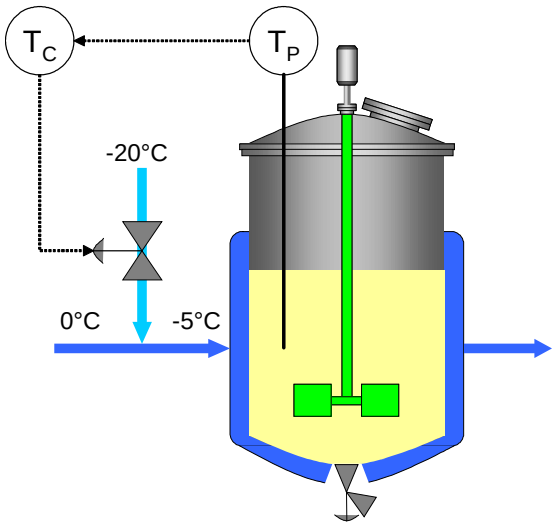
EUROPEAN COMMISSION

Integrated Pollution Prevention and Control

Reference Document on
Best Available Techniques for the Manufacture of

Organic Fine Chemicals

August 2006



4.3.7.4 Joint pretreatment of waste water streams by wet oxidation with O_2

Description

088I,X operates a waste water treatment platform offering the options of wet oxidation of concentrated waste water streams, biological treatment and wet oxidation of sludges (see Figure 4.68). Where necessary, solvents can be removed from individual waste water streams to enable wet oxidation. Blending enables a wide range of input and the wet oxidation runs autothermally in normal operation. The wet oxidation of waste water streams eliminates about 80 % of the COD load with the remaining COD load being highly biologically degradable (organic compounds with low molecular weight). The conversion of critical compounds (e.g. active ingredients) is very high (usually >99 %). Finally, all waste waters are treated in the biological WWTP. Heavy metals are separated after wet oxidation as metal oxides. Overall (wet oxidation and biological treatment), an average COD elimination of >99 % is achieved. The sludges from the biological treatment are also treated by wet oxidation, but under less drastic conditions (lower water content). The effluents from the wet oxidation of the sludges are fed back to the biology.

Table 4.63 gives selected examples for waste water streams pretreated by wet oxidation.

