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Evaluation of the photo-catalytic oxidation process with commercial ZnO for real textiles wastewaters treatment.

Célia R. G. Tavares[1], Valquíria A. S. Ribeiro[2], and André L. S. Volpe[3]
[1, 2, 3]*Department of Chemical Engineering, State University of Maringá (UEM), D-90, 87020-900, Maringá, PR, Brazil,*

Abstract:- The textile industry uses a very great amount of water in their process and then, produces high quantities of colorful wastewater containing pollutants like suspended solids, heavy metals and other inorganic and organic compounds. In this study, real textiles wastewaters were processed in an oxidative photo-catalytic slurry reactor, using commercial ZnO as the catalyst, in order to evaluate its efficiency, the effect of pH, the effect of catalyst loading and its kinetics. The process was tested in a batch reactor, in bench and semi-pilot scales, with excellent data reproducibility observed in the scale-up. Moreover, decolorizations of 97.43 %, BOD and COD reduction were obtained, showing good applicability of the process. According to regional environmental agencies, the final effluents parameters were checked showing good acceptance for the use of ZnO, except for the presence of Zn^{2+} in the effluent as a disadvantage.

I. INTRODUCTION

The nature of pollutants and their concentrations in industrial wastewater depends on their source. Industrial wastewater typically leaves the units at higher temperatures than communal and agricultural wastewater. Because of the high concentrations of toxic materials in industrial wastewater, it is necessary to apply specific processes for their separation, transformation, and further decomposition. A variety of biological, physical, and chemical processes and their combinations are available for these purposes, but each technique has its inherent limitations in applicability, effectiveness, and cost [1].

The wastewaters generated by the textile industry are among the most polluting because of the presence of dyes, fabrics fiber, and various other substances considered dangerous for the environment, besides the large amount of water that is discarded in the effluent. Because of that, many studies have been realized in order to find even better treatments for these wastewaters, such as the photo-catalytic oxidation.

Catalytic processes for wastewater treatment offer several advantages. They can be performed under milder conditions (temperatures and pressures). Another great advantage of catalytic methods is the possibility to treat only a single pollutant, or a group of similar pollutants, out of a complex mixture of pollutants (as in selective catalytic reduction). This opportunity is of special interest when a mixture of pollutants and useful compounds should be processed. By proper choice of the catalyst, it is possible not only to control the degree of conversion of pollutants but also to select different reaction routes, in order to select the optimal reaction intermediates and products and avoid the formation of secondary pollutants [1].

The photo-catalytic oxidation has been widely studied because it is able to mineralize organic compounds without producing other compounds that harm the environment, and does not produce significant amounts of silt. The process consists of irradiating the effluent in the presence of a semiconductor, which generates radicals that accelerate the destruction of organic compounds.

When illuminated with an appropriate light source, these semiconductors generate electron/hole pairs, with electrons promoted to the conduction band and leaving positive holes in the valence band. The generated electron/hole pairs initiate a complex series of chemical reactions involving vestigial organic compounds adsorbed at the surface of the semiconductor that might result in the complete degradation of the adsorbates [4]. The zinc oxide (ZnO) has been widely studied as a semiconductor for the degradation of several environmental pollutants due to its high photo-sensitive, chemical stability, non-toxicity and low cost [4, 6, 7, 18].

II. MATERIALS AND METHODS

a. The Reactors.

In the laboratory scale, the slurry reactor was built using a becker of 2000 mL positioned onto a magnetic stirrer, in order to keep the solution homogenous with the effluent in constant agitation. A thermostatical bath kept the temperature in 25 ^{o}C. Using a support, 4 germicidal lamps of 15 W for the UV irradiation were fixed onto the becker, and the system was isolated from the external radiation. Commercial ZnO was used as the catalyst, with specific superficial area - BET of 0.00636 m^2 Kg^{-1}. The effluent pH was adjusted using sulfuric acid and sodium hydroxide solutions with undefined concentrations. The catalyst was added to 450 mL of the effluent, hence was submitted to agitation for 10 minutes in the dark in order to

complete the homogenization of the solution, after these 10 minutes 50 mL of the solution were collected as the initial sample and then, the 400 mL remaining in the reactor were submitted to the UV irradiation during 4 hours.

