EFFICIENCY OF TECHNIQUES FOR PURIFICATION OF CONDENSATE FROM WOOD DRYERS

MILJÖEFFEKTER AV OCH RENINGSTEKNIK FÖR KONDENSAT FRÅN TORKNING AV TRÄ FÖR FRAMSTÄLLNING AV PELLETS

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ABSTRACT

Previous studies have showed that dryer condensate from steam drying of sawdust is toxic to aquatic organisms and that this toxicity correlates with high levels of organic compounds. Drying of sawdust for the production of fuel pellets is increasing due to the transition to renewable fuels. Recirculation of the drying medium reduces both emissions to air and energy consumption, but creates a liquid condensate containing organic compounds. Authorities have in several cases prescribed sand filtration as a purification technique for biomass dryer condensate. An alternative treatment method is biodegradation using adapted microorganisms found in biological treatment plants of pulp mills. This study investigated the effectiveness of sand filtration regarding toxicity, bioaccumulation and biodegradability; and the effect of dryer condensate on pulp mill wastewater microorganisms. A condensate produced from spruce in a steam dryer under atmospheric pressure was treated efficiently. Toxicity was extremely high before filtration, medium after filtration through a new filter, and almost low when the filter had been in use for two months. Bioaccumulation potential decreased after filtration, and the filter kept its efficiency over time. Readily biodegradable organics were present in lower amounts after filtration. Regarding COD, the sand filter exceeded the efficiency of a MGA-filter. BOD decreased from 250 to about 40 mg/l. The microorganisms had a similar oxygen uptake rate in condensate as in water. The results show that filtration through sand makes a significant difference and that it is also possible to treat the condensate by rerouting it to a pulp mill biological treatment plant. A condensate produced from forest residue wood chips in an industrial steam dryer at 3 bars was studied regarding the efficiency of sand filtration and found to be less treatable; while there was initially an effect on COD and pH, it deteriorated rapidly and then the condensate was almost unaffected by filtration. Thus the feasibility of sand filtration differs considerably for different biomass dryer condensates.

INTRODUCTION

A step towards the creation of a sustainable society is the transformation of our energy system towards renewable energy sources. An important part of this is the manufacture of fuel pellets from sawdust. The sawdust is dried to 10-12% moisture content before being made into pellets. When wood is dried, both volatile and less volatile substances are released into the air, the latter by steam distillation. The authorities in many industrial countries have issued permits for pellets plants with increasingly stringent demands for low emissions of hydrocarbons to air, as well as demands for low emissions of dust and low noise levels. Many pellet manufacturers use cyclones and filters, but another way to reduce emissions to air is to recirculate the drying medium or use steam drying. To recirculate all or part of the drying gas is favorable both in order to reduce air emissions and to increase the energy efficiency of the drying process. The downside is that it creates a condensate, a liquid comprised of the water that was dried of from the wood and various substances that left the wood during drying.

The standard way to access the environmental impact of a wastewater stream is to see if it contains substances that are toxic, bioaccumulative or persistent. The toxic compounds may damage or kill organisms in the recipient that receives the wastewater stream. The bioaccumulative substances are stored in the organisms, usually in their fatty tissues, and the substances stored can eventually reach toxic levels. Finally, it is important to find out if the substances are persistent. If the substances are broken down slowly in the environment, the risk of adverse effects is greater. The substances or waste streams that have two or three of these properties are considered as environmentally hazardous.

During drying of wood, both volatile and less volatile compounds can be emitted to air, the latter by steam distillation. The volatile compounds emitted are primarily monoterpenes (Granström, 2003; Granström, 2009; Sandberg & Granström, 2011). The less volatile compounds include fatty acids, resin acids, diterpenes and triterpenes. During high temperature drying, thermal degradation of wood gives rise to formic acid, acetic acid, alcohols, aldehydes and furfurals (Bridgwater et al., 1995; Fengel & Wegener, 1984; Münter et al., 1999), which has also been found in condensate from vacuum drying along with terpene alcohols (McDonald et al., 1999). It has not been established how high the temperature has to be before thermal degradation products are formed. Broege et al. give 130°C as an estimate (Broege et al., 1996), whereas Bridgwater et al. report 200°C (Bridgwater et al., 1995). The less volatile compounds emitted during drying have high boiling points, but sufficiently high vapour pressure to leave wood at 180-220°C. The above mentioned compounds condense with recirculation and are found either in the condensate or as a coating at the condensate surface.

