Narain Madhavan
Inactive member
Xylem Water Solutions (XWS)
India

Brendan van Wyk
Inactive member
Xylem Water Solutions (XWS)
South Africa

Jens Gebhardt
Inactive member
Xylem Water Solutions (XWS)
Germany

Alexis Metais
Inactive member
Xylem Water Solutions (XWS)
France

PULP & PAPER MILL WASTE WATER DECOLOURATION WITH OZONE

SUMMARY

The Pulp &Paper industry invests a lot to save water, using and treat their wastewater with state-of-art technologies such as coagulation/flocculation, anaerobic/aerobic processes. However, there are still some problems around the removal of substances left in the wastewater, such as hard COD (chemical oxygen demand), unpleasant odour and colour.

Colour prevents the possibility of waste water re-use and causes aesthetic problems in the receiving waters. This has led to government restrictions for the discharge of coloured waters (a target of a strict direct discharge limit, regulated by CPCB, Central Pollution Control Board), and the drive for the industry to invest in new technologies in order to meet these more stringent regulations.

Ozone can be used in different positions within the waste treatment plant to obtain different results. It has successfully been shown to be a cost effective polishing step in treating pulp and paper mill secondary effluents. Additional to the very successful results in decolouration, ozone brings further benefits like disinfection, improved BOD/COD-ratio,reduced AOX and reduction of odour. The use of a low ozone dose prior to effluent coagulation/flocculation helps to reduce the amount of floc required while improving the effluent colour.

It is proved that waste water or recycling water can be treated in an environmentally-friendly way by ozonation without creating sludge or concentrates, while reducing the amount of sludge and concentrates that are generated in other processes.

This paper will examine the technical and economic benefits of using ozone to reduce the colour load in pulp and paper mill effluents with some case studies, incl. various bench scale, pilot scale and full scale studies.

The Pulp and Paper industry generates large volumes of effluent that is dark in colour. The colour is hard to remove as it is made up of lignin and other non-biodegradable organic compounds[1]. This means that it simply passes through the secondary biological treatment steps. The colour of the treated effluent then prevents the possibility of water re-use and causes further aesthetic problems in the receiving waters where it is finally discharged.

The CPCB has published the following table showing the future discharge limits for India. As the table shows, colour will be limited to less than 150CPU.

Table 1 : CPCB EFFLUENT DISCHARGE LIMITS

Main parameter	Unit	
COD	mg/L	< 200
BOD	mg/L	< 20
TSS	mg/L	< 30
Color	CPU	< 150
TDS	mg/L	< 1800
AOX	mg/L	< 8
SAR	mg/L	< 10

LITERATURE

Coagulation is one of the cheapest options for removal of colour, however, this results in a large volume of toxic sludge that needs to be disposed of in an environmentally sustainable manner. This increases the post treatment costs and environmental impact of the mill. The process also does not necessarily reduce the pollution levels to below legal discharge standards, resulting in more treatment and treatment costs being implemented.[2]

Ozone has successfully been shown to be cost effective in treating pulp and paper mill effluents.

Additional to the very successful results in decolouration, ozone brings further benefits like disinfection, improved BOD/COD-ratio, reduced AOX and reduction of odour.

The use of ozone prior to effluent flocculation helps to reduce the amount of flocculants required while improving the effluent colour.[3]

The design of a decolourisation system with ozone depends mainly on the colour causing compounds and the COD background load in the water. There is a close relationship between the ozone demand for colour removal, and the COD concentration, even though the reaction chemistry for ozone on colour is far quicker (in minutes) than that for COD (up to hours). Therefore, it is possible to design and adapt the decolouration treatment system to meet the re-use or discharge requirements with a selective ozone dose that maximizes the colour reduction potential with the minimum ozone dose. In secondary treatment effluent this COD is considered as refractory, or hard, COD. This means that it is non-biodegradable. On reaction with ozone, this COD is converted to a more biodegradable form, or BOD. So a tertiary biological treatment step would result in an effluent lower in COD as well as colour.[4]

