O$_3$ZOM*AX*

600 Robitaille

Granby, Quebec
Tel: 450--378-0611
Fax: 450-777-0264

FOOD EFFLEUNT TREATMENT CASE STUDY

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Prepared by:
Amir Salama P.Eng, M.Sc.

OZOMAX AOP STUDY

I-Objective

To remove suspended an dissolved COD from food effluent such as Eggs , proteins, cheese waste water effluent which contains high level of COD mainly biodegradable proteins to meet local regulations .
To achieve that objective we propose Ozomax patented AOP technology.

II-Waste Waters Technologies Overview

The technologies available to treat such high COD levels can be summarized as follows:

a- Mixing with domestic effluent (dilution) and then biologically treat the waste waters
b- Physical treatment where the water can be recycled by the use of membranes such as ultra-filtration or reverse osmosis or distillation if low cost energy is available such as geothermal or activated carbon treatment.
c- Physico-Chemical treatment which is the most widely spread for small and medium size installation which consist of coagulation , flocculation and clarification which can take place by DAF (diffused air flotation) or by Lamella clarifiers.
d- Ozone treatment followed by either biological or physico- chemical
e- Ozomax advanced oxidation process (AOP) using O3 in presence of low cost catalysts.

See below general description of the processes identified above

A-Biological treatment

Aerobic & anaerobic

Biotechnology encompasses a range of scientific and engineering techniques for applying biological systems to the manufacture or transformation of valuable materials or the elimination of problematic, often poisonous, liquid, solid or gaseous wastes. Several waste treatment systems based upon aerobic and anaerobic bacterial action have been developed to treat heavily contaminated water such as Food industry, Pulp & paper & textile industry waste water.
The different methods of Biological treatment can be described briefly below

1-BAF systems (biological aerated filters, or biofilters) comprise a submerged packed bed with fixed biofilm which is continually aerated. The reactor must be periodically backwashed to remove excess biomass and trapped solids. BAF systems occupy less space than activated sludge processes (ASP) and treat greater loads of BOD (up to 8 kg/m3 BOD per day, compared with 0.6 kg/m3 BOD per day for ASP and 0.4 kg/m3 BOD per day for trickling filters).

2- RBC biofilm in Rotating Biological Contactors (RBC) is formed on a series of discs which rotate at right angles to an incoming flow of sewage. Excess microbial growth is removed by a combination of predation and mechanical action in a similar manner to the trickling filter. In submerged systems 75–90% of the disc area is immersed, compared with around 40% in an RBC.

3- CSTR continuous stirred tank reactor (CSTR) is similar to that of the ASP. However, anaerobic bacteria are more difficult to precipitate than aerobic activated sludge. In addition, the generation of methane gas produces a flotation effect. Settlement may be aided by degassing followed by a filtration step or clarification through inclined plates. Typical retention times are between two and five days.

4- Uflow sludge blanket system uses granular sludge taken from existing plants to form a flocculated sludge blanket through which waste water flows.

5- Expanded bed reactor, completely mixed reactors and biofilm reactors may be combined into a system in which biofilm-covered particles are mixed by gaseous treatments and effluent recycle processing. Completely mixed systems (fluidised beds), or less vigorously mixed assemblies (expanded beds), are available.

Biological Treatment costs (case studies)

