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Advanced Oxidation with Nanofilm Photacatalyst'S on Stainless Steel Wire as Secondary Treatment of Wastewater

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Abstract: In this paper, authors reported the results of wastewater treatment of discharges from sanitary facilities and laboratories from de Metropolitan Autonomous University Azcapotzalco campus in Mexico city in a pilot plant integrated with a unit of coagulation-flocculation and sedimentation of suspended particulate and multilayer filtration with sand, zeolite and anthracite that filtered particulate higher than 5 nanometer of diameter as primary treatment and advanced oxidation based in the use of hydroxyl radical through ozonation and UV Photocatalysis with zinc oxide, zinc oxide doped with silver and zinc oxide doped with zirconia as fine films photocatalysts on a US 100 stainless steel wire as secondary treatment, and finally with activated carbon adsorption as final polish. COD and ORP were evaluated after each step as representative of BOD stablished as MAC's in Mexican regulation on wastewater effluents, obtaining values that comply with the regulation.

Key words: Advanced oxidation, nanofilms photocatalyst, secondary wastewater treatment.

1. Introduction

In Mexico, the wastewater treatment in general is carried on with biological oxidation of organic matter as secondary treatment. Treatment that has been effective to urban wastewaters. However, over the past decade instrument sensitivity has led to a wide detection of ng/L levels of emerging pollutants or organic micropollutants that include pharmaceuticals, personal care products, steroids, hormones, industrial chemicals and pesticides [1, 2]. Pollutants that are refractory to conventional biological treatment.

In this paper, authorsreported the results of the treatment with nano film photocatalyst as secondary treatment of waste water from the Metropolitan Autonomous University, Azcapotzalco campus in Mexico city, waste water that additionally of discharges from sanitary facilities have chemicals from laboratories and workshops that uses inks and pigments, that are released in continuous and batch discharges during the operating hours of the day, from Monday to Friday.

These discharges require new approaches in wastewater treatments. Photochemical processes are alternative to water treatments since UV irradiation in combination with other processes (e.g., ozonation, peroxidation or both) can remove bacterial substances from solution as well as dissolved organics. These photochemical oxidation reactions are now referred to as Advanced Oxidation Processes based in the ºOH oxidant (AOPs) [3] and recently the UV heterogeneous photocatalysis is included in this technique [4].

Advanced oxidation present advantages on conventional chemical oxidation because the process generates the oxidants in situ, there is no use of chemicals consumables as supplies, and as different from biological oxidation advanced oxidation could

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be a batch process and is not necessary to maintain a microbial population when there are toxics or exists abrupt changes in the temperature or pH in the raw water and the generation of residues are less than biological oxidation.

Additionally, biological oxidation use specialized microorganisms with the enzymes required to metabolize the substrate to generates energy and new biomass that require to be disposed in a safe manner. Microorganisms are present in consortiums and the ability of the microbial community to mineralized the organic matter is a function of their metabolic versatility [5].

Table 1 shows the general features of biological oxidation.

Biological reactors work 24 hours and must keep appropriate conditions in order that oxidize organic matter in terms of temperature, pH, available nutrients and oxygen as electron acceptor as well the substrate amount to support the oxidation process.

Microbial activity involves many reactions, according with the metabolism of carbohydrates that comprise the organic matter with lipids and proteins, the process involves at least four steps: glycolysis with 9 reactions to transform glucose C6 to Two pyruvates C3; pyruvates that when the supplied of oxygen is adequate is oxidatively decarboxylated to acetyl CoA which enters to citric acid cycle, where in 6 reactions, it is oxidized to carbon dioxide and water and trough electron transport in the respiratory chain that involves the transfer of electron to the oxygen as final acceptor in 6 reactions [7].

Transfer of electrons are involved in all the oxidation-reductions reactions, oxidation must be accompanied by simultaneous reduction, and the energy required for the removal of electrons in oxidation is supplied by the reduction, electron transport explain how oxygen enter the metabolism [7].

