80% for DMAD carbons. A key problem associated with the use of such carbons is their high propensity towards metal leaching at acidic pH values (Fitzmorris et al, 2006). At the reaction conditions studied in this work, final pH of the reaction solutions were ranging from 3 to 7, most probably due to a combined action of low chain carboxylic acids formation during CWAO and the more or less basic nature of the SBACs. All metals under investigation (Fe, Cu, Cr, Mn, Mg and Ca) leached into solution (see table 13.1). Carbons exhibited a greater tendency towards leaching Ca (for DMAD: 1 to 20 ppm and for DRAW: 0 to 75 ppm) and Mg (for DMAD: 3 to 61 ppm and for DRAW: 5 to 67 ppm). However, these metals were not considered to pose a significant problem. Catalytically active and more toxic metal ions such as Cu and Fe were leached in quantities below or close to the established threshold values for surface discharge (1 ppm for Cu and 10 ppm for Fe). Most stable, almost leaching free, carbons were the DRAW carbon carbonised at 1000\(^\circ\)C and the K\textsubscript{2}CO\textsubscript{3} activated carbon leading to a final pH of solution of 7.1 and 6.9, respectively. This corroborates the findings of Fitzmorris et al. (2006) who reported that metal leaching is pH dependent and strongly reduced at neutral values. Control of pH of the reaction medium can therefore be a simple and efficient solution to prevent or reduce undesirable metal leaching of sludge based carbons, that otherwise would require a posterior treatment of the effluents coming from the CWAO process.

Table 13.1 Metal concentration measured after 4h batch reaction: P\textsubscript{O2}=4 bar, T=160\(^\circ\)C, C\textsubscript{Ph,0}= 5 g/L, W= 2 g.

<table>
<thead>
<tr>
<th>SBAC</th>
<th>[Fe] (ppm)</th>
<th>[Cu] (ppm)</th>
<th>[Cr] (ppm)</th>
<th>[Mn] (ppm)</th>
<th>[Mg] (ppm)</th>
<th>[Ca] (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DM-SA</td>
<td>13.1</td>
<td>1.3</td>
<td>3.0</td>
<td>1.9</td>
<td>15.2</td>
<td>16.2</td>
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<tr>
<td>DM-CO\textsubscript{2}</td>
<td>21.9</td>
<td>1.2</td>
<td>0.4</td>
<td>1.1</td>
<td>61.0</td>
<td>4.0</td>
</tr>
<tr>
<td>DMK_A</td>
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<td>0.0</td>
<td>0.3</td>
<td>3.1</td>
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<tr>
<td>DMK_W</td>
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<td>0.0</td>
<td>0.0</td>
<td>56.9</td>
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<tr>
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<td>0.0</td>
<td>2.8</td>
<td>59.7</td>
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</tr>
<tr>
<td>DR-SA</td>
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<td>0.1</td>
<td>16.7</td>
<td>n.a.</td>
</tr>
<tr>
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<td>0.0</td>
<td>0.1</td>
<td>60.7</td>
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</tr>
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<td>0.0</td>
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<td>75.0</td>
</tr>
</tbody>
</table>
Batch oxidation of phenol, o-cresol, o-chlorophenol and p-nitrophenol over sludge based active carbons.

Real waste water effluents are in general of complex composition and it is important to assess the catalytic potential of SBACs for other phenolic compounds. Oxidations tests of substituted phenols performed with a selected carbon prepared from each sewage sludge feedstock allowed establishing the following order of catalytic reactivity of compounds: o-cresol > phenol > o-chlorophenol >> p-nitrophenol. The same order was found for all carbons tested (DRAW-SA, DMAD-K$_2$CO$_3$ and commercial AP4-X). Very close and high compound and TOC removals were observed for commercial AP4-X and sludge based carbons in the case of o-cresol, phenol and o-chlorophenol (see figures 13.), whereas p-nitrophenol proved to be very refractory to oxidation over active carbon at the given conditions of temperature and oxygen pressure. Recent results reported by Santos et al. (2006) and Suarez-Ojeda et al. (2005) on two other highly active commercial active carbons from Merck and Chemviron Company (Industrial React) are in line with our study and reaffirm the promising catalytic potential that have sludge based carbons in the oxidation of certain substituted phenolic compound families.

![Oxidation of phenolic compounds over sludge based activated carbons: batch operating conditions: $P_{O_2} = 4$ bar, $T=160^\circ C$, $C_{Ph,0} = 5$ g/L, $W=2g$.](image)

Conclusions.

A mayor conclusion of the oxidation experiments performed in a batch reactor is that the reactivity of sludge based carbons in CWAO of phenolic effluents is strongly dependent on the preparation method applied. The following order starting with the lowest catalytic performance can be established from the results: carbonised sludge based carbons < carbons prepared by steam or CO$_2$ activation < physically activated carbons with posterior acid washing < chemically activated carbons < chemically activated carbons with posterior acid washing ≈ commercial carbons. However, an improvement in catalytic performance is associated with the use of more expensive activation reagents or 2 steps treatment (activation plus acid washing) and ergo adversely affects the overall production costs of the carbon. It has to be pointed out that the most efficient preparation method (chemical activation plus acid washing) is capable to provide sludge based carbons for the CWAO that are fully competitive with the most reactive carbons commercially available (among others Chemviron AP4-X, Chemviron Industrial React and Merck,). These latter carbons perform on a par with many of the noble metal or (mixed) metal oxide supported catalysts tested in CWAO of phenol (see Table 2 in Eftaxias et al., 2005, Bhargava et al., 2006, Arena et al., 2008, Nousir et al., 2008, Pintar et al., 2008, Resini, et al., 2008Wang et al., 2008).

CATALYTIC WET AIR OXIDATION OVER SLUDGE BASED ACTIVE CARBONS IN CONTINUOUS TRICKLE BED REACTOR.

Industrial waste water treatment requires the use of active and stable supported catalysts in continuous reactors such as trickle bed reactors to treat the high volumetric quantities of waste water effluents generated. In order to assess the long term activity and stability of SBACs, oxidation tests of 3 days were conducted in a laboratory trickle bed reactor to determine adequate operating conditions for catalyst activity and stability, i.e. resistance to burn off, metal leaching and mechanical attrition. Selected carbons were the economically more attractive steam activated DMAD and steam activated hardened DRAW carbons.
**Determination of operating conditions for CWAO of phenol in Trickle Bed Reactor.**

A stable activity over 72 h can be only observed at 140°C and 4 bar of partial oxygen pressure. The two steam activated DMAD and DRAW carbons performed phenol conversions of 20-25% compared to 50% in case of the commercial AP4-X carbon. Contrary to batch oxidation, both DMAD and DRAW carbons show now a similar activity in continuous operation (see figure 13.8b). To recover a phenol removal of 50% it is enough to raise the reaction temperature by 20°C to 160°C (at same oxygen partial pressure of 2 bar). However, at this temperature the carbons (commercial AP4-X included) exhibited a certain loss of activity over time certainly due to enhanced carbon burn off (see figure 13.8b).

**Figure 13.8.** a) TBR conversion of phenol for DMAD obtained at different operating conditions after 72 h of TOS and b) TBR conversion of phenol versus TOS for commercial AP4-X, steam activated DMAD and hardened DRAW obtained at 160°C and 4 bar of oxygen partial pressure.

**Determination of carbon burn off during continuous CWAO of phenol.**

CWAO itself is a very soft surface treatment and depending on the operating conditions (temperature and oxygen partial pressure) some burn off of the carbon surface and carbon weight loss after oxidation has been observed (Fortuny et al., 1999). In our TBR experiments carbon burn off becomes only noticeable at temperatures of 160°C or 4 bar of oxygen partial pressure, though attaining in the worst case approximately 35% after 72 h of operation (see table 13.2).

**Table 13.2.** Weight loss of SBACs after 72 h of continuous CWAO (ΔW).

<table>
<thead>
<tr>
<th>Experiment</th>
<th>ΔW (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSA-140-2</td>
<td>12.4</td>
</tr>
<tr>
<td>DMSA-160-2</td>
<td>-18.3</td>
</tr>
<tr>
<td>DMSA-160-4</td>
<td>-33.4</td>
</tr>
<tr>
<td>DRSA-H-140-4</td>
<td>-12.1</td>
</tr>
<tr>
<td>DRSA-H-160-4</td>
<td>-35.5</td>
</tr>
</tbody>
</table>

**Determination of carbon hardness and metal leaching during continuous CWAO of phenol.**

A significant finding is the low propensity of the SBACs towards toxic metal leaching during continuous operation despite their high mineral fraction. Lowest metal leaching underwent the second generation of the hardened DRAW carbon with metal concentration in the reactor exited samples of 1 to 5 ppm for Fe and below 1 ppm for Cu. The steam activated DMAD carbon leached somewhat more Fe and Cu with mean values of 6 ppm and 1 ppm, respectively. Surprisingly, the commercial AP4-X carbon exhibited the highest propensity towards Fe leaching with mean concentration of 8 ppm and 15 ppm at 140°C and 160°C, respectively.

Mechanical stability of carbons was only a problem in the case of the steam activated DRAW carbon. The hardness of pellets obtained from DRAW carbon powder was very low and attrition readily provoked undesired clogging of the Trickle Bed Reactor. Several hardened forms of the DRAW carbon were thus tested in continuous operation. It appears that lignosulphonate based binder material is the best option to pelletise DRAW carbons with an adequate mechanical strength for use in continuous reactor operation.

**Conclusions.**
The two carbons prepared by steam activation from DRAW and DMAD sewage sludge feedstock performed a stable activity and high resistance to both metal leaching and mechanical attrition during 72 h of continuous CWAO of phenol at 140°C and 4 bar of oxygen partial pressure. However, at this temperature the catalytic activity of the carbon is too low for the efficient destruction of phenolic waste water contaminants (only 20-25% of phenol conversion). Higher conversions can be readily obtained by increasing the temperature to 160°C, but the improvement of activity is set off by a significant loss of stability due to enhancement of carbon burn off reactions. Nevertheless, there exists several possible solutions to mitigate this problem, i.e. the use of chemically activated or/and acid washed sludge based carbons that are much more active or the surface impregnation of carbonised or physically activated sludge based carbons with small amounts of iron (Fe). The latter alternative has been already demonstrated to strongly enhance the catalytic activity of commercial active carbons for the catalytic wet air oxidation of phenol in trickle bed reactors (Quintanilla et al., 2005, Baricot, 2008).

It must be stressed that the potential and economical perspective of CWAO lies in its smart utilisation as a pre-treatment (and not a total remediation) of organic wastewater to improve their biodegradability to safe levels for subsequent biological end treatment. The exact determination of the required oxidation deepness or biodegradability of the effluent stream is then the key factor that determines the process economics and ergo the successful application of CWAO. Biodegradability enhancement (sum of readily and slowly biodegradable COD) can be assessed by fast respirometric experiments (Orbon et al., 1997). This technique only measures the readily biodegradable COD fraction of a specific effluent, but avoids the extremely time-consuming determination of the total biodegradable COD (Brouwer et al., 1998). Further research work is required to obtain suitable indicators that establish the partial oxidation degree of a treated CWAO effluent necessary for safe discharge into the biological end treatment.

CFD INVESTIGATION OF PILOT SCALE TRICKLE BED REACTOR AT COLD AND REACTING FLOW CONDITIONS.

**CFD hydrodynamic predictions of moderate- to high-pressure trickle-bed reactors.**

Two Computational Fluid Dynamics multiphase frameworks were developed for the hydrodynamic analysis aiming to predict the liquid holdup and pressure drop in the trickling flow regime with a three-dimensional computational grid. Euler-Euler and Volume-of-Fluid multiphase models were optimized in terms of mesh density, time step, convergence criteria, discretization schemes and Reynolds Averaged Navier-Stokes turbulence models (Lopes and Quinta-Ferreira, 2008; Lopes and Quinta-Ferreira, 2009a; Lopes and Quinta-Ferreira, 2009b). Several computational runs were performed querying the effect of gas and liquid flow rates, operating pressure and temperature on liquid holdup and two-phase frictional pressure drop. Multiphase flow distribution was investigated with different gas-liquid distributors using the Eulerian framework (Lopes and Quinta-Ferreira, 2009c), whereas hysteresis phenomena and wetting efficiency in trickle beds were evaluated with the Volume-of-Fluid model (Lopes and Quinta-Ferreira, 2009d).

**Quantification of axial and radial profiles bulk temperature and Total Organic Carbon conversions in continuous trickle-bed reactors.**

The kinetic parameters of CWAO were further integrated within the Euler-Euler and Volume-of-Fluid models where the reaction aspects as well as the transport mechanisms were accounted for in a high-pressure trickle-bed reactor so that both multiphase CFD frameworks were evaluated for either cold flow or reacting flow conditions. Axial and radial profiles of hydrodynamic and reaction parameters were evaluated at different operating conditions (Lopes and Quinta-Ferreira, 2009e). The influence of gas and liquid flow rates as well as the effect of temperature and pressure were investigated in terms of total organic carbon (TOC) conversions. TOC removal efficiency depends heavily on the bed temperature while the operating pressure has minor influence in final conversion. Whereas the effect of liquid flow rate was mainly related with the reaction time, the influence of gas flow rate led to a maximum on TOC conversion. Moreover, higher values of inlet pollutant concentration led also to higher conversions (Lopes and Quinta-Ferreira, 2007a; Lopes and Quinta-Ferreira, 2007b). The multiphase Eulerian predictions handled agreeably better the effect of different numerical solution parameters either supported at non- and reacting flow conditions with respect to Volume-of-Fluid model.

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13.4. Impact of the WP on its industry or research sector.

RESEARCH IMPACTS.

Pioneering the utilisation of sewage sludge based carbons as catalytic materials for waste water treatment of phenolic effluents in Trickle Bed Reactor.

The work performed in workpackage 13 focus on the innovative utilisation of low costs carbons prepared from sewage sludge as novel catalysts for the waste water treatment of phenolic effluents. A key impact is that the catalytic activity of sludge based carbons can be readily tuned by adequate preparation methods to provide catalytic materials that are fully competitive with both commercial carbon catalysts and many metal or metal oxide supported catalysts. A mayor drawback that is the burn off of carbons occurring during continuous operation was evidenced, however strategies to mitigate this problem are proposed. It is therefore hoped that this work has made a convincing and stimulating case for the scientific and industrial community to continue investigating the perspective of sludge based carbons as catalysts for waste water treatment and ergo to develop low cost processes that can be integrated at industrial scale.

Scientific publications and congresses.

One of the key outputs will be the production and subsequent publication of two publications in international scientific journals. The first paper highlights the influence of preparation of SBACs on their catalytic activity and stability to metal leaching in the catalytic wet air oxidation of phenolic contaminants in batch reactor. The writing of this paper is completed to 90% and will be submitted soon to the journal Applied Catalysis B: Environmental for peer review. The second paper is under preparation and will analyse in detail the body of results obtained in the continuous trickle bed reactor experiments.

Part of the results has been already presented in two international congresses hold this year in Biarritz (Carbon09, the annual world conference on carbon, June 14-17 of 2009) and Venice (GPE09, the 2nd international congress on green process engineering, June 14-17 of 2009). The contribution sent to Venice received an excellent evaluation and the scientific congress committee invited us to submit a full paper for
possible publication in the journal International Journal of Chemical Reactor Engineering. Further dissemination of some relevant findings is scheduled to take place during the 8th World Congress of Chemical Engineering organised in Montreal, August 23-27 of 2009. Our 6 pages extended abstract has been accepted as an oral presentation in the technical program of the congress with the possible option of publication in a special issue dedicated to the congress (not decided yet).

Regarding the scientific output generated by the Computational Fluid Dynamics studies, up to eight articles are already published in the following leading peer-reviewed research journals in the chemical and environmental related sciences: Chemical Engineering Journal, Chemical Engineering Science, American Institute of Chemical Engineers, Industrial and Engineering Chemistry Research Journals.

SOCIAL AND ENVIRONMENT IMPACTS.

In the European Union as a whole, the annual production of sewage sludge exceeds 10 millions tons a year (Laturnus et al., 2007). Consequently, its safe handling and disposal has become the most pressing problem of the wastewater treatment sector. If this problem is not appropriately dealt with in the near future, it will exert a strong negative impact on the environment and human society.

Workpackages 12 and 13 have demonstrated in close collaboration that sewage sludge can be valorised into active carbons that among other applications as adsorbent may serve as an efficient catalyst for the remediation of phenolic wastewater. The conversion of sewage sludge into valuable products is therefore a highly viable and environmentally friendlier alternative to the existing disposal (land filling, agriculture) routes and thermal incineration. Some of the main advantages that if can offer are briefly described below.

- The production and subsequent use of SBACs is a sustainable and environmentally friendlier option than land filling, disposal and incineration of produced sewage sludge.
- SBAC production should receive better public acceptance than land filling, agricultural disposal and incineration of sewage sludge.
- A 60-80 wt% reduction in dried sludge mass by physical activation is possible.
- The presence of phenolic compounds in WWTP streams is harmful to the active biomass and generates extra sewage sludge during the biological treatment. The partial remediation of phenolic effluents prior to their discharge into a WWTP using sludge based active carbons would therefore benefit from an in-situ reduction of the production of sewage sludge. Moreover, the sewage sludge in its valorised form would return to the WWTP where it was originated and would help to close the life cycle of sewage sludge.
- The quick disposal of generated sewage sludge into production of active carbon could mitigate the problem of malodours in the surroundings of WTTTP which stems from the release of hazardous gases (H_{2}S) produced during anaerobic microbiological decomposition processes (Ansari et al., 2005).
- Irrespectively of the benefits that will generate reduced sludge volumes, a mayor social and environment impact is the opportunity that low cost sludge based carbons combined with CWAO technology offer to decontaminate waste water that contain biorefractory organic compounds and ergo are not amendable to direct biological treatment.

