Combination of coagulation and catalytic wet oxidation for the treatment of pulp and paper mill effluents

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Abstract Wet oxidation (WO) is a well established process for purification of concentrated municipal and industrial wastewaters. Many attempts have been made to modify the WO process or to create a suitable combination of processes. This work was undertaken to investigate wet oxidation integrated with coagulation, i.e. to treat the sludge remaining after coagulation with a WO process. The possibility of regeneration of the used coagulant was also considered. Two waters from paper mills were used: TMP (thermomechanical pulp) circulation water and membrane concentrate. About 50% of the COD in the original water can be removed by coagulation using Fe₂(SO₄)₃. The results from the wet oxidation experiments show the positive effect of iron in the chemical sludge as a catalyst. The efficiency of the WO process was enhanced almost by 100%. The remaining dissolved organic matter can be easily removed biologically.

Keywords Biodegradability; catalytic wet oxidation; coagulation; membrane concentrate; thermomechanical pulp

Introduction
Treatment of wastewaters by coagulation is a well established technology suitable for concentrated wastewaters of pulp and paper mills containing large amount of colloids and dissolved compounds. Many coagulants have been used to improve the characteristics of water, but lime or ferric sulfate have been found to be economically preferable (Panchapakesan, 1991; Chen and Horan, 1998). Coagulation has been used for colour and COD removal by dual-polymer system on the effluent from bleached kraft mill (Hodgson et al., 1998). As a result, 60% colour removal and 80% reduction of dioxins, which are toxic compounds in bleaching kraft mill effluent, was observed. However, coagulation produces large amounts of chemical sludge which has to be dewatered before disposal or incineration.

Wet oxidation (WO) is a well known process for the purification of concentrated municipal and industrial wastewaters. The process has been studied for the treatment of process waters in pulp and paper mills to reduce organic contaminants or to close paper mill water cycles, since closed-loop operation minimises the risk of polluting the hydrosphere (Andersen et al., 1994; Verenich et al., 2000). During recent decades many attempts have been made to modify the process or to create a suitable combination of processes to increase the efficiency of the oxidation process. Different heterogeneous catalysts have been applied to decrease the pressure and the temperature of the process (Luck, 1996; Zhang and Chuang, 1998; Verenich et al., 2000). The results of these researches showed that the organic load can be reduced by using heterogeneous catalysts, such as Pd/Al₂O₃, Pt-Pd1Ce4/Al₂O₃, Fe/Mn-C, Cu/Co/Bi-C, by up to 60–80% under relatively mild conditions (423–463K and pressures of 1–1.5 MPa) in the case of pulp mill effluent. However, wet oxidation in the presence of hydrogen peroxide is the most attractive process (Sanger et al., 1992; Debellefontaine and Foussard, 1996). The use of heterogeneous catalysts can lead to leaching of active metals into the treating water, which makes post-treatment
necessary for metal removal. At the same time, hydrogen peroxide is a harmless catalyst and its addition showed significant improvement in the oxidation of water pollutants.

Numerous homogeneous catalysts have been tested to increase the rate of the WO process. Among the long list of traditional catalysts, such as Fe, Mn, Zn, etc., Cu is the most popular and effective catalyst due to its high activity. (Collyer et al., 1997; Imamura, 1999). The studies of Debellefontaine and Foussard (1996) showed that ferrous salts are also very efficient as catalysts in WO. The research was done by oxidising potassium oxalate. The addition of Fe$^{3+}$ and Fe$^{2+}$ allowed an increase in organic removal of 2.6 and 32.2 times, respectively, over a non-catalytic system under the same conditions. Chowdhury and Ross (1975) have studied different catalyst combinations for oxidising strong wastewater and have found that the most promising combinations were hydrogen peroxide coupled with Fe$^{3+}$, Fe$^{2+}$ and Cu$^{2+}$.

WO has been integrated with filtration processes or evaporation (Lei et al., 1998; Verenich, 1998). A hybrid process of nanofiltration followed by the WO process allows the water effluent to be concentrated before the WO treatment. The oxidation of paper mill ultrafiltration concentrate showed 45% COD removal at 443K and biodegradability was observed to be enhanced by up to 80% (Verenich et al., 2000). The OXYMEM process combines wet oxidation and nanofiltration. In this process a nanofiltration membrane is used to retain molecules in a wet oxidation reactor until they have been oxidised to the desired extent (Hellenbrand et al., 1997). As a result, the permeate obtained from the integrated process had better characteristics than that from conventional WO. Another way to improve the efficiency of the process is to use sonication or to combine membrane filtration, sonication and WO. These are so-called SONIWO and MEMSONIWO processes (Ingale and Mahajani, 1995; Dhale and Mahajani, 1999).

