Influence of physico-chemical treatment on the subsequent biological process treating paper industry wastewater

Mouhamed el khames Saad, Younes Moussaoui, Asma Zaghbani, Imen Mosrati, Elimame Elaloui and Ridha Ben Salem

ABSTRACT

The present paper presents the main results of the biodegradation study of paper industry wastewater through physico-chemical treatment. Indeed, around 60% of chemical oxygen demand (COD) removal can be achieved by electroflocculation treatment. Furthermore, a removal efficiency of the COD of almost 91% has been obtained by biological treatment, with activated amount of sludge for 24 h of culture. Concerning the physico-chemical pre-treatment of the untreated, filtered and electroflocculated rejection effluents, it has been investigated through the degradation curve of COD studies.

Key words | activated sludge treatment, biodegradation, electroflocculation, filtration, pulp and paper mill effluent

INTRODUCTION

The pulp and paper industry has been considered not only as one of the major energy and natural resources for consuming factories, but also as one of the most important producer of pollutants that affect the environment (Rigol et al. 2003; Pokhrel & Viraraghavan 2004; Francis et al. 2006; Malinen et al. 2006; Sarwar Jahan et al. 2007; Wanrosli et al. 2007). As a matter of fact, the pulp and paper mill industry, using the Alfa as a raw material, is a water-consuming industry that generates a large amount of wastewater. This wastewater is produced by the manufacturing process (Kukkonen 1992; Smook 1992; Wrisberg & Van Der Gaag 1992; Sillanpaa 1996; Leiviska et al. 2008). It is the type of wood material and the pulping process technology that determine the nature of the paper industry effluents.

As far as the environment is concerned, the pulp and paper mill wastewater is extremely hazardous. These liquid effluents are among the most serious causes of anthropogenic humic-like materials on water surface. In fact, the manufacturing process (shredding, pulp washing and bleaching, conditioning, etc.) requires the use of different quantities of chemicals to improve certain characteristics of the pulp and paper (Mikesell & Boyd 1986; McKague 1990; Ali & Sreekrishnan 2001; Pokhrel & Viraraghavan 2004). Regardless of the pulping process, various toxic chemicals occur. This includes resin acids, chlorinated phenolic compounds, adsorbable organic halides, unsaturated fatty acids, terpenes, chlorinated resin acids, inorganic dyes (Paasivirta 1980; Kringstad & Lindstrom 1984; Tana 1988; Makris & Banerjee 2002; Lacorte et al. 2005; Rigol et al. 2003; Pokhrel & Viraraghavan 2004; Amat et al. 2005; Catalkaya & Kargi 2007; Bedoui et al. 2009). Although, pulping is the initial stage in the paper manufacturing industry, it is the most important cause of pollution in the whole process of papermaking. A large quantity of wastewater is generated at different stages in this process. These effluents cause considerable damage to the discharged and untreated received water because these effluents have high levels of biological oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (SS) and dye compounds (Ali & Sreekrishnan 2001; Aksu & Gönen 2004).

Nowadays, despite the regulations and the measures adopted to reduce pollution and protect the environment,
the effluent treatment is a real challenge to carry out in paper industry. Therefore, considerable attention has been devoted to studies of paper wastewater. Physico-chemical treatment of wastewater is widely used in pulp and paper industrial effluents. Some treatment methods require pre-treatment and several steps or a combination of both to curb the effluents. Due to the presence of non-biodegradable compounds in paper wastewater, some developed physico-chemical processes have the potential of treating industrial wastewater efficiently. Thus, various internal processes are necessary in order to reduce pollution and facilitate the biological treatment.

The present work aims at balancing the influence of physico-chemical pretreatment with the subsequent biological step when treating pulp and paper industry wastewater. In this study, two physico-chemical pre-treatment processes are conducted: the electrofloculation, the filtration and their combination. Consequently, biological treatment is performed by using activated sludge.

METHODS

The studied sample of wastewater was taken from the pulp and paper industry located in Kasserine (Tunisia). The sample was conserved in amber bottles at 4°C.

