INNOVATIVE COMPACT TREATMENT SYSTEM FOR WASTEWATER FROM PAPER MILLS PRODUCING WET-STRENGTH PAPER

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Abstract. Production of wet-strength paper requires use of chemical products with a significant environmental impact. The wet-strength process may take place under acidic or basic conditions, with different types and quantities of reagents and therefore different concentration and properties of the wastewater produced.
Austep, in collaboration with the Cordenons Group, has developed a biological treatment process for wastewater from the production of wet-strength paper under both acidic and neutral conditions. It has also conducted pilot tests to determine the yields of both solutions and constructed an industrial plant with the capacity to treat 230 m^3/h. Study of the pilot tests permitted assessment of the efficiency of removal of nitrogenous pollutants and COD and of AOXs (if neutral gluing is used).
The plant oxidates organic substances and nitrifies ammoniac acid. Biological sludge is separated using Double-Treat® technology with a third generation DAF flotation device. The plant is therefore extremely compact, occupying a smaller area than would have been required by conventional active sludge technologies employing sedimentation or anaerobic biomass.

Keywords. Wet-strength, nitrification, active sludge, AOX,

1. INTRODUCTION

European legislation (law governing wastewaters and IPPCs) is setting increasingly strict limitations on parameters applicable to wastewaters released into bodies of surface water. Following recent implementation of these regulations in Belgium, it has become necessary to review the wastewater treatment process employed for wastewater coming from the paper machine in the Cordenons Group’s mill in Malmedy by adding a biological treatment stage.

The conditions applying to the project required development of innovative solutions for the following reasons:

- The plant is located adjacent to residential areas (1-2 m from the nearest house)
- There must be no noise (< 55 dB) or foul odours
- Limited space
- Need to keep ammonia nitrogen values below 2 mg/l
- Need to eliminate slowly degradable compounds such as AOXs

During execution of pilot tests a number of different plant configurations were tried, and the most compact, best-performing treatment system was identified as the one described below.

2. WET-STRENGTH PAPERS

Wet-strength papers, both coloured and white, are produced by adding chemical products to the mix that ensure that the paper does not flake if immersed in water. A number of different types of chemical products are used for this purpose:

- Ureic-melamine resins and melamine-formaldehyde resins
- Polyamides containing chloro-organic compounds (such as epichlorohydrin)

Ureic-melamine resins and melamine-formaldehyde resins react with fibre in an acidic environment (pH 4-5); polyamides with a neutral-alkali pH (6,5-8,5).
Polyamides containing organic chlorine are polymers composed of adipic acid, diethyl-triamine and epichlorohydrin.
Following polymerisation:

Adipic acid–NH–diethylamine–NH–Adipic acid

the external amine is replaced with epichlorohydrin (1-chlorine-2,3-epoxyipropane, C_3H_5ClO).
Mono-chloro-propandiol is produced during hydrolysis of this compound.
It has been demonstrated that epichlorohydrin is degradable biologically and aerobically with long resistance times, about 20 hours (1).

3. DESCRIPTION OF THE DOUBLE TREAT® PROCESS

Wastewater treatment with active sludge centres around separating out sludge. Separation of sludge permits sludge to be kept in the tank, and the more stable and efficient the process, the better prepared the plant will be to deal with overloads, and the more versatile.
Active sludge may be separated out in biological suspended biomass oxidation plants by means of:

- Sedimentation by gravity
- Dissolved air flotation (Daf)

- Filtering on a membrane

All the systems listed perform two functions: clarifying effluent and thickening sludge, which must be recycled in the tank.

The DOUBLE TREAT® treatment system is based on use of a dissolved air flotation stage and, where necessary, refining with sand filtering of the clarified effluent after flotation (Figure 1).

