EESj
Vol. 5, N° 1, 2021

Journal of Energy & Environmental Sciences

A publication of
CINCADER
Centre of Research and Training for Regional Development
Online at www.journals.cincader.org

ISSN 2523-0905
DOI: https://doi.org/10.32829/eesj.v5i1.126

Influence Modeling and optimization of sulphide removal by catalytic oxidation of tannery fur effluents [Modelamiento y optimización de la remoción de sulfuros por oxidación catalítica de efluentes de pelambre de curtiduría]

Jorge Mendoza Bobadilla*[a], Adolfo Guerrero Escobedo[b], Walter Moreno Eustaquio[c], Marina Ponce Zavaleta[a], Luisa Carbajo Arteaga[a]

[a]Laboratorio de Investigación en Aguas, Ingeniería Ambiental, Universidad Nacional de Trujillo, Perú.
[b]Laboratorio de Investigación en Físicoquímica, Ingeniería Química, Universidad Nacional de Trujillo, Perú.
[c]Laboratorio de Investigación en Residuos Peligrosos, Ingeniería Ambiental, Universidad Nacional de Trujillo, Perú.
*jmendoza@unitru.edu.pe

Received: 20 May 2021; Accepted: 3 June 2021; Published: 13 June 2021

Resumen

Los efluentes residuales de la etapa de pelambre de la Industria de curtiduría de pieles de vacuno se caracterizan por presentar una concentración elevada de sulfuros. El objetivo de este estudio fue evaluar los efectos del tiempo de aireación y pH en los efluentes residuales de la etapa de pelambre de la curtiduría, con los catalizadores MnO_2 y $MnSO_4$ por separado; así como, determinar modelos de ajuste mediante la metodología de la superficie de respuesta y los intervalos óptimos de las mejores condiciones que conlleven a un mayor porcentaje de remoción de sulfuros. Por tal motivo, se evaluó el porcentaje de remoción de sulfuros, de muestras extraídas de la etapa de pelambre, mediante tratamientos de oxidación catalítica; variando el catalizador, el pH y tiempo de aireación. Los catalizadores empleados fueron dióxido de manganeso (MnO_2) y sulfato de manganeso ($MnSO_4$) y para cada catalizador se varió el pH en los valores de 8,5; 9,5; 10,2 y 13,4; así mismo se varió el tiempo de aireación en los valores de 30, 60, 90, 120, 150, 180, 210 y 240 minutos. Se realizaron 64 tratamientos, con 3 repeticiones cada uno, reportando los valores promedio de porcentaje de remoción de sulfuros. Se utilizó la metodología de superficie de respuesta para ajustar la correlación de las variables a un modelo cuadrático; así mismo, mediante los gráficos de contorno se identificaron fácilmente las regiones con mayor porcentaje de remoción de sulfuros y mediante la superposición de gráficos de contorno se determinó los rangos óptimos de las variables pH y tiempo de aireación para porcentajes de remoción mayores a 98%. En función de esta evaluación, se propone para los tratamientos con dióxido de manganeso, tiempos de aireación entre 160 a 240 min y pH entre 8,5 a 9 y para los tratamientos con sulfato de manganeso, tiempos de aireación entre 110 a 240 min y pH entre 8,5 a 9,8. Los coeficientes de determinación múltiple R^2 para los modelos con catalizador MnO_2 y $MnSO_4$ fueron de 97,51% y 95,12% respectivamente. Con el catalizador $MnSO_4$ se alcanzaron mayores porcentajes de remoción a menor tiempo de aireación, en comparación con los tratamientos realizados con el catalizador MnO_2.

Palabras clave: Efluentes residuales, pelambre, curtiduría, catalizador, remoción.

Abstract

The residual effluents from the fur stage of the bovine leather tannery industry are characterized by having a high concentration of sulfides. The objective of this study was to evaluate the effects of aeration time and pH in the residual effluents of the leather stage of the tannery, with the catalysts MnO_2 and $MnSO_4$ separately; as well as, determine adjustment models through the response surface methodology and the optimal intervals of the best conditions that lead to a higher percentage of sulfide removal. For this reason, the sulphide removal percentage was

Please cite this article as: Mendoza J., Guerrero A., Moreno W., Ponce M., Carbajo L. Influence Modeling and optimization of sulphide removal by catalytic oxidation of tannery fur effluents, Journal of Energy & Environmental Sciences, vol. 5, no 1, 2021, pp. 20-28. https://doi.org/10.32829/eesj.v5i1.126