Wet air oxidation is a process commonly integrated with biological treatment (Chakchouk et al., 1994; Scott and Ollis, 1995). As already known, oxidising agents can break organic compounds into components of smaller chain length, increasing at the same time the compounds’ biodegradability.

This work was undertaken to investigate a hybrid process of coagulation and wet oxidation. The sludge formed in coagulation contains a lot of coagulant (Fe$_2$(SO$_4$)$_3$) that acts as a catalyst in the subsequent wet oxidation process. For this reason iron sulphate was used as a coagulant because Fe$^{3+}$ ions are known to have catalytic activity in WO.

**Experimental**

*Materials.* For the coagulation and wet oxidation experiments, thermomechanical pulp (TMP) circulation water and membrane concentrate after ultrafiltration were obtained from paper mills in Finland. The properties of the wastewaters are presented in Table 1.

*Coagulation material.* Al$_2$(SO$_4$)$_3$·18H$_2$O and Fe$_2$(SO$_4$)$_3$·H$_2$O with iron content of 21–23 wt %.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>TMP-water</th>
<th>Membrane concentrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>4.8–6.5</td>
<td>5.0–5.2</td>
</tr>
<tr>
<td>COD (mgO$_2$/L)</td>
<td>1,900–2,100</td>
<td>7,100–7,300</td>
</tr>
<tr>
<td>TOC (mgC/L)</td>
<td>1,600–700</td>
<td>1,800–2,100</td>
</tr>
<tr>
<td>BOD/COD (%)</td>
<td></td>
<td>24–28</td>
</tr>
<tr>
<td>Turbidity (FTU)</td>
<td></td>
<td>828</td>
</tr>
<tr>
<td>Solid content (g/L)</td>
<td>1.5–2.1</td>
<td>8.0–8.5</td>
</tr>
<tr>
<td>Ash (g/L)</td>
<td>0.35–0.37</td>
<td>3.1–3.4</td>
</tr>
</tbody>
</table>
Experimental set-up. Coagulation jar experiments were conducted using a 70 ml water sample in a 100 ml beaker, stirring by magnetic stirrer. The temperature during the jar test was maintained at 293K within ±1K. After pH adjustment with NaOH, or if necessary, with H₂SO₄, the designated dose of coagulant was added. After 5 minutes of fast stirring the stirring speed was reduced to 100 rpm. After an additional 20 minutes, the sample was removed and allowed to settle for 60 minutes at which time sludge was decanted from the clean water and stored.

The wet oxidation experiments were performed in a stainless-steel high-pressure reactor (Parr Instrumental Co, USA) with an inner diameter of 63 mm and a volume of 200 ml, capable of performing batch experiments at pressures up to 8 MPa and temperatures up to 623K. The maximum rotation speed of 900 rpm was chosen to ensure proper mass transfer of oxygen from the gas to liquid phase. Pure oxygen was used as the oxidising agent and it was obtained from an oxygen cylinder connected to the reactor.

The operating procedure of the experiments with wet oxidation was as follows. 175 ml of water sample was put into the reactor and then the reactor was heated to the desired reaction temperature (393–453K). When the selected reaction temperature had been reached, pure oxygen was introduced into the reactor and the reaction was assumed to have started. At designated time intervals, liquid samples were taken from the reactor and analysed for pH, Fe-concentration, BOD and COD contents.

Methods. Analysis of Fe³⁺ ion concentration was conducted by atomic adsorption spectrophotometer (Shimadzu AA-680, Japan).

COD was analysed by the closed reflux dichromate method (Standard Methods for the Examination of Water and Wastewater, 1989) using a COD reactor (Hach Company, USA), and spectrophotometer DR/2000 (Hach Company, USA).

Biological oxygen demand was assessed by standard BOD tests (Standard Methods for the Examination of Water and Wastewater, 1989).

Results and discussion

Coagulation study. The influence of the coagulant concentration, pH (4–11) on the performance of the coagulation was examined at room temperature for the two studied waters. The impact of the coagulant concentration is presented in Figure 1 as process efficiency, i.e. percentage of COD removal, and Fe iron ion concentration plotted against coagulant dose.

