

Performance of a Demonstrative (Scale-Pilot) Double Advanced Oxidation Wastewater Treatment Plant to Treat Discharges from a Small Community in Morelia, Michoacán, México

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Abstract: This paper, reports the performance of a wastewater treatment scale-pilot plant to treat 2 GPM (Gallons per Minute) discharges with 5,205 mg/L of pollutants expressed in COD (Chemical Oxygen Demand), from “Lomas de la Maestransá” a small community in Morelia City, Michoacan, Mexico. The scale-pilot plant is a train with (1) pretreatment with a triturated pump for floating solid, (2) primary treatment with “in line” coagulation, and rapid filtration to retain suspended colloids and dissolved solids higher of 5 μm diameter, (3) double advanced oxidation as secondary treatment with ozone and heterogeneous photo catalysis to oxidize volatile solids, and (4) tertiary treatment with activated carbon to retain refractory compounds. Plant performance was analyzed by a certified laboratory that belongs to Potable Water, Sewage and Sanitation Department from Morelia City Government. Results show that treated water effluent complied with the Mexican Official Standard NOM-001-SEMARNAT-1996 for discharges into national waters, with exception of fecal coliforms, since the raw water contains an average of 64,228,351 MPN/100 mL of fecal coliforms, and in spite that we obtained a 99.998% efficiency, the maximum level allowable 2,000 MPN/100 mL standard, was exceeded by 400 MPN/100 mL. After this experience, the wastewater treatment plant is equipped with a residual chlorine tank to keep a 1.5 ppm chlorine residual concentration to keep the treated water clean. This project was possible because we had the support of the Morelia Sanitation Department.

Key words: Secondary treatment, advanced oxidation, heterogeneous photo catalysis, “in line” coagulation, nitrogen compound reduction.

1. Introduction

In Mexico, the wastewater discharges from urban domestic must complied Mexican Official Standards NOM-001-SEMARNAT-1996 for discharges into national water bodies and NOM-002-SEMARNAT-1996 for discharges into

urban or municipal sewage systems. At present these discharges are treated in the country by 2,642 plants with a 194,715.32 L/s, capacity, 761 of these plants are activated sludge's treating 69,337.3 L/s and 140 UASB treating 1,201.4 L/s [1].

These treatments have been effective to comply with the Mexican Official Standards. However, recently in Morelia City have been detected emerging pollutants at ng/L concentration levels [2], which

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include pharmaceuticals, personal care products, steroids, hormones, drugs metabolites, industrial chemicals, and pesticides, Refs. [3, 4] reporting a global reduction efficiency of 25.8%, treated with activated sludges, authors suggesting advanced oxidation processes to treat this kind of pollutants. The CONAGUA (National Water Commission) recommended advanced oxidation processes as tertiary treatment to treat these pollutants [5] since they are refractory to conventional biological treatment.

In this paper, we report the results to treat urban wastewater discharges from a small community located in Morelia Capital City of Michoacan State in México, with double advanced chemical oxidation, using ozone and heterogeneous photocatalysis, to oxidize dissolved and volatile solids, as secondary treatment. Emergent pollutants were not measured; these pollutants also can be destroyed using advanced oxidation, as secondary treatment.

The wastewater treated comes from the community named “Lomas de la Maestransá” located in Morelia City suburbs at 19°41'15" latitude and 10°11'94.92" longitude and 6742 FAMSLS, with 804 houses for 2,432 habitants, where 783 are connected to public sewage services.

The photocatalytic Advanced Oxidation Processes are a single instantaneous reaction independent of temperature and additionally does not generate sludges [6], since pollutants are destructed and there is not a transfer to another medium. The hydroxyl radical is a short-lived, extremely potent oxidizing agent, capable of oxidizing organic compounds mostly by hydrogen abstraction, as well with electron transfer

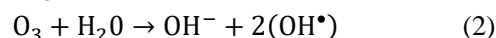
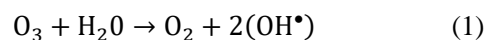
to hydroxyl radicals and radical-radical recombination [7].

The photocatalytic treatment is recommended for an organic load or COD (Chemical Oxygen Demand) lower than 2,000 mg/L [8] and the expected COD was between 250 and 1,000 mg/L [9] for municipal wastewater.

The treatment train is described in Fig. 1.

