10th International IFAC Symposium on
Computer Applications in Biotechnology
Preprints Vol.1, June 4-6, 2007, Cancún, Mexico

PAPERMILL WASTEWATER TREATMENT: MODEL DESIGN AND VALIDATION ON PILOT PLANT

Catherine Cadet[1], Jean-François Béteau[1], Agnès Guillet[2], Marc Aurousseau[2], Cindy Bassompierre[1,2]

[1] LAG – INPG, BP46-38402 St-Martin d'Hères Cedex, France,
e-mail: Jean-Francois.Beteau.@lag.ensieg.inpg.fr, Catherine.Cadet@lag.ensieg.inpg.fr

[2] LGP2 – EFPG, 461 Rue de la papeterie, BP 65, 38402 Saint Martin d'Hères, France,
e-mail : Agnes.Guillet@efpg.inpg.fr and Marc.Aurousseau@efpg.inpg.fr

Abstract: Pulp and paper industry discharges a very important amount of effluent, which includes a major part of carbonaceous pollution. This wastewater is usually treated by biological treatment. This paper deals with the design of a model dedicated to paper mill wastewater treatment. Validation is carried out on a real industrial effluent thanks to a semi-industrial pilot plant.

Keywords: Modeling, Wastewater Treatment, Process Model, Paper Industry, Validation

1. INTRODUCTION

Pulp and paper mill industry is a very important industry in the world, and production increases to meet human requirements. The wood pulping and the paper products manufacturing generate a so considerable amount of pollutants that it is considered as the third largest polluter in the United States (Pokhrel and Viraraghavan, 2004) and is estimated to be responsible of about 50% of all wastes dumped into France's waters.

Pulp and paper discharges varieties of pollutant, which depends for example upon the type of the process, type of the wood materials, applied process technology. Even if an internal process change is a reliable solution to reduce the pollution at the source, the treatment of the wastewater by various external processes is essential. In the secondary treatment processes, activated sludge is the most commonly used process, and literature (Pokhrel and Viraraghavan, 2004), has shown that such a process can remove all the pollutants types relevant to the pulp and paper industry.

Even if for urban effluent treatment many sensors have been developed, they cannot be used in industrial context (specificity of industrial effluents, aggressive environment …). Moreover, efficient on-line sensors are expensive to use and many developing countries cannot buy and maintain them. For all these reasons, the modeling approach is interesting to gather the most of phenomenological knowledge on such processes. Such a model is the basis to be included in a monitoring tool, which achievement will be directly linked with the model pertinence.

This paper deals with the design and the validation of a model of paper mill wastewater treatment with an activated sludge process. The model has to include as much as phenomena as possible but has also to be sufficiently simple to be used in a monitoring tool. The approach is based on the reduction of the Activated Sludge Model (ASM) n°1 developed by the task group of the International Association on Water Quality (IAWQ) (Henze, *et al.,* 1986). This model can be considered as the reference model, since this model triggered the general acceptance of the WWTP modeling first in research community (Gernaey *et al.*, 2004).

In a previous work, (Cadet, *et al.*, 2003), the reduced model proposed by (Jeppsson, 1996), for urban application, has been tested on a real paper mill wastewater treatment plant, and has shown that a specific model has to be designed. This paper proposes a simple model to fit to industrial

requirements of low cost and reliability in use. The hypotheses have been verified by experimentations each time it has been possible.

A semi-industrial pilot plant has been carried out to obtain a tool which is independent from industrial constraints, although reproducing real operating conditions. Paper mill effluent has a very high pollution load to be treated, and paper production changes or machine washes lead to very roughly load and effluent flow changes. Consequently, the pilot plant has been dimensioned to fit to a large range of operating conditions.

In the following part, experimental setup (pilot plant and paper mill effluent) is described. Then the model design is proposed in part 3. Finally model validation on experimental data is presented.