Energy transfer in the system is measured by difference in potential. In the biological oxidation,

Table 1 Biological oxidation requirements.

Microorganisms		
Energy source	Energy Source	
Humidity	pH	
Nutrients	Temperature	
Not Toxicity	disposal of metabolites and excess of biomass	not competitive microorganisms
BIOLOGICAL OXIDATION		

Source: Adapted from Cookson [6] and Sutherson [7].

oxygen has the highest oxidation system in the living cell, and the process is catalyzed by enzymes which functions in combination with coenzymes or electron carriers [7].

According with the previous concepts, biological oxidation involves many steps and additionally uses the oxygen as final electron acceptor which has an oxide reduction potential or ability to accept electrons (1.23 V) lower than oxidants used in advanced chemical oxidation such as hydroxyl radical (2.8 V), anion superoxide O^{-} (2.42 V), and ozone (2.07 V) [8]. In contrast, chemical oxidation involves less reactions and is faster than biological.

ºOH is an extremely reactive radical it reacts as soon as it is formed, additionally the hydroxyl radicals react non selectively with different compounds in the water. The amount of hydroxyl radicals formed is the limiting factor in these reactions, and there is a competition between compounds for the hydroxyl radicals [9].

Wastewater discharges from the UAM Azcapotzalco campus have an elevated organic content from sanitary and food facilities, as well as chemicals, solvents, acids and bases from laboratories of chemical environmental, and metallurgical engineering disciplines and additionally discharges from workshops such as pigments, inks and paints, substances that are refractories to biological oxidation.

Additionally, the discharges of raw material to feed the microbial population occurred from 6:00 to 21:00 hours in the day from Monday to Friday, without discharges Saturday and Sunday and holydays, that

means that in these periods, there are not organic matter as substrates to support biological oxidation.

At the present, the campus has a wastewater treatment plant with a treatment train that receives triturated effluents, that are conducted to a coagulation-flocculation-sedimentation train, post filtered with anthracite, oxidized in a contact tank of ozone and finally filtered with activated carbon, before discharged to city sewer.

This study proposed to increase the treatment train with advanced oxidation with photocatalysis trough a nanofilm of zinc oxide over a stainless steel wire to obtain zero discharge using the treated wastewater to irrigates the campus gardens.

The proposed systems have the next features after triturate the raw water as pre-treatment as shown in Fig. 1.

1.1 Advanced Oxidation Principles

The conventional chemical oxidation use as oxidants consumable chemicals such as: chlorine, chlorine dioxide, sodium hypochlorite or potassium permanganate, substances that need storage with risks associated as well as expensive consumption.

Advanced oxidation implies the in situ formation of the hydroxyl ion ºOH by photocatalysis, as well as others oxidants by secondary reactions, such as superoxide anion O_2^-, and hydrogen peroxide, oxidants that have an oxide- reduction potential, ORP higher than conventional oxidants as show in Table 2.

Hydroxyl radical could be formed from ozone in presence of water according the next reactions:

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

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

And by photocatalysis using a semiconductor, SC such as titanium oxide TiO_2 or Zinc Oxide ZnO, that exposed to UVC radiation lesser than 300 nm, liberate a free electron e^- that leaves a hole with a positive charge, since was in equilibrium, as shows in Fig. 2.

$$UV + MO \rightarrow MO\ (h + e^-) \quad (3)$$

The free electron moves from the valence orbital exposed to the UV radiation to a conduction orbital and translate to a final electron acceptor such as dissolved oxygen in water to avoid the reversible.

