Assessment of electrochemical and chemical coagulation as post-treatment for the effluents of a UASB reactor treating cellulose pulp mill wastewater

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Abstract This paper presents results from exploratory experiments to test the technical feasibility of electrolytic treatment and coagulation followed by flocculation and sedimentation as post-treatment for the effluent of an UASB reactor treating simulated wastewater from an unbleached Kraft pulp mill. The electrolytic treatment provided up to 67% removal of the remaining COD and 98% of color removal. To achieve these efficiencies the energy consumption ranged from 14 Wh.l\(^{-1}\) to 20 Wh.l\(^{-1}\). The coagulation-flocculation treatment followed by settling required 350–400 mg.l\(^{-1}\) of aluminium sulfate. The addition of a high molecular weight cationic polymer enhanced both COD and color removal. Both post-treatment processes are technically feasible.

Keywords Coagulation; electrolytic treatment; Kraft pulp effluents; post-treatment; UASB reactor

Introduction

The need for ever increasing pollutant removal efficiencies from chemical plants has produced a renewed interest in electrochemical and photochemical treatment processes, as recently published papers indicate (see, for instance, Korbatti and Tanyolac, 2003; Chen et al., 2003; Torres et al., 2003; Kim et al., 2002; Panizza et al., 2000; and Motheo and Pinheiro, 2000). One application of these processes is as post-treatment for color removal from pulp mill wastewaters. Due to the chromophoric structure of the lignin compounds it is known that biological processes of treatment are not effective to remove the color content of those discharges (Sierra-Alvarez, 1990). Thus the biological treatment usually needs to be combined with another process when it is necessary to remove color from wastewaters, however the costs are relatively high when compared with the other stages of the treatment plant.

The electrochemical treatment is an established technology for metal removal in the plating and photo finishing industry and has been researched for use, among other applications, in the treatment of textile wastewaters (Kim et al., 2002), removal of organic recalcitrant compounds as the lignin (Chiang et al., 1997), removal of poliaromatic organic compounds (Panizza et al., 2000), wastewaters that contain phenolic compounds (Torres et al., 2003; Korbatti and Tanyolac, 2003), sanitary sewage treatment (Vlyssides et al., 2002) and humic acids removal (Motheo and Pinheiro, 2000). In spite of these uses the electrochemical reactors still lack operational cost effectiveness to be used in large-scale operations such as those encountered in the pulp and paper industry. The main problems with these systems are related to the electrical energy consumption and sludge production. Also, in this particular project, little is known about the application of an electrochemical reactor as the post-treatment to an anaerobic effluent, so the main objective of this work is to increase knowledge in this area.
On the other hand the coagulation–flocculation method of treatment for color removal is well known and there is a great number of research papers and applications of this technology available to the practitioner. This treatment has a mechanistic similarity with the electrochemical process. Thus, for comparison purposes, it was chosen as the other post-treatment for the effluents of a bench-scale UASB reactor treating a simulated wastewater from unbleached pulp mill.

**Materials and methods**

**Materials**

A UASB-type reactor with a total volume of 15.01 L was used to treat a synthetic wastewater that simulates the effluents of an unbleached Kraft pulp mill, providing the influent for the post-treatment studies. The reactor was kept in a constant temperature environment (30 ± 1 °C) and was inoculated with granulated sludge from a full-scale UASB reactor treating effluents from a poultry slaughterhouse. Black liquor from a pulp mill was the main component of the synthetic wastewater, as described in Buzzini and Pires (2002). The influent COD was kept constant (1,400 mg l⁻¹) and the hydraulic retention time (HRT) was kept around 30 h. During the whole experimental period the UASB reactor kept its stability concerning COD removal efficiency, alkalinity, volatile acids concentration and methane concentration in the biogas. Table 1 shows the main characteristics, concerning electrochemical treatment, of the UASB reactor effluent. Sulfuric acid or sodium hydroxide solutions were added to adjust the pH of the wastewater to the desired value for the experiments.

**Methods**

**Treatment I.** The first series of experiments was performed using a laboratory-scale electrochemical cell consisting of a sandwich of two aluminium plates as electrodes separated by a 5 mm machined Teflon plate that formed the reaction chamber with a total volume of 10 mL. A Prominent Gamma G/4b peristaltic pump, with maximum flow rate of 2.31 L h⁻¹, was used to provide the recirculation of the wastewater under treatment. Sodium chloride was added as electrolyte. This system was operated in batch mode using a 2.01 reservoir for feeding and recirculation. Preliminary assays indicated that good results could be obtained with two hours of electrolytic treatment and afterwards the solution was homogenized and transferred to a graduate cylinder for a 30 minute sedimentation period. An undisturbed sample of the supernatant was collected for examination at the end of the sedimentation phase. The following variables were evaluated: current density (19 mA cm⁻², 38 mA cm⁻² and 76 mA cm⁻²); recirculation flow rate in the electrochemical cell (0.45 L h⁻¹, 0.901 L h⁻¹ and 1.80 L h⁻¹) and initial pH (7.3, 6.3 and 8.3).