INDUSTRIAL AND ECONOMIC IMPACTS.

The industrial and economic impacts of this work go hand in hand and have been grouped together under a single heading. Probably the most viable option to utilise CWAO technology and sludge based carbons is their integration into the wastewater treatment facilities operated by the own plant to remediate the arising process effluents. The idea of this approach is to improve in-situ the biodegradability of phenolic effluents to levels that allow for posterior discharge into the existing biological end treatment of the industrial plant. Figure 13.9 gives a schematic illustration of the combined process of CWAO and biological WWTP.
Figure 13.9. In-situ remediation of process water produced at the plant site: Integration of CWAO technology using TBR and sludge based carbon catalyst for the treatment of factory own phenolic effluents.

Since waste water treatment is mandatory to preserve the environment, the treatment costs must be kept as low as possible in order not to adversely affect the net benefits of the industrial plant. It is in this sense that CWAO of organic effluents using sludge based active carbon in trickle bed reactor can positively interfere in the overall cost balance. However, to fully exploit the potential of this technology, some prerequisites are required at the plant site:

- Existence of a biological wastewater treatment in the industrial plant (Harf et al., 1999), i.e. CWAO should be applied at the source of wastewater production (Levec and Pintar, 2007).
- Intelligent management of the different wastewater streams produced at the plant, i.e. process water polluted with biotoxic organic compounds should be directly discharged to the CWAO unit to avoid both undesired dilution of the TOC fraction and high liquid volumes to be treated.
- Availability of adequate system for the recollection and/or separation of wastewaters originated at the plant site.

In the aforementioned scenario, the following relevant items of cost savings/revenues would arise from the utilisation of CWAO-SBAC-TBR technology integrated in existing WWTP facilities.

It was assumed that if the phenolic wastewater effluents were pre-treated by CWAO then the cost of externally incinerating the effluents would be obviated. This will lead to substantial cost savings for the company given the low treatment costs of CWAO, in particular with respect to incineration. Among the commercial oxidation processes or thermal incineration applied at industrial scale, the estimated costs per m$^3$ of effluent treated are 10-15 €/m$^3$ for CWAO (Nippon Sokubai process) compared to 15-30 €/m$^3$ for WAO (ZIMPRO process) and 210-280 €/m$^3$ for thermal incineration (see table 13.3).

**Table 13.3.** Estimated treatment costs per m$^3$ effluent for WAO, CWAO and thermal incineration.

<table>
<thead>
<tr>
<th>Process</th>
<th>T (ºC)</th>
<th>P (bar)</th>
<th>tres (min)</th>
<th>Conversion (%)</th>
<th>Costs (€/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WAO (Zimpro)</td>
<td>200-325</td>
<td>20-210</td>
<td>10-90</td>
<td>80-99</td>
<td>15-30*</td>
</tr>
<tr>
<td>CWAO (Nippon)</td>
<td>130-250</td>
<td>20-50</td>
<td>10-60</td>
<td>98</td>
<td>10*</td>
</tr>
<tr>
<td>Incineration</td>
<td>900-1000°C</td>
<td>1</td>
<td>--</td>
<td>99</td>
<td>210-280**</td>
</tr>
</tbody>
</table>

* as reported in Levec, 1997,
** costs estimation obtained from incineration plant of Constanti (Tarragona) called Gestió Residual Especials de Catalunya, S.A.

Moreover, CWAO conducted in TBR was evaluated to become economically attractive for treating organic effluents with an initial COD content superior than 10 g/L. Beyond this COD limit, adiabatic operation of the CWAO reactor is thermally self-sufficient due to the exothermic nature of the oxidation reactions (Katzer et al., 1976 and Farha et al., 1978). Then, CWAO is highly cost effective compared with other advanced oxidation processes (O$^3$) or biological processes (BIO) as shown in table 13.4 (Lenntech). This table also
highlights the fact that according to economic evaluations of Lenntech Water Treatment & Air Purification Holding, B.V., the treatment costs per m³ effluent are strongly dependent on the pollution level of the effluent stream.

Table 13.4. Treatment costs (€/m³) versus initial COD.

<table>
<thead>
<tr>
<th>COD (g/L)</th>
<th>CWAO</th>
<th>BIO</th>
<th>O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>5.1</td>
<td>8.4</td>
<td>45.4</td>
</tr>
<tr>
<td>50</td>
<td>15.9</td>
<td>41.3</td>
<td>227</td>
</tr>
<tr>
<td>100</td>
<td>29.6</td>
<td>82.5</td>
<td>454</td>
</tr>
</tbody>
</table>

Important savings in operation costs can be also expected from the replacement of more expensive supported noble metal/metal oxide catalysts or commercial carbons by low cost SBACs (see table 13.5). CWAO requires only low grade application carbons, which therefore can be benefit from a significant retail of the market price of commercial carbons. An economic study of the production plant of a steam activated SBAC undertaken by ICL revealed thus an overall cost of only 51€ per tonne of carbon. In 2007 a commercial coal-based steam-activated granular activated carbon retailed in the region of 720 €/tonne (Roskill Information Services Ltd, 2008). From table 13.5 it is also seen that the prices of supported metal oxide and noble metal catalysts compared to commercial carbons strongly increase by about one and two orders of magnitude, respectively. This therefore makes the use of low cost SBACs highly viable for CWAO of organic wastewater streams at industrial scale.

Table 13.5. SBAC production cost and market prices of CWAO catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>SBAC</th>
<th>AP4-X</th>
<th>1%CuO/Al₂O₃</th>
<th>1%Pt/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cost (€/tonne)</td>
<td>51</td>
<td>1500*</td>
<td>~9000**</td>
<td>~50000**</td>
</tr>
</tbody>
</table>

*bulk price as offered from Chemviron Company
**price offer from catalyst manufacturer

The treatment cost with integrated CWAO+WWTP technology will be further decreased if one takes into account that only partial oxidation of the TOC fraction of the organic wastewater effluent is required. This will result in significant savings of equipment and operation costs if lower temperatures and pressures can be applied to CWAO process.

Finally, integrated CWAO + WWTP technology should be oriented towards the remediation of process water for their potential reuse in or recycle to the industrial plant. The cost of tap water is constantly increasing and on average one cubic meter prices now about 1.5 – 2.5 €. Upon that, when extracting groundwater, a levy of 0.15-0.2 € must be added. The same trend holds for draining off waste water, which has risen by 20% in the past 5 years. The reuse of treated process water will thus further contribute to save a company additional expenses arising from the renewal of fresh tap water and draining off process water.

CONCLUSION.

Overall, the utilisation of SBACs as a CWAO catalyst for the partial oxidation of phenolic effluents in continuous Trickle Bed Reactor combined with subsequent biological end treatment can extremely lower the company's costs to pay for external waste water treatment. Application of chemical activation or HCl washing to enhance the SBAC performance may be required and will augment the production costs of carbon; however the margin of cost reduction expected for CWAO+WWTP technology remains strong even under these circumstances.

REFERENCES.


14. **Utilisation of activated carbon as catalyst in AD-OX process.**

14.1. **Summary description of project objectives, work performed and end results, elaborating on the degree to which the objectives were reached.**

**PROJECT OBJECTIVES.**

This work-package aims to investigate the feasibility of a new potential water treatment process: AD-OX, with sludge based activated carbon. AD-OX is a sequential process based on: first room temperature adsorption and second regeneration by catalytic wet air oxidation at higher pressure and temperature. The main advantage of this process would be to provide in situ regeneration of the spent activated carbon which is a waste in industrial waster water treatment. SBAC are to be prepared by the work-package “production of activated carbon from sludge”.

**WORK PERFORMED.**

As Sludge Based AC (SBAC) was provided only after month 14 and in rather few varieties and few quantities, a large part of the work has been achieved using commercial AC.

First both commercial and sludge based AC were thoroughly analysed and compared before and after being used as adsorbent and oxidative catalysts.

The sequential AD-OX process being based on two major steps, adsorption and oxidation, these two steps have been extensively investigated, first separately, with various commercial and sludge based AC and with various organic pollutants: phenol, phenol derivatives, mixtures of these phenols, pharmaceutical compounds, dyes, and real effluents issued from industrial wastewater treatment plants.

In parallel two reactors have been built up: a small automated reactor for multiple adsorption-oxidation cycle tests and a semi industrial pilot plant reactor for preliminary scale up. They have been used to carry out AD-OX process with selected commercial AC and sludge based AC. A global modelling of the two AD-OX steps has been derived.

As oxidative regeneration by pressurised air was not as efficient as expected, several other alternative advanced oxidation techniques have been tested. Especially Fenton oxidation was more intensively investigated.

**END RESULTS.**

SBAC provided the work-package “production of activated carbon from sludge” have very high ash content including metal oxides and low surface area compared to commercial AC. Nevertheless they offer rather acceptable adsorption capacity and catalytic activity for pollutant oxidation (about half that of commercial AC).

Most of pollutants investigated in this work-package were conveniently adsorbed then oxidized on AC and SBAC in the AD-OX process. The main problems are due to:

- Relatively low regeneration of AC and SBAC as soon as the first oxidation has been carried out, the adsorption capacity dropping to about 25%, but being quasi stabilized for other AD-OX cycles.
- Poor mechanical properties of the best SBAC (SA_DRAW: steam activated dewatered raw sludge). This SBAC is not strong enough to support high pressure and shear stresses of a fixed bed and was crushed leading to bed clogging. Trials for strengthening it were not successful due to foaming and metal leaching. More work is still necessary to design (WP12) and test (WP14) convenient SBAC.

Other regenerative oxidations (photocatalytic, UV, ultrasonic, Fenton...) are only slightly better than air oxidation (standard AD-OX). Preliminary tests on electrochemical regeneration are very promising. Concerning economy aspects standard AD-OX will be highly profitable for actual industrial effluent treated with commercial AC (1350€/ton), if corrosion is prevented at reasonable cost. Concerning SBAC, due to its low cost (about 250€/ton according to WP12), it does not deserve uneasy partial regeneration and should be very profitably used as adsorbent for single use and, to less extend, as oxidative catalyst in CWAO, according to WP13.
14.2. Methodologies and approaches employed.

AD-OX is a sequential water treatment process proposed by Partner 5. It is based on two main steps: 1- adsorption on activated carbon at room temperature to remove pollutants from aqueous effluents 2- batch oxidative regeneration of AC by pressurised air (or other stronger oxidant). The advantage of wet air oxidation is that AC is the catalyst of its own regeneration.

The methodology selected to get a deep knowledge of such process was to investigate separately the two steps in simplified conditions and equipments with respect to the pressurized AD-OX reactors to be built in parallel.

Adsorption was first characterized by adsorption isotherms at room temperature for a variety of commercial AC. Adsorption capacity of different non biodegradable pollutants was linked to AC physicochemical properties (surface area, micro-meso porosity, metal content, surface function acidity...).

Similarly wet air oxidations were carried out in aerated autoclave reactor containing AC in a basket. Oxidation rates were compared for same ACs and pollutants, on several successive runs, to observe the decay of adsorption capacity. The pollutant concentration was followed but also the Total Organic Carbon or the Chemical Oxygen Demand. The evolution of AC properties after several uses was also linked to adsorption and oxidation deactivation.

The results of these two investigations gave orientations to select convenient operation conditions (temperature, pressure, reaction time), and to ask for specific Sludge Based Activated Carbon properties to WP 12 in charge of providing SBAC.

An important aspect concerning the significance of this work with respect to actual industrial waste water has been addressed in this work: in addition to phenol as the usual pollutant model, a large variety of other non biodegradable pollutants has been investigated, separately or in mixtures - actual effluents being always complex mixtures. Finally true effluents, withdrawn at the exit of industrial waster water treatment plants, have been treated.

As the economy of AD-OX process is strongly connected with the number of reuses of AC it is important to be able to carry out long series of AD-OX cycles in pre-selected convenient conditions. For this a mini automated AD-OX reactor has been designed and built up during the first year. It can move from (1) adsorption step to (2) liquid batch heating and pressurization, then (3) oxidation and (4) cooling and depressurization, by following UV adsorbance of the liquid effluent at adsorption exit (Æ2), temperature and pressure (Æ3) in the reactor, CO2 concentration at gas exit (Æ4), temperature in the reactor (Æ1). The small size of the fixed bed of AC will limit the adsorption time and give faster results.

In addition a much larger pilot plant, previously used as continuous fixed bed for CWAO, has been modified to be used for AX-OX cycles with batch oxidation and liquid recycle in a loop. This equipment is of less easy use but performs a first scale up for predictive design of a future industrial plant.

As regeneration by wet air oxidation was not as efficient as expected several other advanced oxidation processes have been tried to be involved in a modified AD-OX process.

Modelling of the complete process has been achieved with significant simplifications as the description of the detailed batch recycled oxidation step is out of reach, due to time and space variations of temperature in the fixed bed reactor during this step. On the contrary the adsorption step, the useful one with respect to water purification, has been much more precisely represented.

14.3. Achievements of the project related to the state of the art.

INTRODUCTION: STATE OF THE ART ON ACTIVATED CARBON USE AND REGENERATION.

One of the major techniques for the treatment of low concentrations of toxic organics in water is based on adsorption by activated carbon (AC), either in powdered or, most often, in granular form. AC adsorption can fully replace biological treatment but better it can be effective for separating biorefractory organics from water leaving conventional biological waste water treatment plants. AC adsorption as end step is the best technology according to Sarp Industries-Veolia (private communication, 2009).

However, the saturated AC must be regenerated before reuse. The first commercial-scale adsorption plants used to burn the spent AC. Over the years a variety of regeneration techniques have been suggested, evaluated and applied. These methods are based either on desorption, induced by increasing temperature or by displacement with a solvent, or on chemical decomposition of the adsorbed species induced by thermal,
chemical, electrochemical or microbial processes, as presented on Figure 14.1 according to Sheintuch and Matatov-Meytal (1999).

The most commonly used regeneration, thermal regeneration, based on either desorption with inert gas or reactive decomposition by water vapour or flue gas needs very high temperature (700-1000°C) and then should only be achieved in few very large specialized units.

**Extractive regeneration** methods that use volatile solvents (*solvent regeneration*) have been investigated, but current applications of this technology with AC are not known. Ethanol regeneration has been proposed but in any case a subsequent separation is still needed to recover the solvent. Supercritical fluid extraction exhibits enhanced mass-transfer properties over liquid solvent extraction. However, complete regeneration of AC loaded with organics like phenolic compounds, with supercritical fluid extraction using CO₂, could not be achieved and a large amount of CO₂ would be required. As main drawback, these *solvent regeneration* serves only to transfer the contaminant from one location (AC) to another (solvent or surfactant) and do not destroy the pollutants which have to be treated subsequently.

**Reactive regeneration** methods appear much more attractive as they destroy the adsorbed organics by chemical (including acid–base or oxidative transformations, microbial or electrochemical processes. The chemical methods may involve complete mineralization of the adsorbed species (to carbon dioxide and water), transformation of complex molecules into simpler compounds and the conversion of hazardous materials to more desorbable, water-soluble or more biodegradable compounds. Chemical oxidation using various oxidants -chlorine, chlorine dioxide, hydrogen peroxide, Fenton, ozone and potassium permanganate (Horn and Tseng, 2008, Liang et al., 2009, Bento and Rein, 2007, Huling et al., 2005, Arnold, 2006, Toledo et al., 2003, Alvarez et al., 2005) has been tested and at least partial restoration of AC adsorption capacity was demonstrated. Similarly unconventional techniques including ultrasound (Weng and Hsu, 2008), electrochemistry (Zhang, 2002, Zhou and Lei, 2006, Weng and Hsu, 2008, Narbaitz and Karimi-Jashni, 2009) microwaves (Ania et al., 2005) electrodialysis (Drouiche et al., 2006) and plasma discharges (Qu et al., 2009) have been tried.

These advanced oxidation processes, however, have not fully proven technically feasible for continuous operation and nor to be economically viable.

An established technology for regeneration of spent AC with organics or oxidizable inorganic compounds is *wet air regeneration* (*WAO*) but this method is rather expensive because of the required large investments in high pressure equipment (~200 bar) and the high cost of running the regeneration at high pressure and temperature (Gonzalez et al., 2002, Shende and Mahajani, 2002).
Catalytic regeneration methods may enhance the decomposition rates and enable to carry the regeneration at lower temperatures and lower residence times. They could use either desorption followed by catalytic liquid-phase oxidation, or direct oxidation of the adsorbed species on an AC-adsorbent modified with a catalyst. In the former approach, the water is not contacted with the catalyst and metal dissolution is not a problem. In the latter approach, metal dissolution may occur and should be controlled.

The great improvement to be expected would be to achieve direct oxidation only with activated carbon which in this case catalyses its own regeneration. This is the purpose of AD-OX process proposed by Institut National Polytechnique de Toulouse leader of this work-package.

CHARACTERIZATION OF THE 6 SLUDGE BASED AC PROVIDED BY WORK-PACKAGE “PRODUCTION OF ACTIVATED CARBON FROM SLUDGE”. COMPARISON WITH COMMERCIAL AC.