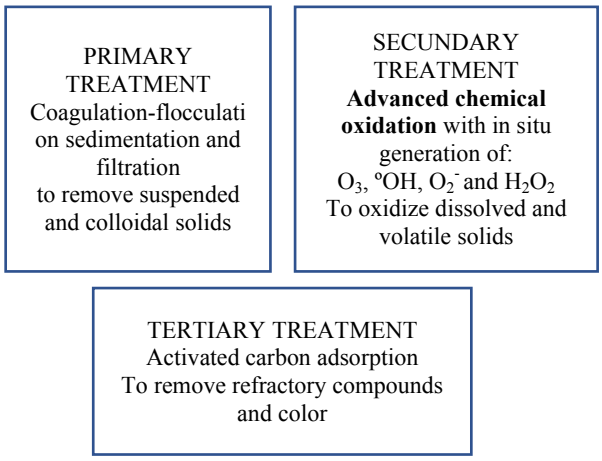

Fig. 1 Proposed system.

Table 2 Oxide-Reduction Potential—ORP of advanced and conventional oxidants.

Oxidant	E, Volts
•OH	2.8
O_2^-	2.42
O_3	2.07
H_2O_2	1.78
ClO_2	1.57
Cl_2	1.36
O_2	1.23

Source: Siegrest, et al. [2].

The free electron and the positive hole generated, reacts in presence of water as:

$$h\nu + (SC) \rightarrow e^- + h^+ \quad (4)$$

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

$$e^- + O2 \rightarrow \bullet O_2^- \quad (6)$$

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

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

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

$$RH + \bullet OH \rightarrow \bullet R + H_2O,\ y \quad (9)$$

$$^oR + \bullet OH \rightarrow ROH \rightarrow CO_2 + H_2O$$

The photocatalytic effect has:

(a) Oxidative reactions:

$$h^+ + H_2O \rightarrow H^+ + \bullet OH \quad (11)$$

$$2\ h^+ + 2\ H_2O \rightarrow 2\ H^+ + H_2O_2 \quad (12)$$

$H_2O_2 \rightarrow 2\ \bullet OH$, and

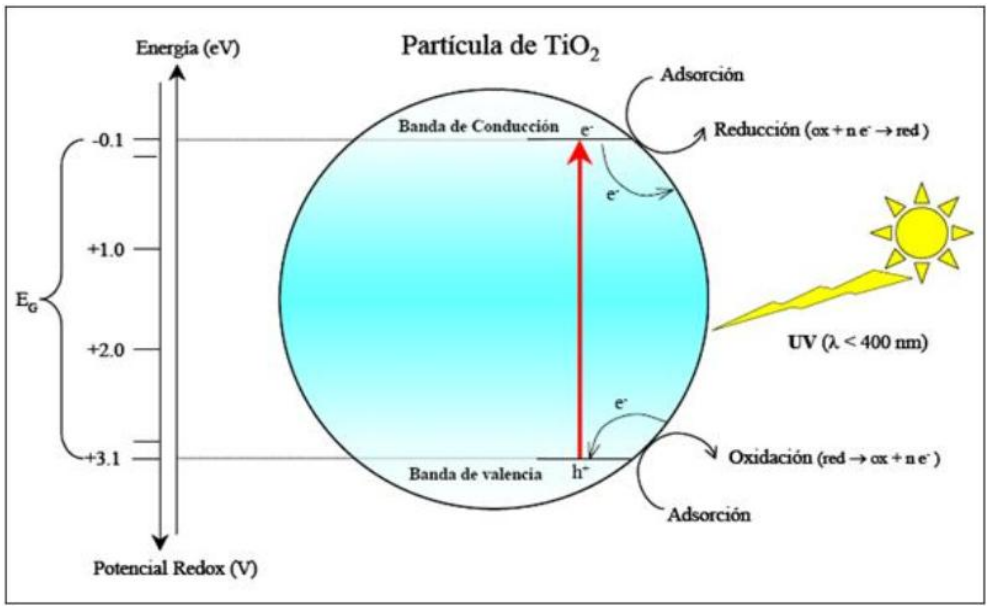

Fig. 2 Photocatalytic process [10].