**Treatment II.** The second set of experiments consisted of laboratory jar-test assays to choose the adequate coagulant dosage, pH, time and mixing gradient. Since aluminium was used in the electrodes of treatment I, aluminium sulfate (Al₂(SO₄)₃·16H₂O) was tested as the chemical coagulant to allow a closer comparison of processes efficiencies.

**Table 1 Main characteristics of the UASB reactor effluent**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD (mg l⁻¹)</td>
<td>210–240</td>
</tr>
<tr>
<td>pH</td>
<td>7.0–7.5</td>
</tr>
<tr>
<td>Conductivity (µS cm⁻¹)</td>
<td>600–630</td>
</tr>
<tr>
<td>Color (U.C.)</td>
<td>1,150–1,350</td>
</tr>
</tbody>
</table>
The following dosages were tested: 150, 200, 250, 300, 350, 400 and 450 milligrams per litre. For the three best aluminium sulfate dosages the concomitant application of a high molecular weight cationic polymer (Bayer) using the following dosages: 1.0; 2.0; 3.0; 4.0; 5.0 and 6.0 milligrams per litre was also evaluated.

The jar-test assay was performed with two litre standard flasks using fixed operational conditions: rapid mixing with an 800 s⁻¹ gradient and 20 seconds mixing time; slow mixing with a 50 s⁻¹ gradient and 20 minutes mixing time. During the sedimentation period the samples were collected at the following velocities: 5.0; 2.5; 1.0; 0.5 and 0.24 centimetres per minute.

The COD, pH, volatile acid concentration, alkalinity, apparent color and conductivity were determined according to the methodology described in the *Standard Methods for the Examination of Water and Wastewater* (1995). The composition of the biogas was monitored by gas chromatography, using a Gow Mac chromatographer.

**Results and discussion**

Table 2 presents a selected set of results obtained with the use of aluminium electrodes. The maximum COD removal efficiency with the electrolytic treatment was 67%, while color removal reached 98%.

The results from Table 2, together with preliminary experiments with other electrodes, indicate that the initial pH, the recirculation flow rate and the electrode composition had an influence on removal efficiency and are factors that must be taken into consideration for the optimization of this process.

It should be pointed out that it was not possible to achieve the best results for color removal and COD removal efficiencies simultaneously in these experiments. The color removal efficiency was three percentage points lower in assay I.1 compared with experiments I.5–I.7, however the COD removal efficiency in assay I.1 was higher by 13 percentage points, if compared to assays I.5 and I.6 and 32 percentage points when compared to assay I.7. Notwithstanding, 95% color removal efficiency, as obtained in assay I.1, may be good enough for many cases.

In most of the electrolytic assays the additional COD removal, although above 50%, would not justify the use of this treatment for removal of the remaining organic load; however the color removal efficiency can be considered very high and this may be a valid option as post-treatment for some of the biological wastewater treatment processes. In this case most of the organic load would be removed by the biological treatment while the electrolytic process would be optimized only for color removal.

These results also confirmed that the wastewater characteristics and the electrode composition have a great influence on the electrolytic treatment performance (Motheo and Pinhedo, 2000; Szpyrkowicz et al., 2001; Diniz et al., 2003), emphasizing the importance

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**Table 2** Best results with the electrolytic treatment and aluminium electrodes

<table>
<thead>
<tr>
<th>Assay</th>
<th>Operational conditions pH; flow rate; current density (pH units – l.h⁻¹ – mA.cm⁻²)</th>
<th>COD removal efficiency (%)</th>
<th>Color removal efficiency (%)</th>
<th>Energy consumption (Wh.l⁻¹)</th>
<th>Electrode consumption (mg.l⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.1</td>
<td>8.3 – 1.80 – 76</td>
<td>67</td>
<td>95</td>
<td>17.0</td>
<td>377</td>
</tr>
<tr>
<td>I.2</td>
<td>7.3 – 0.90 – 76</td>
<td>64</td>
<td>95</td>
<td>24.3</td>
<td>372</td>
</tr>
<tr>
<td>I.3</td>
<td>7.3 – 1.80 – 76</td>
<td>62</td>
<td>96</td>
<td>14.2</td>
<td>353</td>
</tr>
<tr>
<td>I.4</td>
<td>8.3 – 1.80 – 38</td>
<td>61</td>
<td>93</td>
<td>7.0</td>
<td>198</td>
</tr>
<tr>
<td>I.5</td>
<td>6.3 – 0.45 – 76</td>
<td>54</td>
<td>98</td>
<td>18.1</td>
<td>406</td>
</tr>
<tr>
<td>I.6</td>
<td>6.3 – 1.80 – 76</td>
<td>54</td>
<td>98</td>
<td>19.6</td>
<td>342</td>
</tr>
<tr>
<td>I.7</td>
<td>6.3 – 0.90 – 76</td>
<td>35</td>
<td>98</td>
<td>20.3</td>
<td>409</td>
</tr>
</tbody>
</table>
of choosing the correct operational conditions for each case. Another point that should be evaluated is the scale factor since hydrodynamic patterns, thus the mixing conditions, may vary considerably when the size of the reactor changes even if its shape is kept the same.

