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Advanced Oxidation Wastewater Treatment of 3 LPS of an Avocado Sauce Company, at Morelia, Michoacan, Mexico

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Abstract: This paper describes the wastewater treatment of 3 liters per second of capacity of discharges of capacity, from the avocado washed, as well as the production of avocado sauce. Effluents were pretreated with a grease and oil trap and contained small amounts of oil and grease, dissolved and total solids, organic matter and trace of organic and inorganic compounds from the vitamins and minerals of avocado. The treatment train is located in an small surface and the train is integrated with coagulation in line with alumina in a static mixer, rapid filtration in two steps, double advanced oxidation with ozone and heterocyclic photocatalysis with a nanofilm of zinc oxide as, photocatalyzer_and final adsorption of refractory compounds with activated charcoal. The treated wastewater meets the environmental regulation to urban sewerage discharges of the city, according to the results of a Mexican Certified Laboratory.

Key words: Wastewater primary treatment, rapid filter performance, static mixer.

1. Introduction

Congeladora y Empacadora Nacional is an Avocado Sauce industry located in Morelia, Michoacan, Mexico that generates wastewater from the washing of the avocado raw material as well as containers which transport internally the material, the surface where the avocado sauce was prepared and the tools were used in these operations. The wastewater comes from intermittent operations with an average volume of 2 L/s and is discharged to the urban sewerage system of the city, the plant was designed for 3 L/s.

Wastewater contains oil and grease, dissolved and total solids, organic matter and traces of organic and inorganic compounds from the vitamin and minerals of avocado. There are not agrochemicals neither pesticide in the wastewater.

The factory treated wastewater removing floating materials with one screen and oil and grease with a trap to meet the NOM-002.SEMARNAT-1996, standard that is applied to city sewerage systems discharges.

The industry must comply with the rule NOM-002-SEMARNAT-1996, to discharge to city sewers or municipal drainage.

From the analysis of laboratory discharges values:

- No metals exceed limits.
- BOD (Biochemical Oxygen Demand), exceeds 16 times the limit.
- Oil and grease exceeds 8.15 times limit.
- Total suspend solid exceeds 16 times limit.
- Fecal coliform are present.

Discharges have the following characteristics:

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- Are intermittent as function of personnel meal schedule (breakfast, lunch and dinner), where personnel attend the restaurant of the company, as well as from changes in process.
- Have a wide range of oxidized organic and inorganic matter concentration between 100-8,000 mg/L of Chemical Oxygen demand (COD) as function of work shifts and operations and unit processes developed.
- Have a solid floating material with a low sedimentation rate.

2. Material and Methods

For the design of treatment train, we measured turbidity as less than 15 Nephelometric Turbidity Units (NTU) and TDS (Total Dissolved Solid) as 391 mg/L and the ORP (Oxide-Reduction Potential) -38.7 mV, it indicates the nature of the water as oxidant or reducer, and assumed that the wastewater:

(1) Has a low suspended total material, since turbidity was less than 15 NTU and according to Crittenden et al. [1], with turbidity values less than 100 NTU, the suspended solids (in mg/L) have been shown to be approximately equal to the turbidity,

(2) Has a low redactor power,

(3) The organic content as BOD_5 (Five-Day Biochemical Oxygen Demand) and TDS could be eliminated through advanced oxidation after suspended and dissolved solids are removed.

In addition, the Company only has a surface available for the WTP (Wastewater Treatment Plant) of 42 m^2 and is located in the southeast, (Figs. 1 and 2) which is the final discharge point to city sewer, close to washing area of containers and boxes, one of the main generators of wastewaters, with coordinates N: 19°41′49.0″ and O: 101°124′42.7″.

In order to reduce oil and grease discharges, the Company installs a successful floating solid screening tower and a three-chamber oil and grease trap, to reduce the oil and grease discharges as a first step for regulation comply.

From the discharge characteristics and surface available for the WTP, the Company explores a process that could produce a wastewater treatment, with potential to reuse internally in work yard surface cleaning, and restroom flushing at minimum.

The technology selected is based on advanced oxidation, where the oxidants ozone and hydroxyl radical are generated in situ, after the screening of floatable solids and reduce the oil and grease with a three-stage trap.

The process requires a small area, and a minimum of consumables, without generation of biological sludge.

The plant proposed is a train integrated with:

- Trituration of Total Suspended Solids (TDS) presents in the wastewater.
- Primary treatment: coagulation in line with alum to remove colloidal solids.
- Rapid filtration in two steps with silica sand and anthracite to remove coagulated and suspended solids.

➢ Secondary treatment: Double advanced oxidation; with 30 g/h of ozone to reduce turbidity and starting oxidation and OH (Hydroxyl Radical) generated by heterogeneous photo catalysis by radiation with Ultraviolet-C (UVC) on a 12 inches stainless steel US 100 mesh covered with a thin film of zinc oxide to finish the oxidation process, where UVC radiation also contributes to photolysis.

➢ Tertiary treatment: clarification with activated carbon.

➢ Disinfection with 1.5 ppm chlorine at the final discharge to avoid biological pollution after the treatment.