2. EXPERIMENTAL SETUP

2.1 Pilot plant

To have as generic results as possible, a semi-industrial pilot plant has been carried out. Indeed, a laboratory-scale pilot prevents from direct scaling up of the results, by ignoring hydrodynamics influence on the process behavior. Consequently, a medium pilot scale is suitable. The semi-industrial pilot plant is displayed in figure 1.

Fig. 1. The activated sludge pilot plant

The pilot configuration has been designed to be adjustable so as to reproduce most of full-scale encountered configurations and to treat all types of effluents (industrial and urban). It may be used for a wide range of experiments as for example: toxicity tests, fungi treatment tests instead of bacteria use, hydrodynamics influence studies, biological modeling and control strategies validations, which may be long-term essential for biological treatment process optimization.

The table 1 represents the operating parameters range linked with the equipment limitations. The dissolved oxygen concentration has been measured on the reactor, and the maximum value corresponds to the saturation of oxygen concentration.

Table 1. Pilot plant operating parameters range

Operating parameter	Min.	Max.
Reactor volume (L)	100	300
Input flow ($m^3.d^{-1}$)	0.25	1.5
Recirculation flow to input flow ratio	1	3
Residence time (h)	0.8	15
Dissolved oxygen concentration ($mg.L^{-1}$)	anoxic	8.9

The pilot plant (Fig. 2) represents the entire secondary biological treatment, using real effluent taken from the primary settler. It includes a modular biological reactor which allows adapting process configuration (Potier, *et al.*, 2005), a settler, a sludge recycling system and additional equipments (an industrial supervisor, a synoptic screen display, on-line industrial sensors, flow meters, a cooled storage tank for an effluent supply, a buffer tank for pH and nutrient adjustments, an independent electrical safety device). For more details see (Guillet, *et al.*, 2006).

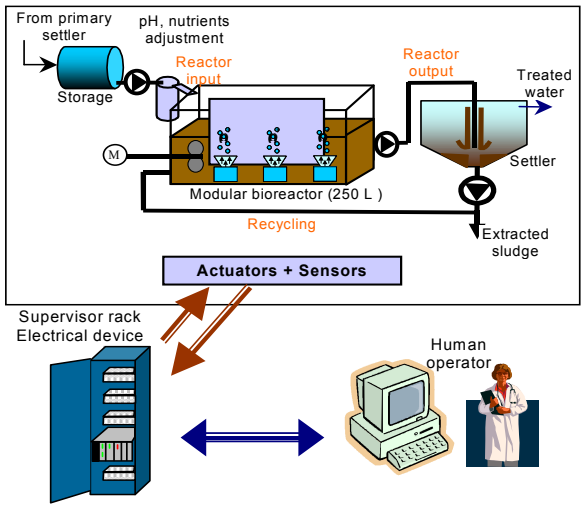

Fig. 2. Activated sludge pilot plant scheme

2.2 Paper mill effluent

A real industrial paper-mill effluent has been used for the experiments. The paper plant produces coated paper with a mixture of mechanical pulp (produced *in situ*) and bought Kraft chemical pulp.

Standard measurements used to characterize the wastewater in industrial plants are:

- The chemical organic demand (COD): measurement of the oxygen quantity needed to oxidize all oxidable compounds (organic and inorganic matters).
- The biochemical organic demand: measurement of the dissolved oxygen consumed by a biomass to oxidize biodegradable organic matter in 5 days (BOD_5) or 21 days (BOD_{21}).
- The volatile suspended solids (VSS) and total suspended solids (TSS).

We characterize the real effluent according to these parameters with the average value and the standard deviation σ:

- Chemical Oxygen Demand: 1100 $mg.L^{-1}$ (σ = 170 $mg.L^{-1}$)
- Biological Oxygen Demand (on 5 days): 560 $mg.L^{-1}$ (σ = 150 $mg.L^{-1}$)
- Total Suspended Solids: 150 $mg.L^{-1}$ (σ = 100 $mg.L^{-1}$)

Some analyses have shown that this paper mill effluent does not contain nitrates, nitrites or phosphate compounds. Consequently, ammonia nitrogen and phosphorus are added as nutrients in accordance with the industrial ratio BOD/N/P of 100/5/1.

