Recovery and reuse of TiO_2 photocatalyst in the treatment of slaughterhouse wastewater with sunlight.

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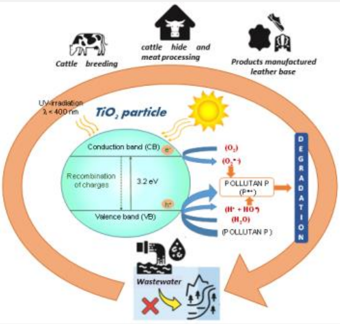

This research focuses on studying the photocatalytic treatment of wastewater from a slaughterhouse. The characterization of the sample indicates the complexity of the wastewater revealing high concentrations of solids, which makes it necessary to include sedimentation and coagulation-flocculation prior to the advanced oxidation process (AOP). Both artificial lighting and sunlight photocatalysis provide very favorable results in terms of COD removal. However, the solar photochemical process achieved the best depuration results (99% COD removal). Recovery tests and FT-IR analysis of TiO_2 from solar experiments indicated that once the wastewater is treated, the photocatalyst still contains impurities. However, with thermal treatment, the material is purified. A 2^{nd} experimental cycle indicated that TiO_2 still maintains its photocatalytic activity by achieving 98% COD removal.

Introduction

The wastewater generated in the centers where meat is processed, such as the municipal slaughterhouses contain a high concentration of thick solids, coat, grease, blood and organic matter (proteins, fats), surfactants as well as and disinfectants used for floor cleaning which makes their treatment difficult [1,2].

In Mexico there are more than 1000 meat processing plants leading to the generation of more than 8 million m^3 of wastewater per year [2]. Unfortunately, in this Latin American country there is no compliance at the regulations of these effluents, and they are often discharged into bodies of water without any treatment generating environmental and public health problems [2,3].

One of the technological proposals for the treatment of complex wastewater is advanced oxidation processes, such as heterogeneous photocatalysis using titanium dioxide. However, there is the challenge of recover and reuse this photocatalyst.

In this project, the efficiency of TiO_2 in the secondary treatment of wastewater from a slaughterhouse was investigated, using artificial and solar light. In addition, the recovery of TiO_2 was studied, then this photocatalyst was reused in a second photo-treatment cycle of this type of effluent.

Material and Methods

The wastewater studied came from a slaughterhouse in central Mexico, to which a gravity sedimentation was applied to separate the heavier solids. Then, coagulation-flocculation was applied using 0.5 g/L of ferric chloride ($FeCl_3$, Golden Bell grade ACS) to remove the solids that could hinder the photocatalytic treatment.

The recovered clarified was then treated via heterogeneous photocatalysis using titanium dioxide (TiO_2, Evonik Aeroxide® P25), in a 250 mL Pyrex glass reactor, using 9-unit LED lighting system (Exulight brand, 30 W). The optimal dose of TiO_2 was studied testing with 0.25, 0.5 and 0.75 g/L irradiated with UV-A light for one hour, to determine the highest percentage of elimination of the parameters analyzed, which were the chemical oxygen demand (COD), total solids (TS), total dissolved solids (TDS) and total suspended solids (TSS), turbidity, conductivity and pH.

Solar photocatalytic treatment was performed for 1 h using the optimal dose of TiO_2 determined in the previous phase, to identify the type of light source more efficient in the depuration of the wastewater samples. Irradiance was measured with a Delta OHM photoradiometer, HD 2102.1 (315-400 nm).

After the solar experiment, the TiO_2 was recovered by sedimentation and drying at room temperature. The mass recovery of photocatalyst was determined. Then, an analysis of the main components of the recovered material via Fourier-transform infrared spectroscopy (FT-IR) was required.

Finally, a treatment at 150 °C in an oven was applied to the recovered TiO_2 to eliminate the impurities found, until completing the mass quantity necessary to carry out the treatments of the 2nd photocatalytic cycle evaluating the photocatalytic activity of recycled TiO_2 in the elimination of organic matter and other parameters from slaughterhouse wastewater.