The slurry reactor in semi-pilot scale consisted of a fiberglass tank with a capacity of 0.320 m^3 and the following dimensions: base diameter of 0.77 m, top diameter of 0.96 m and 0.50 m high. An engine that produces 800 rpm and 2 shovels with width of 0.06 m each, and the total diameter of the agitator of 0.17 m did the agitation. The stirring blades were positioned at 0.10 m high from the base. A structure of baffles was assembled, with six baffles with width of 0.050 m and 0.30 m high, to avoid the formation of vortex. The 44 germicidal lamps of 15 W used in the tests were fixed in a stainless-steel plate of 1.00 m of diameter which was fitted onto the tank. A rubber was fixed at the edge of the reactor to minimize the impact of the stainless-steel plate and to prevent leakage of ultraviolet radiation to the exterior of the tank.

The slurry reactor in semi-pilot scale was built in an industrial laundry of the town, for the treatment of effluent generated. The effluent was fed into the reactor by gravity and the volume transferred was measured by a hydrometer. The effluent pH was adjusted to 4.0 using concentrated sulfuric acid. Commercial zinc oxide was used as the catalyst, with specific surface area - BET of 0.00636 m^2 Kg^{-1}. In all experiments, 0.100 m^3 of effluent were treated, using 3.0 Kg m^{-3} of zinc oxide. During the tests the reaction time was 4 hours, initial and final samples of the solution were collected to evaluate the decolorization, reduction of COD and "apparent" color of the effluent.

b. Analytical Methods.

The COD was determinated using the micro-method [5], and the BOD was determined from the standard method [21].

The pH was measured using a Digimed's pHmeter model DM20, according to the methodology described in the manual of the equipment.

The samples were centrifuged in a rate of 3000 rpm for 20 minutes to completely remove catalyst particles, and then were submitted to spectrophotometric analysis.

The apparent color, that is the color of the dissolved materials plus the suspended matter, and turbidity were determined in a HACH spectrophotometer, model DR/2010, at a wavelength of 455 nm and 860 nm, respectively, according to the methods described in the manual of the equipment.

The spectrophotometric scans were performed on a spectrophotometer HACH-LANGE, model DR/5000. The decolorization of the effluent was determined at the wavelength of maximum absorbance (λ_{max}) of each effluent. These decolorizations have been calculated as:

$$Decolorization\,(\%) = \frac{(Abs_i - Abs_f)}{Abs_i} \cdot 100$$

where Abs_i is the absorbance of the solution before the treatment and Abs_f is the absorbance of the solution after the treatment.

The metals: Lead (Pb), Copper (Cu), Chrome (Cr), Iron (Fe), Nickel (Ni) and Zinc (Zn) were measured by atomic absorption spectroscopy using the method called the Fast Sequential Atomic Absorption Spectrometer, model AA240FS according to the methodology described in the operations manual of the equipment. The calibrations curves of the metals occurred through the use of specific standards for each metal at different concentrations. Only the determination of the Pb concentration to construct the curve occurred with standards of Pb in ppb.

c. Development.

Throughout the study, six effluents were collected from an industrial laundry located in Maringá, Paraná State, in Brazil; at different periods of the year. These effluents were characterized for the following parameters: pH, "apparent" color, wavelength of maximum absorbance, turbidity, COD, BOD and heavy metals.

Initially, experiments were performed in bench scale in order to determine the initial pH of the solution in which it was obtained the better efficiency of the process of photo-catalytic oxidation. After that, the concentration of zinc oxide that provided better results of decolorization of the effluent was also analyzed. With the optimum conditions determined, experiments were realized to determine the kinetics of the process, in which samples of 10 mL were collect at intervals of 30 min during the 4 hours of experiment using a pipette. The 10 mL of samples were chosen to not quite interfere in the total volume, what could change the conditions of the process, and were enough for doing the analysis.

In addition to the bench scale tests, other tests were conducted in the semi-pilot scale photo-reactor built in the laundry where industrial effluents were collected to analyze whether the optimum conditions of the experiment obtained at bench scale would lead to the same good results in the semi-pilot scale.

III. RESULTS AND DISCUSSIONS

3.1. Effluents Characterization.

Information from the laundry told that the chemicals most used were: reactive dyes, chlorine, sodium hydroxide, potassium permanganate, sodium metabisulfite, enzymes, optical brighteners, humectants, sequestrants, dispersants, reducers, softening, hydrogen peroxide, detergents among others with more specific uses but in smaller quantities.