Three samples were used in physico-chemical pre-treatment processes. Thus, the results reported are the average of three values found.

Electrofloculation: Experiment was carried out in cell equipped with a two aluminum electrodes (anode and cathode) which were positioned approximately 2 cm apart from each other and were dipped in the effluent. The total effective surface area of electrodes was 12 cm². The current input (1A) was supplied by a potentiostat (electric generator). Each time 250 mL of wastewater was poured into the electrolytic cell for 30 min of continuous flowing. Then, sodium chloride (NaCl) was added to the aqueous solution to promote the generation of Al-sorbent in the cell equipment.

Filtration: Filtration of pulp and paper mill wastewater was carried out by using Whatman filter paper.

Biological treatment: Biological treatment of untreated and pre-treated wastewater (electroflocculated effluents, filtered effluents) was performed by using activated sludge. An activated amount of sludge reactor including a control reactor was operated at room temperature. Aeration and mixing (200 rpm) within the reactor were achieved by filling air through diffusers.

Phenolic compounds of samples are evaluated by measuring the average absorbance at 276 and 390 nm (Ming et al. 2006; Zhang et al. 2009) by using a Beckman Coulter (DU800) UV–Vis.

COD was determined by a colorimetric method using the dichromate reflux according to Standard Methods (APHA 1995).

SS was determined as follows: a volume of 1 L was filtered through combusted, pre-washed and pre-weighed 60 mm diameter glass Whatman fiber filters. The filters were dried at 95°C, re-equilibrated with room temperature and re-weighed. The difference in weights gives the amount of SS.

The pH of the solution was adjusted to the desired value by adding sodium hydroxide or sulfuric acid. The pH was measured with a pH-meter (model pH 510, Cyberscan).

RESULTS AND DISCUSSION

Characterization of the effluent

The nature and the characteristics of the wastewater are related to the type of wood material and the applied process. However, BOD₅, COD, SS, and color were chosen as design parameters to evaluate the biodegradability of toxic matter. The general characteristics of wastewater generated by various processes of pulp and paper industry are summarized in Table 1.

The BOD₅/COD ratio is 0.3, indicating that this wastewater is poorly biodegradable. Besides, this effluent has a high pH (10.9) and high levels of SS. Therefore, this effluent needs a pre-treatment to be ready for a biological treatment.

Physico-chemical pre-treatment

Electrofloculation

Electrofloculation is a complex process occurring via electrolytic reactions at electrodes surfaces. Compared with traditional flocculation and coagulation, electrofloculation has, in theory, the advantage of removing the smallest colloidal particle formation of coagulants and adsorption of pollutants on coagulants (Pouet & Grasmick 1995; Gurses et al. 2002).
At the aluminum electrodes, the main reactions are:

Anode: \( \text{Al}(s) \rightarrow \text{Al}^{3+} \text{(aq)} + 3e^- \)

Cathode: \( 3\text{H}_2\text{O} + 3e^- \rightarrow (3/2)\text{H}_2(\text{g}) + 3\text{OH}^- \text{(aq)} \)

\( \text{Al}^{3+} \) and \( \text{OH}^- \) ions generated by the electrodes react to form various monomeric species such as \( \text{Al(OH)}^{2+} \), \( \text{Al(OH)}_2^{2+} \) etc. Nevertheless, when pH is higher than 10, these monomeric anions finally transform into \( \text{Al(OH)}_3(\text{s}) \) (Gurses et al. 2013). The latter formed precipitate has a relatively large surface area, which is available for rapid and efficient absorption of many soluble organic compounds. This formed gelatinous suspension \( \text{Al(OH)}_3(\text{s}) \) in the aqueous stream, can remove pollutants from wastewater either by complexation or by electrostatic attraction, followed by coagulation. The obtained agglomeration of particles suspended in water into larger particles (flocs) that can be removed from aqueous medium on sedimentation or flotation (Yilmaz et al. 2005). On the other hand, aluminum sorbent (Al-sorbent) was produced in a parallel-plate electrochemical reactor by anodic dissolution of aluminum electrodes in a dilute sodium chloride (NaCl) aqueous solution. The NaCl in the solution effectively reduced the power of consumption and promoted the sorbent generation. This was obtained by depassivating the aluminum–water electrochemical system (Yang & McGarrahan 2005). At very high pH values, however, almost all the free chloride ions, present in the medium, exist as hypochlorite ion (\( \text{ClO}^- \)). This is known as a powerful disinfectant of water which can contribute to the degradation of organic matter (Yang & McGarrahan 2005).