Previous studies have shown that untreated condensate from the drying of softwood sawdust are extremely toxic to common microorganisms (Bicho et al., 1996), especially if the sawdust is dried to below 10% moisture content (Sandberg & Granström, 2011), which is common in the pellets industry (Olsson, 2001; Ståhl et al., 2004). This toxicity correlates with high levels of organics (measured as chemical oxygen demand, COD) in the condensates (Sandberg & Granström, 2011). Wood condensates have also tested as cytotoxic (Mark et al., 1995; Mark et al., 1996; Singer et al., 1995). Terpenes show high acute toxicity to fish and crustaceans of the genus Daphnia (Falk-Filipsson et al., 1998). Bioaccumulative compounds in wood dryer condensate include fat-soluble resin acids and fatty acids (Ek et al., 2000). Resin acids are notoriously found in the bile of perches living in waters outside of pulp- and paper mills (Kostamo et al., 2004). This strongly suggest that condensate from wood drying should not be released to natural recipients. How is one then to proceed with treatment of the condensate? A summary of the environmental licenses for pellet producers in Värmland, Dalarna and Gävleborg (Granström, unpublished data) has shown that authorities have in several cases prescribed sand filtration and pH adjustment as a purification technique for condensate from biomass dryers. In a sand filter, particles are expected to be separated from the condensate and contained in the filter, surfactants such as resin acids and fatty acids could be adsorbed on the sand grains, and possibly a biofilm could form the sand which would add biological degradation of organic material (Tchobanoglous et al., 2003). Other treatment methods reported to decrease the toxicity of biomass dryer condensate are biological treatment, filtration through active carbon, and reverse osmosis membrane filtration (Ek et al., 2000). These methods, however, is not prescribed or required. An alternative treatment method the authors of this paper have previously suggested (Sandberg & Granström, 2011) is biodegradation using adapted microorganisms found in biological treatment plants of pulp mills. The aim of this project is to establish the effectiveness of sand filtration; and to further examine the potential of biological treatment by studying the effect of dryer condensate on microorganisms derived from pulp mill wastewater treatment.

METHODS

Condensate was produced by drying spruce sawdust in a spouted bed dryer situated at Karlstad University (the KaU dryer) (figure 1). The temperature was 240 °C at the dryer inlet and 120 °C at the dryer outlet. The dryer works at atmospheric pressure. The sawdust had a moisture content of 54% and was dried to 9-10% (wb). The steam was led through a cooler system with Allihn condensers and the resulting condensate either analysed or stored frozen. The produced condensate had a COD of 1030-1080 mg/l, whereof the content of volatile fatty acids was 43.5 mg/l and aldehydes 1.5 mg/l.

Figure 1. The KaU dryer (and adjoining pellets press).

Condensate was also collected from an industrial biomass dryer, a fluid bed steam dryer owned by Borås Energi AB and located at Ryaverket in Borås. The dryer has been in use since 1994. Steam from boilers is used as drying medium. Wood chips are dried from 50% (wb) moisture content to 20-25% at a pressure of 3 bar. The wood has often been chipped about a year before being dried. The residence time in the dryer is six seconds to six minutes depending on the size of the wood chips (Münter et al., 1999). The condensate from the Borås dryer had a COD of 1120-1190, whereof the content of volatile fatty acids was 397 mg/l and aldehydes 2.93 mg/l.

A sand filter was constructed from plastic tubes of transparent PVC, length 170 cm and width 6 cm, filled with Rådasand® 0.6-0.8 mm to a height of 85 cm (figure 2). The specifics of the Rådasand can be seen in table 1. The sand filter was rinsed with water before the experiments with condensate commenced.

Figure 2. The sand filter.

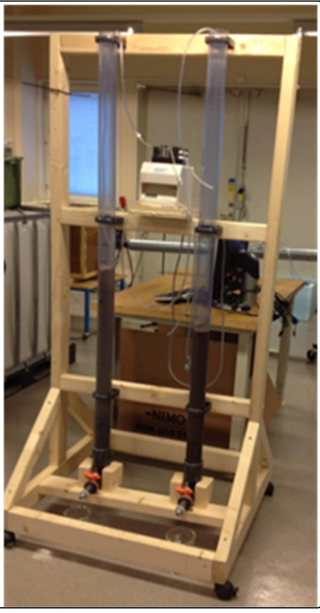

Table 1. The filter sand, sold as Rådasand 0.6-0.8.