Table 2 : EXAMPLES OF DIFFERENT OPTIONS FOR COLOUR REMOVAL WITH OZONE

Influent	Low COD	Low COD	High COD
Effluent	No COD limit	COD limit	COD Limit
STEP	Coloured water	Coloured water	Coloured water
1.	↓	↓	Biological treatment
2.	Ozonation	Ozonation	Ozonation
3.	↓	Biological treatment	Biological treatment
	↓	↓	
	Reuse / Discharge to Receiving waters		

As Table2shows, based on the discharge requirements of the water, and the incoming COD level, there are a few options available for ozone treatment for colour removal. It is possible to use a pure ozone treatment solution to reduce colour if the influent COD is low and there is no COD discharge requirement need to be met. However, where COD levels are high and the discharge limits are low, then a secondary biological treatment step for COD reduction, followed by ozonation to destroy colour and crack the refractory COD to BOD, which is then removed in a tertiary biological process, is required. This system allows for the reduction of COD while reducing the colour to meet discharge requirements.

RESULTS AND DISCUSSION

Xylem has carried out a number of laboratory trials on the use of ozone for colour removal from pulp mill effluents.

Case Study 1 : Colour removal

The latest results are from a pulp mill in India.The main target of the trial was the removal of colour while maintaining, or reducing the final COD levels to be discharged.

The sample obtained had a colour level of 168 CPU and a COD level of 175mg/l respectively.

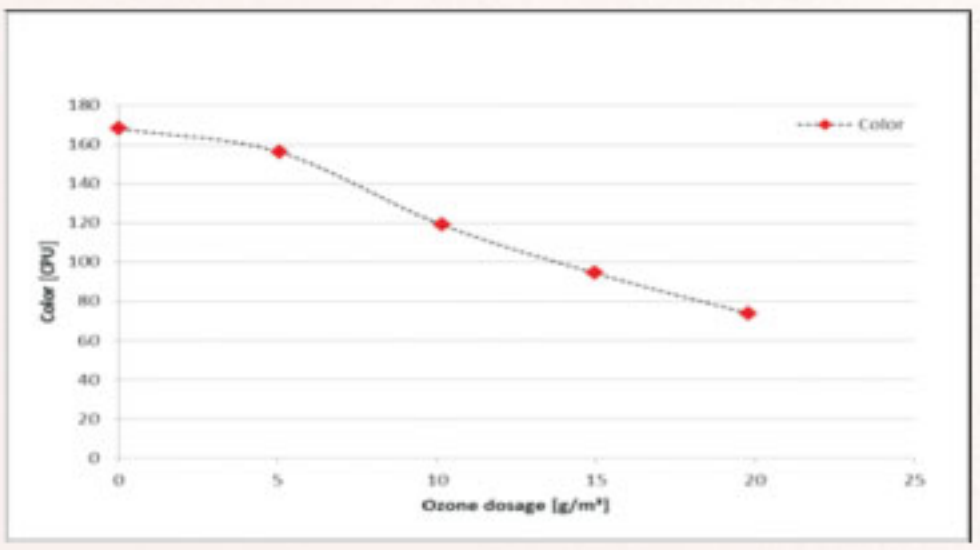


Figure 1: COLOUR Vs OZONE DOSE

By dosing at maximum 20 g O_3/m^3 the colour of the samplecould be significantly lowered from 168 CPU to 73.8 CPU(>55%) while the $COD_{homog.}$ in the waste water remained relatively constant at around 175 mg/l.

Figure 2 : COLOUR REDUCTION LEVEL

Case study 2: Colour removal, Disinfection

The other trial was done for a mill in the Netherlands. The objective of the trial was decolouration, improvement of UV transmittance and disinfection. By dosing a maximum of 10g O_3/m^3 the colour of the sample could be obviously lowered from 3.71 1/m to 2.01 1/m, while reducing the COD slightly from 60mg/l to 52mg/l. This improved the sample transmittance by 45.3%, with a 2-Log Reduction in plate count for Total coliforms.