											Operating costs
	COD in ppm	% D	Flow rate M3 per day	**Cost of Capital/M3 US $**	Power Required Kwatt	Cost of Energy $/kg COD $0.08/kwh	Sp. parts + Maintenance $/kg COD per day	SPACE required m3	Chemicals per M3	Total cost per KG COD	Total cost per M3 US $
Biological											
Biodegradable COD Only											
Extended Aeration domestic (1)	250	75	5000	**260 $**	350	0,72 $	0,385 $	V. large	0,01 $	1,14 $	0,29 $
Extended Aeration domestic (2)	250	90	400	**425 $**	50	1,07 $	0,525 $	V.large	0,01 $	1,63 $	0,41 $
Extended Aeration domestic (3)	250	90	50	**1 400 $**	8	1,37 $	1,728 $	V.large	0,01 $	3,13 $	0,78 $
Extended Aeration OXYDO (4) ssteel	250	70	90	**1 700 $**	4	0,49 $	2,698 $	110	0,01 $	3,23 $	0,81 $
Extended Aerattion OXYDO(5)st-steel	250	80	90	**1 900 $**	4	0,43 $	2,639 $	140	0,01 $	3,11 $	0,78 $
Extended Aeration OXYDO (6)st-steel	250	90	90	**2 200 $**	4	0,38 $	2,716 $	190	0,01 $	3,14 $	0,78 $
Extended Aeration OXYDO (7) painted steel	300	90	90	**1 100 $**	3	0,24 $	1,132 $	140	0,01 $	1,40 $	0,42 $
Up Flow Blanket Aeration Stream painted st	300	90	90	**1 000 $**	3	0,24 $	1,029 $	265	0,01 $	1,30 $	0,39 $
SBR (sequential Batch Reactor)	250	90	110	**1 100 $**	21	1,63 $	1,358 $	Large	0,01 $	3,03 $	0,76 $
Anaerobic septic tank concentrate	18000	45	4	**15 000 $**	0,1	0,01 $	0,772 $	Large	0,01 $	0,78 $	14,01 $

B- Physical Treatment

<u>Ultrafiltration & Reverse Osmosis</u>

The ultrafiltration & R.O membrane flux (volume of permeate produced per unit membrane area per unit time) is mainly dependent on the initial COD concentration, the concentration factor needed for size reuse, temperature, degree of membrane fouling, pressure and reject flow rate.

Ultrafiltration is a low pressure membrane filtration process used for separating macro-molecules and suspended solids from water .
A semi-permeable microporous membrane performs the separation. Water and low molecular weight solutes pass through the membrane and are removed as permeate. The feed stream flows parallel to the membrane surface. This cross-flow characteristic differs from the perpendicular flow of ordinary filtration. For ordinary filtration, a filter cake builds up on the filter surface, resulting in frequent filter replacement or cleaning. In ultrafiltration, the cross flow conditions prevent filter cake build up and high filtration rates or fluxes can be maintained continuously.
Various polymeric materials are used for membrane preparation : cellulose acetate, polyamide, polysulphone and zirconium oxide .

TABLE .1
COMMERCIAL ULTRAFILTRATION MEMBRANES

Manufacturer	Membrane Type	Module Configurations	pH Range	Temperature Range (°C)
A	Cellulosic	Tubular/	3 - 9	60
B	Non-cellulosic	Spiral	2 -13	90
C	Dynamic	Tubular	3 - 10	100
D	Non-cellulosic	Plate & Frame	3 - 11	60
E	Cellulosic	Plate & Frame	3 - 8	50
F	Non-cellulosic	Tubular	3 - 12	70
G	Cellulosic	Linear Thin	3 - 8	30
H	Non-cellulosic	Channel	3 - 12	70
I	Non-cellulosic	Hollow Fibre	3 - 11	60
			2 -13	75

TABLE 2
RANGE OF ULTRAFILTRATION MEMBRANES

Nominal Molecular Weight Cut-off	Apparent Pore Diameter (A)	Water Flux* (M/m2h)	Temperature Range °C	pH Range
500	21	9	60	3,0 - 11,0
2 5000	24	15	45	1,5 - 9,0
5 000	30	68	75	1,5 - 13,0
10 000	38	60	75	1,5 - 13,0
30 000	47	920	75	1,5 - 13,0
50 000	-	-	75	1,5 - 13,0
50 000	66	305	50	1,5 - 13,0
80 000	-	-	50	1,5 - 13,0
100 000	110	1 000	60	3,0 - 11,0
300 000	180	600	60	3,0 - 11,0

*Flux at 367 kPa

Ultrafiltration Module Types

The membranes are assembled into several different module types:

- tubular
- plate and frame
- spiral
- hollow fibre

Typical ultrafiltration flux rates are in the range 10 - 200 litres of product per m2 of membrane area per hour (M/m2h) and this is about 1/200th of that in normal barrier filtration. Thus membranes must be packed into a small volume leaving little space for a flow channel and no room for a filter cake. Hence UF modules are operated in the cross-flow mode with two outlet streams: the product (permeate) and the concentrate (reject).