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 oxide-reduction potential ORP (Oxide-Reduction Potential), 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:



Ozone produces 1 mole OH^\bullet /1.5 mole O_3 [12, 13].

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 [7].

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).

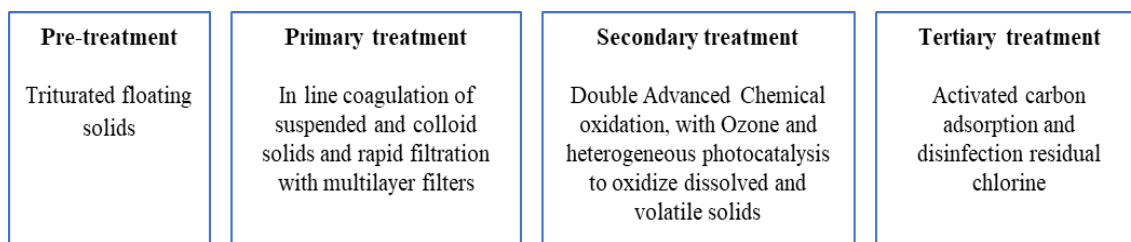


Fig. 1 Wastewater treatment train.

Table 1 ORP of advanced and conventional oxidants [10, 11].

Oxidant	ORP (mV)
Fluorine	3.06
OH•	2.8
O ₂ ^{-•}	2.42
O ₃	2.08
H ₂ O ₂	1.78
KmnO ₄	1.70
ClO ₂	1.57
Cl ₂	1.36
O ₂	1.23
ClO ₂	1.57

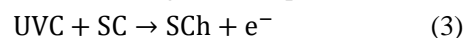
Instead of quantum, we used the quantum yield (ϕ) defined as number of molecules reacted (or mole) per photon absorbed (or Einstein) [11].

Using H₂O₂ as indicator (reaction 10), and according to Kormann et al. [12], the quantum yield ϕ of H₂O₂ in illuminated aqueous suspension of ZnO was found to be one order of magnitude higher than corresponding value for TiO₂. Also ϕ (OH•) is reported as 0.98 for H₂O₂.

In addition, ozone irradiated with UV also generates OH• and H₂O₂, Payton and Glaze cited by Legrini et al. [6] proof that hydrogen peroxide is the primary product of ozone photolysis.

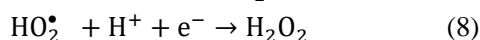
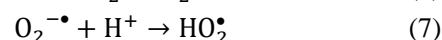
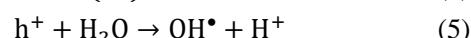
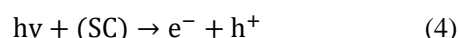
In this study, we used photocatalysis with a ZnO

(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 Fig. 2 and Eq. (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 [13].

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 [15, 16], according to next reactions:



The photocatalytic effect generates:

(a) Oxidation reaction

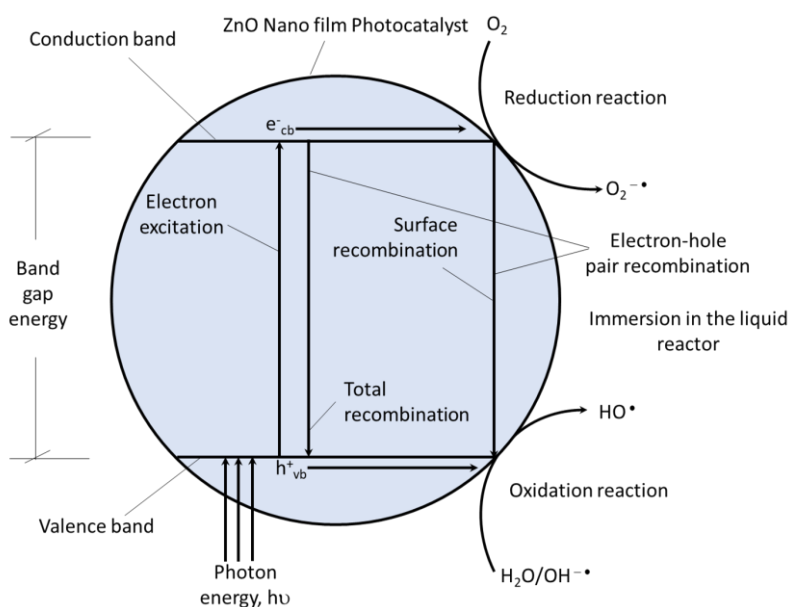
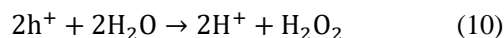
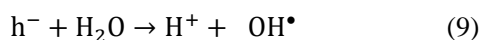
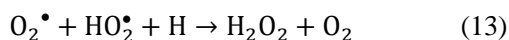


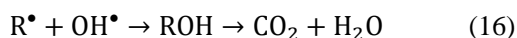
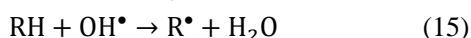
Fig. 2 Photocatalysis processes, adapted from Crittenden [14].