First a complete comparison of usual characteristics of the 9 AC (3 commercial ones and 6 sludge based – 5 from Imperial College of London, 1 from Université-École des Mines de Nantes) tested in this work-package have been performed using the same equipment and methods.

From Imperial College of London:
- C_DRAW is a Carbonised Dewatered Raw sludge.
- C_DMAD is a Carbonised Dewatered Mesophilic Anaerobically Digested sludge.
- SA_DRAW is a Steam Activated Dewatered Raw sludge (the same has also been “hardened”).
- SA_DMAD is a Steam Activated Dewatered Mesophilic Anaerobically Digested sludge.

From Université-École des Mines de Nantes:
- C+CO2A is a Carbonised and CO2 Activated sludge.

The results are given in Table 14.1 showing much less surface area of sludge based AC (from 90 to 265 m²/g) when compared to commercial ones (from 980 to 1860 m²/g). Interestingly the pore size does not vary very much though larger in sludge based AC. Theses 6 SBAC have smaller microporous volume than mesoporous ones. The best SBAC in terms of surface area, is SA_DRAW, a steam activated AC obtained from Dewatered Raw sludge. Conversely carbonized then CO2 activated SBAC showed a lower surface area and pore volume. As SA_DRAW has the best characteristics and the best performances (as it will be shown later) it has been selected to be hardened by adding 5%PVA as a binder. No significant variations of main characteristics were observed due to the binder, except foaming when used in trickling flow.

### Table 14.1. Properties of commercial AC and SBAC (Sludge Based Activated Carbons).

<table>
<thead>
<tr>
<th>Active carbon</th>
<th>BET Surface m².g⁻¹</th>
<th>Mesoporous volume cm³.g⁻¹</th>
<th>Microporous volume cm³.g⁻¹</th>
<th>Pore Ø Å</th>
<th>Apparent density /kg.m⁻³</th>
<th>%Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>MERCK 2514</td>
<td>980</td>
<td>0.2</td>
<td>0.37</td>
<td>22</td>
<td>1032</td>
<td>0.014</td>
</tr>
<tr>
<td>PICA L27</td>
<td>1860</td>
<td>0.48</td>
<td>0.77</td>
<td>25</td>
<td>552</td>
<td>0.008</td>
</tr>
<tr>
<td>PICA S23</td>
<td>1230</td>
<td>0.04</td>
<td>0.49</td>
<td>17</td>
<td>1013</td>
<td>0.012</td>
</tr>
<tr>
<td>C_DRAW</td>
<td>180</td>
<td>0.08</td>
<td>0.07</td>
<td>27</td>
<td>1710</td>
<td>4.4</td>
</tr>
<tr>
<td>C_DMAD</td>
<td>125</td>
<td>0.11</td>
<td>0.05</td>
<td>44</td>
<td>1837</td>
<td>5.4</td>
</tr>
<tr>
<td>SA_DRAW</td>
<td>265</td>
<td>0.17</td>
<td>0.11</td>
<td>35</td>
<td>1471</td>
<td>4.8</td>
</tr>
<tr>
<td>SA_DMAD</td>
<td>155</td>
<td>0.15</td>
<td>0.06</td>
<td>45</td>
<td>1730</td>
<td>6.2</td>
</tr>
<tr>
<td>Hardened SA_DRAW</td>
<td>200</td>
<td>0.16</td>
<td>0.08</td>
<td>37</td>
<td>1519</td>
<td>5.0</td>
</tr>
<tr>
<td>C+CO2A</td>
<td>90</td>
<td>0.03</td>
<td>0.03</td>
<td>25</td>
<td>1932</td>
<td>0.66</td>
</tr>
</tbody>
</table>

DMAD = Dewatered Mesophilic Anaerobically Digested sludge
DRAW = Dewatered Raw sludge
C = Carbonised
Hardened SA_DRAW : binder PVA 5%
SA = Steam Activated, CO2A = Activated on CO2
BET surface area and poros volume measurements on Micromeritics ASAP 2010 Analyser
- mesoporous volume calculated from BJH model
- microporous volume calculated from Horvath-Kawazoe model
- average pore diameter (from single point adsorption)
- apparent density calculated from porous volume (micro + meso) and true solid density (helium pycnometer)
An additional chemical characterization of these SBAC has been performed by element analysis, as metal content, especially iron, is supposed to play a very important role on AC catalyst activity. Results are reported on Table 14.2 showing much higher ash and metal content in SBAC than in AC, which may be explained by the way of production and the material origin respectively.

Table 14.2. chemical analysis of commercial AC and SBAC.

<table>
<thead>
<tr>
<th>Active carbon</th>
<th>%Fe</th>
<th>%Cu</th>
<th>%Zn</th>
<th>%Mn</th>
<th>%ash from Merck/PICA or ICL/GPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>MERCK 2514</td>
<td>0.014</td>
<td>0.007</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>&lt; 6</td>
</tr>
<tr>
<td>PICA L27</td>
<td>0.008</td>
<td>0.011</td>
<td>0.003</td>
<td>0.006</td>
<td>8.3</td>
</tr>
<tr>
<td>PICA S23</td>
<td>0.012</td>
<td>0.007</td>
<td>0.001</td>
<td>0.001</td>
<td>3.2</td>
</tr>
<tr>
<td>C_DRAW</td>
<td>4.4</td>
<td>0.058</td>
<td>0.026</td>
<td>0.012</td>
<td>68.5</td>
</tr>
<tr>
<td>C_DMAD</td>
<td>5.4</td>
<td>0.072</td>
<td>0.11</td>
<td>0.058</td>
<td>79.0</td>
</tr>
<tr>
<td>SA_DRAW</td>
<td>4.8</td>
<td>0.067</td>
<td>0.061</td>
<td>0.015</td>
<td>63.5</td>
</tr>
<tr>
<td>SA_DMAD</td>
<td>6.2</td>
<td>0.069</td>
<td>0.12</td>
<td>0.063</td>
<td>81.0</td>
</tr>
<tr>
<td>Carbonised DRAW sludge</td>
<td>5.0</td>
<td>0.073</td>
<td>0.066</td>
<td>0.016</td>
<td></td>
</tr>
<tr>
<td>C+CO2A</td>
<td>0.66</td>
<td>0.055</td>
<td>0.053</td>
<td>0.042</td>
<td>53.0</td>
</tr>
</tbody>
</table>

4 days lixiviation in a 50% vol. acid solution (3 vol. HCl, 1 vol. HNO₃) under stirring at ambient Temperature + mineralization (95°C during 15 min).

## ADSORPTION ISOTHERMS ON SBAC. COMPARISON WITH 2 COMMERCIAL AC.

Phenol has still been selected as model molecule for adsorption characterisation and the first comparison of the 6 SBAC was achieved on adsorption isotherms using the usual method yet described in previous reports. Adsorption isotherms are reported on Figure 14.2 where also the data corresponding to 2 commercial AC are recalled.

![Figure 14.2](image-url).

Figure 14.2. Adsorption isotherms of Phenol on various commercial AC and sludge based AC (provided by the work-package "production of activated carbon from sludge").
As expected the 5 SBAC appear to be less attractive adsorbents than commercial AC. First they have less adsorption capacity than commercial AC, from 30% to 70% depending on what SBAC and what commercial AC, but this loss in adsorption capacity is moderate compared to the surface area ratio. The most dramatic loss concerns the initial slopes which are much lower for SBAC, with the exception of SA_DRAW which appear as a potential convenient AC for adsorption. These data have been analysed by fitting the well known Langmuir and Freundlich models.

As a conclusion of this preliminary work on phenol adsorption on the 6 available SBAC:

- Only low surface area SBAC was provided by ICL and GPA. These SBAC have very high ash content which is not desired for adsorption but might have a positive effect on oxidation.
- Adsorption performances on these SBAC are low compared to commercial AC but not as low as expected from surface area ratios.
- Only SA_DRAW, the steam activated AC from dewatered raw sludge, shows conveniently shaped isotherm (Langmuir type) and adsorption capacity for potential use in AD-OX process.
- This SA_DRAW when hardened with PVA is still a convenient adsorbent though about 20% less efficient.

**AUTOCLAVE OXIDATION ON SLUDGE BASED AC. COMPARISON WITH 2 COMMERCIAL AC.**

Oxidation runs have first been carried out with the 5 SBAC provided by ICL and GPA using the autoclave yet described in previous reports. Phenol as the reference model pollutant has been selected. All tests have been performed in similar conditions, same temperature and pressure, with the same initial concentration. In order to separate adsorption and oxidation effects the aqueous solution of phenol was heated to the reaction temperature and pressure under nitrogen during 12 hours to reach adsorption equilibrium before starting the oxidation step by starting the pressurized air flow.

Due to different adsorption capacities of the various SBAC the “initial” concentrations -after preliminary adsorption and before oxidation - were no longer identical and results are reported as variations of normalized concentrations by dividing by the “initial” oxidation concentration.

The poor mechanical quality of most of these SBAC did not give the opportunity to use several times these materials as adsorbents then catalyst in order to follow their ageing and ability to be used in successive AD-OX cycles. A strong recommendation was addressed to SBAC providers, in order to procure harder SBAC, able to be used without crushing in pressurized fixed beds. Same oxidation procedure has then been used for the “hardened” AC prepared by ICL from SA_DRAW.

Figure 14.3 shows oxidation tests of the 6 SBAC and, for comparison, of the 2 commercial AC previously used in this WP14 (PICA S23 and MERCK 2514). The two commercial AC gave better oxidation kinetics but, as for adsorption, the SA-DRAW -steam activated AC from dewatered raw sludge performed rather well.

The 4 other SBAC were clearly less active for catalytic oxidation and especially the less active was also the less efficient for adsorption and the less porous (carbonated and CO\(_2\) activated). Hardening SA_DRAW with PVA 5% results in lower catalyst activity but still acceptable.
As it was shown on commercial AC that catalyst activity was significantly reduced when reusing the same AC sample in successive oxidations, deactivation has also been tested on the best SBAC, hardened SA_DRAW. Results are presented on Figure 14.4. Very peculiar features were observed: nearly no oxidation at the first recycling run and very fast reaction rate increase in the second recycling run due to delayed iron leaching favouring oxidation. Such effect has also been observed in continuous oxidation at URV (WP13), where oxidation was found to accelerate after about 15hrs, which roughly corresponds to the total reaction time at the third use. Up to now there is no clear explanation on why iron leaching occurs so late, may be PVA needs some time to be dissolved or modified in the reaction medium. In any case this hardened SBAC is not suitable for AD-OX process due to this iron leaching.

The mini automated plant for fast AD-OX tests has first been used with commercial AC for verification then for a preliminary selection of AC and operation conditions.

The first AC been loaded in this mini automated plant was PICA L27. It was selected intuitively due to its mesoporous type which was supposed to be less modified by heavy oxidation by product deposition in the pores. Indeed this PICA L27 was not strong enough to undergo large pressure variations in the 50 bar runs and it was dramatically crushed leading to bed clogging, abnormal pressure drop and finally no more flow through the bed. Knowing this has been useful to ask WP12 for strong SBAC.

New experiments were carried out with microporous PICA S23 mechanically much stronger. The oxidation step has been investigated during three days with an aqueous solution of 4-hydroxyl-benzoic acid. A complete recording of a three day oxidation run is presented on Figure 14.5.

A clear agreement was found by the two independent analyses. The main feature is the strong decrease of CO2 and 4HBA concentrations after a short peak corresponding to 4HBA desorption due to heating. This CO2 and phenol decrease proves the oxidation to occur slower and finally to stop at a plateau after about 5hrs which may be considered a convenient oxidation time.

New experiments have then been carried out with the hardened SA_DRAW, supposed to be the best SBAC after preliminary adsorption and first oxidation runs. It was first crushed at about 1mm. Phenol has been selected as a model pollutant. Surprisingly lot of foam was formed during the oxidation step which was leaving the reactor by the gas exit, damaging the CO2 analyzer and leading to the stop of the run and the rejection of this SBAC for AD-OX process.
To operate AD-OX with SBAC the only choice, accounting for SBAC availability, strength, size and preliminary tests, was to use C_DMAD. The results in terms of successive adsorption breakthrough curves and concentration profiles during oxidation are presented on Figure 14.6 and 14.7 respectively.

Figure 14.7 clearly shows a dramatic decrease of the adsorption capacity – or breakthrough time, after the first oxidation. This was yet observed in successive batch oxidation experiments but not clearly quantified.
AD-OX FOR PHARMACEUTICAL WASTEWATER TREATMENT.

After preliminary runs of adsorption isotherms then batch oxidation in autoclave reactor on Levodopa and Paracetamol to check various AC and operation conditions a complete AD-OX experiment was carried out for 3 successive cycles in the semi industrial pilot plant for 1g/L Paracetamol aqueous solutions.

In order to verify the adsorption capacity the complete breakthrough curve was first derived, even the proposed AD-OX process does not follow the same procedure, stopping the adsorption step before complete breakthrough to maintain low pollutant concentration at the AC bed exit. The complete breakthrough curve gives much more information on the bed capacity and, when comparing several successive runs, on the loss of adsorption capacity due to AC deactivation due to oxidation.

The results of three successive adsorption runs, starting from fresh AC are presented on Figure 14.8.
The first breakthrough corresponding to fresh AC was used to verify the adsorption capacity of AC. Convenient agreement was found with about 10% difference with respect to adsorption isotherms. The two following breakthrough curves show important reduction of adsorption amount of Pa positive racetamol, confirming that the oxidation step is harmful for the adsorbent. Nevertheless the third adsorption does not exhibit significant additional reduction when compared to the second one. AC deactivation seems to occur at the first oxidation and not to progress later.

Two successive batch oxidation steps have been carried out after complete adsorption steps (presented just above). Very similar behaviours have been obtained as shown on Figure 14.9.

Paracetamol is progressively degraded during oxidation as expected from autoclave data.

Surprisingly in these two runs, after a while, a dramatic increase of DCO was measured. Such phenomena did not occur in the previous AD-OX investigations using Merck 2514 as Activated carbon and aqueous solutions of phenol and hydroxybenzoic acid as model pollutants. Additional investigations are required but it seems that PICA L 27 could react with pressurized air to form some organic compounds not yet identified.

![Figure 14.8. Breakthrough curves for paracetamol in AD-OX process (AC: PICA L27).](image1)

![Figure 14.9. 1st and 2nd oxidation steps of paracetamol in AD-OX process.](image2)

Similar AD-OX experiments have been carried out with PICA S23 which was proved more stable and more efficient for adsorption. Results are reported on Figure 14.10 showing two remarkable phenomena:

- After all night stops the concentration dramatically dropped, then rapidly increased up to recover the previous level. This means that during these experiments of adsorption breakthrough, the activated...
carbon is not fully saturated—despite high exit concentration, due to diffusion which goes on during night time.

- More importantly the third breakthrough curve (after 30hrs oxidation) shows better adsorption capacity recovery than the 2nd one (after 14hrs oxidation).

![Breakthrough curves for paracetamol in AD-OX process (AC: S23).](image)

**Figure 14.10.** Breakthrough curves for paracetamol in AD-OX process (AC: S23).

**FENTON AND OTHER ADVANCED OXIDATION PROCESSES FOR AC REGENERATION.**

As shown in the previous sections AC regeneration by CWAO is not perfectly convenient as only 20 to 25\% of adsorption capacity of activated carbon may be recovered whatever the selected AC or SBAC and the model pollutant (phenolic compound or actual industrial effluent).

In order to improve this adsorption capacity regeneration several other advanced oxidation techniques have been tested in WP14: ultrasound, UV, photocatalysis, Fenton oxidation, electrochemical oxidation. Among them the best results have been obtained very recently (June 2009) with preliminary tests of electrochemistry, which seems also to perform according to Weng and Hsu (2008).

Fenton oxidation ($H_2O_2 + Fe^{2+}$) gives interesting results as compared to US, UV and Photocatalysis. First it has been verified that Fenton reagent does not interact with activated carbon and does not alter its adsorption capacity. Then successive adsorption runs followed by Fenton oxidation at room temperature, on the same AC sample, have been carried out in different concentration solutions.

A typical result is shown on Figure 14.11 proving the Fenton oxidation to be very fast, the resulting TOC variation being probably controlled by pore diffusion phenomena. Best conditions (iron and hydrogen peroxide concentrations) were obtained with fast stabilization (1st recycle) at about 50% adsorption capacity.

These results are not as promising as reported by Huling et al. (2005). The main drawback of Fenton regeneration is the progressive consumption of $Fe^{2+}$ which could be avoided by photo regeneration (Photo Fenton). Preliminary work on Photo Fenton proved it to be the most efficient AC regeneration technique, with 65% adsorption efficiency at the 2nd use, better than 50% with usual Fenton and 25% with air. Such investigation has not yet been published in open literature. Nevertheless the technical and economical feasibility of this photo Fenton process (not mentioned in literature) at industrial scale appears questionable, due to both uneasy scale up of UV irradiation and much higher cost of $H_2O_2$ than compressed air and vapour.
Some experiments have been conducted on Fenton regeneration of SBAC using the few remaining SBAC after the tests described earlier. This SA_DMAD was sieved at 1-1.6mm. Very similar trends were obtained with SBAC and with commercial AC. Fenton regeneration is again slightly better than usual air oxidative regeneration.