ULTRAFILTRATION COSTS

TABLE 3

COSTING OF ULTRAFILTRATION PLANT OF 405 m2 MEMBRANE AREA FOR DESIZING EFFLUENT DUTY (200 M3/day) at 5000 PPM of COD

Membranes	**$ US**
Module Housings	108 000
Tanks	50 000
Pumps	62 000
Valves	12 500
Pipework	12 500
Prefiltration	30 000
Process Control	15 000
Electrical	8 000
Consumption	15 000
Engineering	30 000
Contingency	35 000
TOTAL	**460 000**

Ultra filtration is an economic solution if the concentrate can be used but if not possible to re-use the concentrate then this will represent a problem as the operating cost will increase and payback will be no longer there.

C- Physico -Chemical

Coagulation , Electro-coagulation and Flocculation

The coagulants removes any S.Solids from the effluent, lowers the pH and reduces chemical oxygen demand. The suspended solids settle rapidly at the primary settlement stage at the sewage works, producing clear water but could not remove dissolved COD. The cost of coagulants & flocculents will be economically prohibitive for high COD levels.

On the other hand Electro-Coagulation (EC) s are used for removing dissolved and suspended particles from waste-water streams without or minimal use of chemicals. EC units utilise a process of passing a controlled electric current through a water stream to cause destabilisation of particles to form a stable precipitate, which is then removed.

The EC systems provide an efficient means of non-chemical water treatment that allows waste-water streams to be reduced in volume by reuse and recycling, and/or a reduction in discharge waste-water and sludge volumes, along with a reduction in the associated costs.

Operating Principles

The EC technology is based on the principle of passing an electric current through water causing destabilisation of most suspended particles, including metals, hydrocarbons and organic compounds.

Once destabilised, oppositely charged ions and particles attract (or coagulate), forming a precipitate which is highly stable. The precipitate is then separated from the clarified water via a number of secondary separation techniques such DAF (diffused air flotation or clarifiers and sometime screen & drum filtrations.

The problem arises with EC with water with low conductivity and with dissolved organics which will not break down easily to form the charged ions to form a precipitate. In that case all the energy goes into heating the waste water rather then breaking down the organics.

D- Ozone treatment

Ozone (O3) is an allotrope of oxygen (O2). It is 1.5 times as dense as oxygen and 12.5 times more soluble in water and leaves no residuals or byproducts except oxygen and a minimal amount of carbon dioxide and water. Ozone is thought to decompose accordingly (Miller 1978, 167-168):

O3 + H2O - HO3 + OH-

OZONE + WATER - HYDROGEN TRIOXIDE + HYDROXIDE

HO3+ + OH - 2HO2

HYDROGEN TRIOXIDE + HYDROXIDE - HYDROGEN DIOXIDE

O3 + HO2 - HO + 202

OZONE + HYDROGEN - HYDROXIDE + OXYGEN

HO + H02 - H2O + O2

HYDROXIDE + HYDROGEN DIOXIDE - WATER + OXYGEN

The free radicals (H02 and HO) react with a variety of impurities such as metal salts, organic matter including microorganisms, hydrogen and hydroxide ions. They are more potent germicides than hypochlorite acid by factors of 10 to 100 fold and disinfect 3125 times faster than chlorine Experimental evidence indicates gram-negative bacteria to be on the order of 10-fold more susceptible than viruses to ozone .

Oxidation involves the introduction of oxygen into the organic molecule, with or without degradation of the organic compound. At the last stage of the oxidation reaction of organic compounds with oxidants, involve the production of carbon dioxide and water .