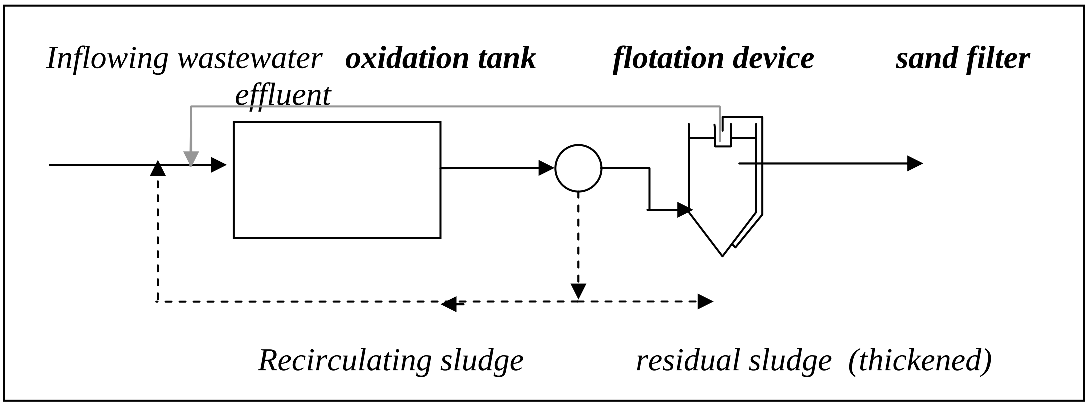


Figure 1 – Diagram illustrating the DOUBLE TREAT® process

Note the following disadvantages of secondary sedimentation:

a) large footprint
b) high recirculation capacities: normally 50 to 100% of the inflow and sometimes up to 150%
c) problems frequently associated with formation of light sludge and/or bulking, sludge which floats on the surface
d) large volumes of residual sludge to be extracted and sent to the sludge line.

Whereas if a membrane system is used for a separation of the biomass, the disadvantages are:

a) High electricity consumption per m^3 of water treated
b) Need for frequent cleaning
c) High plant cost for high capacities
d) Low membrane durability and frequent maintenance work
e) Relatively high volumes of residual sludge to be extracted and sent to the sludge line.

For these reasons, in order to preserve the simplicity, low initial investment and high yields of the active sludge process, especially in treatment of industrial wastewaters, Austep has developed a dissolved air flotation system (also referred to as DAF flotation) specifically designed for separation of active sludge. It may be used as the sole clarification treatment in new plants, or in combination with secondary sedimentation already in existence in operating plants.

The scheme applied is pressurisation of recirculation of clarified water, as shown in Figure 2.

Legend: Acqua chiarita – clarified water

Fanghi sedimentati – sedimentated sludge

Fanghi flottati – flotated sludge

Chemicals

Acqua grezza – raw water

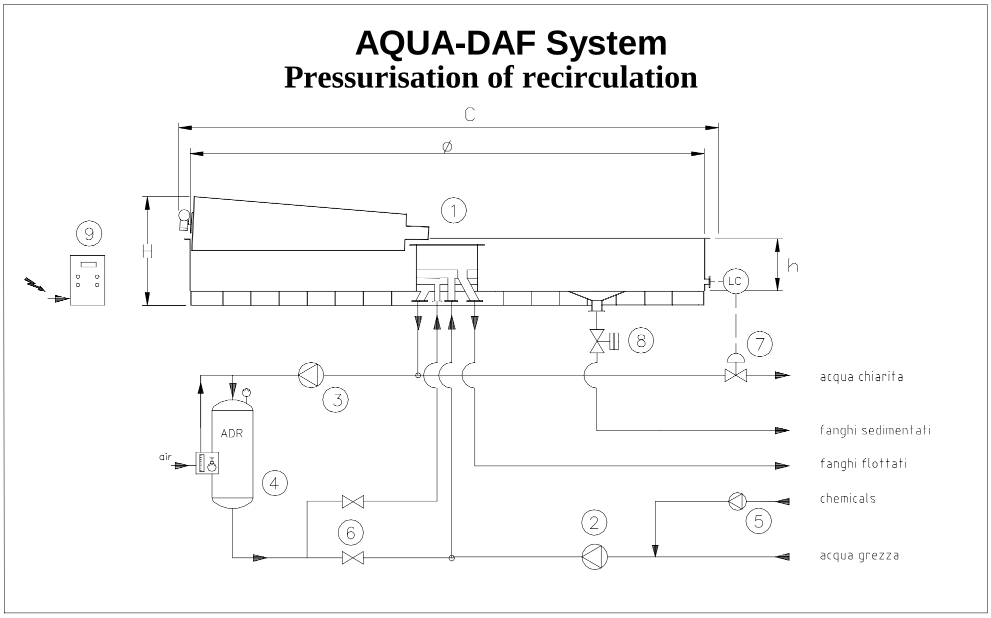


Figure 2 –Diagram illustrating pressurisation of recirculation

The flotation system is normally used for thickening sludge. In this case, the load of solids and concentration of thickened sludge that may be applied in treatment plants is as shown in table n. 1.

Table n. 1 Thickening of residual active sludge by DAF flotation – Typical Values –

	without polyelectrolyte	with polyelectrolyte
Solid content, Kg SS/m^2h	5 ÷10	10 ÷ 12
Concentration of flotated thickened sludge, dry percentage	2 ÷ 3	3 ÷ 4

The concentration of solids in the flotated sludge depends not only on the functional parameters of the flotation device (air/solid ratio, above all), but also on the properties of the sludge, especially its volume index (SVI). Note that if the flotation device is used for secondary treatment, it replaces not only the conventional sedimentation system but the sludge thickener, where necessary.