Definition [a]			
Effective grain size, d10 [b]		0.6 ± 0.1	mm
d60 [c]	max	0.8	mm
Irregularity of form d60 :	max	1.4	
Grain less than 0.4 mm	max	1	%
Grain more than 1 mm	max	1	%
Characteristics			
Grain shape		round edge	
Turbidity	max	4	FNU
SiO_2	<	82	%
Solubility in HCl	<	0.7	%
Iron Content	<	0.1	%
Humus	<	1 000	mg/l
Particle density [d]		2.6	Mg/m^3
Bulk density [e]		1.38	Mg/m^3
Voids [e]		47	%

a) definition values were measured using filter sand standard SS-EN 12901, 12902 and 12904.
b) d10: effective grain size, the mesh size emitting 10 percent by weight of the sand.
c) d60: the mesh size at which 60 percent by weight of the sand is emitted.
d) measured in accordance with EN 1097-6.
e) measured in accordance with EN 1097-3.

In order to access the effects of both fast filtration and slow filtration, the condensate was added batch-wise. The filter was filled with condensate that was allowed to trickle through the sand, and this fast purified condensate was analysed. Then condensate was left in the filter for one week, before being analysed again. This process was repeated over a time period of two months in order to see if any buildup took place with the use of the filter. Fast filtration was 7000 litre per square meter filter per hour, and slow filtration was 20 $l/h*m^2$. The condensate was vigorously shaken before being added to the filter to avoid separation issues.

Acidity was analysed as pH. The pH of the condensate was measured using a Mettler Toledo Seven Easy pH-meter.

Toxicity was analysed using Microtox, a standardized test which gives a measure of the acute toxicity of a compound on the bacterium *Vibrio fisheri*, which is a model organism for aquatic environments. Microtox test has been shown to correlate well with acute toxicity to fish (Blum & Speece, 1990). The value given is the concentration of added condensate that inhibits the microorganisms by 50% after a given number of minutes. Thus, the lower the Microtox value, the more toxic the condensate.

Bioaccumulation potential was gauged using the condensates content of fat-soluble substances, which was measured as surface tension. Surface tension was analysed using a Lauda Tensiometer TD 1. This method has been shown to correlate well with the content of fatty acids and resin acids in pulp and paper wastewater (Sandberg & Rixen, 2012).

Biodegradability is estimated from the BOD/COD-value. The content of organic matter in the wastewater is often determined by analyzes of BOD (biological oxygen demand) and COD (chemical oxygen demand). COD is a measure of the total content of organic matter in the wastewater, while BOD shows the content of easily degradable organic material. Thus the quota BOD/COD show the proportion of the organic material that is easily biodegradable. COD was analysed with a Hoch-Lange cyvette test LCK 214. BOD was analysed by Eurofins, using the method SS-EN 1899-1. To get more detailed data on the composition of organics in the condensate, volatile fatty acids were analysed using a Hoch-Lange cyvette test LCK 365, and aldehydes were analysed using a Hoch-Lange cyvette test LCK 325. All Hoch-Lange cyvette tests were analyzed in a DR 2800 VIS-spektrofotometer.

The resilience of microorganisms from pulp- and paper mill wastewater treatment to the condensate was tested using their oxygen uptake rate. If the condensate is in some way toxic to microorganisms, it will affect their activity and lessen the rate with which they consume oxygen. Thus, the content of dissolved oxygen will decrease at different rates depending on the toxicity of the microorganisms' environment. 25 ml of a selected inoculum of microorganisms chosen from the aerated biological treatment of a pulp- and paper plant was added to 200 ml of either water or condensate in a stirred beaker placed in a 35 °C water bath. The mixture was oxygenated via a diffuser to about 10 mg of oxygen per liter. A parafilm lid was added to avoid oxygen diffusing in from the surface. The decrease in the concentration of dissolved oxygen was measured with a Hach Lange LDO optical oxygen meter. As a control, the dissolved oxygen for pure condensate was also measured. The oxygen uptake rate of the microorganisms was calculated as mg of oxygen per minute.

RESULTS AND DISCUSSION

The results and discussion section deals first with the condensate from the dryer at Karlstad university, then the Borås Energy dryer have a section devoted to it, a finally the differences between the condensates are discussed.

That sand filtration has a purifying effect is clearly visible to the naked eye, see figure 3.

