TOOLS FOR ENVIRONMENTAL CONTROL USED BY PAPER AND PULP MILLS

Ana Luiza Fávaro Piedade e Tatiana Heid Furley

APLYSIA Environmental Research., Vitória - Brazil

ABSTRACT

It is known that, in the cellulose production, there is the formation of a great variety of compounds which can cause adverse effects to the organisms. For instance, the natural constituents of wood (phenolics, greasy and resinic acids), especially the ones present in the liquor, can be the responsible agents of toxicity. The dioxins and organochlorinated found in the chlorine-based bleaching effluents are potential inductors of the EROD activity. This way, the treatment of these effluents becomes very important. Paper and pulp mills usually have a biological treatment for their effluents. However, there is a great difficulty in obtaining and/or maintaining the highly effective treatment. In order for the final effluent to be properly launched in the receiving body with the adequate treatment, it is necessary to take some treatment control tools on consideration. The present essay presents some of the tools being used worldwide by paper and pulp mills, such as:

1. Balance of the sectorial effluents toxicity- with this tool it is possible to identify which effluent(s) contribute(s) with greatest toxicity for the microorganisms of the wastewater;
2. TIE (Toxicity Identification Evaluation) – this technique allows the identification of the compound or compound group inside the effluent, which could be responsible for the effluent toxicity and, then, with the data, it is possible to take more directed measures.
3. Monitoring the microorganisms of the wastewater - the secondary effluent treatment is a biological process in which, mainly bacteria and protozoan oxidate the organic substance in an aeration basing where the effluent is launched. The treatment effectiveness depends directly on these organisms, but their richness and density vary, depending on the environment where they are being developed, i.e., the physical and chemical parameters. The nature of the present micro fauna is characteristic of the temperature, the mean cell residence time, the saprobicity, the water quality level, the quantity of organic biodegradable substance, the effluent toxicity etc (CETESB, 1992; Jenkins *et al.*, 1993; Furley *et al*., 2001). This way, the microscopical analysis of the flocs, the protozoan and the filamentous organisms which are present in the effluent have been used as a helping tool in the control and operation of wastewater in many countries, such as The USA, Italy, Denmark, Australia, Germany and Brazil;
4. TIE of the treated effluent - tool used to identify the secondary treatment effectiveness and the quality of the effluent to be launched in the recipient body;
5. Receiving body monitoring studies:
   5.1 – Benthic biodiversity of the receiving body;
   5.2 – Mussel bioaccumulation studies – by the use of bivalve marine and fresh water mussels, it was possible to monitor the environmental quality of the sectorial effluents and recipient bodies about the presence of organochlorinated contaminants, heavy metals, pesticides, fecal coliforms, among others. The bivalve mussels are excellent bioindicators, because they can bioaccumulate the contaminant in concentrations of 1,000 to 10,000 times superior to the water, providing as a result the average of the last days, not only an up-to-date data.
   5.3 – Toxicity tests of the sediment that is adjacent to the launch site of the effluent in the receiving body.

KEY WORDS: toxicity, wastewater, monitoring.

1 INTRODUCTION

It is known that, in the cellulose pulp production, there is the formation of hundreds of different compounds which may cause adverse effects to the aquatic organisms and many of them are unknown (Pacheco e Santos, 2002 e Pellinen *et al*., 1993). One research made by Gaete *et al*. (2000) has shown that pulp mills cause effects in aquatic organisms of different trophic levels, and numerous publications around the world have indicated that paper and pulp mill effluents can affect various aspects of fish reproduction and also the breaking of biochemical and phisiological systems, morphological abnormalities and dislocation in the structure of fish population and benthic invertebrates (Martel, Kovacs e Voss, 2003). That is why, according to Sibley *et al.* (1997) the paper and pulp mills has been increasing its actions concerning environmental protection practices and focusing mainly the aquatic ambience.
According to Gaete *et al*. (2000), the quality control of the ecotoxicology of industrial effluents based in the individual chemical compounds does not guarantee suitable protection to aquatic life. Gallardo *et al*. (1996) claims that the presence of the own chemical compound is not effective to predict its biological effects concerning additive or synergetic interactions that occur among the mix components, when the toxic components are not known and the chemical characterization has not been made, what makes it necessary to make a more accurate analysis.
Toxicity tests consist of the direct exposition of the organisms to the effluents and the observation, or non observation, of chronic effects over these organisms. This way, the use of bioessays allows the analysis of potential effects over the environment (Gallardo *et al*., 1996).
Thus, it is extremely important to consider the ecotoxicological evaluation in the effluent quality analysis of pulp mill.