2.3 Experimentations

The experimentations were conducted in nominal conditions, with the pilot fed with the paper mill effluent previously described. The nominal parameter values are then:

- Input flow rate $Q_{in} = 0.28\ m^3.d^{-1}$
- Recirculation flow rate $Qr = 2.35\ Q_{in}$
- Reactor volume $V = 250\ L$

Consequently, the nominal volumic load was:

$$C_V = \frac{Q_{in} \cdot [BOD_5]}{V} = 0.62 \text{ kg } BOD_5.m^{-3}.d^{-1}. \quad (1)$$

which corresponds to a medium volumic load. During our experiments, the input flow rate was doubled, increasing the volumic load to 1.34 kg $BOD_5.m^{-3}.d^{-1}$ (which was still in the medium volumic load range).

It may be noticed that the volumic load range of the pilot for such an effluent goes from Cv_{min}=0.56 kg $BOD_5.m^{-3}.d^{-1}$ up to Cv_{max}=3.36 kg $BOD_5.m^{-3}.d^{-1}$, which enlightens the interest of creating an adjustable pilot.

3. MODEL DESIGN

3.1 Cell metabolism and reaction schemes

The metabolism of bacteria is presented in figure 3. In our case the substrate is the pollution to be treated. It may be either organic nitrogen, or a carbonaceous organic chain. A great number of biochemical reactions are involved in the metabolism, with the main following steps:

- The substrates are hydrolyzed outside the cell by exo-enzymes in order to reduce the length of the carbon chains. The hydrolyzed compounds diffuse through the cell membrane by permeation or by active transport.
- The short carbon chain compounds are used by the cell in catabolism in order to produce energy and monomers, which can be stored in the cell.
- The monomers and the energy can be used in the anabolism phase to construct biological materials leading to the cell duplication (biomass growth). Some residuals can also be produced.

Cellular death produces partly biodegradable products, which are reintroduced in the degradation sequence of carbonaceous matter.

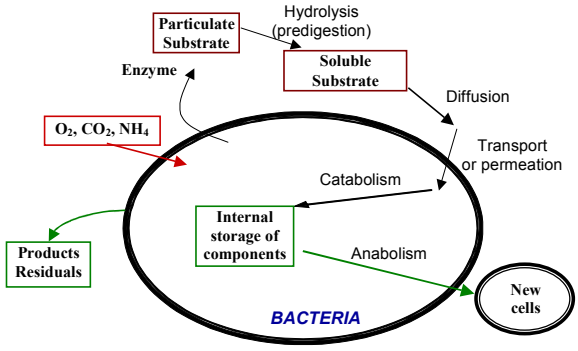

Fig. 3. Metabolism of bacteria

Catabolism and anabolism are very general reactions, and for that reason the process is usually represented by the figure 4.

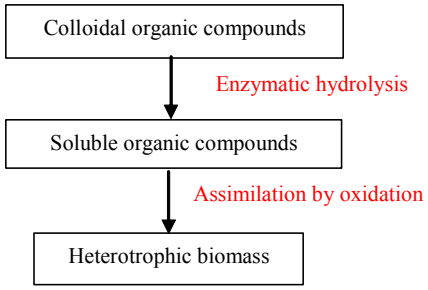

Fig. 4. Degradation mechanism of carbonaceous compounds in biological processes (based on Cardot, 1999)

The reaction may be represented as:

substrate $\xrightarrow{\rho}$ biomass + products

The coming back line means that initial biomass is needed to produce new biomass by cellar division. For each reaction, the reaction kinetic is given by the product of the reaction rate (ρ) and the yield (Y), for a given component. The global kinetic is given by the sum of each reaction kinetic where the component appears, which lead to the general form:

$$r_j = \sum_i Y_{i,j} \cdot \rho_i \quad (2)$$

3.2 Model equations design

Discussion about the choice of the ASM model. The ASM1 model focuses on both carbon and nitrogen degradation. The degradation of carbonaceous compounds is based on the hydrolysis reaction, which imposes slow kinetic to the global process. The ASM2 model adds the phosphorus compound and the ASM3 model introduces a storage state variable for carbonaceous pollution.
Phosphorus is a nutrient in paper mill effluent case, and has not yet been included in the proposed model for reason of simplicity: the model design has been based on keeping the fewest state variables. The