The removal efficiency of the COD and the absorbance at 276 nm (Abs 276 nm) evolutions were quantified along the treatment time (Figures 1 and 2).

**Table 1 | Characteristics of wastewater samples**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Untreated effluent (a)</th>
<th>Electrofloculated effluent (b)</th>
<th>Filtered effluent (c)</th>
<th>Filtered-electrofloculated effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>10.9</td>
<td>9.14</td>
<td>10.9</td>
<td>9</td>
</tr>
<tr>
<td>SS (mg/L)</td>
<td>1,250</td>
<td>400</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>680</td>
<td>275</td>
<td>620</td>
<td>260</td>
</tr>
<tr>
<td>Abs 276 nm</td>
<td>2.048</td>
<td>0.832</td>
<td>1.218</td>
<td>0.389</td>
</tr>
<tr>
<td>Abs 390 nm</td>
<td>0.375</td>
<td>0.150</td>
<td>0.242</td>
<td>0.075</td>
</tr>
<tr>
<td>Color</td>
<td>Brownish</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>BOD₅</td>
<td>210</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

**Figure 1 | Removal efficiency of the COD versus time of the electroflocculated sample.**

**Figure 2 | Variation of the absorbance at 276 nm versus time of the electroflocculated sample.**

Figure 1 shows that the output of removal efficiency of the COD is about 60%. In the same way, Figure 2 shows that the absorbance at 276 nm decreased by half in 30 min, which indicates a decrease in phenolic compounds present in the effluent (Pouet & Grasmick 1995; Shen et al. 2003; Yilmaz et al. 2005).

The picture of the wastewater before and after electrocoagulation (Figure 3) shows that the electrofloculation allows a significant color removal, which can be explained...
by the oxidation of the lignin and its derivates that are responsible for brown coloration (Figures 2 and 3).

Table 1 presents the obtained results of pulp and paper wastewater characterization of untreated and electrofloculated effluent. It can be observed, at the end of treatment, that the pH increased despite the adjustment of pH to 7.5 at the beginning of the electrofloculation treatment. This behavior can be explained by the production of hydroxyl ions (OH⁻) which are generated by water reduction according to the reaction (Yang & McGarrahan 2005):

\[ 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \]

In addition, 68% of the SS was removed from the wastewater by electrofloculation after scraping the formed flocs. In fact, the production of H₂ and O₂ facilitates the flotation of the organic matter flocs (Yilmaz et al. 2005). The study of the evolution of the removal efficiency of the COD, as function of the electric charge, shows that the effectiveness of treatment is proportional to the value of electric charge (Acher & Dunkelblum 1979) (Figure 4).

### Filtration

The filtration has a decrease in COD (Table 1) and a decrease in color (Figure 3) and a noticeable efficiency to remove total SS (Nazar & Rapson 1980; Mehna et al. 1995; Diez et al. 1999; Hamoda et al. 2004). Color in paper industry wastewater is largely due to lignin derivated and polymerized tannins (Sundman et al. 1981; Crooks & Sikes 1993; Reeve 1991).

### Association of filtration and electrofloculation

The filtered effluent undergoes an electrofloculation treatment has given results mentioned in Table 1. The combination of two treatments leads to an improvement in the removal efficiency of some parameters as SS and the color of the effluent due to the decrease of absorbance at 390 nm.