ISSN 2523-0905
DOI: https://doi.org/10.32829/eesj.v5i1.126

evaluated from samples extracted from the pellet stage, by means of catalytic oxidation treatments; varying the catalyst, pH and aeration time. The catalysts used were manganese dioxide (MnO_2) and manganese sulfate ($MnSO_4$) and for each catalyst the pH was varied in the values of 8.5; 9.5; 10.2 and 13.4; likewise, the aeration time was varied in the values of 30, 60, 90, 120, 150, 180, 210 and 240 minutes. 64 treatments were carried out, with 3 repetitions each, reporting the average values of the sulfide removal percentage. The response surface methodology was used to adjust the correlation of the variables to a quadratic model; Likewise, through contour graphs the regions with the highest percentage of sulfide removal were easily identified and by superimposing contour graphs the optimal ranges of the variables pH and aeration time were determined for removal percentages greater than 98%. Based on this evaluation, it is proposed for treatments with manganese dioxide, aeration times between 160 to 240 min and pH between 8.5 to 9 and for treatments with manganese sulfate, aeration times between 110 to 240 min and pH between 8.5 to 9.8. The coefficients of multiple determination R2 for the models with catalyst MnO_2 and $MnSO_4$ were 97.51% and 95.12% respectively. With the $MnSO_4$ catalyst, higher removal percentages were achieved at a shorter aeration time, compared to the treatments carried out with the MnO_2 catalyst.

Keywords: Waste effluent, pelt, tannery, catalyst, removal.

1. Introduction

The tanning industry is considered one of the most polluting industrial activities in the world, which generates effluents that contain persistent pollutants and has been recognized as a serious environmental threat due to high levels of salinity, organic and inorganic matter, suspended solids, dissolved ammonia, total nitrogen, sulfur, sodium chloride, chromium, among others. (Kothiyal et al, 2016; Salas, 2005). However, it should be noted that tannery wastewater can vary significantly, depending on the nature of the tanning process, the processing capacity, the amount of water used and the storage process of the hides. (Caliari et al., 2019). In the tanning process, the stage that generates the greatest pollutant load, bad odors and the greatest use of water is the pelt stage, which consists of subjecting the hides to a treatment with a solution of sulfides in an alkaline medium, with the aim of depilate the skin, completely removing the keratin material (hair, hair roots and epidermis). In its wastewater from this process, sulfur (S^{2-}) becomes one of the most important pollutants in different aqueous solutions and aquatic media, as well as in the air, because it is released in the form of hydrogen sulfide (H_2S) at $pH <9$, being a real threat to human life due to its high toxicity and, at lower concentrations, a serious odor nuisance. Once emitted, it can be reabsorbed and oxidized in the aqueous film that covers concrete surfaces (for example, in a sewer system), causing severe corrosion in concrete. (Guzmán and Luján, 2010; Wilk et al., 2020). Therefore, there is considerable interest in the development of efficient and low-cost systems for the removal of sulfur from the gas and especially from the aqueous phase. (Cunha et al., 2016).

The removal of sulfur has been investigated using different methods such as adsorption with absorbents such as activated carbon, alumina, silica and zeolite; biological processes such as biofilters and microorganisms supported on activated carbon, these being studied to be able to oxidize sulfides in sulfur-containing species such as elemental sulfur, polysulfides, thiosulfate, tionates and sulfate in aqueous medium; precipitation of dissolved sulfides with iron salts to form ferric sulfide, which is non-toxic, sparingly soluble, and thermodynamically stable in neutral and basic solutions (if $FeCl_3$ is used, sulfides are also partially oxidized); photo-assisted electrochemical oxidation processes with UV light to remove sulphides from tannery wastewater (liming); and / or catalytic oxidations. (Wilk et al., 2020; Cunha et al., 2016; Selvaraj et al., 2019). Catalytic oxidation makes it possible to transform sulfides into a much less toxic compound such as sulfur or sulfates in an efficient, selective and reliable way by means of low molecular weight

ISSN 2523-0905
DOI: https://doi.org/10.32829/eesj.v5i1.126

oxidants such as oxygen, ozone, hydrogen peroxide or chlorine and their compounds. It was suggested that two characteristics are important for an active system, that is, a surface redox group to exchange electrons with sulfide species and an electron conductive structure to promote oxidation. The main advantages of the route include high reactivity under ambient conditions, high sulfide decomposition rate, high selectivity to a single milder product (sulfoxide is much less toxic than an over-oxidized sulfone or hydrolysis by-products), and high capacity in activity. catalytic. Several catalytic systems have been developed, including transition metals, noble metals, polyoxometalates, nitrogen oxide, halides / nitrates, among others. Research over the years has shown that metal oxides can effectively remove dissolved sulfides from aqueous solution, among which manganese (IV) and iron (III) oxides are the most important. (Wilk et al., 2020; Cunha et al., 2016; Hong et al., 2019).