The dimensions of the DAF flotation device used for secondary treatment depend on the application scheme and properties of the water to be treated.

In general, surface hydraulic load values (also considering the recirculation capacity of the clarified effluent) vary from 5 to 9 m^3/m^2 h, while mass load (or solid flow) may reach values of more than 20 Kg SS/m^2 h.

A circular form is preferable for flotation systems, both due to the ease of collecting flotated sludge and because of the improved distribution of incoming flow.

Modern third generation flotation systems have very low liquid heights (0.8 to 1.2 m) in stainless steel tanks and can be positioned on top of oxidation tanks to save space.

Use and dosage of polyelectrolyte depend on the “good” quality of the sludge. With volume indexes under 100 ml/g dry concentrations of 2 ÷ 3 % can be achieved without use of polyelectrolyte even at high loads of 5 ÷ 10 KgSS/m^2h.

The values shown in Table n.1 should be considered approximate, and the variability of the properties of sludge means it is difficult to make predictions without conducting tests using a pilot plant.

The need for use of polyelectrolyte depends on the required effluent quality (SST).

Austep’s latest generation flotation system remains stable even when the rate of flow of inflowing wastewater changes, and with mass and hydraulic loads much higher than those that can be handled by conventional secondary gravitational sedimentation systems. This means they can operate with high active sludge concentrations in oxidation tanks, so that the biological process is more stable and efficient and involves no risk of loss of suspended solids due to entrainment or other reasons.

Active sludge rapidly returns to the tank, the site of metabolism and bacterial respiration, without undergoing alteration.

If sedimentation of sludge is difficult due to bulking, flotation effectively separates it out using polyelectrolyte. If the difficulties are due to presence of oily and greasy substances, flotation is the ideal solution.

This solution also offers the following benefits:

a) it rapidly returns aerated sludge to the tank, maintaining its metabolism and respiration activity.

   The energy used in flotation compensates the greater energy cost of oxidation for transition from anoxic conditions (absence of oxygen) at the bottom of the sedimentation tank to oxygen concentration in the tank.

b) sludge is already thickened, as dry concentration is altered from 0.6 ÷ 0.8% (1÷1.2 % max) to 2 ÷ 3%.

   This hugely simplifies the operation of the sludge line.

c) average stay in the oxidation tank is longer, with the same incoming flow, reducing the amount recycled.

If overloading of the secondary sedimentation tank is combined with bulking (which can occur frequently in treatment of industrial wastewaters), the benefits of use of the flotation system are even greater.

4. RESULTS

4.1. Description of the treatment plant for the Cordenons Group’s Malmedy mill

The system was designed on the basis of the following project data:

Table n. 2 Project data

	Project values	Unit of measurement
Rate of flow	230	m^3/h
pure COD	400-800	mg/l
filtered COD	< 300	mg/l
SST	300-500	mg/l
Total nitrogen	10-20	mg/l
AOX	1200	µg/l

The following goals were set for construction of the plant:

- Removal of COD
- Removal of ammonia nitrogen by nitrification
- Removal of AOXs
- Possibility of treating wastewater from wet-strength paper production under acidic conditions (urea-melamine resins)