**AD-OX ON REAL EFFLUENTS.**

Finally a long range of successive AD-OX cycles (20) has been carried out on real water effluent at the exit of conventional biological treatment for industrial wastewaters. Despite the chemical complexity of this effluent only characterized by its COD and its significant salt concentration very similar features were observed: after the first severe cut of its adsorption capacity at about 25%, the activated carbon appeared approximately stabilized without further significant loss of adsorption capacity (about 20% of fresh AC after 20 cycles).

This similar behaviour has also been observed when investigating separately adsorption and oxidation: salt has no noticeable effect on the two steps of AD-OX process. This set of data has no equivalent in the open literature as industrial effluents are very rarely investigated and due to tedious repetitions of many cycles. It provides very important information when thinking to the economy of this process which is now to be investigated in details. At the actual coast of the corresponding AC (1350€/kg) AD-OX process is highly profitable with regards to consumable costs (pressurized air and water vapour instead of AC). The main economical issue is the equipment cost, as true wastewater are highly chlorinated and then highly corrosive at temperature conditions required by CWAO regeneration. In addition a synergetic corrosion effect occurs with AC: three usual stainless steel reactors (316L) were perforated during the 20 AD-OX runs with this chlorinated effluent.

**CONCLUSION.**

The SBAC proposed by WP12 have been analyzed and used as adsorbent, oxidation catalyst and finally in AD-OX process. All the specifications for convenient use of SBAC in oxidation step have not been fulfilled and improvements of mechanical strength, prevention of leaching and of foaming are still to be achieved. Adsorption capacities were not as low as it could be expected from surface area and especially the Steam Activated-Dewatered Raw Sludge showed promising adsorption performances, both capacity of about half of commercial AC and isotherm Langmuir shape, with stiff initial slope. Due to its current inadequacy to undergo regenerative oxidation and to the relatively high cost of this regeneration a single adsorption process followed by incineration seems the most appropriate use of SBAC available for WP14.
The other contributions of WP14 have shown that AD-OX might be used in profitable conditions as an end process after biological or physicochemical treatment of industrial wastewater when corrosion issues will be managed. It was also validated for pharmaceutical wastewaters (Levodopa and Paracetamol) but here again the selection of AC is a crucial point as it should remain inert with pressurized air at oxidation temperature (about 150°C).

Among the variety of new AC regeneration techniques tested by WP14 Fenton oxidation process gives interesting results especially when coupled with UV as a Photo Fenton process. At the very end of this 3 year programme an electrochemical regeneration has been successfully tested and should be investigated in much more details.

REFERENCES.


WO/2007/032998 International Application No.: PCT/US2006/034925

Title: Chemical regeneration of activated carbon


Weng C.H., Hsu M.C. 2008, Regeneration of granular activated carbon by an electrochemical process Separation and Purification Technology, 64, 2, 227-236


14.4. Impact of the WP on its industry or research sector.

ABSTRACT.

Adsorption on granular AC is the best process for reducing hazardous compound concentration and global COD in aqueous effluents leaving water treatment plants (either biological or physicochemical). The main drawback of adsorption is the uneasy, ex situ and non sustainable, thermal regeneration of AC. In industrial waste water treatment this ex situ regeneration is even forbidden. WP14 has succeeded in performing economic in situ partial regeneration of AC in a sequential water treatment process: AD-OX (room temperature adsorption- wet air batch regeneration at 150°C). Technical feasibility was proved with actual aqueous effluent from industrial wastewater treatment using commercial AC and with model bio refractory pollutants using Sludge Based AC. Economical analysis shows AD-OX is profitable with commercial AC as soon as it may be used more than ten times at 20%. The main issue concerns the severe corrosion due to chlorinated compounds in actual effluents: a convenient material selection has to be performed to estimate the equipment cost. Concerning SBAC, if they are actually produced at low cost (about 250€ as expected by WP12) they would be more profitably used in single adsorption without AD-OX regeneration.

WP14 has two major impacts on its industry and research sector: first concerning the technical and economic feasibility of AD-OX process aiming to save Activated Carbon (AC) by improving its in situ regeneration, second concerning AD-OX application with Sludge Based Activate Carbon (SBAC).

Clean water is vital for public health and ecosystems. Water treatment is thus a major activity for mankind welfare, as well for producing drinkable water as for reducing pollution of sewage effluents to be returned in natural environment. The European Community considers that about 20% of its superficial waters are threatened by pollution. Improving water treatment is then more and more necessary due to both increasing agricultural and industrial activities which produce large amounts of chemical pollution in aqueous effluents in addition to urban wastewater and to more drastic regulations on water quality. The Water Framework Directive aims to ensure the good chemical status of both surface water and groundwater bodies across Europe. For surface waters this goal is defined by limits on the concentration of specific pollutants of EU relevance, known as priority substances (or micropollutants). To date, 33 priority substances have been identified. A new Directive, Directive 2008/105/EC of 16 December 2008, establishes limits, known as Environmental Quality Standards (EQS), for these 33 substances and for an additional 8 substances regulated under previous legislation.

For eliminating most of these priority substances generally present at low or very low concentration the best economical technology is undoubtedly the widely spread process of adsorption on Activated Carbon (AC). Though very commonly used for more than a century in water treatment, either in powdered or, most often, in granular form, adsorption on AC indeed remains the most adequate technology for eliminating biorefractory compounds not destroyed by usual biological water treatment plants. According to Sarp Industries-Veolia (private communication, 2009) AC adsorption will be more and more used as end treatment after biological or physicochemical treatment, due to more severe regulations on TOC (Total Organic carbon) of aqueous effluents. The main advantages of AC adsorption are its flexibility, being able to face large concentration and flow rate variations, its simplicity and its large spectrum of compounds to be adsorbed.

According to “The Economics of Activated Carbon” (8th edition, published 01/10/2008, Roskill metals and minerals reports) world activated carbon consumption is estimated at 650,000t in 2007. Growth in consumption in current markets is forecast to be 5%py through 2015. Growth will be led by water treatment applications both in the USA, to control disinfection by-products in drinking water, and in the industrialising countries, to upgrade the quality of drinking and wastewater. In China, 10,000 wastewater treatment plants are scheduled for construction by 2010, raising the proportion of wastewater treated from 29% to 50%.

The next five years could see the emergence of the largest-ever market for activated carbon with the use of powdered activated carbon to control mercury emissions from coal-fired power plant flue gas in North America. Driven by state environmental legislation in the USA and limitations on new power plant
construction, this market is estimated to increase from 5,000t powdered activated carbon in 2007 to 125,000t in 2010. Growth in demand for activated carbon could accelerate to close to 400,000t in 2015 if US federal legislation, requiring installation of 600-700 activated carbon injection systems, is introduced. Total world demand for activated carbon therefore has the potential to rise by nearly 10%py to 1.36Mt in 2015, with mercury emission control accounting for 30% of projected total consumption.

Nevertheless these very positive perspectives are seriously counterbalanced by the most important drawback of adsorption processes i.e. the adsorbent saturation: the saturated AC must be regenerated before reuse. The first commercial-scale granular carbon adsorption used to burn the spent AC. Applied research has proposed several regeneration techniques but only few applications at industrial scale are reported. These methods are based either on desorption, mainly thermal, or on chemical decomposition of the adsorbed species, as presented on Figure 15.1 of section 2.3.

The most commonly used regeneration, thermal regeneration, is based on either desorption with inert gas or reactive decomposition by water vapour or flue gas needs very high temperature (about 850°C). It should only be achieved in few very large specialized units (50,000 tons/year), requiring withdrawal of spent AC from the adsorption tower, long transportations, up to 1000km, to produce 85-90% of “new” (slightly degraded) AC.

Furthermore in the case of industrial wastewater treatment by specialised companies, ex situ regeneration is not allowed due to hazardous compounds and the spent AC itself should be considered a hazardous waste needing a special treatment facility, based on uneasy incineration needing special care for environment. The last situation is the worst case not only from economy point of view but also environmentally as it generates large quantities of CO₂ (about ten times what would be produced by the complete mineralisation of adsorbed species).

Thus developing water treatment processes based on AC adsorption with “in situ” regeneration at moderate cost will have a strong economical impact in the field of waste water business. As explained earlier saving activated carbon results also in reduction of carbon dioxide emission produced when burning the spent AC. So from environmental point of view such processes would be twice profitable by improving water quality and also reducing CO₂ emission.

Concerning the possible use of Sludge Based Activated Carbon in AD-OX process, the environmental balance would be even more positive as a waste (raw sludge) is transformed in useful sustainable material for water treatment. Nevertheless as AD-OX regeneration by WAO autocatalyzed by AC is rather expensive compared to SBAC itself (estimated at 250€/ton) it appears more profitable to use SBAC in a single adsorption process before incineration. It should also be noticed that, due to very large amounts of available raw sludge, transform it in sustainable AC (able to be regenerated) would rapidly exceed the AC demand. As sludge are continuously produced by bio treatments their valorised by products should also be consumed.

As a conclusion WP 14 results suggest a very attractive utilisation of SBAC as usual adsorbents in end waste water treatment. Despite moderate adsorption capacity, SBAC economical efficiency is much higher than commercial AC. Due to their moderate cost SBAC do not deserve AC regeneration.

Another potential use of SBAC is as catalyst of continuous CWAO (see WP13), but quantities needed are much smaller. In addition prior improvement of their mechanical strength is required and long range oxidation runs are to be checked.

Concerning standard AD-OX with commercial AC and WAO regeneration, its use is profitable on specific effluents (e.g. paracetamol, phenols,...) but corrosion problems are to be solved at convenient cost to treat usual waste water issued from water treatment plants. On another hand the preliminary promising tests with cheap electrochemical regeneration should be confirmed with highly salted effluents which are very difficult to treat. If successful this electrochemical regeneration at room temperature and pressure for concentrated chlorine effluents could have the main impact on wastewater industry.
15. **Utilisation of activated carbon in adsorption processes.**

15.1. **Summary description of project objectives, work performed and end results, elaborating on the degree to which the objectives were reached.**

The main objectives of this WP were to characterize adsorption performances of SBAs produced in WP12 regarding synthetic wastewaters treatment containing molecules representative of industrial pollution. This experimental work included batch and dynamic processes. From optimum SBAs of WP12, four different industrial synthetic wastewaters have been tested: dyes (AR18, BV4 and BB9) and phenolic compounds (phenol and phthalate), metal (nickel and copper) and metalloid ions (arsenic V).

In batch reactors, optimal contact times and corresponding adsorption capacities have been determined. The initial proposition also included adsorption test regarding ammonium pollution, but considering the poor results obtained with copper and nickel ions, we decided to replace ammonium cation by arsenate anion. Some of the best adsorption performances (capacity and kinetic) have been obtained with phthalate pollutant (HPK) and steam activated SBAs (DSBS-H2O and DRAW-H2O): maximum fixation capacities reached after 21 days of contact time and maximum fixation capacities (deduced from Langmuir model) close to 187 mg/g. For comparison, the commercial activated carbon Filtrasorb 400 provided by Chemviron (Partner 16 involved in WP 15) exhibited a capacity of 344 mg/g.

Considering the best batch performance (phthalate adsorption on steam activated SBAs), dynamic breakthrough curves have been determined from fixed beds, including two SBAs (DSBS-H2O and DRAW-H2O) and Filtrasorb 400, and HPK as the pollutant. The design of the reactor was conducted taking into account the following parameters: the amount of SBA in relation with the available mass of adsorbent (one batch of production corresponded roughly to 90 g of SBA), the maximum fixation capacities and the initial concentration of pollutant, and the flowrate of wastewater according to the optimal contact times. The other pollutants had not been tested in dynamic process regarding the demand of European officer (26/02/09). Two main results could be extracted from these dynamic breakthrough curves: the dynamic capacities directly deduced from the curves were similar to batch ones indicating that the reactor design was relevant, and a very fast pollutant breakthrough was observed with SBA and delayed with Filtrasorb 400.

15.2. **Methodologies and approaches employed.**

The methodology used to reach the objectives of this WP is a classical and integrated approach dedicated to adsorption processes. It involved first a detailed characterisation of the adsorbent, in order to find relationships between the properties and the adsorption performances. Then, experiments in batch reactors have been conducted including on one hand, the evaluation of the optimal contact times for each couple adsorbant/adsorbate from kinetic decay curves, and on the other hand, the determination of adsorption capacities from adsorption isotherms. The use of some equilibrium models (for example Langmuir model) allows to estimate the maximum fixation capacity and then, to compare the performances of the different sorbents. Based on these results, the design of a dynamic process like a fixed bed was attainable. Three beds have been performed and breakthrough curves have been obtained until the saturation of the sorbent. Dynamic fixation capacities could be extrapolated and compare to the previous ones: if the design is correctly realised, these values should be similar. Secondly, they also give some information about the behaviour of the bed in terms of breakthrough time (potential leak). With all these information, a conclusion can be made about the feasibility to scale-up towards an industrial trial. All these experiments conducted with SBAs, have been compared with those realised with a commercial activated provided by Chemviron (partner 16).

To comply with this methodology, different approaches have been used. In this section, the production of adsorbents are not presented (see WP12) and their selection has focused primarily on DSBS-H2O and DRAW-H2O, and as a second choice on DSBS-CO2 and DRAW-CO2. Regarding the physico-chemical characterisation, following experiments were realised:

- determination of BET surface area from nitrogen adsorption, micro and meso pore volumes,
- determination of ash content,
- determination of C, H, N, S and O content by elemental analysis,
determination of the contact pH: 400 mg of adsorbent were placed in 40 mL of deionised water for 5 days. Each day, the supernatant of the adsorbent’s suspension was removed (for pH determination) and replaced by 40 mL of deionised water, until the pH remains constant. It has been shown that 24 hours are sufficient for proton exchange in solution.

determination of pHpzc: 50 mL of 0.01 M NaCl solution was placed in closed bottle. The initial pH was adjusted to a value between 3 and 12 by adding HCl or NaOH solutions. Then 150 mg of adsorbent was added and the final pH measured at 48 h under agitation at constant temperature. The pHpzc is the point where the curve pHfinal versus pHinitial crosses the line pHinitial=pHfinal.

lixiviation tests: lixiviation tests have been realised in order to determine the quantity of calcium, copper, iron and zinc ions in adsorbent sample. So, 500 mg of sorbent were placed in 50 mL of HCl 0.5 M and were agitated during 5 days. In the liquid phase, calcium, copper, iron and zinc ions have been measured by atomic absorption. Phosphate has been measured in triplicate, according to a protocol adapted to the norm NF T 90-023/EN ISO 6878. 0.7 g of SBA has been dried at 105 °C during the night, and it has been burned off at 550 °C during 4 hours. Then, samples were placed in 5mL of HCl 0.5 M in a water bath (100°C) for 15min, in order to solubilize all phosphates. A mixture was added to sample: 85.7 % (NH₄)Mo₇O₂₄·4 H₂O + 14.3 % ascorbic acid (10 %). With the presence of phosphate, a bluish coloration appeared after 1h at 37 °C. The concentration was determined by UV-visible spectrometry at 820 nm.

potentiometric titrations: based on Boehm’s method, the determination of acidic functions with different bases (NaHCO₃, Na₂CO₃, NaOH – 0.1 or 0.01M), and dosage of basic functions with HCl 0.1 or 0.01M have been performed. 500 mg of sorbent were agitated in 50 mL of acid or base for 48 hrs. Then, solutions were titrated with base or acid to determine equivalence volumes by derivative functions of titration: dpH/dV.

As far as batch adsorption studies, different pollutants have been tested in synthetic wastewaters. Two metal ions (copper(II) and nickel(II)), three dyes (one acid called Acid Red 18 - AR18, and two basic named Basic Violet 4 - BV4 and Basic Blue 9 – BB9), one metalloid element (arsenic(V)) and two organic compounds (phenol and potassium hydrogenophenolate) have been selected. The procedures were:

Sorption of metal ions: experiments were carried out with 500 mg of adsorbent and 1 L of copper(II) solution (C₀ = 50 mg.L⁻¹). Initial pH was fixed at 4 and 5 with HCl 0.05 M for the kinetic study in order to avoid Cu / Ni precipitation. At regular interval times, some milliliters of solution were removed for analysis. Copper and nickel concentrations were determined by spectrometric atomic absorption.

Sorption of dyes: adsorption kinetics were carried out with 500mg of adsorbent and 1 L of AR18 (C₀, SBA = 30 mg.L⁻¹, C₀, Filtrasorb 400 = 50 mg.L⁻¹), BV4 (C₀, Filtrasorb 400 / DRAW-H₂O / DRAW-CO₂ = 80 mg.L⁻¹, C₀, DSBS-CO₂ = 15 mg.L⁻¹) or BB9 solutions (C₀, SBA = 65 mg.L⁻¹, C₀, Filtrasorb 400 = 150 mg.L⁻¹). Dyes concentrations were measured by UV-Visible spectrometry. The wavelengths are 507 nm for AR18, 596 nm for BV4 and 663 nm for BB9. Adsorption isotherms experiments were undertaken in 125 mL flasks and with 50 mg of adsorbent and 100 mL of AR18 solution. The equilibrium time was fixed at 1200 h.

Sorption of arsenic V: kinetics experiments were carried out with 50 mg of adsorbent and 100 mL of arsenic(V) solution (C₀ = 1 mg.L⁻¹). pH was initially fixed at 5.5 with HCl 0.01 M for the kinetic study. Arsenic(V) concentrations were determined by spectrometric atomic absorption (Spectrometer Perkin Elmer A Analyst 6000). Batch adsorption isotherms experiments were undertaken in 125 mL flasks and with 50 mg of adsorbent and 100 mL of As(V) solution. The equilibrium time was fixed at 144 h.