ASM3 model would have been potentially suitable, but though the ASM3 model is proposed as a better model for carbonaceous behavior it is still widely less use. Finally, the reference model used is ASM1, because improvements from ASM1 to ASM3 should not be described by our reduced model and therefore validated.

State variables selection. Carbonaceous matter takes into account slowly and readily biodegradable substrate, which is considered to be only one state variable. Indeed, the hydrolysis of slowly biodegradable matter is a very complex reaction, which kinetics model in ASM1 includes three parameters. The reduced reaction kinetic will be near the slowest dynamic (linked to hydrolysis) which dominate over the fast degradation of readily biodegradable carbonaceous matter. Due to this difference of time scale, the approximate model will remain reliable.

The biodegradable organic nitrogen (which is represented in particulate and soluble compounds in ASM1) is not present in the effluent to be treated. Linked with the fact that only aerobic phase is proposed, this lead to consider that no nitrate and nitrite nitrogen are present in the bioreactor. This hypothesis has been verified by measurements (Bassompierre, *et al.*, 2006b).
As a matter of fact, it is supposed that the only kind of biomass considered is heterotrophic biomass, i.e. that only the bacteria fauna for carbon oxidation is growing under aerobic environment.
However, nitrogen is added as nutriments in ammonia nitrogen form. This component is kept as a state variable as it is easy to measure on-line and it may be used as an indicator of the state of biomass.
Dissolved oxygen (S_O) is easily measured and this data is a good indicator of aerobic conditions. It may be naturally also considered as a state variable, but in our application it is only measured.

Finally, only three state variables are considered:

- One fraction of organic matter (XSs)
- One type or micro-organisms: heterotrophic biomass (X_{BH})
- One fraction of nitrogen (S_{NH})

Reaction scheme. As only one form of biomass is present, and as the other components are supposed to be readily biodegradable, only two processes are considered: the aerobic growth of heterotrophic biomass and the biomass decay. The biomass decay produces partially some organic components.

The aerobic growth of heterotrophic biomass can be represented by Monod laws, considering saturation of carbon, oxygen and ammonia concentrations.

$$\begin{cases} \rho_1 = \mu . \dfrac{XS_S}{K_S + XS_S} . \dfrac{S_O}{K_{OH} + S_{OH}} . \dfrac{S_{NH}}{K_{NH} + S_{NH}} . X_{BH} \\ \rho_2 = b . X_{BH} \end{cases} \quad (3)$$

where μ is the maximal reaction rate of reaction ρ_1 and b is the coefficient of the decay reaction ρ_2.
K_S, K_{OH} and K_{NH} are the half saturation parameters.

The global kinetic for each component is:

$$\begin{cases} r_{XS_S} = -\dfrac{1}{Y_H} . \rho_1 + f . \rho_2 \\ r_{X_{BH}} = \rho_1 - \rho_2 \\ r_{S_{NH}} = -i_{XB} . \rho_1 \end{cases} \quad (4)$$

where Y_H is the rate of conversion of substrate with respect to the biomass, f is the fraction of organic component generated by biomass decay, and i_{XB} is the nitrogen fraction in biomass.