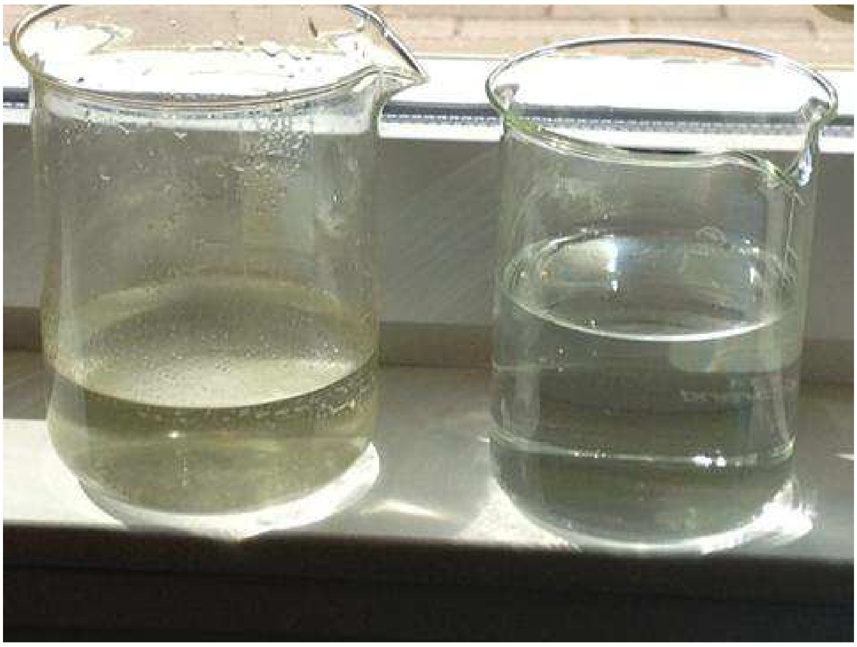

Figure 3. Condensate before (left) and after (right) filtration.

Acidity (pH)

Untreated condensate taken from the condenser had a pH of 4.8. Condensate that was frozen had a slightly lower pH of 4.4 after thawing, a value that was constant throughout the experiments. The condensate trickling fast through the sand filter had a notably high pH value the first day, and then the pH leveled out at or slightly above 6.5 (figure 4). When condensate was allowed to stay longer in the filter, the acidity decreased even more. This effect diminished slightly over time but the difference between fast and slow trickling remained during the entire experiment period (see figure 4). The Rådasand clearly neutralizes the acidity of the condensate.

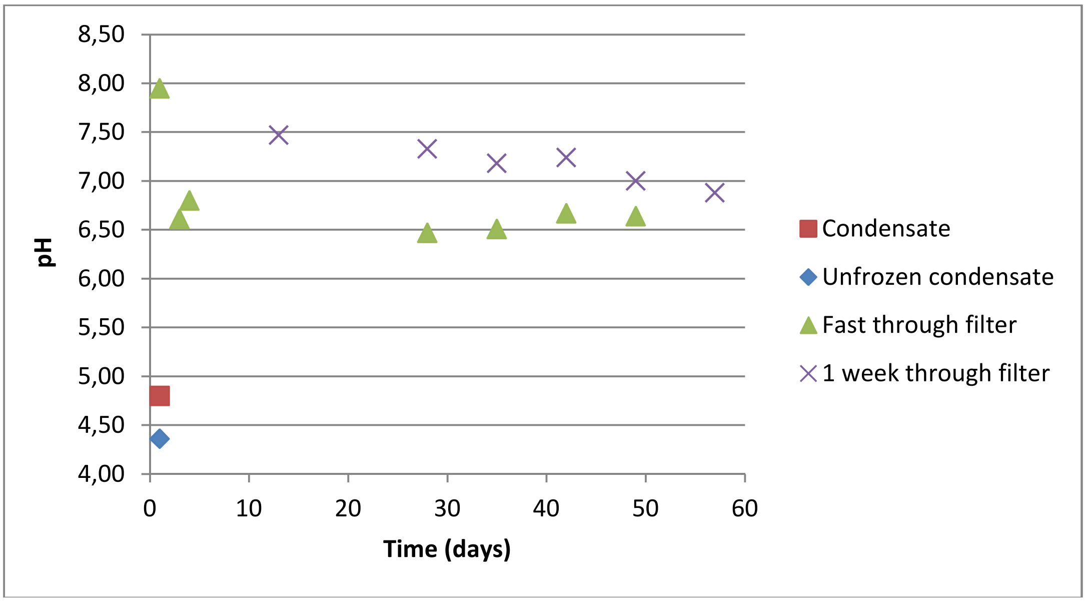

Figure 4. Effect of sand filtration on the pH of the condensate over time.