Sorption of phenol and potassium hydrogenophenolate (HPK): studies were carried out with 500mg of adsorbent and 1 L of phenol and HPK (C₀, SBA = 50 mg.L⁻¹, C₀, Filtrasorb 400 = 200 mg.L⁻¹). Organic compounds concentrations are measured by UV-Visible spectrometry. The wavelengths are 270 nm for phenol and 281 nm for HPK.

Finally, fixed beds have been designed following this procedure: a glass column of 24 cm length and 4.1cm internal diameter was used. The columns were packed with adsorbents (DRAW-H₂O, DSBS-H₂O and Filtrasorb 400) for different heights (2, 6, 8 cm). The bed was rinsed with deionized water until the pH of effluent was equal to the contact pH determined previously. The polluted water was prepared at 100 mg.L⁻¹ of HPK. The flowrate in the column was performed from bottom to head of the column (up flow mode) with volumetric flow rate close to 3 mL.min⁻¹. A peristaltic pump was used to control the flow rate. Samples of effluents were collected periodically and the remaining concentration (C) was analyzed using UV
spectrophotometer. The breakthrough curves of C/C₀ versus time were drawn. The flow through the column was continued until the concentration of column effluent approached the initial concentration.

15.3. Achievements of the project related to the state of the art.

Activated carbon (AC) is a highly effective adsorbent because of its extended specific surface area (exceeding 600 m².g⁻¹), high pore volume, and for some of them the presence of surface functional groups. AC is commonly obtained from various organic precursors such as peat, wood, bituminous coal, coconut shells, polymers (Bansal et al., 1988). In recent years, a growing research interest consists in the production of cost-effective carbon-based adsorbents from a range of residues, mainly industrial or agricultural by-products. In this context, sewage sludge generated during wastewater treatment processes has been identified as potential low cost precursor for activated carbon production (Martin et al., 2003; Otero et al., 2003; Rio et al., 2005; Rozada et al., 2003). Recent studies have shown the feasibility of this conversion, but they rarely determine the effects of activation conditions on surface chemistry and adsorption properties (isotherm and kinetics) of standard industrial pollutants. Considering industrial wastewaters, the sludge based adsorbents show good adsorption capacities of dyes and metal ions compared with commercial ones (Rio et al., 2005; Rozada et al., 2003), but in specific operating conditions (pH), some leachings could occur. The main achievements of this WP are presented below in terms of physico-chemical characterisation, pollutant adsorption performances in batch reactors and in fixed beds.

PHYSICO-CHEMICAL CHARACTERISATION.

From table 15.1, it is shown that steam activated SBA (DSBS-H₂O and DRAW-H₂O) exhibit the highest BET surface and carbon content (excepted for DRAW-H₂O) and the lowest ash content. These values are roughly 4 times lower than Filtrasorb 400. None of the other obtained properties (see D15.1 and technical reports) has clearly led to exploitable results, due to many reasons. For example, the leaching of these materials in acid and base solution (shown by the lixiviation tests) which prevented the determination of surface chemical function and altered the values of pH and pHpzc, or the presence of high mineral content conducting to technical problems with elemental analyser (not adapter for this kind of materials) and not favourable for adsorption performance. Another restriction is the low mechanical resistance of these materials which prevent some industrial implementation. To overcome this drawback, other hardener SBAs have been produced in WP12. Finally, these four SBAs (DSBS-H₂O, DRAW-H₂O, DSBS-CO₂ and DRAW-CO₂) have been selected for adsorption tests, but only the steam activated ones seem to be favourable for use in aqueous pollutant adsorption.

Table 15.1. Main properties of SBAs compared with Filtrasorb 400.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>DSBS-CO₂</th>
<th>DSBS-H₂O</th>
<th>DRAWS-CO₂</th>
<th>DRAWS-H₂O</th>
<th>Filtrasorb 400</th>
</tr>
</thead>
<tbody>
<tr>
<td>S_BET (m²/g)</td>
<td>181</td>
<td>218</td>
<td>215</td>
<td>282</td>
<td>1090</td>
</tr>
<tr>
<td>Mesopore vol. (cm³/g)</td>
<td>0.065</td>
<td>0.084</td>
<td>0.154</td>
<td>0.135</td>
<td>0.097</td>
</tr>
<tr>
<td>Mesopore vol. (cm³/g)</td>
<td>0.080</td>
<td>0.067</td>
<td>0.085</td>
<td>0.049</td>
<td>0.312</td>
</tr>
<tr>
<td>Ash content (% wt)</td>
<td>59</td>
<td>41</td>
<td>70</td>
<td>65</td>
<td>6</td>
</tr>
<tr>
<td>pH after washing step</td>
<td>8.1</td>
<td>7.7</td>
<td>8.9</td>
<td>9.3</td>
<td>8.0</td>
</tr>
<tr>
<td>pHpzc</td>
<td>7.6</td>
<td>8.2</td>
<td>8.6</td>
<td>9.3</td>
<td></td>
</tr>
<tr>
<td>C (% wt)</td>
<td>34.2</td>
<td>37.2</td>
<td>32.4</td>
<td>27.9</td>
<td>88.3</td>
</tr>
</tbody>
</table>

COPPER AND NICKEL ADSORPTION.

No adsorption occurs with these two cations in the operating conditions described previously. It is the reason why it was decided to replace the cation NH₄⁺ by Arsenic V anion (H₂AsO₄⁻).

SORPTION OF DYES.

The sorption of different dyes, namely AR18, BB9 and BV4, is possible (Table 15.2), and if the results are compared after 2 days of contact time, adsorption capacities on BV4 onto DRAWs are better than Filtrasorb 400 (in the same operating conditions) and interesting regarding AR18. DSBSs exhibit clearly poor
capacities and BB9 is the less efficiently removed dye. The nature of the precursor (DRAW compared with DSBS) seems to be the predominant parameter. But after the equilibrium is reached (>50 days for all dyes and all SBAs), the performances of DSBS-CO2 become better than DRAW for BV4 fixation and remain low considering AR18 and BB9. Isotherm curves have shown a multilayer adsorption (DRAW and DSBS with AR18) which prevents to use the Langmuir model to a wide range of concentration. The maximum fixation capacities cannot be deduced which prevents to compare the performance of each sorbent at equilibrium.

Table 15.2. Partial results of dyes adsorption onto SBAs and Filtrasorb 400.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>AR18 (t = 2 days)</th>
<th>BB9 (t = 2 days)</th>
<th>BV4 (t = 2 days)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C₀ (mg.L⁻¹)</td>
<td>Adsorption capacities (%)</td>
<td>C₀ (mg.L⁻¹)</td>
</tr>
<tr>
<td>Filtrasorb 400</td>
<td>50</td>
<td>45</td>
<td>150</td>
</tr>
<tr>
<td>DSBS-CO₂</td>
<td>30</td>
<td>7</td>
<td>60</td>
</tr>
<tr>
<td>DSBS-H₂O</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DRAW-CO₂</td>
<td>30</td>
<td>38</td>
<td>60</td>
</tr>
<tr>
<td>DRAW-H₂O</td>
<td>30</td>
<td>48</td>
<td>60</td>
</tr>
</tbody>
</table>

SORPTION OF ARSENIC V.

From kinetic decay curves, the equilibrium time was found to 6 days for SBAs. The comparison of the adsorption capacities after 2 days showed that only 10% of arsenic was removed with DSBSs, 30 to 40% with DRAWS and 64% with Filtrasorb 400. Adsorption isotherms have been realised and the use of Langmuir model has well described the experimental data (good correlation coefficient as shown in Table 15.3). The maximum fixation capacities were the following (Table 3): near 4 mg.g⁻¹ for Filtrasorb 400, 2 mg.g⁻¹ for DRAW-H₂O and 1.4 mg.g⁻¹ for DRAW-CO₂. One more time regarding these experiments, the nature of the precursor (DRAW compared with DSBS) seems to be the predominant parameter, as well as the activating gas. From the comparison of qₘ values, SBAs exhibits performances 25 to 50% less than Filtrasorb 400.

Table 15.3. Langmuir parameters for adsorption of As(V) onto DRAW-H₂O, DRAW-CO₂ and Filtrasorb 400.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>qₘ (mg/g)</th>
<th>b (L/mg)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filtrasorb 400</td>
<td>3.93</td>
<td>12.84</td>
<td>0.968</td>
</tr>
<tr>
<td>DRAW-CO₂</td>
<td>1.39</td>
<td>0.81</td>
<td>0.969</td>
</tr>
<tr>
<td>DRAW-H₂O</td>
<td>1.98</td>
<td>0.73</td>
<td>0.997</td>
</tr>
</tbody>
</table>

SORPTION OF PHENOL AND HKP.

This section presents the adsorption tests on 2 aromatic molecules: phenol and HKP. It was clear from Table 15.4, that the activating gas was the predominant parameter regarding the fixation capacities.

Table 15.4. Partial results of phenolic compounds adsorption onto SBAs and Filtrasorb 400.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>HPK (t =12 days)</th>
<th>Phenol (t =14 days)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C₀ (mg.L⁻¹)</td>
<td>Adsorption capacities (%)</td>
</tr>
<tr>
<td>Filtrasorb 400</td>
<td>200</td>
<td>56</td>
</tr>
<tr>
<td>DSBS-CO₂</td>
<td>50</td>
<td>56</td>
</tr>
<tr>
<td>DSBS-H₂O</td>
<td>50</td>
<td>67</td>
</tr>
<tr>
<td>DRAW-CO₂</td>
<td>50</td>
<td>53</td>
</tr>
<tr>
<td>DRAW-H₂O</td>
<td>50</td>
<td>62</td>
</tr>
</tbody>
</table>

Better performances were obtained with steam activation, in comparison with CO₂. Moreover, DSBSs presented either similar efficiencies or either better than DRAWS, in the same conditions. The sorption of HKP seemed to be higher than phenol. The equilibrium times have been found to 14 days for HKP and 28 days for phenol. Adsorption isotherms were then performed with each pollutant regarding the selected SBAs

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DSBS-H₂O and DRAW-H₂O. The use of Langmuir model has well described the experimental data (good correlation coefficient as shown in Table 15.5). It was obvious that the sorption of HPK was highly favourable compared to phenol. The deduced maximum fixation capacities were 171 mg.g⁻¹ for DRAW-H₂O, 187 mg.g⁻¹ for DSBS-H₂O and 344 mg.g⁻¹ for Filtrasorb 400. DSBS-H₂O was slightly superior to DRAW-H₂O. From the comparison of qₘ values, SBAs exhibit again performances 25 to 50 % less than Filtrasorb 400 as far as phenol and HPK are concerned.

For the last part of this WP, a selection of the better results has been made. It has been decided to use steam activated SBAs because in most experiments, it was the better activating gas regarding the adsorption performances (As(V), aromatic compounds and dyes), and because this gas allow easier and cheaper industrial production of SBAs than CO₂. Depending of the pollutants, DRAW-H₂O was more or less efficient than DSBS-H₂O. So, DRAW-H₂O and DSBS-H₂O were the best SBAs.

### Table 15.5. Langmuir parameters for adsorption of HPK and phenol onto DRAW-H₂O, DSBS-H₂O and Filtrasorb 400.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>qₘ (mg/g)</th>
<th>b (L/mg)</th>
<th>R²</th>
<th>qₘ (mg/g)</th>
<th>b (L/mg)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filtrasorb 400</td>
<td>344</td>
<td>0.0270</td>
<td>0.996</td>
<td>278</td>
<td>0.42</td>
<td>0.959</td>
</tr>
<tr>
<td>DSBS-H₂O</td>
<td>187</td>
<td>0.0346</td>
<td>0.987</td>
<td>74</td>
<td>0.93</td>
<td>0.999</td>
</tr>
<tr>
<td>DRAW-H₂O</td>
<td>171</td>
<td>0.0260</td>
<td>0.951</td>
<td>65</td>
<td>1.22</td>
<td>0.933</td>
</tr>
</tbody>
</table>

**COLUMN EXPERIMENTS.**

The first selected pollutant was HPK: equilibrium time of 14 days (in comparison with 6 for As(V), 28 for phenol, and more than 50 for dyes) and best qₘ values (half of Filtrasorb 400) for the 2 SBAs. The results were expressed in terms of breakthrough curves (Figures 15.1, 15.2 and 15.3).

![Figure 15.1. Adsorption breakthrough curves of HPK onto Filtrasorb 400 in column.](image)

The dynamic capacities at saturation extrapolated from the curves, were approximatively close to the maximum capacity at equilibrium obtained in batch reactors (300 mg.g⁻¹ for Filtrasorb 400, 170 mg.g⁻¹ for DSBS-H₂O and 130 mg.g⁻¹ for DRAW-H₂O) indicating that the design of the beds was correct.
Moreover, it can be seen in Figure 15.2 and 15.3 and considering a breakthrough for C/C₀=0.1, that the breakthrough time was immediate in comparison with Filtrasorb 400. It meant that the leak of pollutant was not delayed and occurred at the beginning of the test, which could be unfavourable to HPK removal at industrial scale depending on the desired outlet concentration. A way to improve these results is to increase the amount of SBAs so as to increase bed thickness until being higher than critical thickness. This alternative has not been tested considering the high amount of SBAs to provide and the resulting column height in the case of column scale-up for industrial applications. However, the other experiments have not been conducted following the demand of the European Officer (end of February 2009).

CONCLUSIONS.

From these adsorption experiments (kinetic decay curves, adsorption isotherms and breakthrough curves), some conclusions can be presented:

- adsorption tests have been performed, but the duration of experiments has been underestimated due to very long kinetic reactions.
- as far as metal ions are concerned, no adsorption has been noticed. Some different results have been published in the literature, but it seems greatly depend on the nature of sludge (calcium or lime
content), the conditions of production, the technology of the oven... To confirm this, SBAs coming from London (DRAW) show in the most cases, better performances in comparison with Nantes sludges (DSBS). Moreover, activation of chars with H₂O leads to greater adsorption capacities than CO₂ activation.

- in terms of results, the optimum contact times are high in all cases, maybe excepted for arsenic(V). As it is true also for the tested commercial activated carbon, a great hope was in the behaviour of the breakthrough curves. However, the curves corresponding to SBAs exhibit an immediate leak of pollutant in the case of HPK (the only pollutant tested in dynamic condition on demand on European officer). Considering the adsorption capacities, performance of SBAs are generally ranged between 25 to 50 % of those obtained with the tested commercial activated carbon.

For all these reasons, the application of these SBAs in industrial adsorption processes for wastewater treatments does not appear as a promising development. Others SBAs has been produced in WP12, with different operating conditions (chemical activation, de-ashing procedure, addition of hardening additives...) and for which, some specific applications could be found. But the selection made in this WP has focused of parameters like: low production costs in term of number of required treatments or simple activating gas leading to low-cost SBAs as much as possible, available amounts of SBAs... In terms of structure, the leaching of minerals within different pH conditions, the low mechanical resistance and the fact they can not qualified as “activated carbon” because of their carbon and ash content, lead to restrictions for their applicability to industrial scale. In terms of performance, results show capacities ranged between 25 to 50 % of those obtained with Filtrasorb 400. They could be interesting, since SBAs would be considered as low-cost sorbents. However, a commercial activated carbon is generally regenerated and at the end of use, incinerated to produce 6% of ashes. In case of SBAs, regeneration tests were not relevant to do since adsorptions were low, and after combustion, 40 to 70 % of ashes were produced (Table 15.1) and intended to landfill disposal.

REFERENCES.


15.4. Impact of the WP on its industry or research sector.

Due to the large amounts of activated sludge generated around the world, it seems very attractive to find a potential reuse which could be an alternative to incineration/landfill disposal or landfarming. In terms of sustainable development, this approach should have very positive environmental, social and economical aspects. For these reasons, the conversion of sludge into activated carbons for wastewaters treatment appeared to be pertinent. Different research works have been realised in the past, but the main interest of this WP was to compare different productions of SBA, of various origins, towards many pollutants. Two heavy metals (copper and nickel), arsenic ion and organic compounds like dyes (AR18, BB9 and BV4) and aromatics (phenol and phthalate) have been tested in the same operating conditions. Before the standby of the project, dynamic fixed beds have also been performed with the phthalate. Nevertheless, regarding the obtained results, and especially in terms of fixation capacities (see D15.1 and D15.2), this approach does not seem to be relevant with these particular low-cost SBAs. The main involved characteristics could be the poor carbon content of the produced materials and the high ash content, leading to a low surface area and finally minor fixation capacities. Other SBAs have been produced by WP12 in different operating conditions (chemical activation, de-ashing procedure, addition of hardening additives...) with probably better properties towards adsorption, but we can not wait their availabilities (amounts) to reach the objectives of this WP.
Finally, the mass yields of tested SBA were close to 30%, indicating that great loss of gas and liquid products occurred at a lab scale, but they were not considered for energy production for example.

