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Improving Water Management Efficiency at Industries with Organic Load

WaterReuse Project

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Murcia, May 14th, 2015











Life+ WaterReuse Project

WaterReuse is a project funded by the LIFE Program which is the EU's financial instrument to support environment and climate actions.

From 01/10/2013 to 30/09/2015

Beneficiaries:

Coordinator: Destilerías Muñoz Gálvez, S.A. Associated: Centro Tecnológico Nacional de la Conserva y la Alimentación

Total Project Budget: € 1.688.437.-EU Financial Contribution: € 844.218.-









Project Objectives

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✓ To Develop, Validate and Disseminate a sustainable system for the Re-use of process water from industries with high or refractory organic loads.

✓ To **Recycle** up to a 95% of effluent water.

- ✓ To eliminate TSS (Total Suspended Solids) and reduce COD (Chemical Oxygen Demand) down to parameters suitable for water Re-use.
- To minimize Carbon Footprint by applying computerized optimization systems, renewable energy from solar panels.
- ✓ To avoid the usage of chemicals, organic nutrients and production of sludge.

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Applied Technologies

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 ✓ Ultra and Nano membrane filtration

 Electrochemical Oxidation

✓ Photocatalysis





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Characterization of Effluents

✓ A complete characterization has been carried out.

Industrial Wastewater Sector	COD (ppm)	BOD (ppm)	TOC (ppm)	TSS (ppm)	FOG (ppm)	рН	Electrical Conductivit y (mS/cm)	Microbiology	HPLC- MS GC- MS Pesticides (ppm)	Heavy Metals (ppm)	Ecotoxicology (Equitox /m ³)
Dairy	10500- 28778	20145	3472	3100	1.2	3.42	5-20	Not found	<loq< th=""><th>Not found</th><th>10.57</th></loq<>	Not found	10.57
Candies	45600- 61400	22000- 23500	12100 - 23102	1840 - 22880		3.52- 10.93	1.41-3.25	Enterococos Escherichia coli.	<l0q< th=""><th>Not found</th><th>5.1</th></l0q<>	Not found	5.1
Pickles	9692- 37300	4650- 21500	4576- 6485	480- 2190	26-66	3.76- 4.02	27.70-72.90	Clostridium perfringens	Present	Zn: 1.41- 4.21	10.77
Olive Oil	29416- 22900	14800	86795 - 69150	550- 6475	2-93	4.70	2.49	Escherichia coli 100-65,000 (cfu/100ml)	<loq< th=""><th>Not found</th><th></th></loq<>	Not found	
Fine Chemical	77500- 10700	1000- 25000	2179- 27999	<10- 98	<1-12	3.37- 8.22	1.31-14.68	Not found	<loq< th=""><th>Not found</th><th>8.1</th></loq<>	Not found	8.1

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Ultra and Nanofiltration Treatment

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- ✓ UF and NF have been operated at constant flow rate.
- ✓ Permeate flow rate is a direct linear function of Trans Membrane Pressure (TMP).
- ✓ Permeate flow rate increases rapidly with temperature.



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Photochemical Treatment

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- ✓ The kinetic and space velocity of the photochemical reaction is very low, making impossible to couple with others at Prototype's.
- ✓ System has been only used with supported catalyst and, in some cases, bubbling compressed air but no oxidizing agents have been further added (i.e. water peroxide, persulfate).
- ✓ Largest decrease in achieved COD was 600 ppm, after a long period of treatment.
- ✓ Some mechanical problems have also been found at the catalysts supporting cloth due to movements produced by liquid flow.





Electrochemical Treatment (1)

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- ✓ Electrochemical operation under Galvanostatic control.
- ✓ Current Density applied up to 1.000 A/m².
- ✓ COD decline follows a linear trend under charge control, changing to exponential under mass transport control:

Charge Control:

 $COD = COD_0(1 - at)$ Mass Transport Control $COD_t = \alpha COD_0 \exp\left(-at + \frac{1 - \alpha}{\alpha}\right)$







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Electrochemical Treatment (2)

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- ✓ pH initially decreases due to the production of organic acids. At the end of the process acids disappear due to complete mineralization. Organic acids have been identified and measured by GC and GC-MS.
- ✓ Intermediate oxidized species explain the decrease in the COD/TOC relationship.