Real wastewater contains many other organic compounds than dyes, compared to synthetic wastewater, and the produced hydroxyl radicals from the photocatalysys reacts with any kind of organic compounds, what may decrease the efficiency of the degradation of the dye[19]. The diversity of the process in the laundry and the use of reactive dyes, which have in their chromophore group the structure N = N on the aromatic structure, leads to the use of a wide range of chemicals, giving to the wastewater strong color and high pollution potential, with possible carcinogenic and mutagenic activity, making these effluents dangerous to humans and aquatic ecosystems. The regional environmental agencies recommend values for COD below 0.125 Kg m^{-3}, BOD below 0.050 Kg m^{-3} and for color below 0.075 Kg PtCo m^{-3}.

The effluents were characterized concerning to various parameters and the results are shown in the Table 1 below:

Table 1: Characterization of the brute effluents.

PARAMETER	Effluent 1	Effluent 2	Effluent 3	Effluent 4	Effluent 5	Effluent 6
pH	6.4	7.3	7.2	6.6	7.5	6.7
Color (Kg PtCo m^{-3})	0.218	0.517	0.335	0.572	0.746	0.1056
Turbidity (FAU)	87	112	75	121	93	146
Wave length (nm)	664	481	608	655	660	477
COD (Kg O_2 m^{-3})	0.2464	0.2402	0.2090	0.2361	0.2380	0.2237
BOD (Kg O_2 m^{-3})	*	*	*	0.03785	0.03006	0.03372
DQO/DBO	*	*	*	6,23	7,91	6,63
Lead (ppm)	0.22	0.16	0.31	0.12	0.17	0.18
Copper (ppm)	0.04	0.06	0.05	0.05	0.05	0.15
Chrome (ppm)	0.04	0.05	0.06	0.05	0.05	0.05
Iron (ppm)	0.32	0.17	0.11	0.04	0.16	0.22
Nickel (ppm)	0.03	0.02	0.03	0.03	0.03	0.04
Zinc (ppm)	0.20	0.01	nd	Nd	nd	nd

* - Not performed.
nd - not detected.

The results presented in Table 1 showed that the parameters of color and COD were higher than the recommended by the environmental agencies and the effluent required proper treatment and also showed that the characteristics of the wastewater changes according to the different periods of the year because there was a variation in the activities of the industrial laundry, using more or fewer dyes, what can difficult the treatment of the effluent to ensure that they always be within the limits for disposal in the environment. The effluents also presented high values of turbidity what may difficult the pass of UV rays through the suspension in the reactor, harming the process. The rate COD/BOD showed the difficult of treating the wastewater with biological process since the BOD of the effluents were below 0.050 Kg m^{-3}. According to the metals (Pb, Cu, Cr, Fe, Ni e Zn), the effluent was within the estabilished limits for disposal.

3.2. Effect of initial pH.

The effluents 1, 2 and 3 were used in bench scale experiments to find the pH and the concentration of ZnO in suspension that provide the best efficiency. Therefore, experiments were performed changing the pH of the effluent in a range of 4-10 and the percentage of decolorization was analyzed. The other parameters were adopted as the ones optimized by Veiber [22] as follows: the concentration of zinc oxide was at 2 Kg m^{-3}, the volume of reaction was 400 mL, four 15 W germicidal lamps were used and the reaction occurred in 4 hours. The results of the effluent's decolorization as a function of the pH of the solution are shown in Figure 4.