There are many variables to consider when applying ozone to the industrial process. There are a variety of contaminants which can enter a waste stream at any given point in time.

(see article about O3 oxidation capabilities Amir Salama at www.Ozomax.com).

E- Ozomax AOP Technology

The chemistry involved in free-radical water treatment processes (AOPs) is sufficiently complex that true optimisation of the processes is often difficult without the use of kinetic models or by performing feasibility studies.

This technology combines Ozonation & electro-oxidation in the presence of catalyst freshly produced at the electrodes (see Ozomax patent # **6,315,887 B1)** to break down partially the dissolved organic to form charged radicals & ions to render it insoluble when reacted with the catalyst. This breaking down of the molecules happens at quasi super critical conditions .
The process utilises dissolved elemental oxygen at moderate temperatures up to 60C and pressures to 1-2 atm. The extremely high levels of catalytic activity is comparable to those required for related methods such as supercritical water oxidation and wet air oxidation .

The Ozomax AOP process can achieve either total separation/precipitation of dissolved organics or achieve complete mineralisation even for chlorocarbon, aromatic, phenolic, and a dye, at reasonably low reactor operating temperatures and energy demands.

This promising technology has many applications such as:

- Removal of heavy metals
- Removal of suspended and colloidal solids
- Breaking oil/water emulsions
- Removing fats, oils and greases
- Removing complex organics
- Destroying bacteria, viruses and cysts
- Reducing BOD, phosphates and nitrogen levels

These applications have specific industries in which they are able to be applied:

- Ground Water Clean-up
- Process Rinse & Wash Water
- Portable water treatment
- Sewage effluent treatment
- Cooling Towers
- Pre-treatment for Membrane Filtration
- Abattoirs , Egg & Meat Processing & Rendering
- Automotive manufacturing & machining
- Food Processing
- Laundries
- Pulp & Paper processing
- Textile manufacturing
- Oil & Gas Refining & Petrochemical emulsion treatment

<u>Benefits and Features</u>

AOP offers distinct process benefits over chemical coagulation including the following:

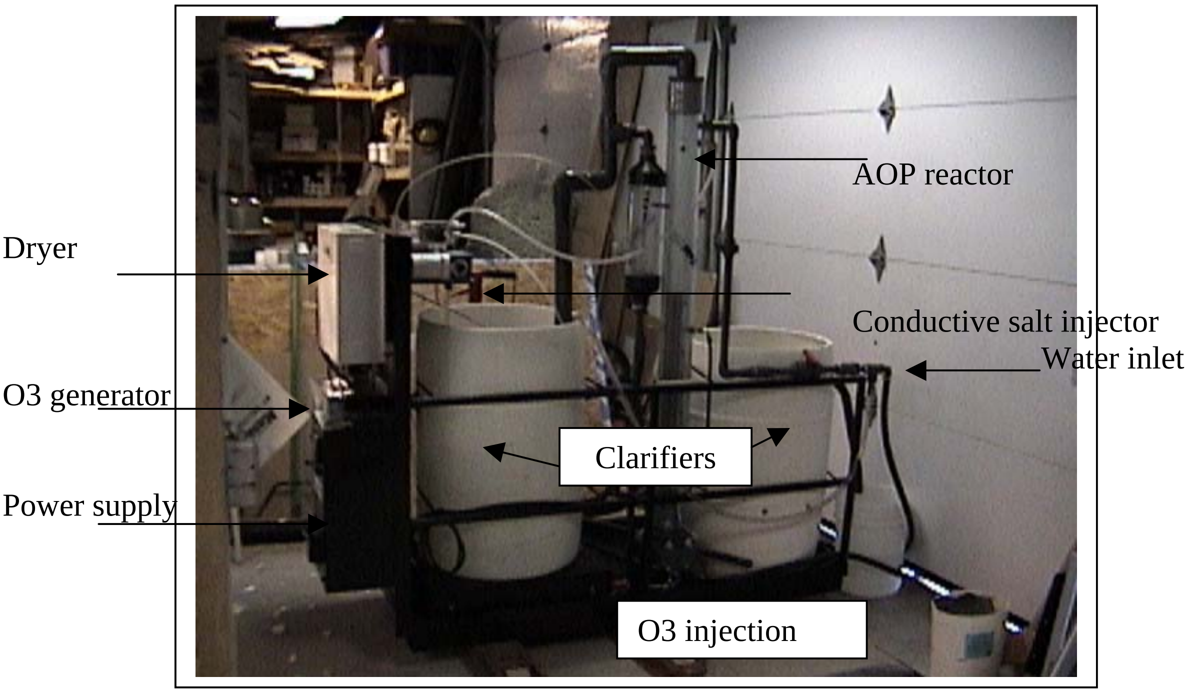
- Cost savings: often the return on capital investment is <12 months.
- Clarified water is usually of high quality, which may allow it to be re-cycled and/or re-used.
- It helps meet EPA and council compliance standards, and/or further reduce discharge fees.
- Smaller volumes of sludge are produced, which are more shear resistant and easily dewatered. This is in contrast to chemically coagulated sludge, which generally have a high bound water content and larger volume.
- The Sludge produced generally passes the US EPA's guidelines for Toxic Characteristic Leaching Protocol (TCLP). This is in contrast to chemically coagulated sludges which are generally unstable metal hydroxides that are classified as hazardous and must be disposed of in secure land-fills.
- The operating costs are significantly less than most standard treatment methods.
- The system requires very little maintenance, supervision or floor space.