(b) Reductive reactions:

$$e^- + O_2 \rightarrow \bullet O_2^-$$

$$\bullet O_2 - + HO\bullet_2 + H^+ \rightarrow H_2O_2 + O_2$$

$$HOOH \rightarrow HO\bullet$$

•OH has properties to attack virtually all the organic compounds including refractories to biological treatment, and compounds of low concentration (ppb), and reacts 10^6-10^{12}, faster than ozone, and generally the mineralization is complete, as different of conventional treatment, with a minimum amount of sludge's and improve the organoleptic properties of treated water [11].

In this project, instead of titanium oxide, authors use nanofilms of zinc oxide on a stainless steel US 100 wire, with a 149 microns open area, as well as zinc oxide doped with traces of silver and zirconium.

The purpose of zirconium doping was to increase the mechanical resistance and the silver doping to reduce the bandgap and increase the •OH formation.

2. Material and Methods

To develop the experiments, authors worked with the next Methodology:

(1) Manufacturing zinc oxide photocatalysis, with hydrolysis of zinc acetate as precursor in an electrodeposition cell, where the hydrolyzed precursor is deposited as zinc hydroxide (Zn_2OH) on the US 100 stainless steel wire, previously cleaned with isopropyl alcohol in an ultrasonic bath, and then calcined two hours at 500 ºC to obtain a ceramic film nanostructured of Zinc oxide (ZnO) as shown in Fig. 3.

(2) Manufacturing the zinc oxide photocatalyst doped with silver and zirconia. Adding traces of zirconium and silver sulfate in the electrodeposition process.

(3) Construction of treatment train (Fig. 3).

(4) Design experiment, using COD and ORP as independent variables after the ozonation and photocatalyst oxidation, and also color as dependent variable of pH.

(5) Characterization of raw water sample, measuring; COD, ORP, suspended solids (SS), Dissolved oxygen (DO), color and turbidity.

(6) Running the experiment by triplicate.

(7) Characterization the same parameters in each experiment phase.

(8) Analysis of data and discussion.

(9) Calculus of results and conclusions.

The Fig. 3, it shows the US 100 Stainless steel wire with and without the semiconductor thin film, this material can support the aqueous environment without

corrosion, and with a low pressure drop to facilitate its use in the wastewater treatment.

The Figs. 4 to 9, it shows different sizes of the thin film electrodeposited on the wire with ZnO ceramic semiconductor and ZnO doped, presenting a big surface area, where the oxidation takes place.

Fig. 10 shows the composition of the material electrodeposited on the US 100 stainless steel wire, where Zn appears as well as the elements that are present in the steel.

Fig. 3 SS US 100 wire with/without a thin film of ZnO photocatalyst.

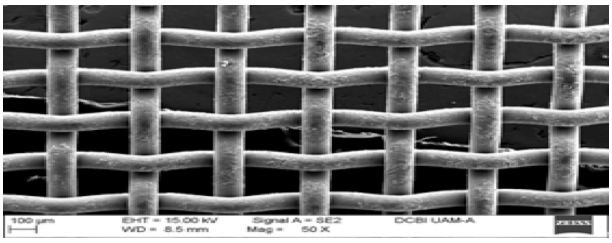

Fig. 4 MEB 50 X image of US 100 wire covered with a thin film of ZnO.

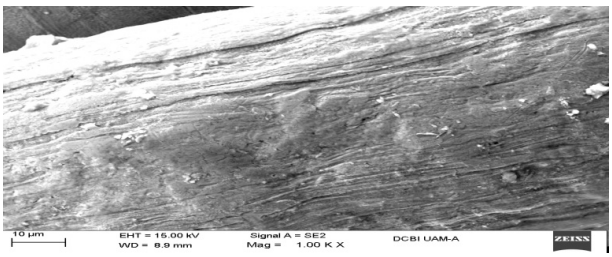

Fig. 5 MEB 1.0 KX image of US 100 wire covered with a thin film of ZnO.