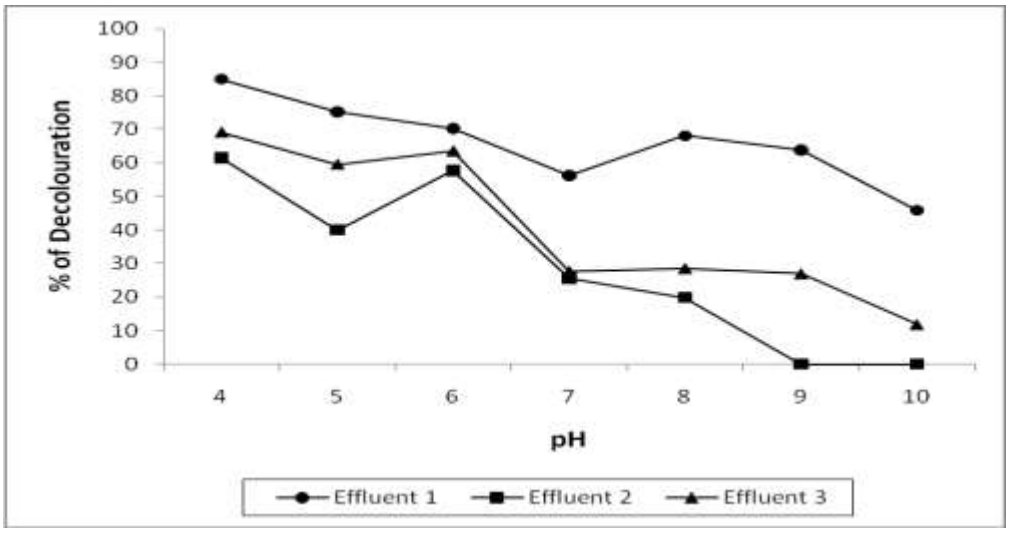

Figure 4: Efficiency of the photo-oxidative process as a function of pH of the solution.

As observed, the pH can be one of the most important parameters in the efficiency of the photodegradation process [23, 12], since it directly influences the surface charge of the particle and also the formation of oxidizing and reducing sites in the catalyst, thus determining the efficiency and stability of the suspension. The pH is related to the ionization of the surface of the reactants and products in the solution, since the degradation of the dye occurs by the contribution of three reaction mechanisms: the hydroxyl radical attack, direct oxidation by the positive gap and the direct reduction by the electron in the conduction band (depending on the nature of the substrate). ZnO is an amphoteric oxide and its point of zero charge is in pH = 9 [12]. The adsorption of the dye molecules in the ZnO surface happens widely in acid pH, when the surface of the catalyst is positively charged, and this may be the reason of higher decolorizations in the acid pH. In alkaline pH, the ZnO surface becomes negatively charged because of the adsorbed OH^-, with less available sites for the dye adsorption. The high concentration of OH^- in the ZnO surface also difficult the adsorption of the molecular oxygen, decreasing the efficiency of the photodegradation [10, 13].

The Figure 4 shows that the highest decolorization occurred in the acid pH = 4, in which were obtained decolorizations of respectively 85 %, 62 % and 69 % for the effluents 1, 2 and 3. The catalytic activity decreased with the increase of the pH, presenting none decolorization for the effluent 3 using the pH of 9 and 10. The difference of the efficiency for the three effluents happened due to the different quantities of chemicals released in the wastewaters by the process of the laundry, changing the conditions of the reaction.

The results are in agreement with those obtained by [23], who studied the photocatalytic degradation of the Acid Violet dye, having a composite of zinc oxide with activated carbon (ZnO: AC) as the catalyst. These researchers have found that the ZnO:AC photo-activation showed a better efficiency in acid pH (2.0), attributing the increase in efficiency in acidic solution to the perhydroxyl radical, which can form the hydrogen peroxide, which then gives rise to hydroxyl radical, promoting the degradation. Another similar result was found on the photocatalytic process using ZnO to the decolorization of "Yellow Cassafix CA-3R" in which the authors obtained the greatest degradation at pH 4.0 [24].

However, these results contradict those obtained by other researchers who used ZnO as the catalyst, and have found the best degradation of dyes in an alkaline solution [2, 6-9]. Since those results were obtained with synthetic effluents, such results might reflect the presence of other compounds in the real wastewater that may be changing the normal optimum conditions.

The pH was not controlled during the experiment and was only measured in the final sample, showing that the final pH of the suspension was between 6.5 and 8.0 for the three effluents. This was attributed to the amphoteric character of ZnO acting as an acid in a basic solution and acting as a base in a acid solution.

The experiments also showed that the effluents with higher “apparent” color were the ones that had less decolorization. This result is in agreement to [2, 3, 6-9, 17, 23]. These authors argue that the efficiency of decolorization is inversely affected by the concentration of the dye, thus the greater the color of the effluent, the lower will be the degradation.