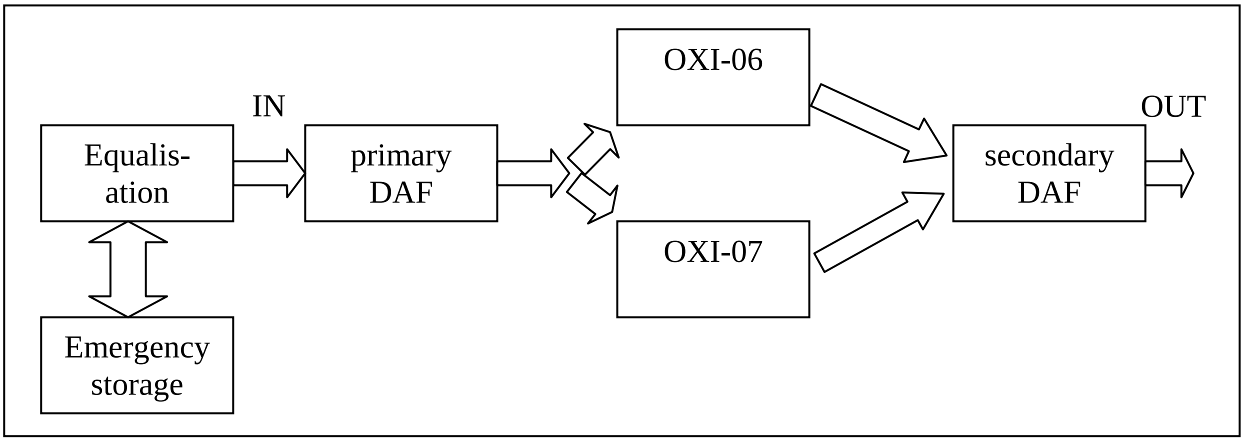


Figure 3 – Block diagram illustrating the treatment system for the Cordenons Group's Malmedy mill

The system is based on the following individual operations and processes, show in the block diagram in figure 3:

- Equalisation and emergency tank off-line
- Primary flotation: for removal of fibre (SST)
- Oxidation tank: for removal of soluble COD, nitrogen and AOX
- Secondary flotation: for separation of effluent from sludge and recycling of sludge

The goal that turned out to represent a limitation was the need for nitrification, which affected not only the quantity of biomass present (greater sludge age) but also its minimum residence time, so that the reaction could be completed.

The system was constructed in two parallel lines with a piston flow to prevent short circuits. The aerated mix is then sent to the DAF flotation system, which permits separation of sludge from treated effluent.

The principal plant engineering data is as follows:

Table n. 3 Plant engineering data

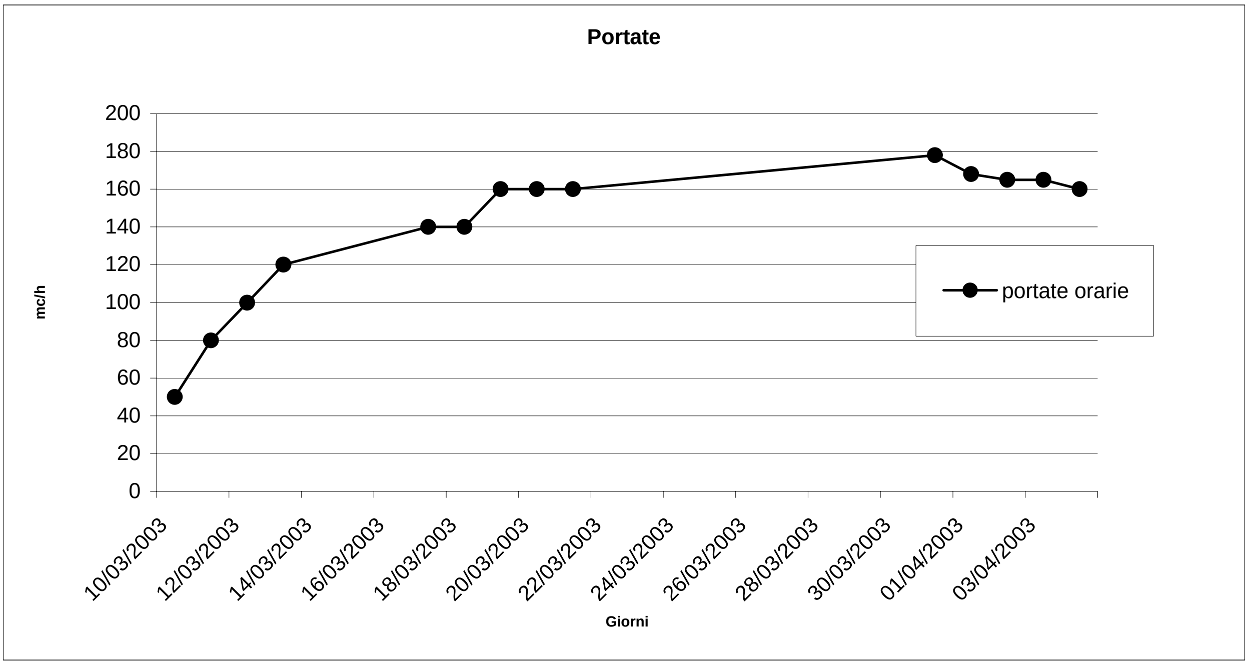
	Project values
Equalisation tank	800 m^3
Emergency tank	1800 m^3
Primary flotation area	40 m^2
Useful tank volume	900-1000 m^3
Flotation area	120 m^2
Biomass present	2-6 g/l

4.2. Operating data

The system began operation at the beginning of February 2003 with a single line, gradually increasing capacity up to full operation. The system was started up with biological sludge taken from the nearby civil wastewater treatment plant in the town of Eupen. Data on incoming wastewater and outgoing effluent was monitored every day and is shown in the graphs below.