Thus the model of the reactor is:

$$\begin{cases} \dfrac{dXS_S}{dt} = \dfrac{1}{V}\left(Q_{in} XS_{S-in} + Q_r XS_{S-r} - Q_{out} XS_{S-out}\right) + r_{XSs} \\ \dfrac{dX_{BH}}{dt} = \dfrac{1}{V}\left(Q_{in} X_{BH-in} + Q_r X_{BH-r} - Q_{out} X_{BH-out}\right) + r_{X_{BH}} \\ \dfrac{dS_{NH}}{dt} = \dfrac{1}{V}\left(Q_{in} S_{NH-in} + Q_r S_{NH-r} - Q_{out} S_{NH-out}\right) + r_{S_{NH}} \end{cases} \quad (5)$$

where indexes *in* represents the input, *r* the recycling input and *out* the output.

This model is suitable to our purpose: the number of state variables and parameters is reduced, so that the model may be easily used for estimation, control and supervision.

4. VALIDATION ON INDUSTRIAL EFFLUENT

4.1 Experimental data

A database constituted from the pilot plant fed with paper mill effluent has been carried out.

The paper mill effluent to be treated (real effluent from industry) is characterized by XSs concentration. The hypothesis that the effluent is biologically inert (no biomass) has been experimentally validated. Thus, XSs is constant and only one measurement is made after each feeding of the storage tank. As no aeration takes place in this tank, there are anoxic conditions (oxygen concentration very low). Ammonia nitrogen and phosphoric acid are added directly in the tank, and measured by samples.

The reactor presents a carrousel configuration and its hydrodynamics behavior was equivalent to a continuous stirred tank reactor (DTS measurements, Bassompierre, *et al.*, 2006a). As the measurements are taken at the two reactor inputs (from the storage tank and the clarifier) and at the reactor output, the number of measurements has been minimized, in order to decrease the delay to obtain the values and the global measurement cost by experimental studies (Bassompierre, *et al.*, 2006b). Thus a reversible linear measurement model has been established, linking XSs to BOD_5 measurement and X_{BH} to TSS measurement, and getting free of the BOD_{21} and VSS measurements.

At the output of the biological reactor, a sampler takes measurements at fixed periods and the measurement model is used to determine XSs and X_{BH}. S_{NH} and S_O are on-line measured, through

sensors and the supervisor. At the input of the bioreactor, where the recycled effluent from the clarifier is injected, XSs and X_{BH} are determined in the same way. S_O is about anoxic concentration.

The COD and S_{NH} analysis have shown that there was no biological activity in the clarifier: the concentrations in the clear water and in the sludge recycling loop were equal to those in the output of the biological reactor (mixed liquor).

4.2 Parameter identification

A first database has been carried out for parameter identification. A step, shown in figure 5, has been made on the input flow of the pilot plant, which corresponds to a usual event in paper mill production. The magnitude of the step is twice the nominal input flow rate. Figure 6 shows the input carbon concentration. Each point corresponds to a storage tank feeding.

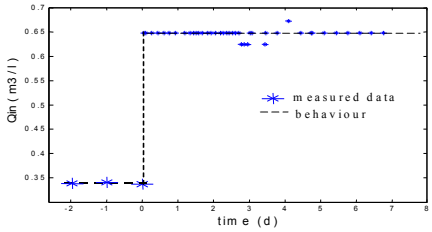

Fig. 5. Step on the input flow

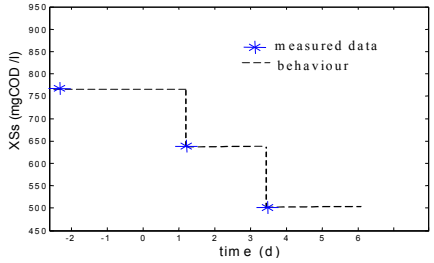

Fig. 6. Input carbon concentration

The re-circulated inputs are not presented here. The behavior of XSs, X_{BH} and S_{NH} are obviously much more varying, as shown for the biomass example on figure 7. The great variations are more important than in urban case, and show the major importance of the settler in dynamical behavior. Between day 2 and 3 a rough increase of X_{BH} can be noticed: it is due to artificial feeding of the clarifier with biomass. This event can be considered as a disturbance.