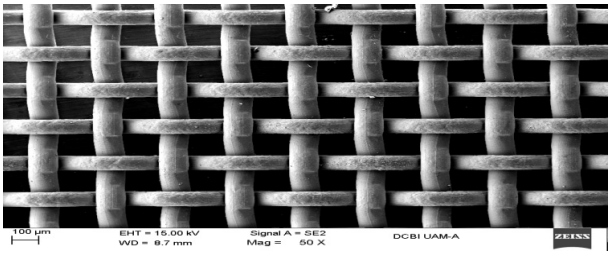

Fig. 6 MEB 50 X image of US 100 wire covered with a thin film of ZnO doped with zirconium.

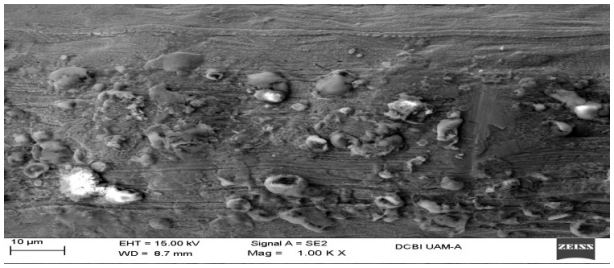

Fig. 7 MEB 1.0 KX image of US 100 wire covered with a thin film ZnO doped with zirconium.

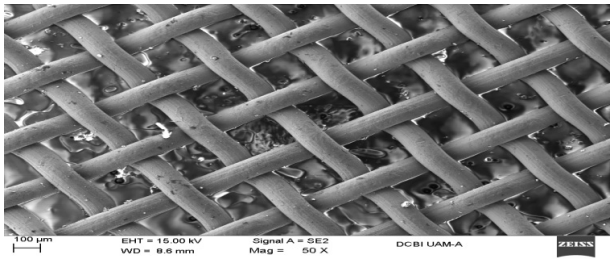

Fig. 8 MEB 50 X image of US 100 wire covered with a thin film of ZnO doped with silver.

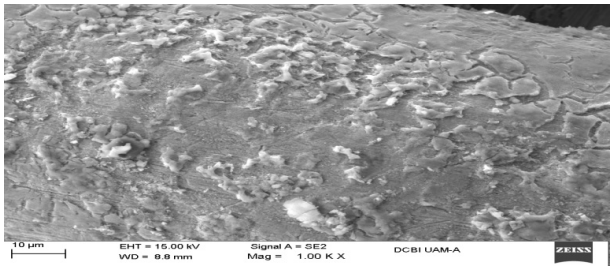

Fig. 9 MEB 1.0 KX image of US 100 wire covered with a thin film ZnO doped with silver.

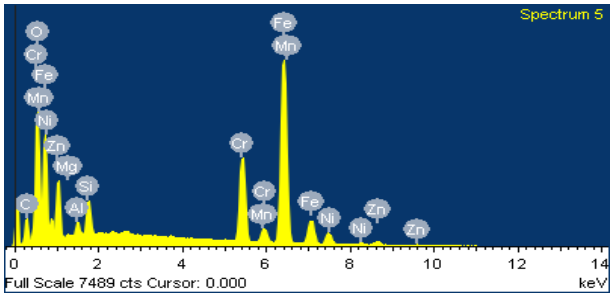

Fig. 10 Thin film ZnO on SS US 100 wire dispersive Energy spectrum.

The difractogramm in Fig. 11, shows the ZnO present in the wire, and the ZnO particulate, is a sample of the material electrodeposited on the surface of the US 100 SS.

The experiment was conducted in the treatment train of Fig. 12, where supplied air in up flow, to promote mixing, increase time of contact, and increment the dissolved oxygen.