2. Materials and Methods

Obtaining samples

The residual water samples from the fur stage were collected from the Junior Tannery SAC located in the Industrial Park of the city of Trujillo - Peru, before being transferred to the Water Research Laboratory of the National University of Trujillo, they were left at rest. for 12 hours in order to settling remains of hair and sedimentable solids.

Regarding the characterization of the samples, the pH and sulfides were analyzed, the pH being analyzed through the Thermo Fisher Scientific multiparameter and the initial concentrations of sulfides determined by Visocolor Eco colorimetric tests and PF-12 Macharey Nagel Photometer in the Water Research Laboratory at the National University of Trujillo. 2 L of sample were used for each experimental treatment.

Experimental design

An experimental design was carried out in order to evaluate the effect of the variables pH (8.5, 9.5, 10.2 and 13.4) and aeration time (30, 60, 90, 120, 150, 180, 210 and 240 minutes) in the percentage of removal of sulphides present in the wastewater of the fur stage from the tannery industry. The pH was varied using phosphoric acid.

Experimental Procedure

The treatments were carried out in aerated batch type reactors with a capacity of two liters in the Water Research laboratory. For the oxidation of the sulfide, manganese sulfate and manganese dioxide were used as catalysts, incorporating oxygen to the system through aeration constantly (4 L/min) for 4 hours, extracting samples every 30 minutes to determine the percentage of removal of sulfides in function of the pH of the solution and aeration time. Each treatment had three replications, presenting as results the average values of the sulfide removal percentage. The variations in pH and aeration time in the proposed ranges were carried out in two groups of treatments: one group with the catalyst MnO_2 at a concentration of 430 ppm and the other group with $MnSO_4$ at 747 ppm in order to maintain the same amount of manganese in both groups.

Statistical Analysis, Modeling and Optimization

An analysis of variance was carried out at pH and aeration time according to the linear and quadratic modeling obtained by the response surface method. To visualize the optimal region of maximum removal, 3D response surface graphs and 2D contour graphs were made; for both tests performed with MnO_2 and $MnSO_4$. The p-test statistic was verified for each factor, in order to evaluate the degree of significance; as well as the coefficient of determination R2. Contour overlay graphs were made for a better visualization of the ranges with the highest removal of sulfides. Statistical evaluations were performed with Minitab 19 software.

EESj
Vol. 5, N° 1, 2021

Journal of Energy & Environmental Sciences

A publication of
CINCADER
Centre of Research and Training for Regional Development
Online at www.journals.cincader.org

ISSN 2523-0905
DOI: https://doi.org/10.32829/eesj.v5i1.126

3. Results

Effect of aeration time and pH using MnO_2

The pellet effluent presented initial pH and sulphide values of 13.4 and 467 ppm respectively. Figures 1 and 2 show the percentages of removal of sulfide ions as a function of pH and aeration time, where it can be seen that the highest removal percentages were obtained using $MnSO_4$ as a catalyst. In addition, it is observed that as the pH increases, the removal percentages decrease both for the treatment with MnO_2 and with $MnSO_4$, since in several studies it has been shown that a decrease in the pH of the reaction solution increases the oxidation capacity. the catalyst; in turn, both the speed and the final oxidation product depend on this parameter. (Herszage and Dos Santos, 2003; Ahmad, 2009; Qiu, 2011; Wilk et al., 2020).