As far as this WP is concerned, the use of SBA produced from rustic activation process, is not recommended for wastewater treatment applications. However, considering basic surface pH of SBA and high mineral content, industrial air treatment application (acid gases and dioxins) would be investigated with more success.
16. **Utilisation of activated carbon in biofilters for elimination of industrial waste gases.**

16.1. **Summary description of project objectives, work performed and end results, elaborating on the degree to which the objectives were reached.**

**PROJECT OBJECTIVES.**

The main target of this work-package has been to evaluate the feasibility of employing activated carbon produced from sludge obtained from a wastewater treatment plant as packing material in biological reactors for the abatement of odours generated in industrial facilities, as, for instance, in solid waste or wastewater treatment plants. The labours framed in this work-package have been grouped in three main tasks: *redesign and start-up of an existing biofiltration setup (task 1), evaluation of biofilter’s performance parameters (task 2) and modelling of the biofiltration units (task 3).*

**WORK PERFORMED.**

During the development of the project a series of bench-scale biofilters packed with commercial organic packing materials and carbon were designed and tested. It is important to mention that, as sludge-based activated carbon (SBAC) was not available on-time, commercial activated carbon (CAC) and sludge-based (non-activated) carbon (SBC) were used instead. Considering the characteristics of the materials (see below) it is expected that very similar results would have been obtained if SBAC had been employed. Also, a general dynamic biofiltration model applied to toluene removal was developed, calibrated and validated. Mathematical equations employed are based on discretized mass balances which take into account the main chemical and physical phenomena involved in the system. Previous experimental results, in which a toluene degrading biofilter inoculated with bacterial populations evolved to a fungal biofilter (Maestre et al., 2007) were used herein as input data to calibrate and validate the biofiltration model. In addition, a statistical procedure was applied to check the confidence intervals of the parameters obtained during the model calibration procedure. Finally, a detailed economical evaluation on the use of sludge-based carbons was also performed.

**END RESULTS.**

The objectives expected for the present work-package have been fully accomplished. A series of organic and inert packing materials, including different carbons, have been characterized. SBC, when mixed with coconut fibre, has proven to be an appropriate packing material in a conventional biofilter. Toluene removal efficiency was commonly above 90% when an inlet concentration around 6 ppmv (similar to what can be found in odorous waste gases) was fed to the bioreactor. Also, it was proved that the use of SBC may represent an economically viable alternative to other commonly employed inert packing materials, as CAC. Total costs may be reduced from 40 to 50% if SBAC or SBC is selected as packing material instead of CAC. Also, a dynamic model to simulate toluene abatement by bacterial and fungal biofilters has been developed, calibrated and validated through a set of different experimental conditions for biofilters with switching populations from bacteria to fungi. The model was able to satisfactorily predict different operation periods, including bacteria-, transition from bacteria to fungi-, and fungi-based operation by means of a relatively small number of parameters. With this, the model developed is a significant tool to help in the design of odour treatment biofilters.

16.2. **Methodologies and approaches employed.**

**BIOREACTOR SETUP.**

A biofiltration setup that had been previously employed for the depuration of toluene-containing vapours and consisting of two parallel biofilters was redesigned and restructured in order to fit the requirements of the REMOVALS project. This plant consisted of four PVC columns (8.8 cm internal diameter) with a packing height of 50 cm, giving a total bed volume of 3 L per reactor. Each biofilter was fed with pre-humidified air regulated with calibrated flowmeters as primary gas flow. A secondary air stream was pumped by a peristaltic pump into a glass bubbler unit containing pure liquid toluene. Both gaseous streams were mixed.
and the resulting gas mixture was fed from the bottom of the reactor. Each reactor had four gas sampling ports located, respectively, at 0, 15, 30, and 45 cm from the gas inlet. Tap water or a nutrient-enriched solution was automatically sprinkled on a daily basis over the biofilter beds to provide additional moisture, the necessary nutrients for the microorganisms and to wash dead cells and the end-products of toluene degradation.

METHODOLOGIES.

For the analysis of the operation of the bioreactor systems (Task 2), gas samples were collected from sampling ports and stored using Tedlar® bags prior to their analysis. Toluene concentration was measured by gas chromatography in a GC 6890N (Agilent Tech., Spain) equipped with a HP-5 capillary column and a flame ionization detector (FID). Leachate samples were periodically collected from the bottom of each reactor. Conductivity and pH of these samples were measured respectively by means of microCM 2100 and MicropH 2001 lab probes (Crison, Spain). Nitrite, nitrate and phosphate of liquid samples were determined by capillary electrophoresis in a Quanta 4000E unit (Waters, Spain). Ammonia concentration was measured by means of a continuous flow analyzer. Packing materials porosity and specific surface area were determined in an external laboratory (Serveis Científico-Tècnics, UB) by BET absorption isotherms in an ASAP2000 porosimeter (Micromeritics, U.S.A.). Materials densities were measured in a helium picnometer. Elementary analysis was performed by combustion under standard conditions using sulphanilamide as standard (EA-1108 ThermoFisher Scientific). Extractable phosphorus was determined by ICP in a Thermo Jarell-Ash model 61E multichannel analyser in standard conditions (Polyscan, U.S.A.). The specific surface area and material densities were determined by the BET technique in a Tristar 3000 apparatus (Micromeritics, U.S.A.). Filter media moisture, organic matter content and pH were determined according to Standard Methods (APHA, 1995). Water holding capacity was measured by keeping the material wet (sparkling constantly tap water for 100 min) and determining the weight changes. Water retentivity was measured by keeping wet material in constant contact with dry air flow circulating through the bed and measuring the loss of weight of the bed. Conductivity, pH and buffer capacity were determined for the materials leachate after submerging them in water for 1 h.

APPROACHES EMPLOYED.

The model (Task 3) was built considering the most relevant phenomena occurring during the biofiltration process like convection, absorption, diffusion and biodegradation. The theoretical model describing the elimination of toluene in a biofilter bed is based on the mass balance in the gas phase and within the biofilm. Important assumptions underlying the model were:

1) Gas phase circulation regime is modelled as plug flow pattern. Thus, axial dispersion is not considered.

2) Gas-biofilm interface equilibrium is described by Henry’s law.

3) Planar geometry and perpendicular diffusion in biofilm are used to derive model equations considering that the solid support size is significantly higher than the biofilm thickness. Diffusion in the biofilm is described by Fick’s law.

4) Biofilm is formed on the external surface of the packing material. Thus, biomass does not grow in the pores of the packing material and reactions only take place in the biofilm phase.

5) Physical properties of the species in the biofilm are assumed to be the same as in water since this is the main component.

6) There is no accumulation of biomass in the filter bed in each period and biomass properties (thickness, specific surface area and kinetic coefficients) are uniform along the bed. This assumption was experimentally verified by monitoring a practically constant pressure drop and reactor weigh in the whole studied operation period.

7) Adsorption of pollutant onto the support is neglected due to the low pollutant concentration and the low adsorption capacity of the packing material. Moreover, under steady-state conditions, the adsorption process is in equilibrium.

In terms of the economical analysis for the comparison of investment and operation and maintenance costs of biofilters packed with different packing materials, a procedure developed by Devinny et al., (1999) was...
revised and adjusted. Such approach was based on the analysis of open-bed biofilters considering all cost related to their construction and operation including packing material replacement.

16.3. Achievements of the project related to the state of the art.

EVALUATION OF BIOFILTERS' PERFORMANCE PARAMETERS.

Even though it has been widely reported that the packing material is one of the main operational parameters, as well as the main one influencing the investment and operational costs in biofilters (Prado et al., 2009), there is still controversy on which are the most important requirements that a packing material must fulfill if long-term, stable performance are desired. In order to clarify this and to value the potential use of SBC, SBAC or other carbons, a complete characterization of the organic packing materials used in the present study was performed prior to their first inoculation. In a posterior study (see below), the performance of these materials was compared to that of SBC. In addition, the four biofilters were characterized for typical parameters such as bed porosity or water content before inoculation. It must be stressed that the pore size, the specific surface area, the material density and the C, H, N, S and P content are inherent to the material and, therefore, comparable to other materials characterized in the literature (Bohn, 1996). It was shown that the pore size showed a high correlation with the toluene adsorption capacity determined by breakthrough curves performed in the biofilters (data not shown). Adsorption tests performed at an inlet toluene load of 100 g·m⁻³·h⁻¹ showed that the bed was saturated after 6, 15, 25 and 34 minutes for the coconut fibre, peat, pine leaves and compost biofilters, respectively. In any case, it is important to mention that high surface areas, with deep pores as these exhibited by compost, may be counteracted due to the biomass growth over the surface of the packing material, thus reducing the sorption capabilities to buffer transient inlet loads. Also, highly mineralized materials such as compost and peat showed low organic matter contents compared to other usual biofilter packing materials, which may lead to a higher resistance to long-term deterioration. Coupled with higher nitrogen content, compost seemed a priori the most suitable material out of the materials tested in terms of physical and chemical characteristics.

A previous study performed under similar conditions as the ones expected to be employed in the current study showed that unacceptably long start-up periods could happen when the biofilters were inoculated with sludge from an urban wastewater treatment plant (Maestre et al., 2007). This same effect has been found in a number of previous studies (Veiga and Kennes, 2001; Prado et al., 2005), as it is a typical operational problem both in biofilters and in biotrickling filters. In order to shorten this start-up time, an innovative start-up strategy was applied. In this study, instead of inoculating the four biofilters with an specific microbial culture able to perform the biodegradation process, they were packed with filter bed materials that had been previously employed in another study and that were, accordingly, already colonized by toluene-degrading strains. The materials selected were pine leaves, a mixture of compost and pine leaves in a proportion 3:1 (v:v), coconut fibre and peat. This would allow to characterize the performance of these packing materials, serving as a first step before the operation with SBC. Subsequently, the performance of all systems was compared.

Effect of the EBRT.

The empty bed residence time (EBRT) is one of the main operational parameters in both biological and physico-chemical gas-treating systems. Previous works have highlighted the influence of the EBRT on the performance of VOC-degrading bioreactors (Deshusses and Hamer, 1993; Zhou et al., 1998). According to the literature, it can be hypothesised that bioreactors packed with different materials can show different responses to EBRT variations. However, there is still controversy on the degree of influence of variations in the EBRT on the performance of biofilters packed with organic materials. In order to clarify this, four conventional biofilters, each packed with one of the four abovementioned organic materials were operated at EBRT values ranging from 90 to 5 s, corresponding to inlet air flow rates from 120 to 2000 L/h. These results will be of special value for the industrial implementation of bioreactors, allowing for a more precise scale-up of the systems and, hence, reducing costs. Although there are a few studies regarding the biodegradation of VOCs at low EBRT (Popov et al., 2005), no previous works have been found in the literature on the removal of toluene in bioreactors at EBRT values as low as 5 s.

All the filter bed materials present in the new reactors had been working in previous systems under steady-state conditions for more than eight months, reason why no pre-adaptation phase was observed. A toluene inlet concentration of 1.1±0.3 g/m³ was set during all the experiment. The reactors were periodically fed 100 mL of the abovementioned nutrient solution twice per day. Each EBRT change was performed after steady-
state conditions had been reached and kept for at least three hours to ensure consistent results. It was observed that a fungal population remained dominant inside the reactor during all the study. Figure 16.1 shows that a decrease in the removal efficiency was found in all four reactors as the EBRT decreased, even though slight differences in their performance could be observed. However, removal efficiencies above 75% were found in all systems when operated at EBRT values above 60 s. In the reactor packed with pine leaves (Figure 16.1a), only a small effect of the EBRT on the removal efficiency was found when operating at EBRT values between 20 and 90 s. Under such conditions, the removal efficiency remained between 75 and 85%. However, at EBRT values as low as 5 s the removal efficiency dropped to 35%. The biofilter packed with a mixture of compost and pine leaves (Figure 16.1b) decreased its performance from 77% at an EBRT of 60 s to below 20% at an EBRT of 5 s.

**Figure 16.1.** Influence of the EBRT on the toluene removal efficiency of four biofilters packed with different organic materials. (a) pine leaves biofilter; (b) compost + pine leaves biofilter; (c) coconut fibre biofilter; (d) peat biofilter.

Both the biofilters packed with coconut fibre and with peat (Figures 16.1c and 16.1d, respectively) showed a similar behaviour to this of pine leaves biofilter. It is remarkable that both of them showed efficiencies around 30 % at EBRT values of 5 s. Except for the reactor packed with compost plus pine leaves, all other reactors showed removal efficiencies between 30 and 35 % at EBRTs as low as 5 s, showing that the elimination of toluene at EBRT values around 5 s can be performed with moderate efficiencies. These results will allow for an optimal scale-up when the systems are to be applied at industrial scale, reducing costs and maximizing efficiency. From results it was hypothesized that design of biofilters with SBC or SBAC for toluene degradation would need of EBRTs above 40 s for achieving removal efficiencies above 80%. This was later check during operation of a biofilter packed with SBC (see next section).

**Influence of nutrients supply.**

The supply of a nutrient solution plays an important role in the biofilter performance, providing the adequate moisture level and the nutrient content needed by the microorganisms. Although it has been stated that organic packing materials usually offer the necessary nutrients to maintain a proper microbial population, an extra-nutrient addition has been demonstrated to be needed when high pollutant loads are being fed (Devinnin et al., 1999). Also, this addition is a key factor for pH control in bioreactors, providing the necessary wash out of by-products. However, considering that a good part of the nutrient elements that are present in the packing material may be in a non-biologically available form, specific experiments need to be undertaken in order to assess the need of nutrient supply to bioreactors. Even though a number of studies have been performed with this purpose (Zhu et al. 1996; Deshusses and Cox 1999; Jorio et al. 2000; Moe and Irvine 2001; Prado et al., 2002), this is the first to date to evaluate the need of nutrient supply in reactors packed with coconut fibre, which may be a reliable and cheap option. In the present study, the reactor packed with
coconut fibre was operated during 100 days under different watering conditions in order to determine the
effect of the addition of a nutrient solution on its performance. The EBRT was kept at a constant value of 60
s during all the study. Initially, the reactor was fed a nutrient solution under the conditions previously
described. The toluene load was set at 107±14 g/m³h during the first 25 days operation. An elimination
capacity of 37±11 g/m³h was found during this stage.

As Figure 16.2 shows, the removal efficiency did not overcome 50%. On day 26 of operation, the toluene
load was decreased to a value of 28±6 g/m³h with the purpose of increasing the removal efficiency prior to
the nutrient limitation stage. Immediately, an increase in the removal efficiency was observed, up to values
around 90 %. pH remained slightly below 2 during this stage. Once a steady-state had been reached on day
39, the nutrient solution was replaced by distilled water. Thus, the biofilter did not receive any external
nutrients between days 39 and 88. The toluene load during this stage was 28±7 g/m³h. Figure 16.2 shows
that the toluene removal efficiency remained above 90 % during more than one month, dropping sharply
after day 80. A progressive increase of the leachate pH was observed, which was related to a decrease in
the production of acidic metabolites. Even though an increase in pH could lead to the appearance of bacteria
overgrowing the fungal population, which, in turn, would decrease the performance of the biofilter, in the
present case the biofilter was predominantly fungal-based during all the study.

![Figure 16.2](image-url)

Figure 16.2. Performance of the biofilter under different toluene inlet loads and nutrient supply conditions.
The dotted lines point the days when the liquid solution supplied was switched. TL: Toluene load. EC: Elimination capacity. RE: Removal efficiency.

A previous work performed under similar conditions (Maestre et al., 2007) proved that the performance of a
series of fungal bioreactors packed with organic media were very stable at pH values up to 4-5. Hence, it can
be concluded that the decrease in the removal efficiency was not due to the pH increase. Subsequently, in
order to assure that it was due to a lack of nutrients, on day 88 the nutrient solution feeding was restored.
Fig. 2 shows that this led to an immediate increase in the removal efficiency, which reached values
comparable to the original ones just after a few days. A concomitant pH drop was then observed. The results
presented herein point out that the operation of toluene-degrading biofilters colonized with fungi may be
carried out temporarily without any nutrient addition, even though a N-containing nutrient solution must be
added when no other nitrogen source is available to keep reactor performance.

Similarly to the results shown herein, biofilters filled with SBC and CAC showed a similar performance in
terms of nutrients requirements both indicating that the high nutrient content of SBC is not bioavailable for
biomass growth and that external nutrients addition is required for proper biofilters performance.

**Effect of the watering rate.**

As biodegradation processes require of high moisture content in the filter bed material, it is a common
practice in bioreactors to supply water in an intermittent manner (Devinny et al, 1999). This leads to an
increase in the pressure drop of the bioreactor. In the present section, an assessment of the pressure drop
variations as a function of different operational parameters is given. In order to determine this, a specific lab-
scale setup was constructed and operated. Several packing materials were tested. These were compost,
coconut fibre, pine leaves, peat, polyurethane foam, immature coal, an innovative material composed of an
inner core of clay externally covered by compost, volcanic rock and SBC. The study was performed at seven
different air flow rates, five moisture content values and three different material porosities. The air flow rates
selected were so as to achieve EBRT values between 5 and 40 s, considered typical in actual bioreactors.
Figure 16.3 shows the results obtained, respectively, for coconut fibre, compost, polyurethane foam and the mixture of clay and compost. It can be seen that, in all four cases, the pressure drop increases when the air flow rate or the water content increase as well or when the porosity decreases. Volcanic rock was the material that led to highest pressure drop values, reaching up to 50 cm water/m column at an air flow rate of 700 L/h, a water content of 8% and a porosity of 0.65. Conversely, the organic materials led to lower maximum pressure drop values.