3.3. Effect of catalyst loading.

The next optimized parameter was the catalyst loading. Thus, experiments were made using different concentrations of ZnO for the effluents 1, 2 and 3. The concentrations 2.0, 3.0 and 3.5 Kg m^{-3} were tested keeping the other parameters fixed like as the previous experiments and the pH was adjusted to 4.0 in the beginning of each test. The results of decolorization are shown in Figure 5:

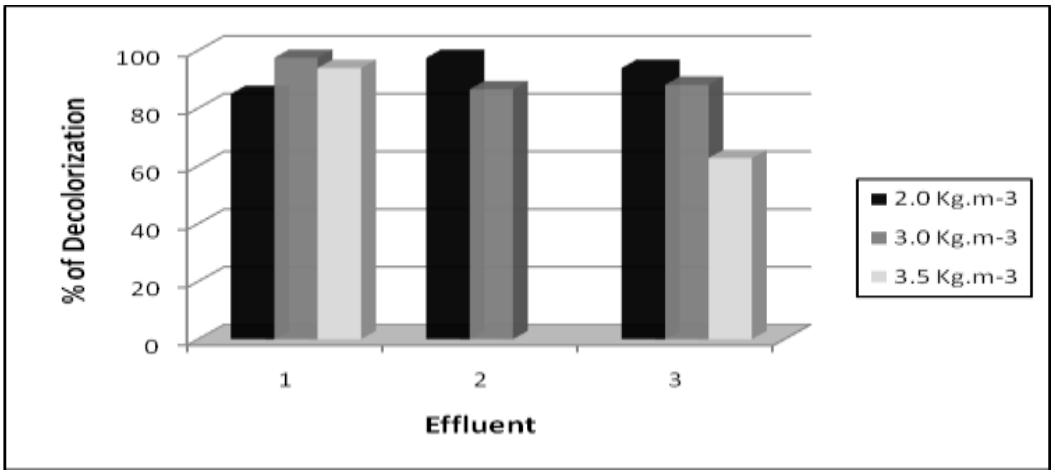

Figure 5: Efficiency of the process as a function of the catalyst loading.
Note: The test with 3.5 Kg.m^{-3} was not performed for the effluent 2.

The concentration of 3.0 Kg m^{-3} of the catalyst provided the higher decolorization for the three effluents according to Figure 5: 97.43% for the effluent 1, 86.53% for the effluent 2 and 88.09% for the effluent 3. It happened because increasing the concentration of ZnO the surface area where the reaction can be catalyzed increases, but very high concentrations can interfere in the pass of the ultra-violet radiation in the solution or result in the deactivation of activated molecules by collision with ground state molecules decreasing the efficiency of the process [2, 6, 8, 9, 11, 14-17, 23]. Therefore, the concentration of 3.0 Kg m^{-3} of ZnO was adopted in the following experiments.

For the tests performed with the concentration of the catalyst of 3.0 Kg m^{-3}, zinc concentrations of 20.8, 31.1 and 28.6 ppm were detected in the final samples for the effluents 1, 2 and 3 respectively showing that part of the zinc in the catalyst was dissolved during the photodegradation process, provided that analysis showed there was no zinc dissolved in the beginning of the experiment. Other author also have obtained similar results with low pH in his study of photocatalytic degradation with ZnO [8, 12]. This makes the effluent unfit disposal, since the CONAMA, which is the National Council of the Environment in Brazil, regulates it in the Resolution 357/2005, the concentration of zinc in the effluent for disposal has to be lower than 0.005 Kg m^{-3}.

3.4. Kinetics study.

The Langmuir-Hinshelwood model, $\ln(C_o/C)=k.t$, where C_o is the initial concentration and C is the concentration at any time (t), was tested in the process and the fit is presented in Figure 6. The process followed the pseudo-first order kinetics [6, 10, 11, 14, 16], with correlation constant for the fit of R^2=0.9793 and the rate constant calculated to be k=0.0073 min^{-1}.