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(b) Reduction reaction



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



OH^\bullet attacks virtually all the organic compounds including refractories to biological treatment and compounds of low concentration (ppb) and reacts in 10^6 - 10^{12} s, faster than ozone, and generally the mineralization is complete, with a minimum amount of sludge and improves the organoleptic properties of treated water [17].

Moreover, in the primary process of photochemistry additionally to excite the electrons to migrate a higher orbital, may disrupt the molecule into fragments that recombine to give the original reactant [7, 14], as shown in Fig. 2.

2. Material and Methods

To construct the wastewater treatment plant, we:

(1) Manufactured the ZnO photocatalysts, from hydrolysis of zinc acetate as precursor in an electrodeposition cell, where the hydrolyzed precursor is deposited as zinc hydroxide $Zn(OH)_2$ on 0.049 m² US 100 SS (Stainless Steel) wire circles, previously cleaned with isopropyl alcohol in an ultrasonic bath,

and then calcined two hours at 500 °C to obtain a nanostructured ceramic film of ZnO (Figs. 3 and 4).

We obtained an average of 1.35 g/m² of ZnO ceramic film, and we prepared 22 SS circles with ZnO film in two sides of the circle, with a total area of 2.17 m² or 0.036 moles with 2.168×10^{22} molecules, to calculate the energy in Einstein KJ or Kcal.

We obtained with the Stark-Einstein law for 254 nm and 0.036 moles energy of 17 KJ, higher than activation energy of many chemical reactions to assure the typical wastewater pollution values from domestic discharges, as well to possible fluctuations in organic load.

It is expected an OH^\bullet concentration between 10^{-11} and 10^{-9} mol/L or 6.02×10^{12} - 6.02×10^{14} molecules of OH^\bullet /L [18], with velocity reaction constants for pollutants dissolved in water of 10^8 to 10^9 L/mole [19].

(2) Constructed a treatment train, with the following elements:

(a) Pretreatment with a 1 HP submerged triturated pump in a 7 ft³ polyethylene tank to remove floating solid and obtain small solids as raw water or influent to primary treatment.

Primary treatment with:

Coagulation “in line” with alumina in a 0.22 ft³ static mixer using the energy from the triturated pump to flash mixing and obtain aluminum hydroxides “pin flocs” as aides of filtration.

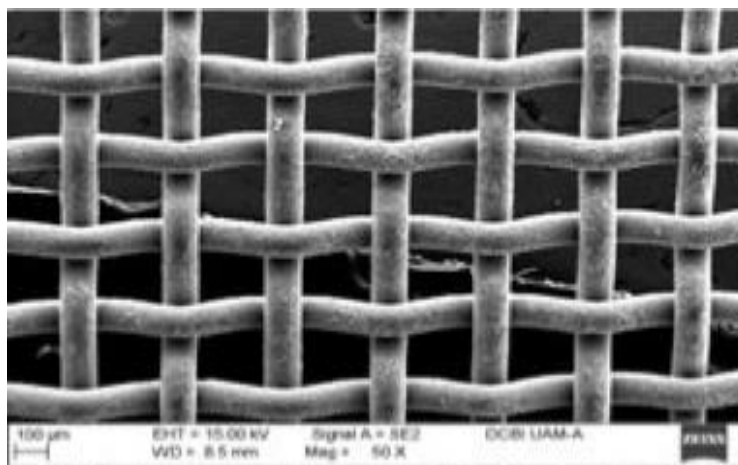


Fig. 3 MEB image 50× of US 100 wire covered with a thin film of ZnO.