It is important to mention that pressure drops in a fixed bed have been already described by different semi-empirical mathematic expressions. Most studies use Ergun’s equation (Ergun and Orning, 1952), shown in Equation 1, to describe the pressure drop.

\[
\frac{\Delta P}{H} = a \frac{\mu v_0}{d_p^2} \left(1 - \frac{\epsilon}{\epsilon^*}\right)^2 + b \frac{\rho v_0^2}{d_p} \left(1 - \frac{\epsilon}{\epsilon^*}\right)
\]

(Equation 1)

In Equation 1, \(\Delta P/H\) is the pressure drop in Pa; \(H\) is the filter bed height in m; \(\mu\) is the air viscosity in Pa·s; \(v_0\) is the superficial air velocity in m·s\(^{-1}\); \(\epsilon\) is the filter bed porosity; \(d_p\) is the spherical equivalent diameter of the particle in m and \(a\) and \(b\) are, respectively, the first and the second parameters of Ergun’s equation. These parameters are related to the friction factor. Some authors have satisfactorily adjusted experimental data to Ergun’s equation by adapting these parameters by means of a correction factor (Delhoménie et al. 2003). Some other authors have developed specific relationships, due to the heterogeneity of the material and to the difficulty inherent to the modelling of the pressure drop using Ergun’s equation (Comiti and Renaud, 1989).

**Figure 16.3.** Influence of the operating parameters on the pressure drop in a bioreactor packed with (a) coconut fibre; (b) compost; (c) polyurethane foam; (d) SBC.

In the present work, parameters \(a\) and \(b\) from Ergun’s equation were adjusted as a function of the material, the porosity and the water content. The pressure drop \((\Delta P/H)\) was adjusted by linear regression as a function of the gas superficial velocity. In all cases, the correlation coefficient was above 0.990, showing a clear linear trend between the operational parameters and the pressure drop. The experimental study incorporates the effect of the water content in the pressure drop, even though this parameter is not present in Ergun’s equation. Accordingly, this allows establishing a modified version of Ergun’s equation which incorporates the effect of the water content on the pressure drop for different packing bed materials. This is a key factor to properly estimate operating cost during biofilters operation.
EVALUATION OF SBC AS FILTER BED MATERIAL IN A BIOFILTER.

After proving that SBC (and, accordingly, SBAC) showed acceptable characteristics in terms of several properties and provided an adequate pressure drop in a wide range of operation conditions, the behaviour of this material as packing bed was assessed in a biofilter treating a mixture of six organic volatile compounds (VOCs) such as hexanal, butyric acid, limonene, methylisobutylketone (MIBK), dimethylsulfide (DMS) and toluene. The experimental time was divided in 2 phases. In the first phase, the inlet concentration was 6±2 ppmv per VOC, corresponding an inlet loading rate of 3.2±1.0 g m$^{-3}$h$^{-1}$, while in the second phase the VOCs inlet concentration was doubled to 10±1 ppmv, corresponding to an inlet loading rate of 5.6±0.6 g m$^{-3}$h$^{-1}$. The biofilter was packed with a mixture of coconut fiber plus sludge-based carbon from a waste water treatment plant (1:1, v:v), supplied by Partner 14 (Imperial College of London). The coconut fiber was added as bulking agent in order to decrease the pressure drop in the biofilter (McNevin and Barford, 2001; Burgess et al, 2001) and aided to hold water content. Growth and immobilization of biomass on SBC were evaluated inoculating the lab-scale plant with activated sludge and studying the abatement of VOCs in the reactor, during 95 days of operation (Figure 16.4). The gas flow rate was kept at 425 l h$^{-1}$ (EBRT of 25 s). The bioreactor was sprinkled once a day with tap water.

In Figure 16.4, the operation and performance of the biofilter in terms of toluene inlet and outlet concentration, and toluene removal efficiency (RE) is represented. The first 10 days correspond to the biofilters start-up phase, in which SBC was basically adsorbing toluene and the immobilized biomass was being acclimatized. Toluene removal efficiencies above 90% were achieved from the first day, corresponding to an EC between 2.5 and 3 g m$^{-3}$h$^{-1}$. Results demonstrate that SBC was able to develop and maintain an active biomass on the surface of the material after a short time of acclimatization, due especially the high surface area and the high water holding capacity. In the first phase, while the biomass was adapting to the operating conditions of the reactor, toluene was being adsorbed on the material. Moreover, the presence of nutrients content in the SBC could contribute to the growth and the maintenance of the biomass immobilized even if this was limited during treatment of higher loads of toluene. On day 69, inlet toluene concentration was increased from 5 to 10 ppmv. The RE decreased gradually, down to values under 75%. This shows a relatively poor performance of this packing material (Devinny et al, 1999) in comparison to other studies where roughlier and more hydrophilic packing materials allowed the microorganisms to fix more easily (Durham et al, 1994). It was hypothesised that bioavailability of nutrients from the SBC was limited, thus limiting toluene degradation at higher loads. Nevertheless, as soon as the inlet toluene concentration was decreased again to 5 ppmv, on day 88 of operation, high RE were reached again. Regarding toluene abatement, the RE reported in the analyzed operation time shows that the mixture of SBC-coconut fibre is an acceptable support media for the biomass, but when feeding toluene concentrations above 10 ppmv the removal efficiency decreases drastically. Removal efficiencies for all six VOCs were maintained above 70 % during the whole experimental time (results not shown). These results can be considered acceptable, although different studies performed by other authors report similar or better performances when using activated carbons (Abumaizar et al, 1998; Moe and Li, 2005; Mathur et al, 2007).
MODEL DEVELOPMENT, CALIBRATION AND VALIDATION.

A dynamic model to simulate toluene abatement by bacterial and fungal biofilters was developed, calibrated and validated through a set of different experimental conditions for biofilters with switching populations from bacteria to fungi. Simple and complex models have been employed to simulate toluene biofiltration under both steady-state and dynamic operating conditions (Abumaizar et al., 1997; Metris et al., 2001; Ottengraf and Van der Oever, 1983; Zarook et al., 1997). In all modeling works reported in the literature toluene removal in biofilters is based on bacterial degradation activity without taking into account fungal operation. The approach developed along the Removals Project allowed us to model the biofilter considering the variation of the biological activity due to the development of different populations of microorganisms, approach that has not previously described in the literature to the research group knowledge.

The model was able to predict satisfactorily different operation periods, including bacteria, transition from bacteria to fungi, and fungi based operation be means of a small number of parameters. Results clearly demonstrate that a higher complex model is not necessary to describe properly the performance of the biofilter. However, a correct procedure in biofilter modeling force to determinate model parameters for each situation instead of taking them from literature. Moreover, the physico-chemical model was checked by model predictions in the operation where biological degradation was not the predominant process. Otherwise, estimation of kinetic parameters corroborated the biomass evolved from bacteria to fungi in both biofilters in concordance to pH changes reported along the entire experiment and microscopic observation. Kinetic parameters confirmed that fungi provide a better capacity to degrade toluene from gas phase. Moreover, a higher affinity was observed between fungi and the pollutant in comparison to pollutant and bacteria consortium. Thus, determination of volumetric maximum growth rate and semi saturation constant for both biofilters with their corresponding confidence interval pointed out that biofilters colonized by fungi showed a better performance than those colonized by bacteria. The model calibration was checked by a novel procedure in gas biofilters modeling based on the Fisher Information Matrix and the model validation was verified using a rigorous statistical test. Deviations on model predictions are explained by biomass modification in the bioreactors obtaining better results at the end of each period due to the pseudo biomass steady-state achieved.

In order to determine the influence of model parameters on the model predictions and to have a practical guide to what parameters are more important to determine from a practical point of view, a sensitivity analysis was performed for each parameter, including all kinetic, stoichiometric and physicochemical parameters. The analysis was performed by examining the effects of parameter variation over the elimination capacity (EC). Sensitivity was assessed by increasing and decreasing by 10% the values of the parameters and comparing the relative change of the state variables to a relative change of the value of the parameter according to Equation 2. Results obtained from sensitivity analyses are shown in Table 1.

\[
\text{sensitivity} = \frac{\Delta V}{V_d} \cdot \frac{\Delta P}{P_d} = \frac{\Delta V}{V_d} 
\]

(Equation 2)

where \(\Delta V\) is the difference between the simulated variable under the new conditions and the value of the variable in the default conditions (\(V_d\)). Similarly, \(\Delta P\) represents the difference between the value of the parameter at the ±10% change and the value of the default parameter (\(P_d\)).
Table 16.1. Sensitivity analysis results for outlet concentration and elimination capacity of the biofilter for the all model parameters in the general model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Definition</th>
<th>Δ</th>
<th>Sensitivity Cg (_{out})</th>
<th>Sensitivity EC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cg(_{in})</td>
<td>Pollutant inlet concentration</td>
<td>10%</td>
<td>1.57</td>
<td>0.79</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-10%</td>
<td>-1.49</td>
<td>-0.83</td>
</tr>
<tr>
<td>Qg</td>
<td>Inlet air flow rate</td>
<td>10%</td>
<td>1.51</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-10%</td>
<td>-1.56</td>
<td>-0.48</td>
</tr>
<tr>
<td>EBRT</td>
<td>Empty bed residence time</td>
<td>10%</td>
<td>-1.49</td>
<td>-0.44</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-10%</td>
<td>1.67</td>
<td>0.45</td>
</tr>
<tr>
<td>a</td>
<td>Specific surface area</td>
<td>10%</td>
<td>-1.47</td>
<td>0.52</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-10%</td>
<td>1.66</td>
<td>-0.59</td>
</tr>
<tr>
<td>Hp</td>
<td>Pollutant gas/biofilm partition coefficient</td>
<td>10%</td>
<td>1.00</td>
<td>-0.36</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-10%</td>
<td>-1.08</td>
<td>0.38</td>
</tr>
<tr>
<td>Db,P</td>
<td>Pollutant diffusion coefficient in the biofilm</td>
<td>10%</td>
<td>-0.78</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-10%</td>
<td>0.88</td>
<td>-0.31</td>
</tr>
<tr>
<td>(\mu^*)</td>
<td>Maximum volumetric rate</td>
<td>10%</td>
<td>-0.70</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-10%</td>
<td>0.80</td>
<td>-0.29</td>
</tr>
<tr>
<td>Ks,P</td>
<td>Pollutant half saturation constant</td>
<td>10%</td>
<td>0.21</td>
<td>-0.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-10%</td>
<td>-0.22</td>
<td>0.08</td>
</tr>
<tr>
<td>δ</td>
<td>Biofilm thickness</td>
<td>10%</td>
<td>0.10</td>
<td>-0.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-10%</td>
<td>-0.05</td>
<td>0.01</td>
</tr>
<tr>
<td>kg</td>
<td>Mass transfer coefficient</td>
<td>10%</td>
<td>0.02</td>
<td>-0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-10%</td>
<td>-0.02</td>
<td>0.00</td>
</tr>
<tr>
<td>Ks,O</td>
<td>Oxygen half saturation constant</td>
<td>10%</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-10%</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Db,P</td>
<td>Pollutant dispersion coefficient in the air</td>
<td>10%</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-10%</td>
<td>-0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>ε</td>
<td>Clean bed porosity</td>
<td>10%</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-10%</td>
<td>-0.01</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Without considering operating parameter, the major impact was obtained for physicochemical parameters such as the specific surface area, the gas/biofilm partition coefficient and the diffusion coefficient in the biofilm. On the other hand, dispersion coefficient and bed porosity presents a nil influence on model predictions. Results were consistent with other studies found in the literature (Baquerizo et al, 2005; Deshusses et al, 1995). Thus, specific surface area, the gas/biofilm partition coefficient and the diffusion coefficient in the biofilm are the 3-most influencing parameters in the model and are recommended as the three that need to be specifically determined in all studies performed with the developed model.

16.4. Impact of the WP on its industry or research sector.

SOCIAL, ENVIRONMENTAL AND INDUSTRIAL BENEFITS OF THE USE OF SLUDGE-BASED CARBON AS FILTER BED IN A BIOFILTER.

As already exposed, the production of activated sludge is one of the main problems generated by the activity of solid waste and waste water treatment plants. Only in the United Kingdom, the yearly generation of this sludge is above 2 billion kg, which increases year after year. This leads to issues associated to the management of this material. Currently, processes as sludge digestion by ozonation and thermophilic microbial digestion have proved their efficiency in reducing sludge generation. However, recalcitrant compounds are accumulated in the remnant sludge, reason why these materials can no longer be biologically treated. Their conversion in activated carbon and posterior utilization as packing bed in gas-treating biofilters are a promising alternative to their disposal. This alternative comprises two benefits which make it especially interesting both from an industrial and an environmental point of view:

1) It means an efficient and environmental-friendly way of managing the sludge generated in solid waste or waste water treatment facilities, valorising a material sludge with no economic interest and converting it into a product that can be employed in a wide series of applications.
2) A material that can be efficiently employed as packing bed in bioreactors is produced at a relatively low cost. The present work has proved that sludge-based activated carbon can serve as an efficient and stable packing material in conventional biofilters, leading to relatively low pressure drop values and serving at the same time as support for the microorganisms and as buffer, eventually helping to control shock loads.

From a social point of view, the use of bioreactors for waste gases treatment means an effective way of controlling gaseous emissions from a wide variety of industries, reducing and even eliminating their pollutant load and the odour associated to them. During past decades, the social concern regarding gaseous toxic and odorous emissions has significantly increased. Only in Spain, more than 18000 industries were denounced for this reason between 2007 and 2008. More than 51 % of the news published in press during that period regarding environmental issues were refered to conflicts due to the emission of odours from industrial facilities. Also, around 78 % of the wastewater treatment plants operating in Spain were denounced at least once in 2007 for reasons associated to the emission of odours (data supplied by a specialised odour-treating company). Currently, it can be affirmed that around 12 % of the operating costs of a wastewater treatment plant are due to the treatment of odours generated in the same facility. If costs due to fines, specific treatments, activity stops, etc. due to problems generated by odours are added, it results that more that 25 % of the operating cost of wastewater treatment plants are due to odour management.

The increase in the social concern regarding environmental issues has lead to a concomitant rise in the legislative pressure. In the last three decades, the number of laws controlling gaseous emissions in Spain has risen six-fold. Currently, the European Union is in the process of developing a law aimed at controlling the emission of odours in industrial sources, which should be out by 2010. By the time that law is approved, a technology that can handle the treatment of such emissions with a high efficiency, robustness and low costs will be needed. The results contained in the present report prove that biofiltration may very well be that technology, at least in the cases where the physico-chemical conditions of the gas current allow for the development of a stable microbial community. Among the different packing materials that can be employed in these systems, sludge-based carbon has proven to be an especially adequate one, due to its mechanical and chemical properties, the availability of nutrients, its buffer capacity and its low cost. Many industries already have, or can have at a relatively low cost, the tools to produce this carbon from the sludge produced in their own facilities. In this case, two problems can be solved at the same time: the disposal of the sludge and the purchase of the packing material for the biological reactors. However, a series of technical and scientific questions had to be answered in advance in order to optimize their use, economically and technically. The studies performed in the frame of WP16 of the REMOVALS project have been aimed at clarifying this. The information obtained during the performance of a series of bench scale biofilters (Task 16.2) and the model developed (Task 16.3) are considered to be of capital importance for the development of real-scale systems.

In a first stage of the present study, the performance of a series of conventional biofilters packed with typically used organic bed materials and employed for the removal of a model volatile organic compound (toluene) was assessed during pseudo-stationary and transient conditions. Breakthrough values for the removal efficiency as a function of the empty bed residence time were established for all four packing materials. Moreover, the influence of the watering rate and of the nutrient supply was assessed. These results will allow for a most precise scale-up of industrial bioreactors, with a consequent decrease in the investment and operating costs. In this sense, one of the main operating parameters is the pressure drop, which may lead to increased maintenance costs after just a few months of operation. The present work has allowed for the characterization of the evolution of the pressure drop as a function of the packing material, bed porosity, gas flow rate and water content. Results suggest that a standardized method for pressure drop control can be developed just by regularly controlling these operating parameters.

Subsequently, the performance of a biofilter packed with a mixture of coconut fiber and SBC from a waste water treatment plant (1:1, v:v) and treating a mixture of six volatile organic compounds was studied. The results show that, at an empty bed residence time of 25 s, a removal efficiency above 70 % could be warranted for all the pollutants. This proves that SBC can serve as an adequate packing material for gas treatment in bioreactors. The environmental and industrial implications of this have been highlighted in the previous sections.

Additionally to experimental results, a theoretical model based on mass balances for pollutants in a biofilter was successfully developed, calibrated and validated. The biofiltration model revealed as a promising tool for further design of biofilters and to intensively test different biofiltration scenarios at low cost compared to experimental testing of biofiltration units. Modelling results additionally showed that the specific surface area of the packing material was the parameter that largely influenced model outputs. Thus, experimental
determination of sludge-based carbons specific surface area appeared as a key factor for successful model usage.

Apart from the improvement of the design of industrial biofilters, the programming environment and interface of the model developed may allow for training of plant operators from industrial facilities at low cost in short periods of time. This is particularly important since the expertise of plant operators in this type of emerging technologies such as biofiltration is significantly limited.

Summarizing, the use of bioreactors packed with sludge-based carbon means a reliable and environmental-friendly alternative to traditional, physico-chemical technologies for waste gas remediation. The results obtained in the frame of WP16 will allow for the design and implementation of cheaper, more reliable and more robust bioreactors.