Table 3 presents the best results obtained with the jar-test assays. To facilitate the comparison with the electrolytic treatment the results are for 30 min of sedimentation, which corresponds to a speed of 0.24 cm.min\(^{-2}\). The jar-test experiment indicated that an increase in aluminium sulfate dosage from 350 mg.l\(^{-1}\) to 450 mg.l\(^{-1}\) without the addition of cationic polymer (assays II.1, II.8 and II.15), increases the COD removal efficiency by approximately 14 percentage points, however the increase in color removal is not significant, being only three percentage points.

For 350 mg.l\(^{-1}\) of aluminium sulfate the addition of 1.0 mg.l\(^{-1}\) of polymer increased the COD removal efficiency by 10 percentage points, but again the increase in color removal efficiency was small. The increase in polymer dosage from 1.0 mg.l\(^{-1}\) to 6.0 mg.l\(^{-1}\) did not significantly affect the COD (two percentage points) or the color (three percentage points) removal efficiency. The same behavior was observed for an addition of 400 mg.l\(^{-1}\) of aluminium sulfate.

It should be pointed out that the recommended sedimentation velocity for settler design is 2.5 cm.min\(^{-2}\) however; in these experiments it was necessary to add the cationic polymer to observe some color and COD removal at this velocity. The best results obtained for this velocity with a dosage of 350 mg.l\(^{-1}\) aluminium sulfate and 6.0 mg.l\(^{-1}\) of polymer were 83% COD removal and 96% color removal. When the aluminium sulfate dosage was increased to 400 mg.l\(^{-1}\) the highest COD removal was 87% and color was 97%. These increases are not significant since they are within the experimental error of the measurement methods.

Figure 1 presents color and COD removal efficiencies as a function of the aluminium ion concentration. The graph shows that the addition of 150 mg.l\(^{-1}\) and 200 mg.l\(^{-1}\) aluminium sulfate, which corresponds to 13 mg.l\(^{-1}\) and 17 mg.l\(^{-1}\) in terms of aluminium ions, was not sufficient to provide significant COD removal. However, a small increase in dosage to 250 mg.l\(^{-1}\) of aluminium sulfate, or 21 mg.l\(^{-1}\) in terms of aluminium ions, increases the color removal to 79%. This increase is not reflected in the COD removal that reaches only 12%.

### Table 3: Best results obtained with the jar-test experiment

<table>
<thead>
<tr>
<th>Assay</th>
<th>pH after rapid mixing</th>
<th>Coagulant dosage(^1) (mg.l(^{-1}))</th>
<th>Polymer dosage(^2) (mg.l(^{-1}))</th>
<th>COD removal (%)</th>
<th>Color removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>II.1</td>
<td>6.0</td>
<td>350</td>
<td>–</td>
<td>76</td>
<td>91</td>
</tr>
<tr>
<td>II.2</td>
<td>5.9</td>
<td>350</td>
<td>1.0</td>
<td>86</td>
<td>94</td>
</tr>
<tr>
<td>II.3</td>
<td>6.0</td>
<td>350</td>
<td>2.0</td>
<td>83</td>
<td>96</td>
</tr>
<tr>
<td>II.4</td>
<td>6.0</td>
<td>350</td>
<td>3.0</td>
<td>86</td>
<td>96</td>
</tr>
<tr>
<td>II.5</td>
<td>6.0</td>
<td>350</td>
<td>4.0</td>
<td>84</td>
<td>95</td>
</tr>
<tr>
<td>II.6</td>
<td>6.0</td>
<td>350</td>
<td>5.0</td>
<td>87</td>
<td>97</td>
</tr>
<tr>
<td>II.7</td>
<td>6.1</td>
<td>350</td>
<td>6.0</td>
<td>88</td>
<td>97</td>
</tr>
<tr>
<td>II.8</td>
<td>5.7</td>
<td>400</td>
<td>–</td>
<td>86</td>
<td>93</td>
</tr>
<tr>
<td>II.9</td>
<td>5.5</td>
<td>400</td>
<td>1.0</td>
<td>89</td>
<td>97</td>
</tr>
<tr>
<td>II.10</td>
<td>5.6</td>
<td>400</td>
<td>2.0</td>
<td>89</td>
<td>97</td>
</tr>
<tr>
<td>II.11</td>
<td>5.6</td>
<td>400</td>
<td>3.0</td>
<td>87</td>
<td>98</td>
</tr>
<tr>
<td>II.12</td>
<td>5.6</td>
<td>400</td>
<td>4.0</td>
<td>88</td>
<td>98</td>
</tr>
<tr>
<td>II.13</td>
<td>5.6</td>
<td>400</td>
<td>5.0</td>
<td>89</td>
<td>98</td>
</tr>
<tr>
<td>II.14</td>
<td>5.6</td>
<td>400</td>
<td>6.0</td>
<td>89</td>
<td>97</td>
</tr>
<tr>
<td>II.15</td>
<td>5.2</td>
<td>450</td>
<td>–</td>
<td>90</td>
<td>94</td>
</tr>
</tbody>
</table>