Chemical oxygen demand (COD)

The content of organics in the condensate was measured as COD in mg per liter. The COD of the condensate before purification was 1030-1080 mg/l (figure 5). In order to see how much of this could be removed by removing the fatty substances at the surface of the condensate, the water beneath it was tested and found to have a COD of 621 mg/l. Cooling the condensate to 15 °C made more fatty substances separate to the surface and the water beneath it had a COD of 566 mg/l. As for the effects of sand filtration, the condensate that was led fast through the filter at the beginning of the experiment period had notably varying COD at 150-400 mg/l, and at subsequent filtrations the condensate had COD of 120-200 mg/l (figure 5). Condensate that spent a week in the filter had about 90 to 400 mg/l with no trend (figure 5). For comparison, condensate filtered through two 45 um MGA filters had a COD of 459 mg/l. Thus, the sand filter was consistently more efficient than MGA filters at reducing COD.

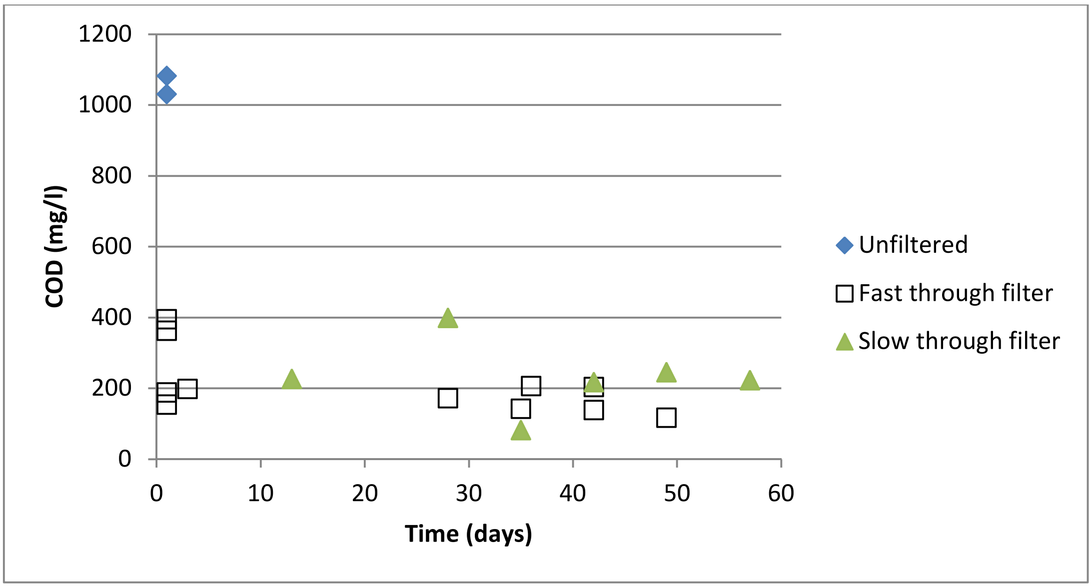

Figure 5. COD in the condensate before and after filtration.

Biological oxygen demand (BOD)

The content of organics in the condensate was 250 mg BOD/l before purification and without the surface fatty layer. Condensate that trickled through the filter the first day had 48 mg/l and when the test was repeated at the last day of the experiment period the filtered condensate had a BOD of 34 mg/l. The purified condensate always lacked a surface layer of hydrophobic fatty substances. As the BOD test has an uncertainty of 30%, there is no significant difference between the values at the start and finish of the filtration period. However, the difference before and after filtration is obvious. The quotient BOD/COD shows the proportion of organic matter that is easily degradable. This was for unfiltered condensate 24%, for filtered condensate at the start of the test period 13% and at the end of the test period 17%.

Aldehydes

The content of aldehydes in the condensate decreased after filtration (see figure 6). The condensate that spent time in the filter had low levels with no notable trend over time, whereas the condensate that progressed fast through the filter had progressively lower levels of aldehydes as the filter was used (figure 6).