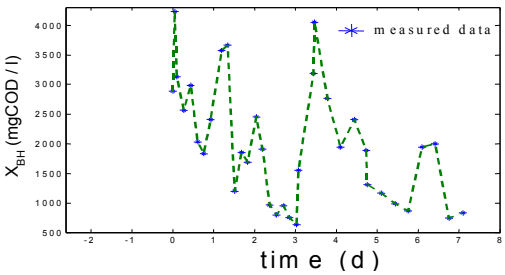

Fig. 7. Recycling biomass concentration

A sensitivity parametric study has shown that the half saturation parameters were much less sensitive to changes in operating conditions than yield and maximum rate parameters. The first ones have been maintained to the ASM1 values and only the second ones have been identified.

Table 2 shows identified parameters in comparison with their ASM1 value. The two last parameters, linked to biomass decay (ρ2) are almost the same as for ASM1 model. Nevertheless, the three first parameters, linked to biomass growth (ρ1) are much smaller than for urban effluent. That means that biomass activity and pollution conversion is lower for paper mill effluent than for urban effluent. It is coherent with the fact that wastewater treatment consumes less nitrogen than in urban case. An explanation may be that the chemical compounds of the effluent are more difficult to assimilate by the bacteria.

Table 2: Identified parameters

Parameter	ASM1 Value	Identified value
Y_H ($g_{COD\_XBH}.g_{COD\_XSs}^{-1}$)	0.67 (oxidation) 1 (hydrolysis)	0.62
i_{BH} ($g_N\ g_{COD}^{-1}$)	0.08	0.016
μ (d^{-1})	4 (oxidation) 3 (hydrolysis)	2.6
f	0.92	0.62
b (d^{-1})	0.3	0.33

Figure 8 presents the modeled output biomass concentration, which is very close to the measured data. The disturbance at day 3 due to the clarifier is correctly taken into account. A global decrease of the biomass is observed, may be due to a limitation in the quantity of supplied oxygen (even if in no anoxic conditions were measured). However, the identified model is able to handle such phenomena.

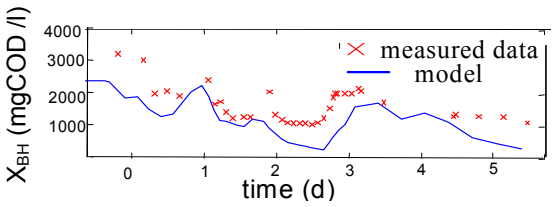

Fig. 8. Output biomass concentration with identification database

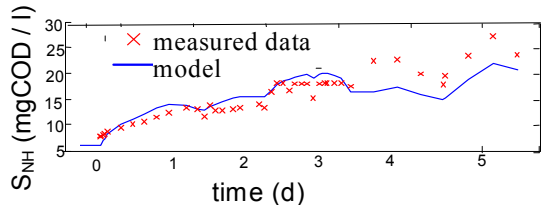

Fig. 9. Output ammonia nitrogen concentration with identification data base

Figure 9 shows a very good behavior of the model for S_{NH}. Its high concentration may be due to the operating conditions of the pilot plant (low temperature, modification of biomass composition because of the input stability...). But it may also be

due to the paper mill effluent, because similar results are noticed on the industrial plant. It is interesting to go further to explain this phenomenon.
Globally, the identified model shows a good agreement with our experimental database.

4.3 Model validation

A second data base is carried out for model validation. Similarly, an input flow step is applied at time 0, from 0.288 m^3/d to 0.576 m^3/d. XSs is constant around 770 mg_{COD}/l. Again some disturbances occurred during experiments: a deflocculation event appears in the clarifier jointly with the flow step. For a good validation, the operating point experimentally achieved is different from the one considered for identification.