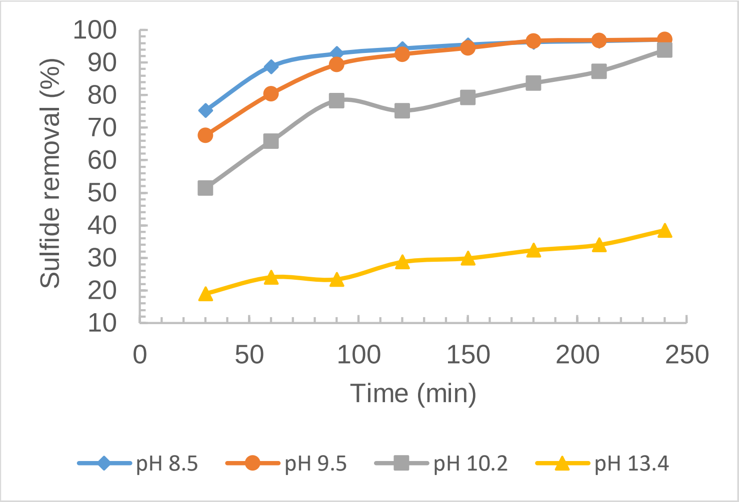

Figure 1. Percentage of sulfide removal as a function of aeration time and pH, in the presence of MnO_2.

Effect of aeration time and pH using $MnSO_4$

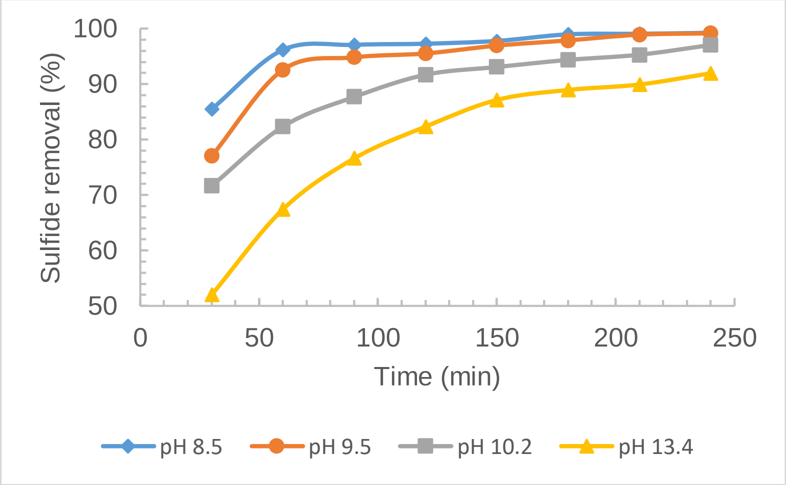

Figure 2. Percentage of sulfide removal as a function of aeration time and pH, in the presence of $MnSO_4$.

ISSN 2523-0905
DOI: https://doi.org/10.32829/eesj.v5i1.126

In catalytic oxidation of sulfides with MnO_2, the dissolution reaction begins through a surface complex formation by adsorption of S^- to the surface of manganese oxide. Afterwards, the transfer of two electrons from the S^- atom to the valence band of MnO_2 occurs, therefore, the surface of the manganese oxide oxidizes the sulfide complex on the surface to zero adsorbed sulfur (direct Mn-S bond) in two steps. There is a suggestion that after the first step an S-free radical could form, which undergoes further oxidation to S^0 after the transfer of the second electron. S^0 can react with excess sulfur present in solution to form polysulfide or with other S^0 to form stable cyclic form S_8. In turn, during this process, a surface complex Mn (III) is formed as an intermediate reaction. Generally, after the Mn-S surface complex is formed, it could follow two different and competing reaction pathways that lead to the formation of S_8 or sulfate. In research carried out, there is clear evidence that Mn (III) is an intermediate in the reducing solution of MnO_2; it is possible and favorable for sulfide species to form a surface complex also with an Mn (III) atom, and that after the formation of a complex (with an Mn (IV) or Mn (III) atom), 2 Electrons could be transferred to reduce one Mn atom (eg Mn (IV) to Mn (II)) or two different Mn atoms (eg Mn (IV) to Mn (III)) in the oxide structure. The distribution of oxidation products has been shown to change with pH, with sulfate being the main product at low pH values and elemental sulfur at near neutral pH. (Herszage and dos Santos, 2003; Wilk et al., 2020). In a study it was determined that elemental sulfur amounted to 80% of the oxidation products formed at pH 8.0. Likewise, in another investigation they studied the changes in the distribution of the reaction products with the sulfide to oxide ratio. The results showed that, at pH 7.5 and for a MnO_2/H_2S ratio equal to 1, sulfur is the main product and the amount of sulfate formed increases with the MnO_2/H_2S ratio. (Hersztage et al., 2003).