➢ Two containers of 5 m^3 for wastewater and wastewater treated.

➢ A room with cabinets of power and control

The WTP will operate with energy from an electrical substation of 440 kV, transformed to 110 V and 220 V with a dry transformer of 75 kV to operate elements with 2 and 3 phases of 220 V and mono phase elements of 110 V, plus illumination.

The WTP consumes a maximum of 150 A, and less of 60 kWh. Configuration of WTP is shown in Fig. 2.

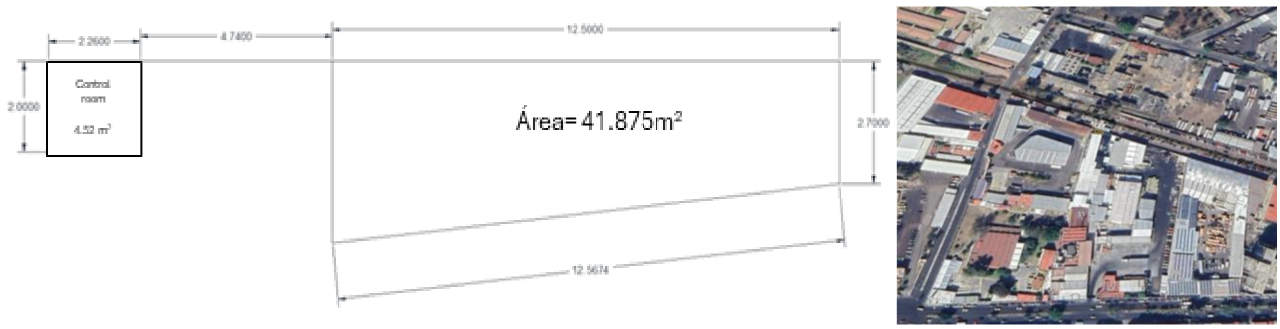

Fig. 1 Available area to WTP.

Fig. 2 Wastewater Treatment Plant.

Coagulation is a chemical process to remove colloidal solids involving many reactions and mass transfer in three separate and sequential steps. Coagulation formation, particle destabilization, and interparticle collisions, occur during and immediately after introducing small highly charged molecules or electrolyte dispersed in rapid mixing where interparticle collision causes aggregate (floc) formation, in this process we use aluminum sulfate as coagulant. $Al_2(SO_4)_3 \cdot 14H_2O$ reacts instantaneously when mixed with the wastewater with a rapid mixing at an static mixer, using the energy of the trituration pump to create aluminum hydrolysis products that cause filterable coagulation species (Fig. 3).

Rapid filtration is enhanced when the wastewater coagulated passed through two sequential filters, a fist one with gravel and silica sand, to remove particles between 100-2,000 μm and the second with gravel and anthracite to remove 5 μm particles. We made jar test in order to obtain the optimum amount of alum as coagulant.

The advanced oxidation is based on the hydroxyl radical $OH^{\bullet}$, the superoxide anion O_2^-, and hydrogen peroxide H_2O_2, oxidants that have an ORP, higher than conventional oxidants as show in Table 1.

The $OH^{\bullet}$ oxidant is generated in situ from ozone in presence of water, according to the following reactions:

$$O_3 + H_2O \rightarrow O_2 + 2(OH^{\bullet}) \quad (1)$$

$$O_3 + H_2O \rightarrow OH^- + 2(OH^{\bullet}) \quad (2)$$

Fig. 3 Static mixer.

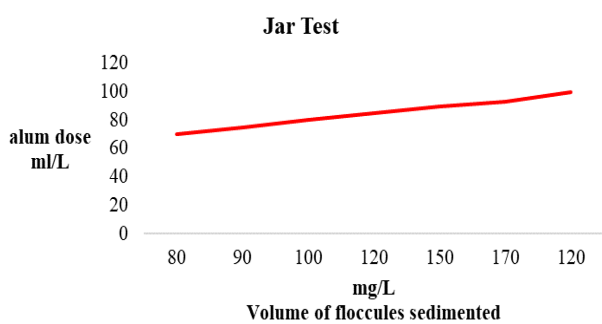

Fig. 4 Optimum amount of alum as coagulant.

Table 1 ORP of advanced and conventional oxidants [2, 3].

Oxidant	ORP (mV)
Fluorine	3.06
$OH^{\bullet}$	2.8
O_2^-	2.42
O_3	2.08
H_2O_2	1.78
$KMnO_4$	1.70
ClO_2	1.57
Cl_2	1.36
O_2	1.23

Ozone produces 1 mole OH/1.5 mole O_3 [4].

According to the first law of photochemistry, the quantum of radiation light absorbed as a primary process, excites electrons from a lower orbit to a higher one, and may cause a chemical reaction as secondary process [5].

The energy E is measuring with the Stark-Einstein law, and for one mole, the energy is generated by 6.02×10^{23} photons or one Einstein.

$$E = \frac{Nhc}{\lambda}$$

where:

N = Avogadro constant = 6.02×10^{23} photons/mol;

h = Planck's constant = 6.626×10^{-34} J s;

c = light velocity = 3.0×10^{8} m/s;

λ = wavelength of light = (254 nm in our case).