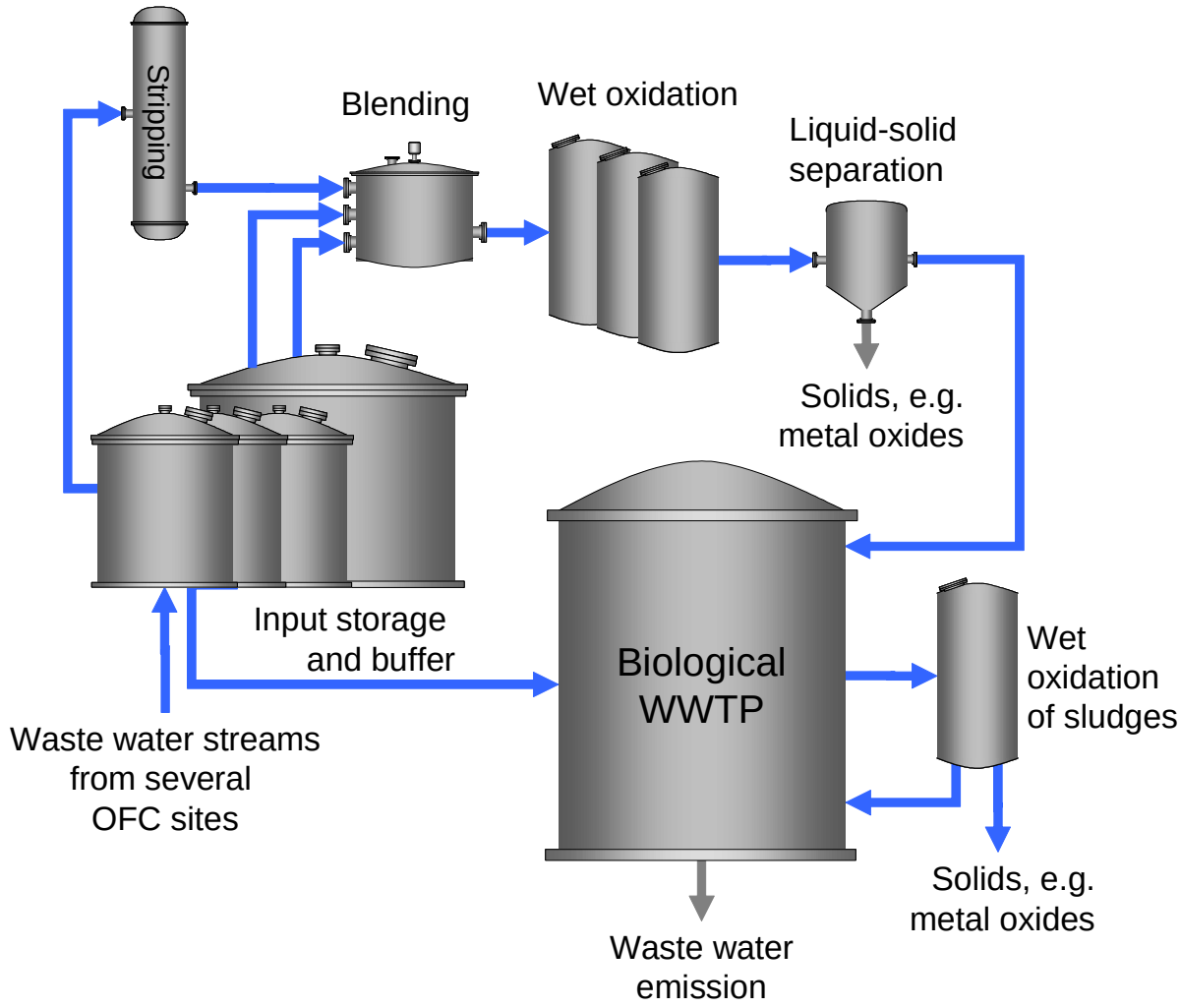


Figure 4.68: Joint pretreatment by wet oxidation with O_2

The main criteria when considering a waste water stream for wet oxidation are:

- the waste water stream contains active ingrdients from API or biocide/plant health product manufacture
- the waste water stream inhibits nitrification in the biological WWTP (inhibition is seen as problematic from 20 % on)
- the waste water stream contains poorly degradable organic load
- the waste water stream contains a high COD load. Independent of the biodegradability, high COD are more efficiently (and more cost effective) treated by wet oxidation
- the waste water stream contains heavy metals
- the waste water stream contains cyanides. Cyanides do not represent a problem since the wet oxidation is operated at pH 12 – 13.

Figure 4.69 shows examples of the assessment of waste water streams and the decisions made.

	Original sample	Wet oxidation	
		Before	After
	mg/l		
Yellow wash-waters from biocide production			
Nitrated and chlorinated benzo trifluorides	9700		<15
COD	23600	21991	3435
Chloride	7090	4727	4963
Solvents	470	470	470
Antibiotic production			
COD	70388	32214	3856
BOD_5		582	2642
BOD_5/COD		0.02	0.69
Kjeldahl N		39060	32970
Suspended solids		16160	4556
Solvents	284	209	199
Antibiotics production			
COD	1570	1486	191
BOD_5	580	549	162
BOD_5/COD	0.37	0.37	0.85
Solvents	52	48	18
API production			
COD	54000	25700	6000
TOC	30000	15000	830
BOD_5	2000	1000	150
BOD_5/COD	0.04	0.04	0.03
Cyanides	35000	17500	<1
Chlorides	85000	42500	42500
Nitrate	<1	<1	7500

Table 4.63: Examples and results for waste water streams treated by wet oxidation with O_2