2 METHODOLOGY

Concerning about the improvement or maintenance of the treated effluent and the receiving body quality, some tools of effluent and/or receiving body control have been widely used by pulp mill worldwide, as they follow:

2.1 Balance of the toxicity of sectorial effluents

According to Scroggins (1986), there are two basic approaches used in the toxicity reduction in paper and pulp mills: internal or external control of the plant. The internal control usually involves loss prevention in the source and/ or reducing the overflows, drainages or closing water circuit. The external control, as primary and secondary treatments, treats the effluent from the moment it left the plant. According to this same author, internal controls are usually preferred over the external one, because the first one brings some feedback to the investment, such as fiber, chemicals and energy regain. Besides that, in many cases, when there is no effluent internal control as, for instance, a drainage, these effluents may arrive at the wastewater with a large toxic level and cause impact to the microorganisms which are responsible for the organic substance remotion, and that brings the treatment effectiveness reduction as a consequence (Furley *et al*., 2002). At the work made by Furley *et al*. (2003), who submitted the several sectorial effluents of the cellulose industry Aracruz Celulose in Brazil, to toxicity tests with MICROTOX, with the alga *Skeletonema costatum* and the urchin *Echinometra lucunter*, it was possible to identify the sectorial effluents that contributed with major toxicity to the microorganisms of the wastewater of the factory in test. Using this, it was possible to take more directed measures to improve this wastewater performance.

2.2 TIE (Toxicity Identification Evaluation)

O TIE is a procedure developed by the EPA in 1980, to characterize and identify toxins in environmental samples (Boucher e Watzin, 1999; Burgess *et al*., 2000 e 2003). According to Cook *et al*. (1998), the EPA has procedures to manage chronic or acute TIEs in non treated effluents that have been the basis for most investigations of TIE for non treated effluent data. EPA guide describes three parts of the TIE that have been used. Phase I comprehends the characterization of the group or groups of contaminants that contribute to toxicity. In Phase II, specific toxins that may be responsible for toxicity are identified. Finally, in Phase III, various tests are used to confirm that the toxicity observed in Phase II is the cause of toxicity in Phase I. According to King *et al*. (2000) e Baummer *et al*. (2000) the TIE has been proven valuable for characterizing and identifying toxicity in effluents and waters of recipient body.

Pedroso and Rachid (2003) showed that the identification of the compound or individual classes responsible for the toxicity of a sample represents a great advance for the environmental control area, because it makes the choice for one or more technologies for the effluent treatment to be base don information about the main compounds responsible for the toxicity, not only for those ones that presented biggest concentrations.

Traditionally, the choice for a certain type of effluent treatment is made due to its physical and chemical characteristics, concerning its being suitable to the current legislation. However, many effluents, after being submitted to ordinary treatment, still show remaining toxicity. In these cases, it is recommended studying toxicity reduction, in which the identification study is one of the main components to investigate the cause of toxicity and to make it possible to adopt measures that may improve the quality of the final effluent (Pedroso e Rachid, 2003). These measures may comprehend, since the replacement of the products used during the production process, to changes in the implanted treatment system (Cook *et al*., 2003).