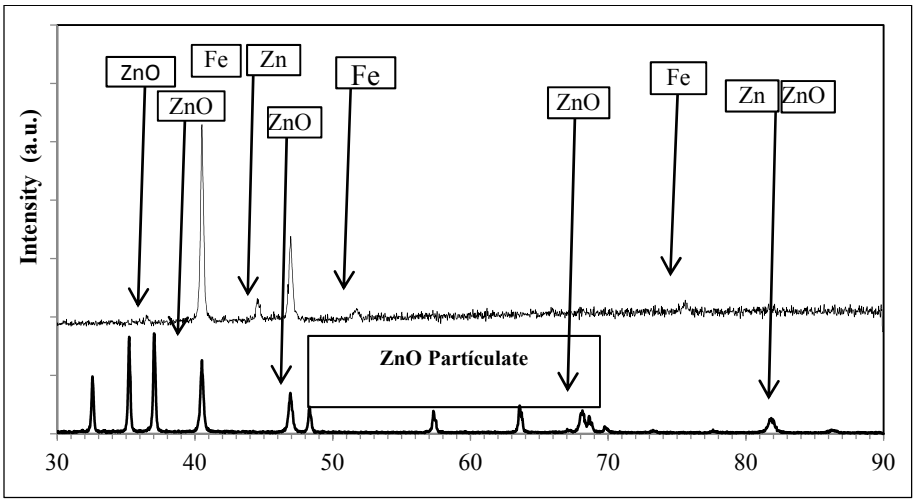

Fig. 11 US 100 SS wire covered with thin film of ZnO difractogramm.

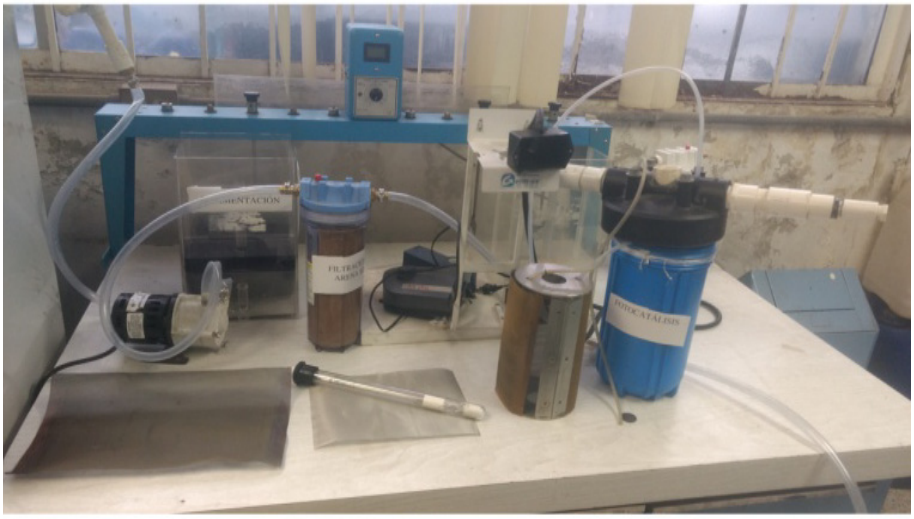

Fig. 12 Treatment train.

Table 3 Parameters trough the different treatment phases.

Sample	pH	SS mg/L	Color NTU	ORP Volt	DO m/L	COD mg/L
Raw water	7.46	384.3	1,400	-60	5.6	1,241.2
Multilayer Filtration	7.59	98.3	533.3	-43	6.3	513.7
Coagulation flocculation sedimentation	6.99	6.33	120.7	-60.7		437.9
Ozonation	7.98	9.0	183.3	-20.5	9.6	240.8
ZnO PC	8.92	9.0	210.33	16.7	9.8	186.3
ZnO PC Zirconium doped	8.71	6.7	154.7	-12.9	10.	195.5
ZnO PC Silver doped	8.55	6.3	155.3	-11.7	10.2	188.2
Activated carbon after ZnO PC	9.62	6.3	74	33.3	11.6	27.8
Activated carbon after ZnO PC zirconium doped	9.9	6.7	78.33	19.27	11.9	51.8
Activated carbon after ZnO PC silver doped	9.9	4.3	81.67	11.1	11.86	31.2

PC = Photocatalyst.

Table 3, shows the results in each phase of the treatment train.