4.3. Inflow data

The graph below (figure n. 4) shows the rate of flow fed to the system during start-up and normal operation. The system was also tested with rates of flow equal to the project capacity, but this capacity has not yet been reached on a continuous basis. The equalisation tank permits proper equalisation of variations in rate of flow.



Portate - Rates of flow

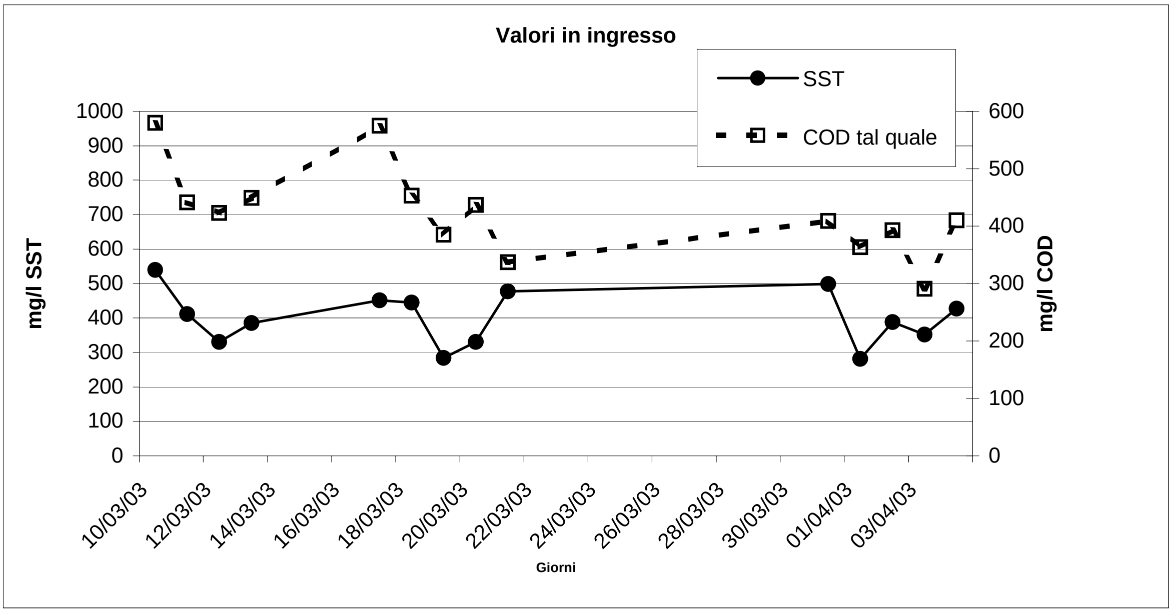
Portate orarie - Hourly rates of flow

Giorni - days

Figure 4 – Figures on rates of flow entering the biological treatment system

The graph below (figure n. 5) represents incoming values for SSTs and CODs prior to primary flotation. It is clear that even though there is an equalisation tank upstream, there is a great deal of variability in suspended solids. The presence of a primary flotation system is indispensable for correct performance of removal of the aerobic biological system downstream.

The off-line emergency tank is used to collect sudden excess flow and for washing the machine twice a week.