\(^1\) Aluminium sulfate  
\(^2\) Cationic polymer
Table 4 presents a summary of the COD and color removal efficiencies for treatments I and II. These results show that even though the COD removal efficiency at the UASB was high the color removal was not significant. After the electrochemical treatment an additional 67% of the remaining COD was removed, which resulted in an overall removal of 94%. The coagulation followed by flocculation and sedimentation treatment provided 98% of color removal and 89% additional COD removal, with an overall efficiency for COD removal of 98%.

All color removal was achieved in the post-treatment. These results indicate that both electrochemical and coagulation followed by flocculation and separation post-treatment are technically feasible. The biological treatment would remove most of the organic load while the physical-chemical treatment would provide a high degree of polishing. Results from preliminary experiments indicate that the physical-chemical treatments by themselves are sufficient to provide a good degree of treatment; however the cost would be much higher. Electrical energy consumption increased with the increase in current density, which indicates that a non-stoichiometric relation exists between the amount of ions discharged in the wastewater and the treatment efficiency. The energy consumption increase was higher when the current density was doubled from 38 mA.cm$^{-2}$ to 76 mA.cm$^{-2}$ than when the increase was from 19 mA.cm$^{-2}$ to 38 mA.cm$^{-2}$.

It should be observed that a lower pH may provide better results, however the assays in this work were limited to more practical values that would not cause severe corrosion or the need to correct the effluent pH to permitted values for discharge. In the case of the use of the coagulation procedure it would be necessary to assess the combination of aluminium sulfate and polymer costs to choose the best operational conditions.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>COD removal (%)</th>
<th>Color removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UASB</td>
<td>80</td>
<td>not significant</td>
</tr>
<tr>
<td>Electrochemical (I)</td>
<td>67*</td>
<td>98</td>
</tr>
<tr>
<td>Coagulation (II)</td>
<td>89*</td>
<td>98</td>
</tr>
<tr>
<td>UASB + electrochemical</td>
<td>94</td>
<td>98</td>
</tr>
<tr>
<td>UASB + coagulation</td>
<td>98</td>
<td>98</td>
</tr>
</tbody>
</table>

*In terms of the remaining organic load after the biological treatment
Conclusions
The best operational conditions for COD removal with the electrochemical treatment were: pH 8.3; flow rate in the reactor 1.80 l.h$^{-1}$; current density 76 mA.cm$^{-2}$ while for color removal these parameters are pH 6.3; recirculation 0.45 l.h$^{-1}$ and current density 76 mA.cm$^{-2}$. With these conditions the maximum COD and color removal reached 67% and 98% respectively. In this experiment the pH, the recirculation flow rate in the electrochemical cell and the current density had a significant influence on the electrolytic cell performance. To achieve the reported efficiencies the energy consumption ranged from 14 Wh.l$^{-1}$ to 20 Wh.l$^{-1}$. The highest COD and color removal efficiencies for the coagulation-sedimentation process were 89% and 98% respectively, reached for 400 mg.l$^{-1}$ addition of aluminium sulfate and 5.0 mg.l$^{-1}$ cationic polymer.

The color removal efficiency presented similar values for both post-treatment processes while the overall COD removal was four percentage points lower with the electrochemical process. It should be noted that this difference is close to the experimental uncertainty of the COD determination. Thus it is possible to conclude that either the electro-chemical or the coagulation-sedimentation process as post-treatment for UASB effluents from cellulose production are feasible from a technical standpoint.

Acknowledgements
The post-doctoral grant awarded to Dr. Andréa Paula Buzzini (Grant 01/06244-1) and financing of this research (Grant 01/05489-0) by FAPESP (Brazil) is gratefully acknowledged, as is Votorantim Celulose e Papel for supplying the black liquor. Dr. E.C. Pires acknowledges the research incentive grant from CNPq Brazil (Grant 300038/88-7).

References