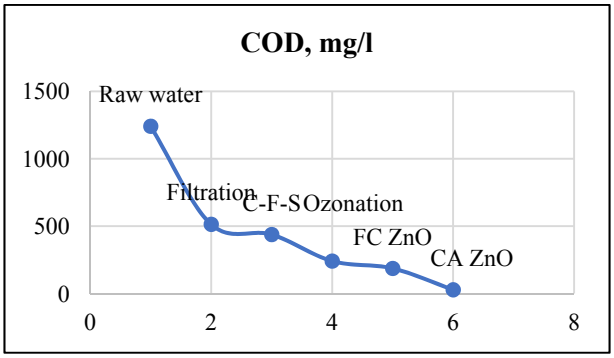

Fig. 13 COD in the treatment phases with ZnO photocatalyst.

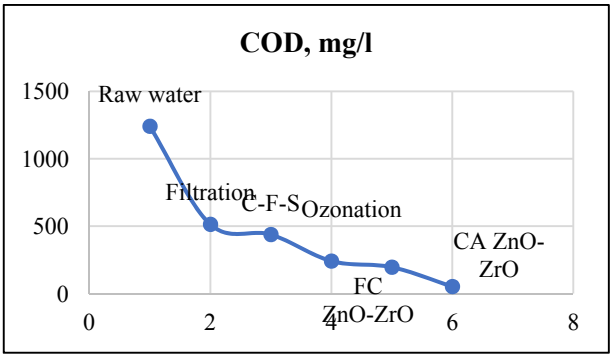

Fig. 17 COD in the treatment phases with ZnO-ZrO photocatalyst .

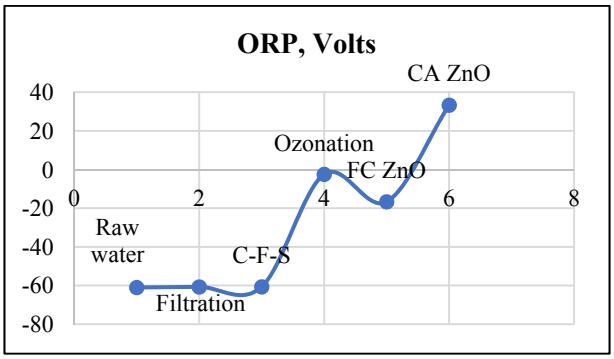

Fig. 14 ORP in the treatment phases with ZnO photocatalyst.

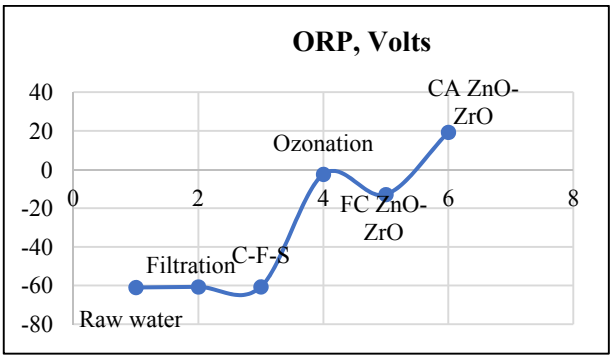

Fig. 18 ORP in the treatment phases with ZnO-ZrO photocatalyst.

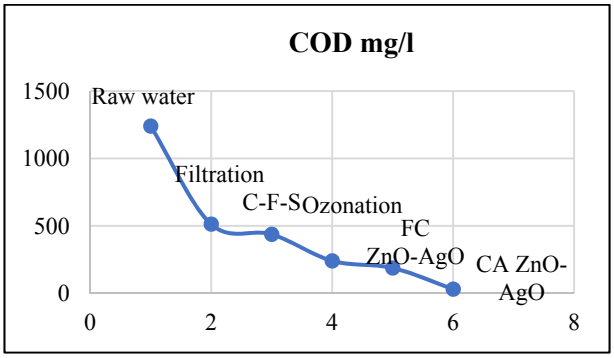

Fig. 15 COD in the treatment phases with ZnO-Ag photocatalyst.