### Biological treatment

A biological treatment has been carried out to evaluate the pre-treatment effect in the biodegradability of pulp and paper mill wastewater, the filtered and the electrofloculated effluents.

This biological treatment was performed by using activated sludge. The activated sludge characteristics are given in Table 2.

Figure 5 presents the removal efficiency of the COD of biodegraded untreated, filtered and electrofloculated effluents. As clearly shown, the maximum of removal efficiency of the COD was reached after approximately 48 h of continuous flowing treatment. However, the removal rates of pollution decreased when the COD loading rate increased. Slightly after 48 h, more than 95, 95 and 96 % of the removal efficiency of the COD was obtained respectively for untreated, filtered and electrofloculated effluent by the activated sludge. During the first 4 h, the removal efficiency is very weak allowing the phase of adaptation of the bacteria to the rejection. The accentuated bacterial growth caused.

### Table 2 | Activated sludge characteristics

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mohlman index (mL/g)</td>
<td>94.60</td>
</tr>
<tr>
<td>VSS (mg/L)</td>
<td>1,750</td>
</tr>
<tr>
<td>SS (mg/L)</td>
<td>2,000</td>
</tr>
<tr>
<td>UFC/mL</td>
<td>$3.49 \times 10^4$</td>
</tr>
</tbody>
</table>
the accentuation of the substrate degradation. This phase reached its maximum after 48 h, and then declined.

The variation of COD of various biodegraded effluents: untreated, filtered and electroflocculated effluents, was presented in Figure 6. As it can be seen, there is a rapid decrease in COD after less than 8 h. After that, insignificant changes can be observed throughout the experimental time. This can possibly be explained by the biodegradability of organic substances in the soluble organic matter.

The differences in evolution of the COD between the three categories of effluent: untreated, filtered and electroflocculated (Figure 6) is explained by the fact that the removal efficiency of the COD depends on the microorganisms/initial COD ratio. The increase in microorganisms/initial COD ratio increases the removal efficiency of the COD. Similarly, COD removal depends on the amount of nitrogen added. The rate of COD removal is higher at low amount of nitrogen (Kargi & Ozmihçi 2004). In the same context, Bedoui et al. (2009) used the UV/H₂O₂ system to treat the pulp and paper mill wastewater. They showed that UV/H₂O₂ treatment cannot sufficiently mineralize the organic matter contained in these effluents.

The time course of the SS variation is studied (Figure 7). The figure presents the growth of the biomass and the substrate degradation. During the first 4 h, the SS variation remains nearly still and the bacteria adapt to the rejection. Subsequently, there is an exponential bacterial growth; however, the substrate is in excess. After 30 h, the bacterial load applied decreases and the substrate starts to be limiting. After 48 h, there is a decline because of the autolysis and mortality of the applied bacterial load.

The presented data can demonstrate that the electrofloculation of wastewater improves biological treatment.

**CONCLUSIONS**

The results of this study show that the physico-chemical treatment has an important role in the removal of the pollution load from the wastewater of the pulp and paper mill. It has been observed that about 60% of removal efficiency of the COD has been reached by electrofloculation. Consequently, the removal efficiency of the COD in electrofloculation process can be considered to be dependent on the current intensity. An almost complete removal efficiency of the COD (91%) can be achieved by biological treatment by activated amount of sludge in batch for 24 h. Studies of the biological degradation of the untreated, filtered and electroflocculated effluent, show that the physico-chemical pre-treatment allows a reduction in the pollution load and facilitates the biological treatment. As
the electrofloculation process has proved to have a noticeable effect on paper wastewater treatment, the present study permits us to predict a possible industrial application of the described system.

ACKNOWLEDGEMENT

We greatly acknowledge financial support of the Ministry of Higher Education and Scientific Research of Tunisia (Ministère de l’Enseignement Supérieur et de la Recherche Scientifique de Tunisie).

REFERENCES


First received 28 September 2011; accepted in revised form 14 February 2012