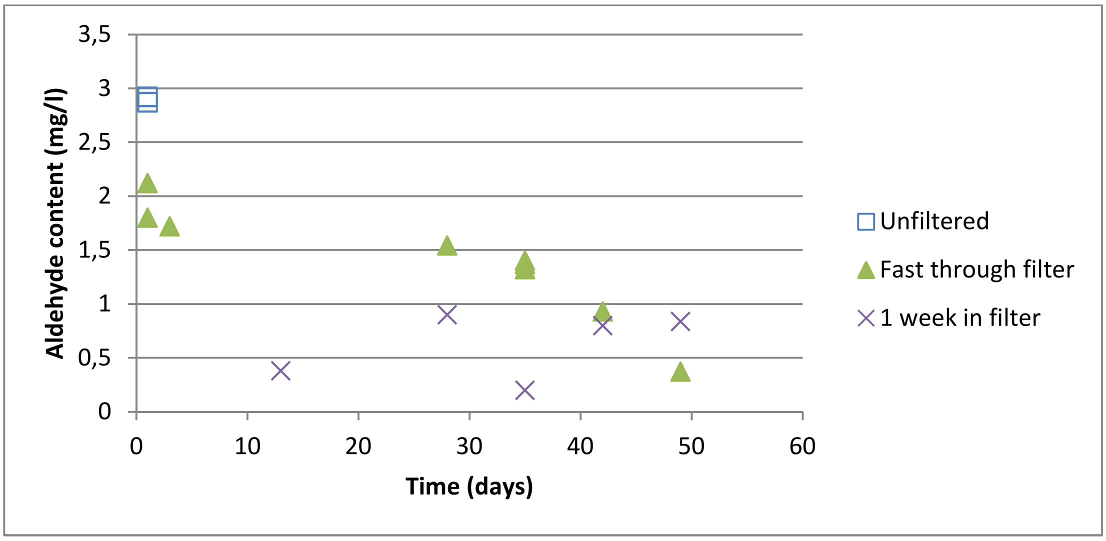

Figure 6. Aldehydes in the condensate before and after filtration.

Surfactants

The effect of a sand filter on the condensates content of surfactants was estimated by measuring its surface tension. The method used on distilled water shows a value of 76. Addition of surfactants, such as resin acids and fatty acids, lowers the surface tension value. Unfiltered condensate had 46.4. As can be seen in table 2, there are no trend over time for the condensate that trickled fast through the filter. Condensate that spent a week in the filter had consistently higher values, as longer residence time caused improved purification. However, this effect decreased over time, possibly as the surfaces on the sand became saturated with surfactant compounds.

Table 2. Surface tension

Day	Fast filtration (mN/m)	Slow filtration (mN/m)
3	51.4	n.r.
13	n.r.	58.2
28	50.2	58.3
35	53.3	56.3
42	51.8	55.8
49	50.2	54.2
57	n.r.	49.3

n.r. = not recorded

Microtox

The microtox test showed, as expected, that the untreated condensate was extremely toxic, see table 3. The toxicity lessened after sand filtration treatment and the effect improved considerably over time. An EC50-value over 45% is considered moderate toxicity. The condensate purified by trickling through the sand filter at the end of the experiment period was reasonably close to that level.

Table 3. Microtox values for condensate before and after filtration.

	Microtox EC10 (%)	Microtox EC20 (%)	Microtox EC50 (%)
Untreated condensate	< 1	1	6
After fast filtration day 1	1	2	13
After fast filtration day 61	2	7	39

Microorganism oxygen uptake rate (OUR)

In the beaker with only condensate, the concentration of dissolved oxygen decreased to 8 mg/l, which is the equilibrium value for water at 35 °C, in 200 minutes and then remained stable (see figure 7). The oxygen uptake rate in the beaker with water and inoculum was 0.05 mg per litre and minute, and for the beaker with condensate and inoculum 0.08 mg per litre and minute. This showed that the microorganisms in the inoculums were active and that these adapted microorganisms actually thrived better in condensate, probably due to the presence of edible organics.