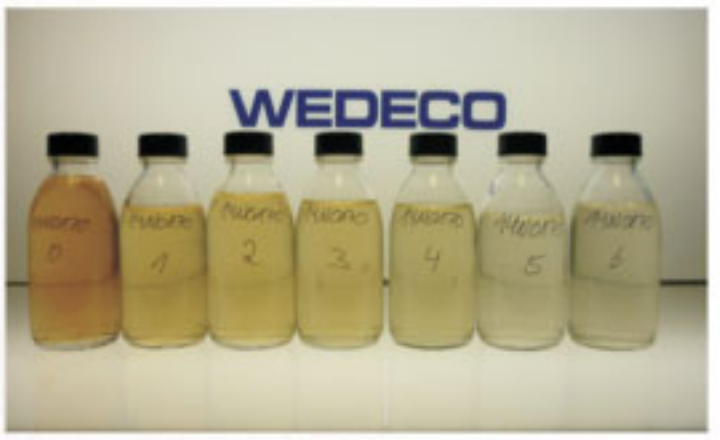


Figure 3 : DECOLOURIZATION OF SAMPLE DURING OZONATION

Case study 3: Color removal and COD reduction

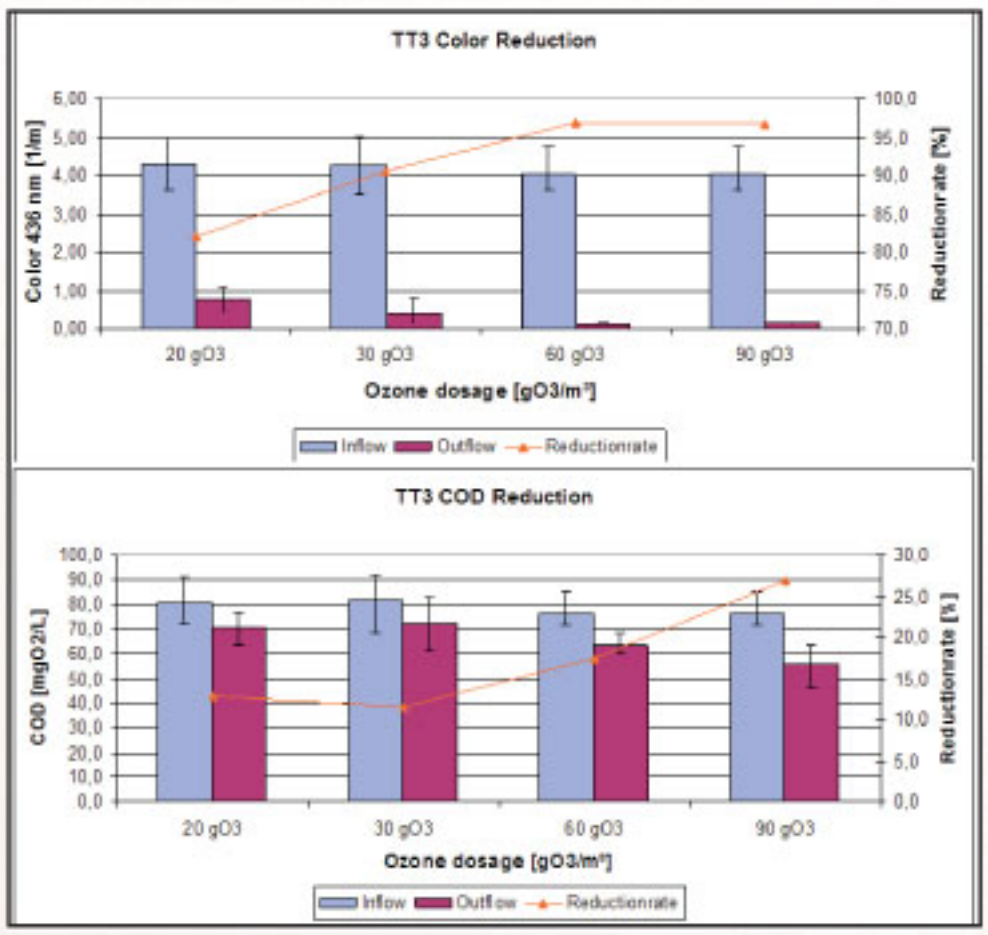
The third Pilot Plant trial was conducted with the objective of colour removal and COD reduction for possible waste water re-use. The pilot trial was carried out at 2 different points in the treatment process; one was after 3FM filtration and one after the MBR. It was found that the most effective position for both colour& COD removal was after the MBR. This stream contained an average of 4,00 1/m colour [@436nm] and 80mg/l COD.