According to Araki *et al*. (1997), the TIE study was also developed in Japanese paper and pulp mills. In Japan, due to the raise of population's ecological consciousness and awareness, it is believed that soon toxicity tests will be used by the government as a restriction item. Several paper and pulp mills around the world have already made TIE tests to fulfill the demands of environmental facilities or simply to foresee future tendencies. Furley *et al* (2004) developed the TIE in the sectorial effluents of the pulp mill Cenibra S/A in Brazil, and identified the group of compounds that most contribute to the general effluent toxicity of the factory. It was possible to provide more accurate measures to reduce toxicity in ETE, based on the found results.

2.3 Wastewater Microorganism Monitoring

Effluent secondary treatment system is a biological process in which specially bacteria and protozoan oxidate the organic substance in an aeration basing where the effluent is launched. The treatment effectiveness is directly dependent on these organisms. However, their richness and density vary due to the environment they are developing, i.e., the physical and chemical parameters. The nature of the present micro fauna is characteristic of the temperature, the mean cell residence time, the saprobicity, the water quality level, the quantity of organic biodegradable substance, the effluent toxicity etc (CETESB, 1992; Jenkins *et al.*, 1993; Furley *et al.*, 2001). According to Schade and Lemmer (1994), the density of protozoan and bacteria that belong to each different group is important to understand the activated sludge performance and its activity. Furley *et al.* (2001) summons that the toxic compounds can lead to meaningful reductions in the number of one specific population of bacteria from the secondary treatment, having as a result the altering of the biodegradation of substances and the final quality of the treated effluent. Other compounds, for example the easily biodegradable or the sulphur-based ones, can promote filamentous organisms overwhelming, causing Bulking, also leading to problems in the sedimentation of biological sludge, resides generating a final effluent with high turbidity and solid concentration (Jenkins *et al.*, 1993). In order to ensure and improve the stability and effectiveness of the biological processes in the wastewater, it is necessary to have better knowledge of the physical, chemical and biological conditions of the secondary treatment process, as well as identifying the main causes of the unbalance (Furley *et al.*, 2001). In the work made by Furley *et al.* (2001) in a pulp mill in Brazil, the microbiological analysis, which is usually disregarded in the wastewater's, was useful as an important tool for the identification of the sources of toxic contaminants to the organisms, as well as for the effects that they may cause indirectly to the effluent quality, when the factory is in general stop period or when it gets boil-out or sporadic drainages. By weekly monitoring the microorganisms from the effluent in the pulp mill Lwarcel S/A in Brazil, made by Piedade *et al* (2004), it could help increasing the effectiveness and improve the factory wastewater performance, also by identifying the filamentary bacteria species that had been causing Bulking and leading to sludge loss in the secondary dry sump in this wastewater. Piedade and Furley *et al* (2003), obtained a R$140,000 saving a year by weekly microbiological monitoring of the effluent from the pulp mill Cenibra S/A, reducing polymeric use as the monitoring made it possible to improve the quality and sedimentability of the biological flocs. This way, the microscopical monitoring of the biological flocs, protozoan and filamentous organisms, present in the effluent has been used as a help tool for control and operation of activated sludge in many countries, such as The U.S.A., Italy, Denmark, Germany and Brazil, what contributes for operation cost reduction involving actions like polymeric and nutrient addition, aeration, sludge discharge, among others.