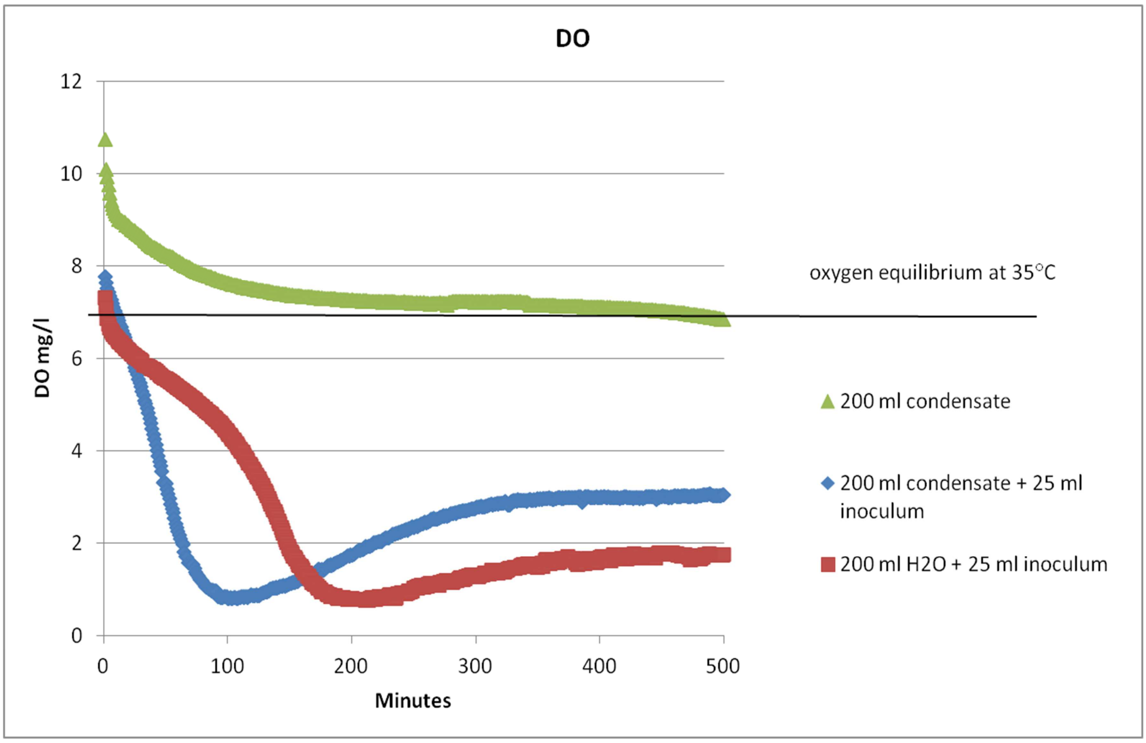

Figure 7. Concentration of dissolved oxygen.

Borås dryer

This condensate was analysed regarding COD, pH, volatile fatty acids, and aldehydes. The load of organics, measured as COD, was similar for both condensates, but the condensate from the Borås dryer had a higher concentration of short-chain fatty acids and aldehydes. The condensate from the Borås dryer had a thicker film of hydrophobic substances on the surface, a film that did not dissolve through shaking, and also had a considerably more powerful smell than the condensate from the KaU dryer. COD and pH was studied over time, which revealed that while there was initially an effect of sand filtration, it deteriorated rapidly and after that the filter was almost useless (figure 8 and 9). The pipe previously used for filtration of KaU condensate (pipe 1) worked less well than a fresh pipe (pipe 2) during the first fast filtration, indicating that an initial presence of small particles had a positive effect but that these are quickly rinsed out. The slow filtration saw no difference between pipe 1 and 2, and thus no long-term effect of a build-up of organics in the sand filter was demonstrated.

For COD, there was possibly a small effect on the slow filtration at the end of the test period (figure 8), but this can not be said to be a significant trend.