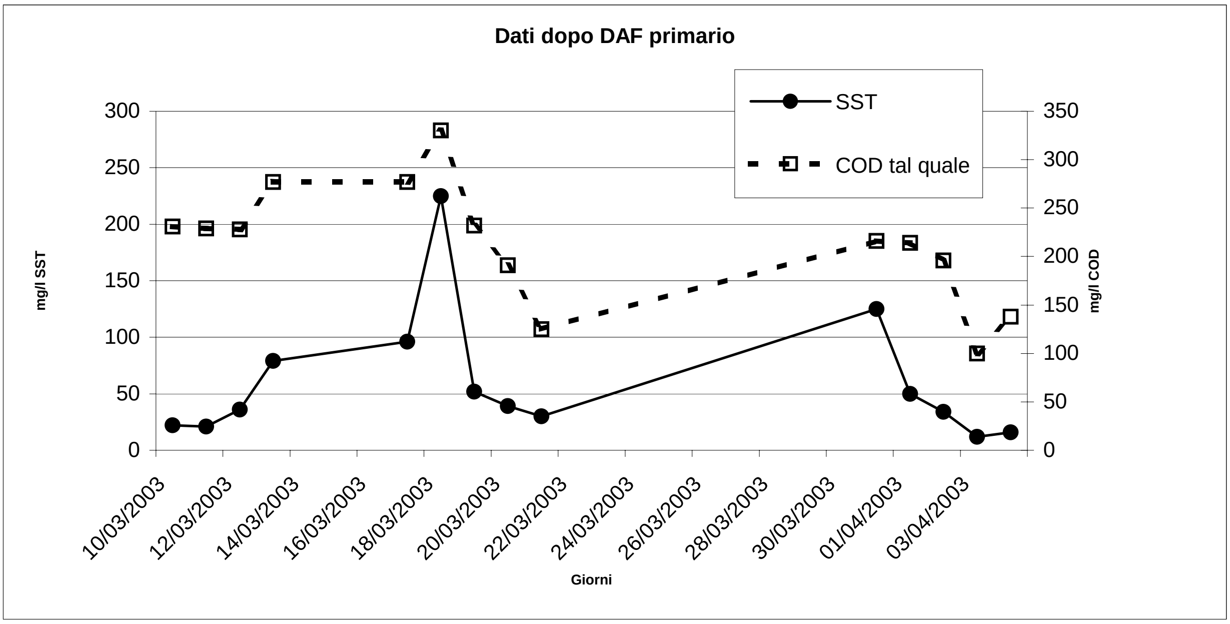
Valori in ingresso - Inflow values

COD tal quale - COD as such

Giorni – days

Figure 5 –COD and SST values for inflow at the primary flotation tank

Figure 6 shows SST and COD figures for effluent from the primary flotation tank and for feeding to the aerobic treatment system. The primary flotation system is conventional (at a hydraulic load of about 4 $m^3/m^2/h$ and a solid load of about 0.6-2.2 kg $SST/m^2/h$) and supplies SST values in effluent of about 40-80 mg/l.



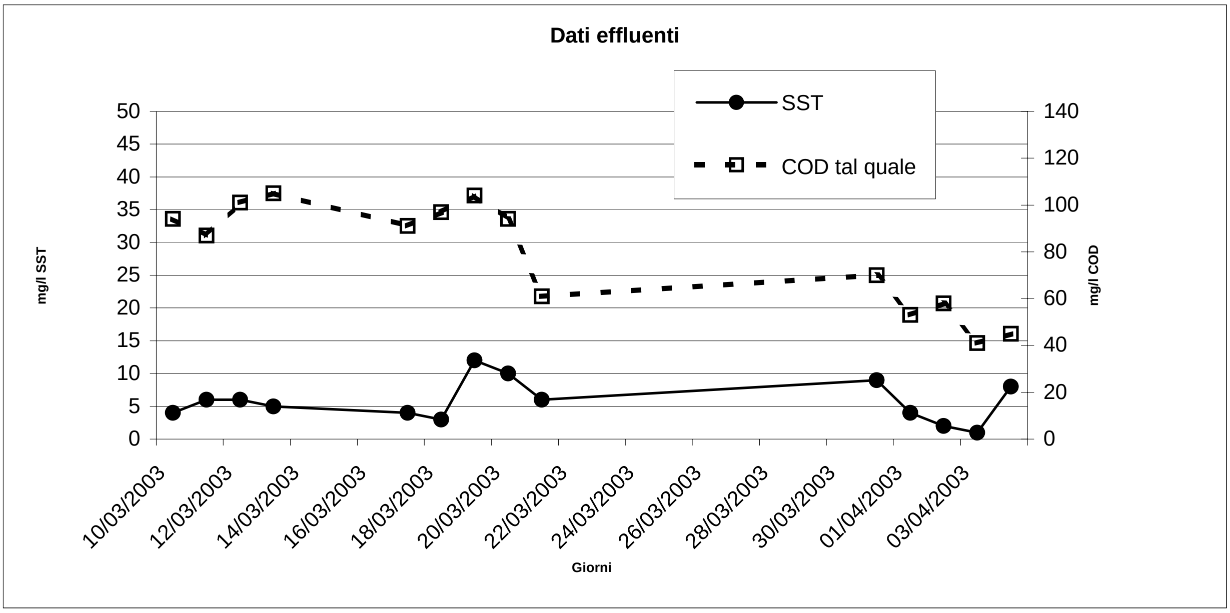
Dati dopo DAF primario - Data following primary DAF

COD tal quale – COD as such

Giorni – Days

Figure 6 – Data on wastewater fed to biological treatment system: COD and SST

Values for effluent from the biological system are shown in figure n. 7.