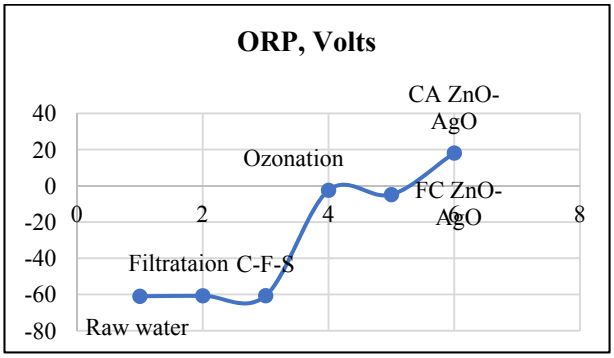

Fig. 16 ORP in the treatment phases with ZnO-Ag photocatalyst.

3. Results and Discussion

These data show the next behavior in the treatment.

COD and ORP are considered as representative of inorganic and organic matter and the differences in each phase of the treatment could be representative of efficiency.

COD is related with BOD, which must be less that 60 mg/L according with waste water discharges on municipal services by Mexican rules, usually COD is higher than BOD.

ORP parameter is an indicator of the oxidation state of the water and it could be measured with an electrode or a direct reading instrument and evaluate the process in fast way, differences in the ORP values means that the oxidation happened.

As seen in the figures from 13 to 18, shows that the COD values were reduced to levels that can comply with the Mexican rule, maximum level allowed concentration, stablished by the Mexican rules, according with the oxidation registered with the ORP

values that were incremented from the raw values to the oxidized water since.

4. Conclusions

Water treatment using these treatment trains, resulted successful, however, the advanced oxidation by itself is not enough to reach values that meet the rule 002, it is required the use of activated charcoal to make this happen.

According to the results shown, the best photo catalyzer was the Zinc Oxide, even though in the three cases, values that meet the rule were reached.

References

[1] Shingai, N., and Perez-Garcia. 2016. "Degrading Organic Micropollutants: The Next challenges in the Evolution of Biological Wastewater Treatment Processes." Front. Environ. Sci. http://doi.org/10.3389/fenvs.2016.00036.

[2] Wols, B. A., and Hoffman, C. H. M. 2012. "Review of Photochemical Reaction Constants of Organic Micropollutants Required for UV Advanced Oxidation Processes in Water." *Water Research* Volum 46: 2815-2827.

[3] Serpone, N. 1995. "Brief Introductory Remarks on Heterogeneous Photocatalysis." *Solar Energy Materials and Solar Cells* 38 (1-4): 1995.

[4] Herrman, J. M. 2005. "Heterogeneous Photocatalysis: State of the Art and Present Applications." *Topics in Catalysis*: 34.

[5] Alvarez, P. J., and Guevara, P. E. 2003. "Biorremediación y atenuación natural de acuíferos contaminados por sustancias químicas peligrosas." CDCH-UC, Venezuela.

[6] Cookson, J. 1995. Bioremediation Engineering Design and Application. N.Y. Mc Graw-Hill, USA.

[7] Sutherson, S. 2001."Natural and Enhanced Remediation Systems." *Arcadis Lewis USA*: 91.

[8] Domenech, X., Jardim, W. F., and Litter, M. 2012. "Advanced Oxidation Processes for the Removal of Pollutants." https://www.researchgate.net/publication/290852253/january 2004.

[9] Siegrest, R. K. L., et al. 2001. "In situ Chemical Oxidation Using Permanganate." Batelle Press, USA pp 7.

[10] Malato, S. 2002. "Solar Detoxification." Chapter 4, edition of UNESCO.

[11] Litter, M. I. 2005. "Introduction to Photochemical Advanced Oxidation Processes for Water Treatment." The Handbook of Environmental Chemistry, Vol 2, Part M, pp. 325-366, Springer-Verlag, Berlin.