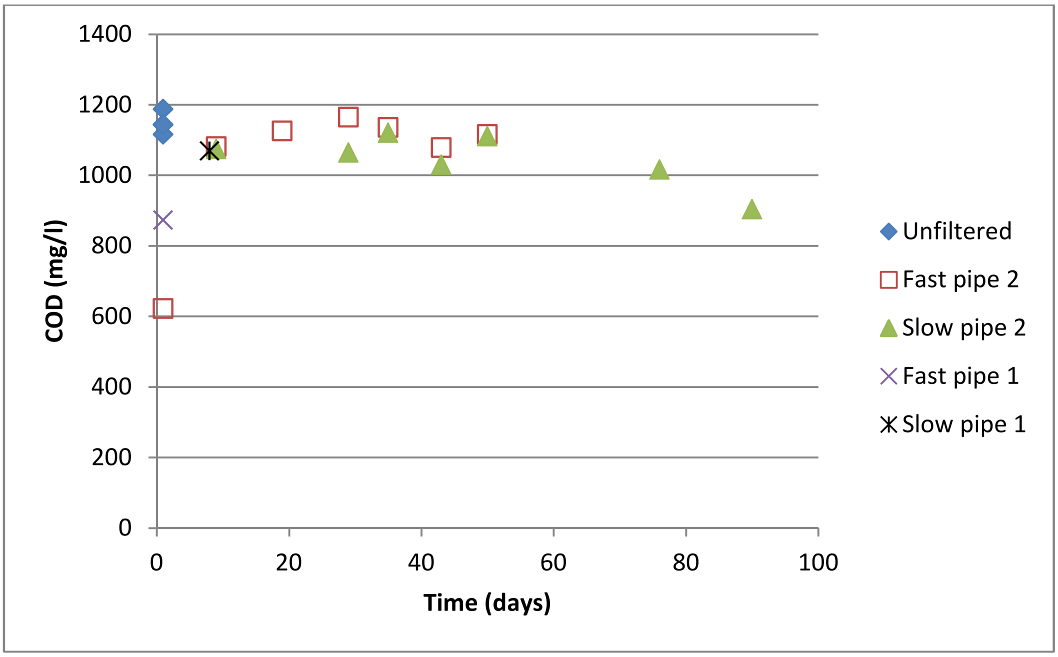

Figure 8. COD in Borås condensate.

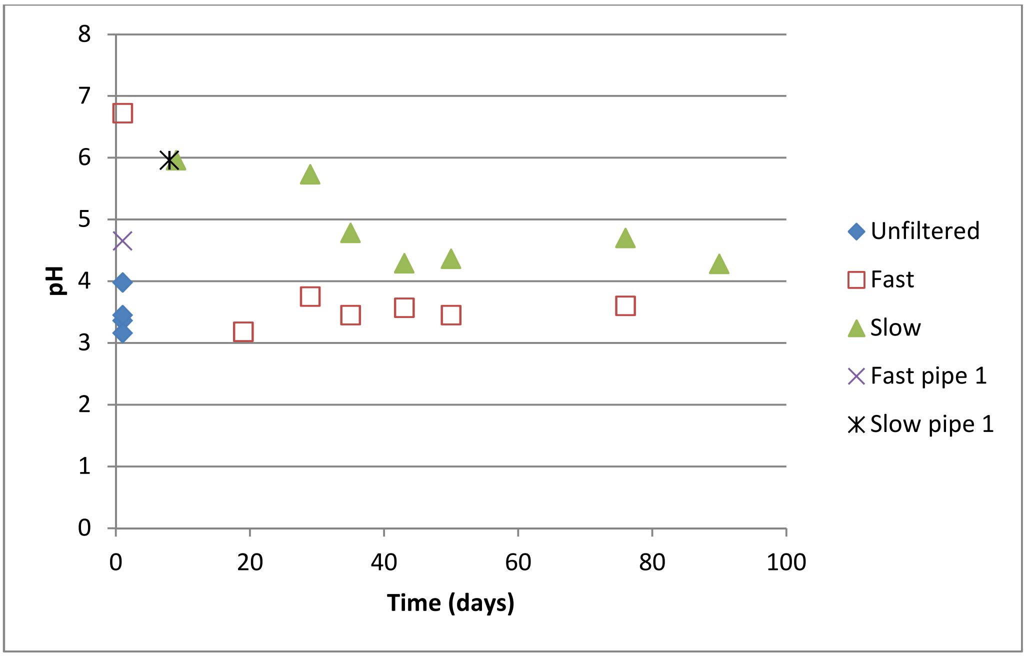

Figure 9. pH in Borås condensate.

Visual inspection of condensate before and after sand filtration showed a difference in clarity, see figure 10.

Figure 10. Borås condensate before (left) and after (right) filtration.

Discussion on the differences between the two condensates

The difference between Borås condensate and KaU condensate is likely due to the different composition of material and drying schedule. The condensate produced from spruce in an atmospheric steam dryer was possible to treat with a sand filter, whereas the condensate produced from forest residue of what was believed to be a mixture of spruce and pine in a pressurised steam dryer was not. It is notable that the COD-value was not sufficient information to detect this difference.

CONCLUSIONS

For the condensate produced from spruce in the dryer at Karlstad University, the sand filter reduced toxicity and bioaccumulation potential but not biodegradability. It served to decrease acidity, organics (BOD, COD and aldehydes), surfactants and toxicity. Slow filtration was preferable for the removal of acidity and surfactants. The effect deteriorated somewhat with use regarding acidity and surfactants, but improved notably regarding toxicity. For the condensate from the biomass dryer at Borås Energi, however, the beneficial effect of the sand filter was short-lived. A sand filter thus treats only some condensates, possibly those from low-extractive woods and/or non-overpressurised dryers. Microorganisms from the wastewater treatment of a pulp and paper plant proved resilient to the spruce condensate and this it would be possible to treat this condensate by rerouting it to such a treatment plant.

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