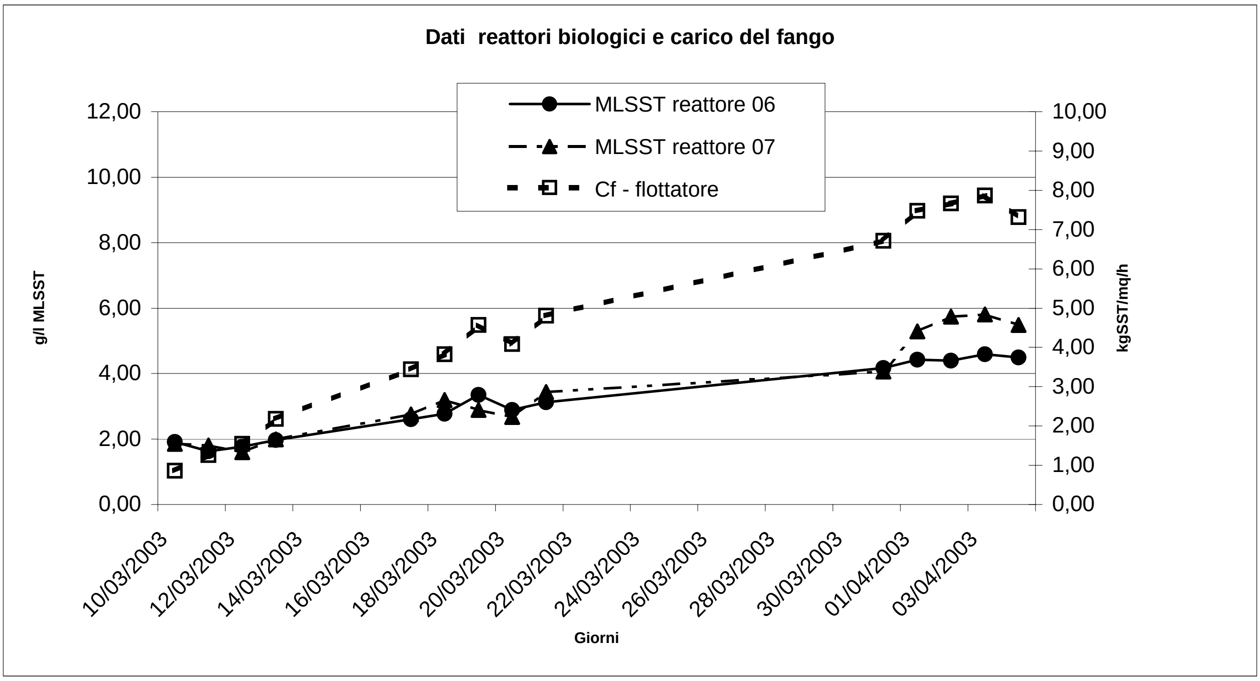
Dati effluenti - Effluent data

COD tal quale –COD as such

Figure 7- COD and SST in effluent from biological treatment system

It is clear that COD values are always below 150 mg/l, and often below 100 mg/l, while suspended solids are practically absent in effluent from the Water-DAF Flotation system: < 15-20 mg/l.

These values are obtained with a fairly high load on the flotation system, up to 8 kgSST/m^2/h, as shown in figure 8, which shows both biomass concentrations in both tanks, OXI-06 and OXI-07, and the corresponding average daily load on the Aqua-DAF flotation system.



Dati reattori biologici e carico del fango - Data on biological reactors and sludge load reactor

Flottattore - flotation system

Reattore - reactor

Giorni - days

Figure 8 – MLSST in oxidation tanks and corresponding sludge load on flotation system