COD removal improved with an increasing dose of coagulant. The concentration of
dissolved Fe$^{3+}$ increased up to 75 mg/L and then diminished rapidly to 4.7 mg/L as the coagulant dose was increased. This point corresponds to a coagulant dose of 155 mgFe/L. It is of interest to note that from the point where the metal ion concentration started to diminish to its minimum, the process efficiency, i.e. COD removal, sharply increased from 20% to 51%. Further addition of the coagulant did not improve the process significantly. For this reason the optimum coagulant dose was assumed to be 155 mg Fe/L.

During coagulation a large amount of chemical sludge was created. The amount of sludge was about 25% of the treated water. The sludge had good settling properties and was fully settled in 60 minutes.

The jar experiments demonstrated that pH has a significant influence on the coagulation process (Figure 2). A notable peak was observed at pH range 5.85–6.0, as expected (Ullmann’s Encyclopedia of Industrial Chemistry, 1996).

Based on the results obtained, the optimum dose of coagulant and optimum pH for TMP circulation water was assumed to be 155 mgFe/L and 5.85, receptively.

Similar experiments were conducted for the membrane concentrate which indicated that the optimum point for this water at a temperature of 294K is pH 5.9 and the optimum dose was found to be 1.2 gFe/L.

Coagulation experiments were carried out at the same time using aluminium sulphate and it was found that in order to reach an efficiency of 50%, as obtained with iron sulphate in the case of ultrafiltration membrane concentrate, the dose of aluminium sulphate should be more than 2.1 g/L.

**Wet oxidation study.** The collected sludges after coagulation had the following characteristics (Table 2).

The experiments were carried out at different temperatures (393–453K) and pressures of 0.2–1.5 MPa. The results of COD analysis are brought together in Tables 3 and 4. In the case of the TMP circulation water, blank experiments were conducted with the original water concentrated to the COD value of the sludge by evaporation. In the case of the ultrafiltration concentrate, the original water itself was used as a blank, without any additional pre-treatment.

**Table 2** Some characteristics of chemical sludge obtained after coagulation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>TMP-water</th>
<th>Membrane concentrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>PH</td>
<td>5.8–6.1</td>
<td>5.8–6.2</td>
</tr>
<tr>
<td>COD (mg O$_2$/L)</td>
<td>7,400–8,700</td>
<td>11,000–14,500</td>
</tr>
<tr>
<td>TOC (mg C/L)</td>
<td>2,100–2600</td>
<td>5,100–6,000</td>
</tr>
<tr>
<td>Fe concentration (g/L)</td>
<td>1.31–1.43</td>
<td>&gt;2.0</td>
</tr>
</tbody>
</table>

![Figure 2](https://iwaponline.com/wst/article-pdf/44/5/145/430451/145.pdf)
As can be seen, a significant effect from the coagulant/catalyst was obtained at medium temperatures (413–433K) and at 403K for the ultrafiltration concentrate only. For the TMP-chemical sludge the increase in COD removal can be clearly seen at temperatures of 413–433K. The Fe-catalyst increased COD removal by 100% in the pressure range of 0.2 to 1 MPa in comparison with a non-catalysed system under the same conditions. For the membrane-chemical sludge, the largest difference between catalytic and non-catalytic wet oxidation was observed at 403K where 38% COD removal was achieved and only 3% in the blank experiment. The effect of the catalyst diminishes with increasing temperature. The reason may be that, at higher temperatures, an energy barrier, which is reduced by a catalyst, can more easily be overcome without the need for a mediator (catalyst). Thus, the effect of the catalyst will gradually disappear with increasing temperature.

The reason for the high COD removal at medium temperature can be explained by the high concentration of the catalyst in the water medium (Figure 3). As can be seen, the concentration of dissolved metal ions have a visible peak at a temperature range of 403–423K, where it reaches a value of 80 mg/L for TMP-chemical sludge and 530 mg/L for membrane-chemical sludge.