2.4 Toxicity Tests at the Treated Effluent

According to Gallardo *et al* (1996), the simple analysis of each substance concentration present in an effluent does not allow the evaluation of synergistic, additive or antagonistic effects occasioned by the existing substance combination. According to the same author, the use of bioessays allows the analysis of potential effects of effluents over the environment. They consist of the direct exposition of the organisms to the effluents and the observation or non observation of the chronic effects over the organisms. Although they do not represent an exact repetition of the natural situation, theses tests provide information about the relative toxicity of an effluent and organs which are struck by its effects. Chronic tests or toxicity tests from a complete cycle of life are projected to expose all stages of the test organism's cycle of life (gametes, eggs, embryonary stages, larva and adults) to a concentration level that includes the sublethal effect edge.
It is known that, in the cellulose pulp production, there is the formation of a great variety of compounds which may cause adverse effects to the organisms. According to Athiainen *et al.* (1996) and Brumley *et al* (1997), the natural constituents of wood (phenolics and resinic and greasy acids) present specially in the liquor, may be responsible for the toxicity. Hewitt *et al.* (1996) summons that the dioxins and organochlorinated found in the chlorine-based or chlorine dioxide-based bleaching effluents are potential inductors of the EROD activity. On the other hand, Kinae *et al.* (1981) believes that either the natural wood extractives or the organochlorinated are the villains of the toxicity in the general effluent in a pulp mill.
Sibley *et al.* (1997) summoned that, in Canada, effluent toxicity test represents an integral component of the program directed to monitor changes in the characteristics of the effluent concerning the implementation of new technologies in the process. Besides this, toxicity test in the effluent is used to evaluate the pulp mill conformity about the existing legislation.
Kovacs *et al.* (2003) comments that some factories in Canada have been regulated by the effluent toxicity since 1972, but, since January 1996, amendments made the regulatory limit to be more strict and applicable to all the factories. Toxicity is determined using trout test (*Oncorhynchus mykiss*) and *Daphnia magna.* The tests are made once a month with trout and once a week with *D. magna*.
According to Furley *et al.* (2001), the toxic compounds may result into meaningful reductions in the number of a particular bacteria population from the secondary treatment, having the substance biodegradation effectiveness altered, as well as the final quality of the treated effluent as a consequence. This way, toxicity tests are biological tools to evaluate the quality of effluents in Kraft pulp mill, as well as changes in the quality of this effluent due to changes in the process (Dube & MacLatchy, 2000).

2.5 Receiving Body Monitoring Studies

2.5.1 Benthic Biodiversity of the Receiving Body

Benthic macroinvertebrates are the organisms that live in the bottom and that usually inhabit substrates during part of their cycle of life. In this habitat, these organisms colonize different places, such as plants, rocks, sandy and muddy sediments. According to Landim (2003), the evaluation of the organisms or the community constitutes an important tool to characterize the quality of water. One advantage in the use of these organisms is that they reflect all environmental impact, which may result into a modification in the community structure. This tool has been widely used for evaluating environmental effects and causes, such as natural factors or the ones with anthropogenic origin.
Among the several biological studies, the benthic one works as an excellent indicator, because these organisms have direct contact with the sediment which, in general, is the silting up site of most contaminants (Sundelin and Eriksson, 1996).
Parker and Smit (1997) claimed that the most common effect at pulp mills is a diminution in the number of species and an increase in the number of organisms of the receiving body of the effluent. Prilha and Lanti (2000) indicated that this happens first due to the eutrophication caused by the excess of nutrients in the pulp mill effluent.

Since 1978 in Brazil, the cellulose industry Aracruz Celulose S/A makes several studies in the area of influence of the effluent launching as, for example, the studies of biological monitoring in marine environment (either in seabord or in water mass). The purpose of this study is to verify occasional environmental changes that may be caused by the effluent. This essay makes a qualitative and a quantitative sampling of the benthos, calculating diversity, richness and relative abundance of these organisms every year in the winter and in the summer. As a result for this work, the industry verified that, in the rocky coast, the benthic community of the entretide zone, did not show directly attributive effects launched in the submarine outfall from Aracruz Celulose (Furley *et al*, 1996).

Thus, by monitoring benthic organisms, the factory can visualize the negative and/or positive impact of possible changes in the industrial process or even the enlargement of production under the environment.

2.5.2 – Mussel Bioaccumulation Studies

Among the various contaminants that can be launched in an effluent, the POPs (heavy metals, organochlorinated, PCBs etc) must be carefully observed. They are not biodegradable, they persist in nature for long time, they are toxic to living organisms in certain concentrations (Mhatre, 1991) and they may be incorporated in the trophic chain (Baby and Menon, 1987).