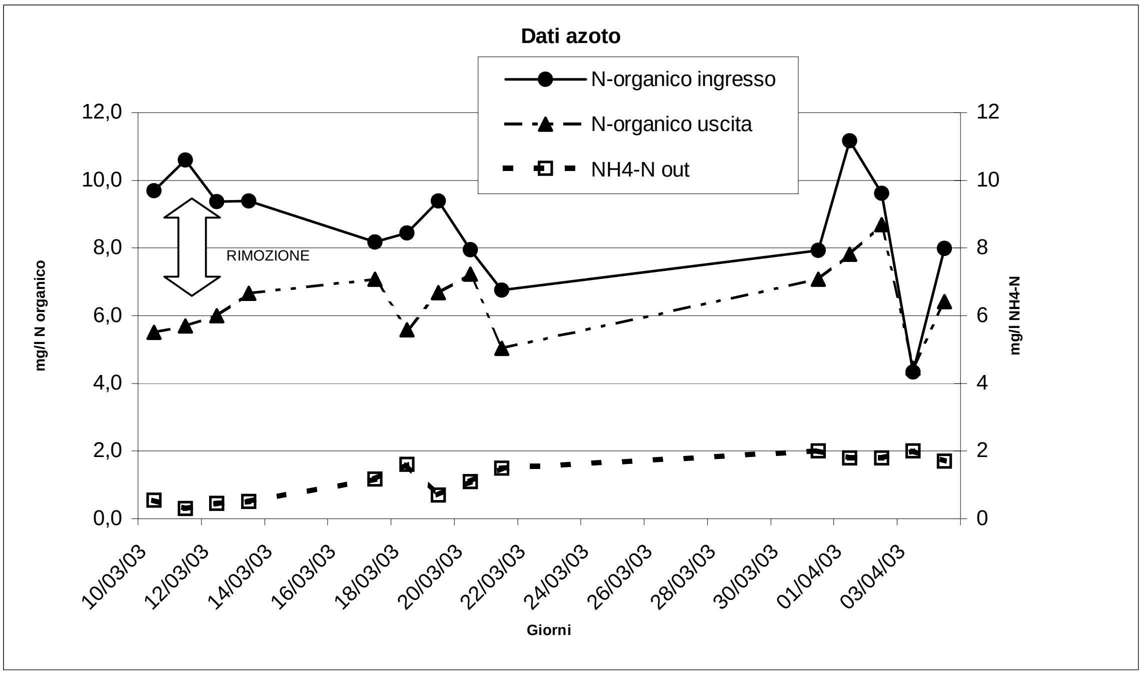
The increase on the load on the flotation system is proportional to both incoming rate of flow and the increase in totals solids in the tank due to bacterial growth and partially due to accumulation of fibre in the tanks. Fibre accumulation, if not excessive, will not disturb the biological process, as shown by COD values in effluent.

4.4. Removal of nitrogen and AOXs

The oxygen content of the wastewater, though not particularly high, requires stable application of nitrification processors as the maximum admissible value for ammonia nitrogen upon release is 2 mg/l.

Nitrogen is present in the wastewater prevalently in organic form, and ammonia nitrogen formed by ammonification is partially used for new bacterial cells (which need a quantity of nitrogen amounting to about 2-2.5% of the COD removed for synthesis), while the remainder is nitrate oxidated.

Organic nitrogen removed is shown in figure 9, which shows that the concentration of ammonia nitrogen is below or close to 2 mg/l. Nitrics are always well below 0.6 mg/l or not measurable.



Dati Azoto - Data on nitrogen

N- organico ingresso - Incoming organic N

N – organico uscita - Outgoing organic N

Rimozione - removal

Giorni - days

Figure 9 – In-out organic nitrogen and ammonia nitrogen exiting the system

Powdered active carbon was used during pilot tests and on the real plant. Dosage of active carbon by the PACT process (3) permits adsorption of slowly degradable substances such as AOXs and surfactants or colour, and permits bacteria to degrade them in an amount of time in excess of their hydraulic residence. AOX values measured during aerobic pilot tests were 800-1200 µg/lt coming in and about 400-600 µg/lt coming out of the system. During the start-up stage, without addition of carbon to the tank, the values measured were much lower, about 50 µg/lt coming in and 20-30 µg/lt flowing out. If these values should rise due to the type of paper produced, carbon dosage will permit higher yields while maintaining AOX values in effluent under 0.8-1 µg/lt as required by Belgian legislation.

4.5. Footprint

More space was needed in the Malmedy paper mill than planned due to removal of nitrogen and AOXs and the impossibility of using deep tanks as there was rock only about 1.5 mt below plane of site. Figures on the amount of space occupied are given below:

Daily load:	1800 kg COD/d
Volume:	1800 m^3
Volumetric load	1 kg COD/ m^3/d
Area occupied	350 m^2

In a paper mill with COD only, or other rapidly degradable substances, with the same applied load COD these figures will be:

Daily load:	1800 kg COD/d
Volume:	600-1000 m^3
Volumetric load	2-3 kg COD/ m^3/d
Area occupied	150 m^2 circa

Lastly, it is important to remember that it would not be prudent to reduce wastewater volumes for paper mills with high rates of flow and relatively low pollutant concentrations (200-500 mg/l).

Reduction of volume is theoretically feasible if the sole parameter taken into account for scaling the system is sludge load, in that the DOUBLE TREAT® system permits maintenance of high biomass concentrations in the tank. But if contact times are reduced excessively, bacterial kinetics could become a limiting factor, leading to mixing problems and short circuit risks.

CONCLUSIONS

Wastewater from paper mills producing wet-strength paper may be effectively treated using active sludge biological systems. Use of DOUBLE TREAT® technology can reduce the amount of space required while continuing to eliminate not only COD but also nitrogen and AOXs.

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