ECONOMICAL BENEFITS OF THE USE OF SLUDGE-BASED CARBON AS FILTER BED IN A BIOFILTER.

Together with the already described social and environmental benefits, the economical advantages of employing sludge-based carbons as packing material in bioreactors are expected to significantly contribute to generate an impact in the sector. Two main economical benefits can be distinguished here: the ones related to the disposal of the waste water treatment facilities sludge, for which no optimal alternative exists, and those related to the savings in the purchase of the bioreactor packing material.

With the purpose of assessing the economical viability of using activated carbon as filter bed in bioreactors, a specific cost-assessment model which includes the main investment, operating and maintenance costs of a conventional biofilter was developed. Specifications on this model can be found in Prado et al. (2009). The total investment costs have been calculated as the sum of the initial site preparation costs, the packing and support materials costs, the equipment costs, the piping costs, the electrical costs, the equipment installation costs, the engineering design costs, the liner costs and the miscellaneous costs. The annual operating costs were calculated as the sum of the electricity and water annual consumption costs, the labor costs and the overhead costs. Among the medium replacement costs, two actions were considered: the disposal of the old packing material and the addition of the new one. All other eventual costs have been considered negligible compared to these. Although a very simple bioreactor was selected as model reactor, the protocol can be applied to different scenarios (as, e.g., biotrickling filters) after few modifications. No nutrient supply was considered for the economical evaluation. The protocol presented herein was applied to a series of biofilters supposedly packed with different packing materials and operating under the same conditions. A gas flow rate of 20 000 m$^3$/h and an EBRT of 60 s were selected for the biofilters, which were considered to be operating for 15 years. The EBRT value of 60 s was selected as previous studies showed that removal efficiencies above 75% may be assured at that EBRT irrespective of the packing material. Seven packing materials were selected for the study: compost, agricultural residues, a mixture of pig manure and sawdust, Biosorbens™ and three different types of activated carbon (commercial activated carbon, sludge-based activated carbon and sludge-based non-activated carbon). The cost and the estimated durability of each material are shown in Table 2. All costs presented herein are estimations for Spain, year 2008. Due to the inherent difficulty to quantify many of the parameters included in the protocol, an error around ±20% was estimated for costs calculated in the present section.

Table 16.2. Average cost and estimated durability of all seven packing materials considered.

<table>
<thead>
<tr>
<th>Material</th>
<th>Cost (€/m$^3$)</th>
<th>Estimated durability (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compost</td>
<td>25</td>
<td>2</td>
</tr>
<tr>
<td>Agricultural residues</td>
<td>75</td>
<td>1</td>
</tr>
<tr>
<td>Pig manure + sawdust</td>
<td>50</td>
<td>1</td>
</tr>
<tr>
<td>Biosorbens™</td>
<td>550</td>
<td>15</td>
</tr>
<tr>
<td>Commercial activated carbon</td>
<td>475</td>
<td>10</td>
</tr>
<tr>
<td>Sludge-based activated carbon</td>
<td>120*</td>
<td>10</td>
</tr>
<tr>
<td>Sludge-based non-activated carbon</td>
<td>80*</td>
<td>5</td>
</tr>
</tbody>
</table>

* Values calculated considering a market cost of 600 €/Tm for SBAC and 400 €/Tm for SBC (as provided by Partner 14) and a carbon density of 0.2 Kg/L in both cases.

Table 3 summarizes the main costs implied in all seven cases. It can be clearly seen that the use of SBC represents an economically viable alternative to other inert packing materials, as Biosorbens™ or
commercial activated carbon. Total annualized costs of 43360 and 42910 €/year have been estimated for SBAC and SBC, respectively, while, in the case of commercial activated carbon, a total annualized cost of 79710 €/year results from the application of the model. This reduction in the costs is a consequence of the much lower purchase price of sludge-based carbons, which, in turn, results of their reduced production costs. The investment cost for this average-sized system ranges from around 56000 € when selecting compost as packing material to around 380000 €, if Biosorbens™ is the chosen bed. Among these, biofilters packed with sludge based carbons fit in the medium cost range (around 115000 and 90000 € for activated and non-activated carbon-based biofilters, respectively). However, the high durability of these materials causes the annualized medium replacement costs to be low in comparison to the others (4200 and 6600 €/year). Only Biosorbens™ which has an estimated durability of the same range as the biofilter total operating time, reason why no medium replacement costs need to be considered, has lower annualized medium replacement costs. Regarding operating costs, as all the scenarios contemplate same air flow rate and empty bed residence time, no differences are found. Overall, only compost is a better option from an economical point of view. However, as previously stated, the use of organic packing materials as compost as packing bed in biofilters may lead to operational problems which may decrease performance. Accordingly, there is evidence that sludge-based carbon may be a promising alternative to traditional packing materials both from an operational and an economical point of view. This is expected to lead to a clear impact in the biofiltration market.

Table 16.3. Investment, operating and medium replacement costs estimated for a series of average-size conventional biofilters packed with different packing materials, with Q = 20 000 m³/h, Vₚ = 400 m³, EBRT = 60 s.

<table>
<thead>
<tr>
<th>COST</th>
<th>BF1</th>
<th>BF2</th>
<th>BF3</th>
<th>BF4</th>
<th>BF5</th>
<th>BF6</th>
<th>BF7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total investment costs (€)</td>
<td>56,500</td>
<td>87,260</td>
<td>71,890</td>
<td>379,570</td>
<td>333,420</td>
<td>114,950</td>
<td>90,340</td>
</tr>
<tr>
<td>Annualized investment costs (€/year)</td>
<td>6,600</td>
<td>10,190</td>
<td>8,400</td>
<td>44,350</td>
<td>38,950</td>
<td>13,430</td>
<td>10,550</td>
</tr>
<tr>
<td>Annual operating costs (€/year)</td>
<td>19,340</td>
<td>19,340</td>
<td>19,340</td>
<td>19,340</td>
<td>19,340</td>
<td>19,340</td>
<td>19,340</td>
</tr>
<tr>
<td>Annualized operating costs (€/year)</td>
<td>25,750</td>
<td>25,750</td>
<td>25,750</td>
<td>25,750</td>
<td>25,750</td>
<td>25,750</td>
<td>25,750</td>
</tr>
<tr>
<td>Packing material replacement costs (€/action)</td>
<td>16,640</td>
<td>36,640</td>
<td>26,640</td>
<td>0</td>
<td>196,640</td>
<td>54,640</td>
<td>38,640</td>
</tr>
<tr>
<td>Annualized packing material replacement costs (€/year)</td>
<td>9,820</td>
<td>46,460</td>
<td>33,780</td>
<td>0</td>
<td>15,010</td>
<td>4,170</td>
<td>6,600</td>
</tr>
<tr>
<td>Total annualized costs (€/year)</td>
<td>42,170</td>
<td>82,400</td>
<td>67,930</td>
<td>70,100</td>
<td>79,710</td>
<td>43,360</td>
<td>42,910</td>
</tr>
</tbody>
</table>


REFERENCES.


Section 2 – Dissemination and use.

Use of cellulolytic enzyme for improving sludge digestibility and rheology.

Result description.
During this investigation enzymatic saccharification was identified as a pre-treatment option for primary sewage biosolids (PSB). This enzyme breaks down complex polysaccharides in the PSB allowing fermentative hydrogen production to take place (Massanet-Nicolau, 2008; Massanet-Nicolau et al., 2008). The saccharification process could be used in a conventional methanogenic digester to improve digestibility. In addition the enzymatic saccharification also causes significant improvement in rheology of the PSB making it easier to pump. This could result in operational savings if deployed in a full scale sewage treatment process. Since the enzyme is a commercial product, designed to be used at full scale, its cost is lower than that of cellulolytic enzymes of research grade. At present the cost of pre-treating a litre of PSB is 3.25 UK pence.

Possible market applications or how they might be used in further research.
Use in further research on sewage sludge digestion is possible with immediate effect since the product can already be purchased in small quantities (<1000L).
Use in industry to improve the digestibility and rheology of sewage would be subject to negotiation of an affordable priced and production of the enzyme in sufficient quantities. Both would require negotiation with the manufacture and a timescale would depend on the outcome of such negotiations.

Stage of development.
Currently the efficacy of the enzyme has been demonstrated at a laboratory scale, however the enzyme is currently available in quantities sufficient to be used at a pilot scale if required.

Collaboration sought or offered.
Currently no further collaboration in this area has been agreed upon but research involving this product is ongoing at the University of Glamorgan.

Intellectual property rights granted or published.
The research leading to this exploitable knowledge has been published by the University of Glamorgan in a peer reviewed, scientific journal.

Contact details.
Further details pertaining to this research can be obtained by contacting:
Dr. Jaime Massanet-Nicolau.
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Faculty of Health, Sport and Science
University of Glamorgan
CF37 1DL Pontypridd
United kingdom
e-mail: jmassane@glam.ac.uk
Tel: +44 (0)1443654388
Conditions appropriate to stable continuous hydrogen production from sewage biosolids.

Result description.
The production of hydrogen from sewage biosolids via anaerobic fermentation, in a continuously fed mode, requires substantial changes in both environmental conditions and operating procedures when compared to those used in a conventional methanogenic digester. The experimental work performed in this package identifies specific criteria that would enable hydrogen to be produced from sewage biosolids at full scale; these include the pH, hydraulic retention time, sparging rates and pre-treatment’s necessary for successful fermentative hydrogen production.

Possible market applications or how they might be used in further research.
The results obtained are of use in further research with immediate effect since the materials and methods can be replicated in any adequately equipped laboratory. The results could also be applied to pilot and eventually full scale anaerobic digestion of lignocellulosic biosolids, particularly sewage sludge.

Stage of development.
The research leading to these results was conducted at laboratory scale but could be adapted to pilot scale research with immediate effect.

Collaboration sought or offered.
Information on the significance and potential application of these results has been presented to Thames Water Utilities. The research forms part of a larger body of expertise regarding anaerobic digestion which the University of Glamorgan uses as the basis of collaborative research with other institutions.

Intellectual property rights granted or published.
These results will be published in peer reviewed journals within the next 12 months.

Contact details.
Further details pertaining to this research can be obtained by contacting:

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Automatic coNtrol for partial nitrification to nitrite in BIOfilm reactors (ANFIBIO).

Result description.
ANFIBIO is an advanced control strategy to be applied in biofilm reactors to treat high strength ammonium wastewater such as the reject water coming from the dewatering of the digested sludge in wastewater treatment plants (WWTP).

Possible market applications or how they might be used in further research.

a) WWTP of new construction. If a new installation is planned to include an advanced treatment of the reject water, and therefore for an optimization of the nitrogen removal, a specific treatment for the high strength ammonium wastewater such the reject water coming from the dewatering of the digested sludge should be implemented. In this case ANFIBIO is the best strategy to be applied in a biofilm reactor to partially nitrify before the denitrification step.

b) Retrofitting of existing WWTP. If an upgrade in terms of nitrogen removal is foreseen for an existing WWTP already treating specifically the reject water, ANFIBIO is the best strategy to retrofit the nitrifying reactor to a high capacity partial nitrification biofilm reactor. This would imply small investment cost and short payback periods, due to the very low price per unit mass of nitrogen removed.

Stage of development.
The test of this developed technology have been carried out at pilot scale with different types of biofilm reactors, always with excellent performance, stability and robustness in the operation, obtaining full partial nitrification to nitrite, with very low concentrations of ammonium and nitrate (both less than 1%).

Collaboration sought or offered.
We seek collaboration for: (i) a full industrial test including retrofitting of an existing WWTP installation already treating reject water; and/or (ii) an industrial high strength ammonium wastewater. Investor partner to commercialize the patented technology is sought as well.

Intellectual property rights granted or published.
Priority application registered in Spain (June 2009) by Universitat Autonoma de Barcelona, Spain.

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Fax: +34 93 581 2013
e-mail: julio.perez@uab.es
e-mail: julian.carrera@uab.es
Automatic control loop based on in-line OUR measurement applied for partial nitrification in an activated sludge system with three-reactors in series.

Result description.
This exploitable result is an advanced control strategy to be applied in an activated sludge system with three-reactors in series to treat high strength ammonium wastewater such the reject water coming from the dewatering of the digested sludge in wastewater treatment plants (WWTP).

Possible market applications or how they might be used in further research.

a) WWTP of new construction. If a new installation is planned to include an advanced treatment of the reject water, and therefore for an optimization of the nitrogen removal, a specific treatment for the high strength ammonium wastewater such the reject water coming from the dewatering of the digested sludge should be implemented. In this case this technology is a good strategy to be applied to partially nitrify before the denitrification step.

b) Retrofitting of existing WWTP. If an upgrade in terms of nitrogen removal is foreseen for an existing WWTP already treating specifically the reject water, this technology is a good strategy to retrofit the nitrifying reactor to a high capacity partial nitrification system. This would imply small investment cost and short payback periods, due to the very low price per unit mass of nitrogen removed.

Stage of development.
The test of this developed technology have been carried out at pilot scale with excellent performance, stability and robustness in the operation, obtaining full partial nitrification to nitrite, with very low concentrations of ammonium and nitrate (both less than 1%).

Collaboration sought or offered.
We seek collaboration for: (i) a full industrial test including retrofitting of an existing WWTP installation already treating reject water; and/or (ii) an industrial high strength ammonium wastewater.

Intellectual property rights granted or published.

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e-mail: julian.carrera@uab.es
Evaluation of re-engineering needed for transformation of MAD into TAD.

**Result description.**

As a result of the project, a full set of knowledge allows assessing the potential re-engineering associated to the migration from Mesophilic Anaerobic Digestion (MAD) to Thermophilic Anaerobic Digestion (TAD). This transformation could include application of pre-treatments to amend the sludge condition and enhance the subsequent TAD. Standard experimental studies at bench-scale will give valuable performance information on COD, TS and VS removal, pathogen destruction and biogas production and quality in a recommended range of operation variables. Economic impact can also be estimated.

**Possible market applications or how they might be used in further research.**

Although especially addressed to those WWTP that have MAD plants in operation and are considering their transformation into thermophilic range systems, it is useful for any WWTP that desires information about the alternatives existing for sludge stabilisation.

**Stage of development.**

Lab- and bench-scale plants are already in use and ready to conduct sludge stabilisation performance analyses. Pre-treatments based in heating and/or peroxidation are also in use. Other pre-treatments can be applied under request and will be developed if needed. Basic procedures and analytical systems are also prepared.

**Collaboration sought or offered.**

We seek collaboration for wider industrial tests for existing WWTP having installed sludge digester working in mesophilic conditions, in order to gain knowledge on correlation between sludge type and TAD performance, including pre-treatments.

**Intellectual property rights granted or published.**

The details of the offer will be freely available in a doctoral thesis with the provisional title “Performance of pre-treatments for the aerobic and anaerobic digestion of excess sludge” and the derived contributions in open literature.

**Contact details.**

José Font Capafons  
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Fax: +34 977 559621  
e-mail: jose.font@urv.cat
CFD assessment of ATAD performance.

Result description.
CFD modelling of ATAD operation will be available as further development of the project. This numerical model will account for simulating gas-liquid hydrodynamics and mass transfer, with and without mechanical agitation, in water phase or sludge. For the latter, rheology and temperature will be considered on both hydrodynamics and mass transfer. Oxygen mass transfer characterisation will be coupled with biological performance, including mass and energy balances. Experimental determination of rheological behaviour and impact on oxygen mass transfer is available through standard protocols.

Possible market applications or how they might be used in further research.
Consistent numerical models are of interest for diagnosis and optimisation of the few full-scale ATAD plants operating throughout the world. Also, designers -included those with proprietary technology- will have the possibility to optimise newly designed systems or existing technology.

Stage of development.
Determination of rheological sludge properties, oxygen mass transfer using classical mixing systems and mixing power requirements to guarantee homogeneous oxygen surplus without local deficit is currently available and can be applied over dedicated designs. The first steps towards the numerical simulation of the ATAD reactor are now taken; one more year (end of the ongoing Ph.D. thesis) is still necessary to complete this part.

Collaboration sought or offered.
We seek collaboration for wider industrial tests for existing ATAD plants, in order to check the model performance in several situations. Collaboration with designers, even if proprietary of the technology, will be welcome.

Intellectual property rights granted or published.
The details of the offer will be freely available in a Ph.D. thesis the derived contributions in open literature.

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jack.legrand@univ-nantes.fr
Extraction protocol of hydrolytic enzymes.

Result description.
The exploitable result is a detailed protocol of extraction, identification and quantification of hydrolytic enzymes from activated sludge. Up to seven enzymes have been identified as they are present in the supernatant recovered after extraction of activated sludge. The extracted enzymes could be used as pretreatment of activated sludge itself or for other industrial applications. The extraction method was optimized using ultrasonication, which means that this method could be easily scaled up for its use in municipal wastewater treatment plants.

Possible market applications or how they might be used in further research.
The results obtained are useful for further research with immediate effect, since the materials and methods can be replicated in any adequately equipped laboratory. The results could also be applied to pilot and eventually full scale extraction of hydrolytic enzymes from activated sludge.

Stage of development.
The research leading to these results was conducted at laboratory scale but could be adapted to pilot scale research with immediate effect.

Collaboration sought or offered.
Currently no further collaboration in this area has been agreed.

Collaborator details (type of partner sought and task to be performed).

Intellectual property rights granted or published.
These results will be published in peer reviewed journals within the next 12 months.

Contact details.
Further details pertaining to this research can be obtained by contacting:
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