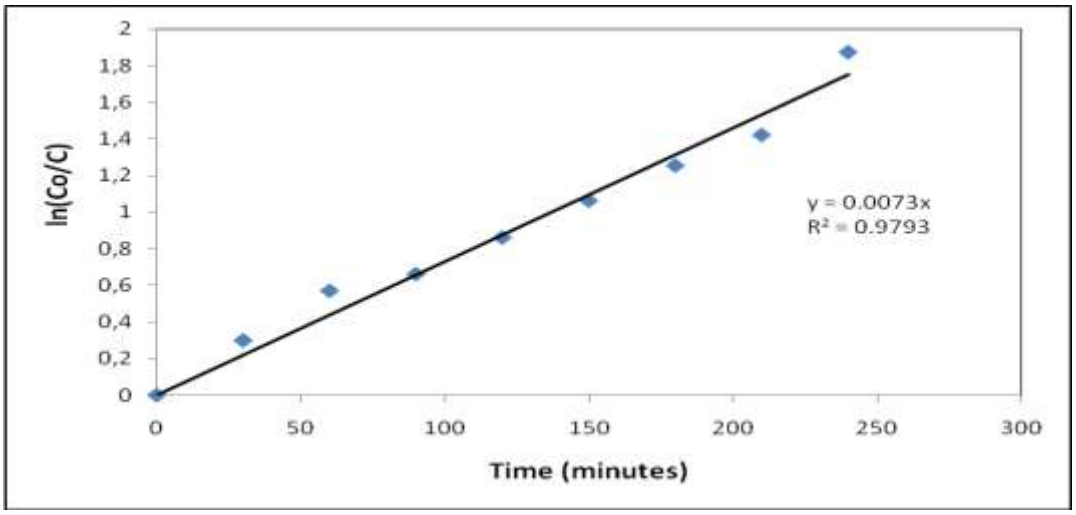

Figure 6: Kinetic fit for the photo catalytic process.

3.5. Experiments in semi-pilot scale.

Photo degradation experiments with the effluents 4 and 5 were performed in the photo-reactor in semi-pilot scale using the optimal conditions obtained previously in order to analyze its reproducibility. The results are shown in Table 2:

Table 2: Evaluation of the photo-degradation in semi-pilot scale.

PARAMETER	Effluent 4	Effluent 5
Inicial Color (Kg PtCo m^{-3})	0.572	0.746
Final Color (Kg PtCo m^{-3})	0.036	0.063
Inicial Absorbance	0.229	0.256
Final Absorbance	0.020	0.013
Decolouration (%)	**91.3**	**95.0**
Inicial COD (Kg O_2 m^{-3})	0.2361	0.2402
Final COD (Kg O_2 m^{-3})	0.1304	0.1217
Reduction of the COD (%)	**44.8**	**49.33**
Zinco Inicial Zinc (ppm)	nd	nd
Final Zinc (ppm)	32.1	34.7

nd - not detected.

The results presented in Table 2 shows that the parameters optimized in bench scale were enough to obtain the reproducibility of the process in semi-pilot scale, providing the color removal and reduction of COD. Again it was observed that the effluent that had higher concentration of color showed the lowest decolorization, and color values below the limit established by CONAMA Resolution 357/2005 for disposal in the environment were obtained for both effluents.

In regards to COD, the process efficiency for the effluent 5 was slightly higher than that obtained for the effluent 4. For the effluent 4, the final concentration of COD was slightly above the limit set by the environmental agencies.

Again, it was found the occurrence of solubilization of the catalyst, leaving the wastewater out of the acceptable standards for disposal, confirming the need of further treatment for zinc removal, in order to fit the environmental regulations.

IV. CONCLUSION

With the characterization of the industrial effluents obtained from the laundry the need of an effective treatment for color removal and COD and BOD reduction before its disposal in the environment can be confirmed, since these parameters were above the limits allowed by regional environmental agencies.

The tests to determine the pH, which provides the activation of the catalysts sites, indicated pH 4.0 as the ideal for better efficiency of the effluents decolorization, but solubilization of zinc oxide was observed in the acid solution, which can be a limiting factor to the use of photocatalysis under these conditions.

The tests to determine the best concentration of ZnO indicated that 3.0 Kg m^{-3} was the concentration that achieved the best decolorization of the effluent, above this concentration the degradation of the dye decreased, losing efficiency significantly. The results showed that the advanced oxidation process using ZnO as the catalyst was efficient in color removal and COD reduction of real textile wastewaters.

It was found that the metals presence in the effluents before the treatment were within the limits established by CONAMA for disposal in the enviroment and remained so after the treatment except for the zinc, which solubilized during the photocatalytic process increasing its concentration in the treated effluent. Thus, the ZnO use as the catalyst under these conditions requires a specific treatment for its removal before the disposal in the environment.

Nomenclature.

ZnO: Zinc oxide

BOD: Biological Oxigen Demand (ML^{-3})

COD: Chemical Oxigen Demand (ML^{-3})

λ_{max}: Maximum Absorbance Wavelenght (L)

Abs_i: Solution's absorbance before the treatment

Abs_f: Solution's absorbance after the treatment

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