In addition, ozone irradiated with UV also generates $OH^{\bullet}$ and H_2O_2, Payton and Glaze cited by Legrini et al. prove that hydrogen peroxide is the primary product of ozone photolysis.

In this study, we used photocatalysis with a ZnO (Zinc Oxide) SC (Semiconductor), that only absorbed radiations lower than 400 nm, and we exposed to 254 nm UVC radiation to liberate a free electron e^- that leaves a hole with a positive charge, since it was in equilibrium, as shown in Equation 3.

$$\mathrm{UVC + SC \rightarrow SCh + e^-} \quad (3)$$

h^+ and e^-, created by UV radiation, have oxidative properties and reduction power, h^+ in presence of water promotes the generation of other oxygenated reactive species [6].

Free electron exposed to radiation, moves from the valence orbital to a conduction orbital and translates to a final electron acceptor such as dissolved oxygen in water to avoid reversible reaction, according to next reactions:

$$\mathrm{hv + (SC) \rightarrow e^- + h^+} \quad (4)$$

$$\mathrm{h^+ + H_2O \rightarrow OH^{\bullet} + H^+} \quad (5)$$

$$\mathrm{e^- + O_2 \rightarrow {O_2}^{-\bullet}} \quad (6)$$

$$\mathrm{{O_2}^{-\bullet} + H^+ \rightarrow HO_2^{\bullet}} \quad (7)$$

$$\mathrm{HO_2^{\bullet} + H^+ + e^- \rightarrow H_2O_2} \quad (8)$$

The photocatalytic effect generates:

(a) Oxidation reaction

$$\mathrm{h^- + H_2O \rightarrow H^+ + OH^{\bullet}} \quad (9)$$

$$\mathrm{2h^+ + 2H_2O \rightarrow 2H^+ + H_2O_2} \quad (10)$$

$$\mathrm{H_2O_2 \rightarrow 2OH^{\bullet}} \quad (11)$$

(b) Reduction reaction

$$\mathrm{e^- + O_2 \rightarrow {O_2}^{\bullet}} \quad (12)$$

$$\mathrm{{O_2}^{\bullet} + HO_2^{\bullet} + H \rightarrow H_2O_2 + O_2} \quad (13)$$

$$\mathrm{HOOH \rightarrow OH^{\bullet}} \quad (14)$$

$OH^{\bullet}$, O_2^- and H_2O_2 oxidize organic compounds (RH) or organic matter, according to the next reactions:

$$\mathrm{RH + OH^{\bullet} \rightarrow R^{\bullet} + H_2O} \quad (15)$$

$$\mathrm{R^{\bullet} + OH^{\bullet} \rightarrow ROH \rightarrow CO_2 + H_2O} \quad (16)$$

$OH^{\bullet}$ attacks virtually all the organic compounds including refractories to biological treatment and compounds of low concentration (ppb) and reacts faster than ozone, and generally the mineralization is complete, with a minimum amount of sludge and improves the organoleptic properties of treated water [7].

Moreover, in the primary process of photochemistry additionally to excite the electrons to migrate a higher orbital, the molecule may disrupt into fragments that recombine to give the original reactant.

3. Results and Discussion

Samples were obtained by certified personnel from Centro de Estudios en Medio Ambiente (CEMA) with reports 24R149-1 of the analysis released on April 4, 2024.

The data in Table 2, show significant concentration reductions of several parameters of the wastewater

Table 2 Reduction efficiency of wastewater parameters with double advanced oxidation.

Parameter	Units	Results		Efficiency (%)	+ MACs NOM-001 SEMARNAT-2021	Efficiency (%)	+ MACs NOM-002 SEMARNAT-1996
		Inlet	Outlet				
pH	pH units	5.8	5.8	NA	6-9		6-9
Floatable matter	-	Not present	Not present	NA	Not present		Not present
Temperature	℃	21.8	21	NA	35		40
Fecal coliforms	NMP/100 mL	4	4	-	NA	-	NA
Escherichia coli	NMP/100 mL	NA	3	NA	500		NA
Helminth eggs	H/L	NA	< 1	NA			NA
Fat oil & grease	mg/L	611.28	6.76		18		75
Settleable solids	mL/L	< 0.1	< 0.1	-	NA		7.5
Total suspended solids	mg/L	3,200	30		72		200
COD	mg/L	NA	138.33	NA	180		NA
BOD_5	mg/L	3,200	83.9		NA		NA
Total Kjeldhal nitrogen	mg/L		1.4		NA		NA
Total nitrogen	mg/L		1.508		30		NA
Nitrates	mg/L		< 0.098		NA		NA

Maximum allowable concentration for agricultural use.

NA = not applicable.

analyzed, complying with most of the maximum allowable concentration of the regulations that apply.

4. Conclusions

According to the results from the accredited laboratory, the project was successful, showing that there are opportunities to be improved if the static mixer increases the efficiency of in-line coagulation.

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