### Table 3  The effect of coagulant/catalyst presence on COD removal, TMP-water

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Pressure (Mpa)</th>
<th>COD removal (%) sludge/blank</th>
</tr>
</thead>
<tbody>
<tr>
<td>393</td>
<td>0.2</td>
<td>0/0</td>
</tr>
<tr>
<td>413</td>
<td>0.2</td>
<td>10/6</td>
</tr>
<tr>
<td>433</td>
<td>0.2</td>
<td>26/18</td>
</tr>
<tr>
<td>453</td>
<td>0.2</td>
<td>35/17</td>
</tr>
</tbody>
</table>

### Table 4  The effect of coagulant/catalyst presence on COD removal, membrane concentrate

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Pressure (Mpa)</th>
<th>COD removal (%) sludge/blank</th>
</tr>
</thead>
<tbody>
<tr>
<td>403</td>
<td>0.2</td>
<td>27/15</td>
</tr>
<tr>
<td>418</td>
<td>0.2</td>
<td>35/13</td>
</tr>
<tr>
<td>433</td>
<td>0.2</td>
<td>27/15</td>
</tr>
<tr>
<td>448</td>
<td>0.2</td>
<td>21/42</td>
</tr>
</tbody>
</table>

**Figure 3** The concentration of Fe ions during catalytic wet oxidation (black data points) for ultrafiltration concentrate and (white data points) for TMP-water
Figure 4 depicts the behaviour of the iron concentration during the wet oxidation experiments at different oxygen partial pressure. All six curves show a sharp decrease in the Fe concentration during the first 10 minutes with a subsequent increase. The decrease in the concentration may be attributed to partial oxidation of Fe to oxides. The increase in the dissolved iron concentration may be explained by a decrease in pH caused by the formation of carboxylic acids during the WO process. However, after 60 minutes, analysis showed a decrease in the concentration of the homogeneous catalyst. At higher pressure, the lower active metal concentration is observed at the end of experiment. This indicates that, at higher oxygen pressures, more dissolved iron might be oxidised than at lower pressures.

Some results concerning biodegradability are presented in Figure 5. It is necessary to point out that the settled water obtained after coagulation had itself quite high biodegradability, within 35–45%. The catalytic wet oxidation (CWO) increased the BOD/COD ratio up to 85%. The pre-heating period undoubtedly contributed some effect on the ratio as can be seen from Figure 5. The difference in “zero-time” points is caused by thermal decomposition during the pre-heating of the sludge sample to the designated temperature.

Process comparison. Finally, a comparison of the processes was done. Figure 6 depicts the results of wet oxidation processes conducted with and without coagulation as a pre-treatment process for the TMP circulation water and the membrane concentrate.

As can be seen, the WO process after coagulation enhanced COD removal to 58% and to 50% under relatively mild conditions for the membrane concentrate and the TMP circulation water, respectively. An interesting phenomenon was observed at a temperature of 403 K for the membrane concentrate where the organic load was reduced 12.7 times more by catalytic wet oxidation (CWO) than by non-catalytic oxidation. At the same time, a reduction of 64% in the volume of the sludge was observed, in some cases up to 80%, for 120 minutes of the CWO treatment. The sludge remaining, containing mostly iron oxides, can be used as a coagulant after recovery by acidification with sulphuric acid.

Conclusions
A combination process of coagulation with Fe$_2$(SO$_4$)$_3$ and subsequent wet oxidation of the chemical sludge was studied for the treatment of paper mill effluents. In coagulation, an efficiency of 51% in COD removal was achieved with the optimum coagulant dose of 155 mg/L. In the wet oxidation process, iron contained in the chemical sludge had a signifi-

![Figure 4](https://iwaponline.com/wst/article-pdf/44/5/145/430451/145.pdf)

**Figure 4** Concentration of Fe ions during catalytic wet oxidation (black data points) for ultrafiltration concentrate and (white data points) for TMP-water
cant catalytic effect. As a result, CWO could reduce the organic load up to 50% and 58% under relatively mild conditions for the TMP-chemical sludge and membrane-chemical sludge, respectively.

During oxidation the chemical sludge was transformed into dense (iron oxide) sludge which can easily be separated from water and the iron can be recovered in the form of Fe₂(SO₄)₃ by acidification. However, the dissolved iron concentration was found to be quite high after CWO of the chemical sludge. This makes the treated water unsuitable for recirculation. The biodegradability of this water was observed to be high, up to 80%, and it can be easily treated biologically. Therefore, future research will be done to improve the water quality to allow the possibility of recirculation of the treated water.

Acknowledgements
The research was carried out in Lappeenranta University of Technology and received financing from Graduate School in Chemical Engineering (GSCE). The authors are thankful to Jose Luque MSc. from Universidad de Barcelona for carrying out most of the experiments.
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