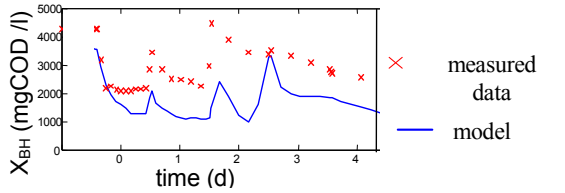

Fig. 10. Output biomass concentration with validation data base

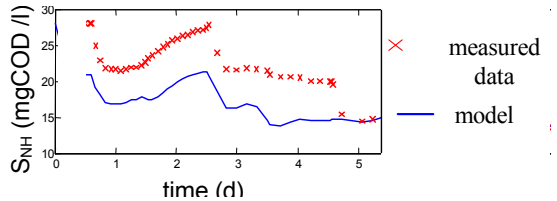

Fig. 11. Output ammonia nitrogen concentration with validation data base

Figure 10 and 11 show good results from dynamical behavior point of view. The observed bias is due to the change in operating point that the model can't completely take into account. Nevertheless, for our modeling objectives, the main goal is to obtain a model able to predict dynamical behavior of the process. This point is essential for example, to help in the best way the operators for plant supervision.

5. CONCLUSION

In this paper, the model design for paper mill wastewater treatment has been assessed. Specificity of paper mill effluents needs a new approach to take into account its composition and its influence on biological treatment operation. The use of a new semi industrial pilot plant is of considerable help to extract relevant information for an accurate modeling. Actually, it is free of industrial constraints such as variability of the effluent composition due to changes in paper making process, which prevent from reaching an equilibrium point in industrial wastewater treatment plants.
A reduced model has been designed thanks to biological considerations and thanks to the dynamical behaviour observed on the pilot plant fed with paper mill effluent. Rigorous identification has been carried out on experimental data, and the model has been successfully validated on another experimental database.

Further work will be to study more specifically the impact of disturbances in the effluent due to pulp and paper making process. Thus a model has been designed and validated on real industrial effluent, though these results need to be strengthened by other experiments. This model may be used now to explain and anticipate biomass state, which will help the operator to stabilize the process.

REFERENCES

Bassompierre C., C. Cadet, J.F. Béteau, M. Aurousseau, A. Guillet (2006a). *Towards an integrated co-operative supervision system for activated sludge processes optimisation*, International Symposium on Advanced Control of Chemical Processes, ADCHEM'06, April 2-5, Gramado, Brazil.

Bassompierre C., Guillet A., Aurousseau M., Cadet C., Béteau J.F., Lenzi F. (2006b), Paper mill wastewater treatment: off line measurement correlations for monitoring, *Environmental Engineering and Management Journal (EEMJ),* September 2006, **5(4)**, 285-296

Cadet, C., N. Lucas, J.F. Béteau, A. Guillet, M. Aurousseau and N. Simonin (2003). Modelling of wastewater treatment of a pulp and paper mill for monitoring. *Environmental. Engineering and Management Journal*. **2(3)**, 163-174.

Cardot C. (1999), *Les traitements de l'eau – Procédés Physico-chimiques et biologiques*, Ellipses, Paris.

Gernaey K.V., M. Van Loosdrecht, M. Henze, M. Lind, S. Jorgensen (2004), *Activated sludge wastewater treatment plant modelling and simulation: state of the art*, Environmental modelling and software, **19**, 763-783

Guillet A., Cadet C., Aurousseau M. Bassompierre C. and Béteau J.F. (2006). *A semi-industrial pilot for paper mills treatment improvement: an innovative conception*. 3rd International Symposium on emerging technologies for pulping and papermaking, 7th-9th November 2006, Guangzhou, China.

Henze, M., Jr. Gredy, W. Gujer, G. Marias and T. Matsuo (1986). *Activated Sludge Model n°1*. IAWQ Scientific and Technical Report n°1.

Jeppsson U. (1996), Modeling aspects of wastewater treatment processes. PhD, Lund Institute technology, Sweden, 428p.

Pokhrel D. and Viraraghavan T. (2004) Treatment of pulp and paper mill wastewater – a review. *Science of the total environment*, **333**, 37-58.

Potier O., Leclerc J.P. and Pons M.N. (2005) Influence on geometrical and operationnal parameters on the axial dispersion in an aerated channel reactor. *Water Research*, **39 (18)**, 4454-4462.