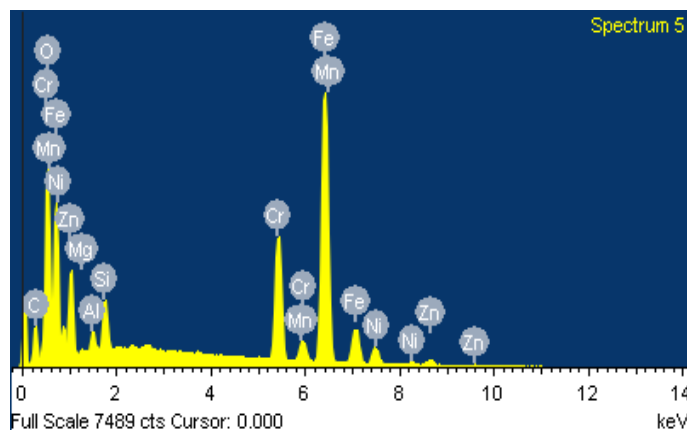


Fig. 4 Thin film ZnO on SS US 100 wire dispersive energy spectrum.

Rapid filtration of suspended and dissolved solids and “pin flocs” with three in line filters, first a 2.45 ft³ poly glass filter filled with grave, sand, and diatomaceous earth; second a 3.9 ft³ poly glass filter filled with anthracite, zeolite, and cationic resin, and a third filter consisted in a 0.0074 m³ polyester housing to retain solids higher of 5 microns.

(b) Secondary treatment by double advanced oxidation to convert organic matter and nitrogen volatile, suspended solids, soluble and suspended solids not soluble to carbon dioxide and water with:

A first oxidation with 12 g/h of ozone or 0.25 moles in 0.05 m³ SS reactor or contact tank, working with filtered water from primary treatment premixed with ozone in a venturi, before feed the contact tank. In total 0.25 moles of ozone produce 0.167 moles of OH•/h or 1.003×10^{23} molecules of OH•/h or 1.67×10^{21} molecules of OH•/min, additionally to start the advance oxidation processes to reduce turbidity.

A second oxidation by heterogeneous photocatalysis in a 0.5 m³ SS reactor, containing SS wire US 100 22 circles of 0.25 m of diameter with an effective surface of 0.048 m² with a total area of 2.1 m², considering both sides. This area is covered by electrophoresis with a thin film of 2.93 g or 0.036 moles of ZnO, activated with five UV 254 nm light lamps that emitted 2,380 KJ/Einstein for mole, with an energy in the reactor of 85 KJ, activation energy that produces between 10^{-11} and 10^{-9} moles/L of OH•/min, or for 7 L/min produces 4.2×10^{13} to $4.2 \times$

10^{15} molecules of OH•/min to oxidize the influent suspended solids and COD.

(c) Tertiary treatment with:

Adsorption of refractory compounds in a 0.11 m³ poly glass filter with activated carbon.

Disinfection with 1.5 ppm sodium hypochlorite to keep residual chlorine and maintain the treated water clean.

(d) The filter tanks have a capacity of 2-6 gal/min, working with a 2 gal/min operation rate.

(e) All the plant is working with 22 amperes to supply electrical energy to:

One 1-HP submerged triturated pump.

One 1-HP SS pump to feed the ozone system.

One 1-HP pump to backwash the filters.

Two ¼-HP pumps to feed aluminum sulfate system and sodium hypochlorite system.

One 12-g/h ozone generator or 0.25 moles O₃/h.

One oxygen concentrator of 5 L/min, and

Five 254-nm UV lamps.

All the tanks were closed for odor control, and the scale-pilot plant was mounted in a 2.22 m² carbon steel platform.

(3) The mounting the wastewater treatment plant as described previously, shows in Fig. 5.

(4) Evaluate the wastewater treatment plant performance with the parameters of NOM-001-SEMARNAT 1996 that regulates the wastewater treatment in Mexico that discharges to national bodies waters.

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Fig. 5 Wastewater treatment double advance oxidation plant.

The sampling and analysis were made by a certified laboratory with number AG-0781-084/17 of EMA (in Spanish) (Mexican Quality Assurance Organism), Laboratory that belongs to the Morelia City Government, named OOAPAS, acronym in Spanish, that means Potable Water, Sewage and Sanitation Operator Organism.

3. Results and Discussion

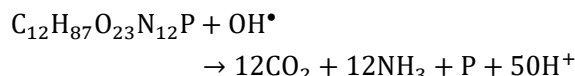
The samples were obtained by certified personnel from OOAPAS with reports 169 R and 170 R of the analysis released on November 8, 2019.