is sometimes conducted to determine whether or not Electro-Coagulation best suits the specific requirements of the application, and to optimise operating parameters.

<u>III- TYPICAL CASE STUDY RESULTS</u>

Initial test results in the lab showed a reduction of about 95% . (see test results in Table III- 1)
First test achieved a reduction from 8500 PPM to 550 PPM COD in about 5 minutes of retention in an AOP reactor of 4 liters in capacity followed by clarification.
Subsequent experiments with different initial COD levels showed that 95% reduction or more can be achieved by going to several steps of AOP & solids separation (clarification).
Tests performed are summarized below in table III-1

<u>Pilot Line description</u>



<u>AOP SKID MOUNTED UNIT FOR ORGANIC OXIDATION BY OZONE</u>

Tests matrix

Variables:

1- Waste effluent flow rate
2- Conductive catalytic salt concentration
3- PH exiting AOP reactor which affects floculation
4- O3 dosage gr/hr
5- Power input for the electro-catalytic

Tests Results

TABLE III-1

Run #	**COD in**	**COD out PPM**	**Continuous**	**Batch**	**Catalyst in reactor**
1 (Lab)	8 500	550		4 liters in 5 min	None
Pilot test	6400	1100	0.1 gpm		None
Pilot test	20 000	3 200	0.2 gpm		None
Pilot test	20 000	2640	0.2 gpm		None
Pilot test	20 000	1920	0.2 gpm		0.2 g/l Al3
Pilot test	20 000	1250	0.2 gpm		0.4 g/l Al3
Pilot test	20 000	2 558		10 liters in 15 min	0.4 g/l Al3
(Batch Ozomax)	20 000	11 200		7 liters in 5 min	P-700
(BatchOzomax)	20 000	13 700		7 liters in 10 min	P-700
(Batch Ozomax)	12000	1100		7 liters in 10 min	None

Conclusions

1- This waste water respond well to the AOP treatment but require some fine tuning
2- 95% COD reduction can be achieved to produce clear water which can be either recycled or disposed off
3- Two types of by-products will be produced solids which can be easily filtered using drum or screen filters and a foamy product which contains small suspended solids and other liquid proteins.
4- The system can operate in a continuous or batch modes

Written by :

Amir Salama P.Eng, M.Sc.A

Ozomax inc.

R&D Director