Philips (1980) observed three basic methods to quantify these contaminants:1. level studies in water; 2. in sediment; 3. in biota members. The pollutant analysis in water is expensive and demanding, besides, there is an extreme weather variation in the concentration levels due to streams, tides and rain. Another problem concerns the estimative of the bioavailable part of these contaminants present in the water (Philips, 1980). As for the sediment analysis, neither it can allow the knowledge of the bioavailable fraction. Due to these disadvantages in water and sediment analysis, the bioindicator organisms have been widely studied and used (Philips, 1980). The biggest advantage of the bioindicator use is to be able to measure the bioavailable pollutants directly, without needing to make studies about all the chemical species present in the environment. The collections can be made from time to time conveniently and they give an indication of the quantity of pollutants in an integrated way, even if the launchings are intermittent (Watling & Watling, 1979) and, finally, some organisms are able to accumulate pollutants at rates of ten to ten thousand times the concentration found in water, and this provides the average of the last days and not a punctual response only (Salazar & Salazar, 1998). The bivalve mussels are the most used organisms in the compound studies. By using marine bivalve and freshwater mussels as an environmental quality tool, it is possible to monitor the environmental quality of the receiving body over the presence of organochlorinated contaminants, heavy metals, pesticides, fecal coliforms among others (Kirnaghan et al, 2003).

Furley *et al.,* (2003), summons that between the years of 1996 and 1997, an “in situ” experiment of bioaccumulation using mussels was led in the effluent launching site at a pulp mill in Brazil. The experiment showed that there was a little accumulation of organochlorinated in the place, but this contamination slightly increased with the STD production implementation and significantly in the general stops for maintenance, situation in which occurs the drainage of the residual contained in the tanks and lines (Furley and Carvalho, 2000). As a result for this work, the factory set a program for industrial effluent drainage during the maintenance period, and this highly contributed to the improvement of the effluent quality during this time.

2.5.3 – Toxicity tests of the adjacent sediment to the launching point of the receiving body effluent.

It is known that, once in the environment, the compounds which are present in the effluent may complex to the material in suspension in the water and, then, lay and accumulate in the sediment. Kukkonen (1992) observed that the organic lipophiliac pollutants of pulp mills can link to the organic material dissolved in the water and/or to molecules of chlorolignin (biggest byproduct of the chlorine-bleached pulp, higher molecular weight than 1,000). According to Chapman (1990), Sundelin and Eriksson (1996 and 1998) and Hämäläinen (2000), various contaminants have the characteristic of adsorbing or linking chemically to non consolidated sediments for long periods of time. This way, turning sediments into very enriched deposits when compared to the water, and may cause chronic effects either for the benthic or for the epibenthic organisms, as well as to organisms that live on them indirectly.

Alves and Oliveira (1994) still quoted that, although surveys on the pollutant concentration in the aquatic environment, obtained by chemical analysis are very important, they do not provide information about the availability of these substances or about their potential effect for the aquatic biota by themselves. Today it is known that many metals often link to the sediment or particular material. Then, a non available way to exercise toxic effect over aquatic organisms is found. This way, toxicity tests in the sediment of the effluent receiving body is an important tool to evaluate the real impact of the effluent to aquatic life.

3 CONCLUSION

It is now to be concluded that all the tools for evaluating the quality of the effluent and the recipient commented above, have been very effective, because they use the effluent entry evaluation, the treated effluent, the sediment and the receiving body organisms that receive the effluent discharge influence.

Using the tools, toxicity surveys of the sectorial effluents, TIE and wastewater microbiological monitoring, the factory is able to evaluate the technological changes or improvements in the production process, as well as enlargements. These tools allow formulating prognostics in environmental impact studies in the production elevation situations. Besides, the factory is able to take more accurate measures concerning problems in the wastewater performance, avoiding change attempts in the industrial process unsuccessfully and, consequently, reducing cost. Another advantage is to maintain the effluent quality according to the internationally accepted patterns.

Making the treated effluent toxicity test periodically and monitoring studies in the recipient body, the factory contributes to the maintenance of aquatic life and shows some ecovision of the company, which helps to environmental quality certification and still prepares industry for future community questionings.

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