The data in Table 2, show significant concentration reductions of several parameters of the wastewater analyzed, complying with most of the maximum allowable concentration of the regulations that apply for agricultural use of wastewater treated.

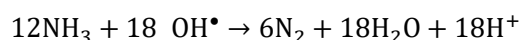
Fecal coliforms reduction was 99.996%, but since the influent value was more than 64 million of NMP/100 mL, we exceed with 400 the 2,000 allowable value. Parameter can be controlled with residual chlorine in the treated water reception tank.

Using the formula for organic matter of Metcalf & Eddie of $C_{12}H_{87}O_{23}N_{12}P$, we proposed the next reactions to explain the results obtained.

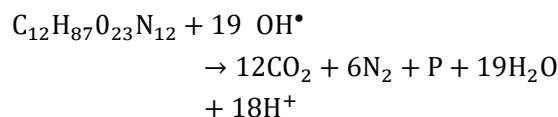
(1) Oxidation of carbon matter and reduction of nitrogen matter.



(2) Oxidation of N-NH₃



(3) Or the global reaction



(4) And $68 H^+ + 68 OH^{\bullet} \rightarrow 68H_2O$

The pH is not modified as appears in the table and in the process, since this parameter was continuously measured and remained around 7.0.

The oxidation occurred with the OH^{\bullet} in excess produced in the contact ozone reactor as well as in the photochemical reactor, where expected an OH^{\bullet} concentration of $10 \times 10^{14} OH^{\bullet}$ molecules/L.

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

Parameter	Units	Results		Efficiency %	+ MACs NOM-001 SEMARNAT 1996
		Inlet	Outlet		
pH	pH units	7.2	6.6	NA	NA
Floatable matter	-	NA	N/A	N/A	Not present
Temperature	°C	24	25	N/A	NA
Fecal coliforms	NMP/100 mL	64,228,351	2,400	99.996	2000
Fat oil & grease	mg/L	33.96	2.24	93.4	25
Settleable solids	mL/L	0.3	< 0.1	66.67	2
Total suspended solids	mg/L	156	< 9.64	93.82	200
COD	mg/L	561.08	< 92.42	83.53	NA
Total Kjeldhal Nitrogen	mg/L	53.9	0.16	99.7	60
Organic nitrogen	mg/L	1.94	N.D.	100	NA
Ammoniacal nitrogen	mg/L	51.96	0.16	99.69	NA
Total phosphorus	mg/L	11.2	0.87	92.23	30
Nitrates	mg/L	0.44	0.18	59.09	NA

+ Maximum allowable concentration for agricultural use.

NA = not applicable.

The OH^\bullet excess is explained, by the sum of OH^\bullet generated in the photocatalytic process plus the OH^\bullet generated by the UV photolysis of the ozone exited from the contact tank due to its low solubility in water, the mass transfer limitations and the short time in the contact tank conditions that generate hydrogen peroxide and hydroxyl radical and the UV present in the photocatalytic reactor with mirror quality has a rate constant in the order of 10^8 to $10^{10} \text{ M}^{-1}\cdot\text{s}^{-1}$ [4]

The nitrogen reductions in the first reaction occurred because the oxidative and reduction power capacity of the pair $\text{e}^- \cdot \text{h}^+$, created in the photocatalytic reactor since the retention time is very short in the entire process and less than a minute between the two advanced oxidation stages.

4. Conclusions

This technology with the approach of wastewater—Secondary Treatment—is successful to treat the pollutants in wastewater regulated in Mexico, without generating solid wastes in the secondary treatment since there is not a biomass growth. All the reactions are at ambient temperature and at pH almost neutral as reported.

Since all the components of the treatment train are closed, there are no nuisances by bad odors and neither significant noise.

In this scale-pilot plant all the treatment train was installed on 2.5 m^2 platform, and we calculated that for a wastewater treatment plan automated of 250 L/s. needs $2,000 \text{ m}^2$ with a total weight of 300 tons with all the components mounted on the surface of a platform that supports the total weight.

This technology can work in a batch or continuous mode, and since the process does not need heating or acclimation, and the reactions are almost instantaneous, is possible turn off and start on the plant operation as needed.

This technology can destroy emergent pollutants that are present in micro concentration but that have significant impacts on the community health and the

ecosystems as general.

Finally, it can work with the visible light region, if doping ZnO with other metals in order to reduce costs and UV risks.

Acknowledgements

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