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Electrochemical Treatment (3)

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- ✓ Electrode Reactions taking place:
 - Reduction at the cathode:
 - Oxidation at the anode:

 $2H^{+} + 2e^{-} \rightarrow H_{2}$ $Cat + H_{2}O \rightarrow Cat(OH \cdot) + H^{+} + e^{-}$ $Cat(OH \cdot) \rightarrow Cat + (OH \cdot)$ (reacting with organic)



Proposed Reaction Pathway:







COD reduction by Membrane and Electrochemical treatments

Industrial Wastewater Sector	Initial COD (ppm)	Final COD (ppm)	Reduction % COD	Permeate membranes COD (ppm)	Membranes COD (kWh/kg)	AH/m ³	H ₂ (kg/m ³)	Electro- chemical (kWh/kg COD)	Consumo energético total (kWh/kg COD)
Candies	43119	20	99.95%	14949	0.98	93600	2.30	52.82	53.79
Pickling (1)	17100	402	97.65%	13900	8.59	55800	1.80	38.31	46.90
Pickling (2)	14200	135	99.05%	12000	12.50	41842	2.35	27.75	40.25
Olive Oil (1)	22900	0	100.00%	9500	2.05	55544	1.80	73.01	75.07
Olive Oil (2)	13200	574	95.65%	4390	3.12	24650	0.80	39.99	43.11
Fine Chemical (1)	54100	21	99.96%	28200	3.25	23250	1.00	29.72	32.97
Fine Chemical (2)	42600	50	99.88%	29300	4.32	37200	2.60	23.03	27.36
Fine Chemical (5)	61200	1.2	100.00%	45600	4.56	132173	3.32	37.80	42.36
Fine Chemical (7)	23200	311	98.66%	15800	8.74	48298	1.41	35.64	44.38
Fine Chemical (12)	10700	255	97.62%	N/A	N/A	46508	1.68	42.81	42.81

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Energetic Considerations



- ✓ Optimization of operational parameters can lead to an estimated reduction of 25% of the above figures.
- ✓ Hydrogen production as by-product has been estimated within the range 0.8-4.9 kg Hydrogen/m³, which helps to reduce energy requirements.

✓ Complete treatment of wastewater demands from 27 to 75 kWh/kg COD, with minimum reduction of 95%.









Optimization strategies to decrease operational costs

Membrane Treatment:

Increase in Temperature and TMP, lead to larger permeate rate increasing efficiency. TMP is also a compromise between production rate and membrane fouling. Operation at 50°C instead of 20°C can double permeate rate (depending on wastewater nature).

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Electrochemical Treatment:

- Increase in Temperature, and Electrolyte conductivity lead to lower energy use.
 Applied Current Density is a compromise between energy costs and treatment rate.
- > Control of the Applied Current Density to avoid operation above the limiting current.

Photochemical treatment:

➤ Use of bubbled air keeps dissolved oxygen at saturation level.







Optimization of Electrochemical treatment

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✓ A reduction of up to 37% can be achieved by operating at higher temperatures, depending on the applied Current Density.





✓ A reduction of 12% can be achieved by increasing electrolyte conductivity.











Carbon Footprint and Renewable energy



✓ Solar panels feed prototype with renewable energy during daylight.

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- ✓ Grid Energy has been contracted with a certified supplier of renewable energy.
- ✓ The PLC/SCADA control system has been programed with a logic function which operates over a PID control. It modifies procedures in order to link renewable energy production with prototype's necessities leading to neutral Carbon Footprint.



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Conclusions

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- ✓ WaterReuse is especially suited to treat difficult wastewaters containing high concentrations of toxic or refractory chemicals.
- ✓ Complete COD, BOD, Eco-toxicity and TSS elimination.
- ✓ It can operate, even more efficiently, with high conductivity wastewaters.
- ✓ Fully-automated operation, with instantaneous start-up and shut-down.
- ✓ Modular construction and easy scale-up, very small footprint.
- ✓ Reduced carbon footprint due to the use of renewable energy photovoltaic cells. Hydrogen production as by-product which can be used for energy recovery.
- ✓ No use of chemicals or additives.
- ✓ No generation of sludge or waste at treatment. Concentrated organics from UF/NF membranes to be reused.







WaterReuse Contact : http://www.waterreuse.eu/

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