Results and Discussion

Slaughterhouse wastewater (SWW) raw showed a COD of 6000 ± 282.84 mg/L, TS of 2020 ± 180 mg/L, TSS of 375 ± 57.70 mg/L, conductivity of 1401 ± 5.05 µS/cm, turbidity of 205 ± 2.83 NTU, and pH of 7.21 ± 0.30. Due to the high concentration of solids containing in the sample it was decided to apply sedimentation and coagulation-flocculation prior to the photocatalytic treatment, achieving 33% and 50% of COD removal, respectively.

Regarding the dose of photocatalyst, 0.25 g/L was found as the optimal value, in tests with LED lighting, when reaching up to 97% of COD removal, while with the other doses of TiO_2 90% of organic matter removal was achieved. Solar photocatalysis achieved an improvement in the removal of organic matter, delivering 99% COD removal.

The behavior of the removal of COD in each stage of wastewater treatment is depicted in Figure 1, where it is confirmed that the photocatalysis is the process that contributes most to the elimination of pollutants in slaughterhouses wastewater.

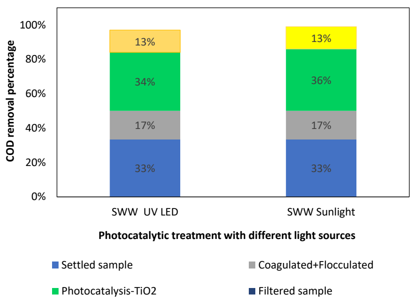

Figure 4. Comparison of the contribution of the elimination of COD of each operation applied to the treatment of SWW.

Once sedimented and dried the TiO_2 after the photocatalytic treatment a mass recovery of up to 88% was obtained.

Analyzing this TiO_2 residual via Fourier-transform infrared spectroscopy the spectra with broad bands between 880 and 500 cm^{-1} was detected that are related to the typical stretching vibration of the Ti-O-Ti and Ti-O-C bonds, while other absorption peaks detected were related to the rest of the organic matter, as shown in Figure 2.

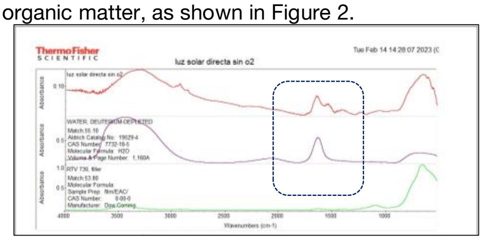

Figure 2. FT-IR spectra of the TiO_2 P25 recovered after solar photocatalytic treatment of SWW.

With the above, it was necessary to purify the recovered TiO_2 by thermal method before using it in a 2nd experimental cycle. The results of the FT-IR analysis of the recovered and heat-treated TiO_2 indicated the disappearance of the atypical peaks related to remaining impurities around 1600 cm^{-1}.

Now, the TiO_2 could be used in a 2nd photocatalytic experiment achieving a 98% removal of COD.

The results of the characterization of the samples treated via photocatalysis are shown in Table 1, where it can be confirmed that although there is an increase in the final concentration of COD for the experiment where recycled TiO_2 was applied, these values are better compared to those achieved with photocatalysis with LED lighting.

Table 1. Physicochemical characteristics of the slaughterhouse wastewater in the main photocatalytic experimental stages.

Sample	COD	TS	Conductivity	Turbidity	pH
	mg/L	mg/L	µS/cm	NTU	
Raw SWW	6000 ± 283	2020 ± 180.10	1401 ± 5.05	205 ± 2.83	7.21 ± 0.30
SWW+TiO_2 UV-LED	160 ± 28.28	242.45 ± 39.14	1014 ± 2.83	10 ± 1.41	7.74 ± 0.36
SWW+TiO_2 Sunlight	80 ± 14.14	161.62 ± 20.80	954 ± 4.35	7 ± 0.71	7.23 ± 0.29
2nd cycle SWW+TiO_2 Sunlight	140 ± 21.21	204.10 ± 42.29	894 ± 5.29	45 ± 2.83	7.80 ± 0.24

Conclusions

The research confirmed the benefit obtained with photocatalysis using TiO_2, within a treatment train of a complex effluent such as slaughterhouse wastewater. Solar photocatalysis means an improvement in the process for two reasons, the use of clean energy and the improvement in the quality of the effluent, which complies with some levels established in Mexican wastewater regulations (NOM-001-SEMARNAT-2021). A significant contribution of the project is the study of the recovery and reuse of TiO2, which demonstrates the effectiveness of using recycled material, providing encouraging results.

References

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