As the graphs below show, colour is fast reacting with ozone and there is a greater than 80% reduction in colour using just a dose of 20g/m^3 of ozone, the COD

wasminor reduced by about 12% at the same time. Optimum design for the system would be to balance colour and COD removal with the cost of ozone. This was shown to be about 80g/m^3 ozone. The resultant investment costs in an ozone system then would be between 0.05 and 0.12 €/m^3 of effluent treated while the operating costs would be in the range of 0.1 to 0.22 €/m^3 depending on the electrical power cost and the cost of oxygen as feedgas for ozone generator.

FIGURE 4 : COLOUR OF SAMPLE AT DIFFERENT OZONE DOSAGES

GRAPH 1 : COLOR AND COD REDUCTION WITH OZONE



Case Study 4 : Full Scale Case Study

A paper mill in Germany was tasked with reducing their specific effluent volume by recycling their effluent stream and reducing their fresh water consumption.

The mill managed to reduce their specific effluent volume from 28.8m^3/adt down to 14m^3/adt. This was brought about by integrating a fine filtration system combined with ozone treatment (Figure 5).

The fine filtration system consisted of a pressure disk filter with 8 disks and total active surface area of 13.5m^2. This system was in operation continually and accounts for about 69% of the operating costs of the system.

An ozone system consisting of the following components was installed:

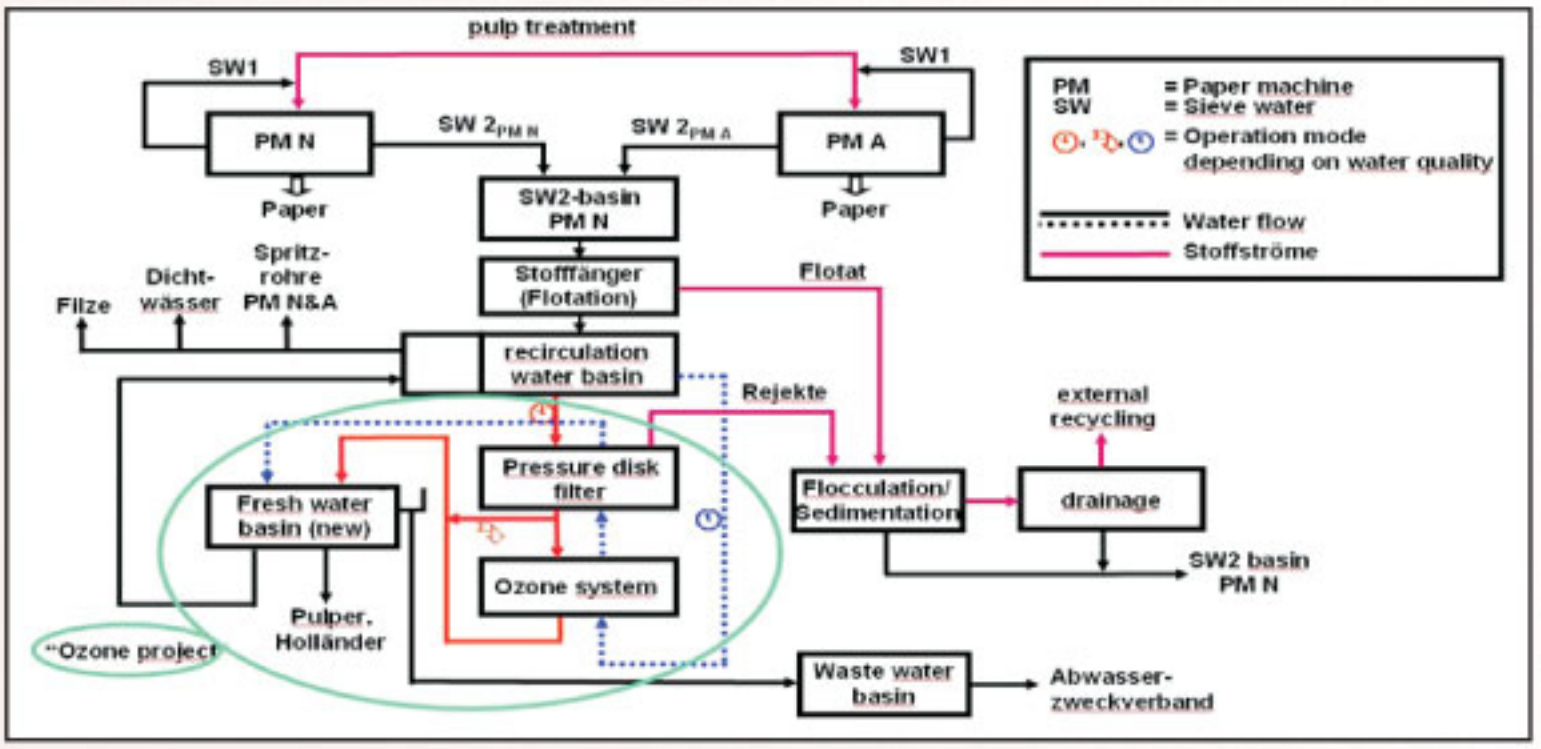


Figure 5: WATER TREATMENT FLOW SCHEME, WITH FILTRATION AND OZONE SYSTEM

- **Two (2) reaction tanks with volume of 4,5 m^3 each tank**
- **Ozone generation from oxygen**
- **Ozone injection by pump injection system**
- **Ozone production capacity: 3 kg Ozone/h**
- **Max. Ozone dose: 100 g Ozone/m^3 at flow rate 30 m^3/h**

The main purpose of the ozone treatment was colour removal and an average ozone dosage of 80g/$m^3$was used to obtain an extensive decolourisation of the waste water. The ozone system did not run continually and was only in operation when the effluent colour was out of specification. The operation of the ozone system then accounted for just 31% of the operating cost of the system.

Pressure disk filter

Ozone system

Figure 6 : OZONE SYSTEM WITH VARIED PARTS

The trial aided in results as below

- **Absorption of >90% of filterable substances**
- **Extensive decolourisation by ozone treatment (80 g Ozone/m^3 waste water)**
- **Water reuse for production purposes is then possible**
- **Considerable reduction of specific water consumption from 28 m^3 to 14 m^3 per ton of paper**
- **50% reduction of fresh water consumption**

As a result of the successful combination of filtration and ozone treatment, the fresh water consumption of the Mill could be reduced by 50% - which is equivalent to 60.000m^3/year.

CONCLUSIONS

It is proved Ozone is effective in treating pulp and paper mill effluents with multiple advantages and the costs can be optimized to affordable levels. Additional to the very successful results in decolouration, ozone brings further benefits like disinfection, improved BOD/COD-ratio, reduced AOX and reduction of odour.

Waste water or recycling water can be treated in an environmentally-friendly way without creating any secondary sludge or concentrates.

In addition to colour removal, ozone oxidation modifies COD into a more biodegradable form, and allows for the reduction in sludge production, it should be considered as a treatment step in front of bio filtration and DAF systems.

It is possible to operate the ozone system on a temporary basis, only using it when colour levels exceed discharge parameters. It is easy to start and stop the system without creating additional problems in the effluent treatment circuit.

Ozone, in combination with other technologies, especially different filtration technologies ranged from disc filters, DAF (dissolved air filtration), media filter, and even MBR will help the mills solve their site specific issues.

References

1. B Chakradhar& Sonia ShrivastavaIndian Journal of Chemical Technology, Vol. 11, (pg 617-621), (*Sept, 2004*)
2. Pradeep Kumar, Tjoon Tow Teng, Shri Chad, Kailas L.International Journal of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering,Vol:5,(No8), (pg 715-720),(2011)
3. A. Metais, Dr. I. Zhu, Dr. JC Hostachy. 7th International Colloquium on Eucalyptus Pulp, Brazil, (May 26-29 2015)
4. M Rosner International Sales Meeting(June 2001)