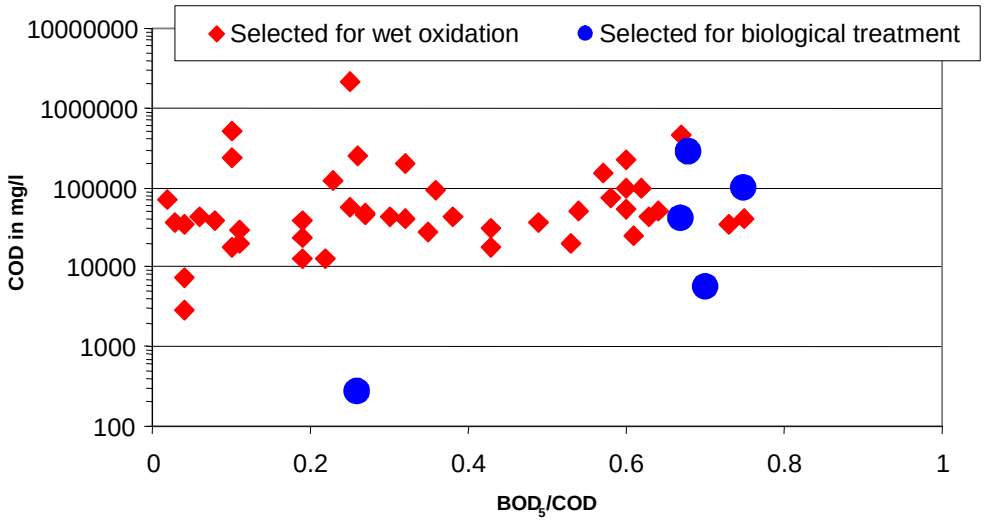


Figure 4.69: Results of the assessment of waste water streams from an external origin

Achieved environmental benefits

- highly efficient combination of pretreatment and biological treatment of waste water streams
- highly efficient elimination of active ingredients, poorly degradable organic loads, heavy metals, AOX and CHCs
- the sludge problem is solved as well.

Cross-media effects

- O_2 consumption
- chemicals for pH adjustment
- energy for pumping.

Operational data

Table 4.64 gives an overview to the operational data of the wet oxidation of waste water streams.

Applicability

The setup is very flexible and provides a pretreatment option for a wide range of waste water streams. The layout for the single unit is possible from 2 to 25 m^3/hour. The relatively high investment costs are better justified for larger multipurpose sites or as, in this example, joint pretreatment. The low treatment costs make wet oxidation with O_2 an attractive alternative to biological treatment of waste water streams containing high COD loads. No corrosion problems occur up to a salt content of 8.5 % w/w.

Other examples where wet oxidation with O_2 is applied or planned:

- *042A,I*: see Section 4.3.7.11
- *102X*: joint treatment platform in construction.

Wet oxidation with O_2			
Input criteria	COD	10000 – 150000 mg/l	Additionally, blending is possible
	Average input COD	40000 mg/l	
	Volatile organic compounds (solvents)	Up to 2000 mg/l	Stripping is offered as an option
	Chloride, bromide	Up to 85000 mg/l	Additionally, blending is possible
Process conditions	Mode	Continuous, autothermal	
	Throughput	18 m^3/hour	
	pH	12 – 13	
	Temperature	About 300 °C	
	Pressure	About 100 – 150 bar	
Stripped solvents	External disposal		
Off gas	Temperature	60 °C	
	Treatment	Scrubbing, thermal oxidation with energy recovery	
Output	Average COD removal	80 %	
	Average biodegradability	>95 %	

Table 4.64: Operational data for the wet oxidation with O_2 on the *088I,X* site

Economics

- high investment cost
- low operating costs
- wet oxidation: EUR 0.20 – 0.25/kg COD.

Driving force for implementation

Need for an efficient pretreatment in addition to biological treatment.

References to literature and example plants

[90, 3V Green Eagle, 2004], [91, Serr, 2004], [92, Collivignarelli, 1999], *088I,X*, *087I*