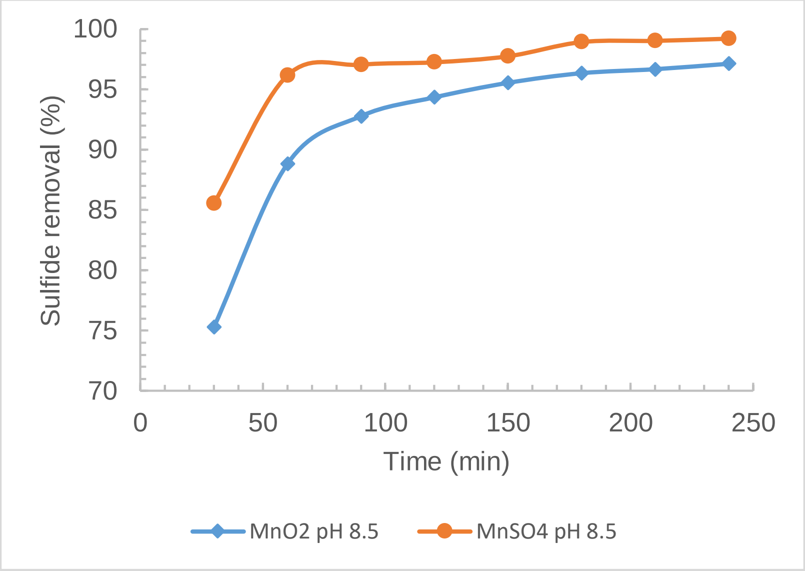

Figure 3. Efficiency of catalytic oxidation of sulfides with MnO_2 and $MnSO_4$, at pH 8.5.

Analyzing figure 3, the best removal percentages for a pH of 8.5 are shown, achieving a removal greater than 95% for both catalysts, evidencing and confirming what was previously stated that the oxidation capacity of the catalyst increases with the increase in acidity in the reaction system. In addition, it must be taken into account that another factor, strongly influenced by the oxidation capacity of the catalyst, is the availability of oxygen. In the case of MnO_2, its activity depends on the relative amount of surface defects (that is, oxygen species adsorbed on the surface), which could activate molecular oxygen and / or water molecules into oxygen species adsorbed on the

ISSN 2523-0905
DOI: https://doi.org/10.32829/eesj.v5i1.126

surface. Therefore, the greater the amount of these species, the greater the catalytic activity. The oxygen lability of the lattice can also influence the formation of surface adsorbed species through complex interaction with oxygen vacancies and molecular oxygen. Oxygen vacancies are common in metal oxides and can serve as adsorption and active sites for heterogeneous catalytic reactions. (Miao, 2018).

Modeling according to the Response Surface Methodology

Figures 4 and 5 show the 3D surface graphs according to the models obtained with the response surface methodology; as well as 2D contour graphics. Theoretically, the highest removal percentages, according to the model obtained for manganese dioxide, are obtained from an aeration time of 180 minutes and pH 8.5 - 8.7 and for the model obtained with manganese sulfate, they are obtained from 50 minutes in a wide pH range.

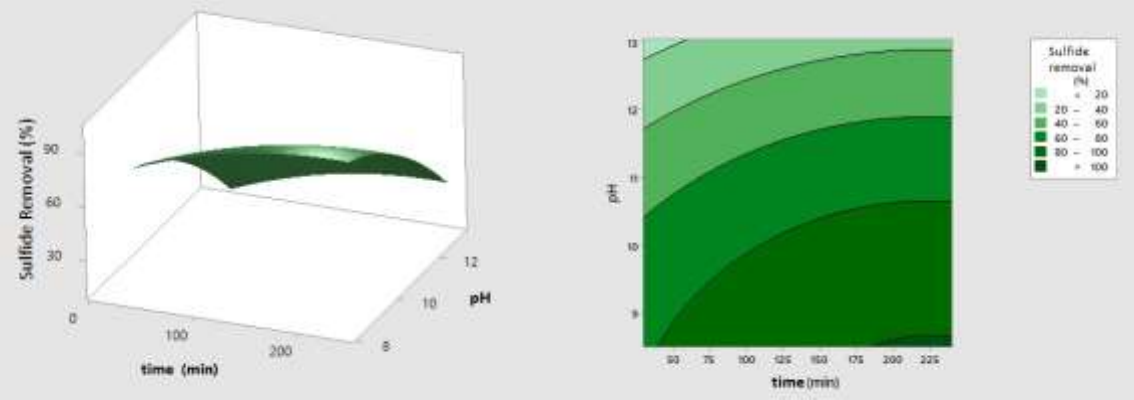

Figure 4. 3D surface and 2D contour graphics to obtain the maximum percentage of sulfide removal, with MnO_2 catalyst.

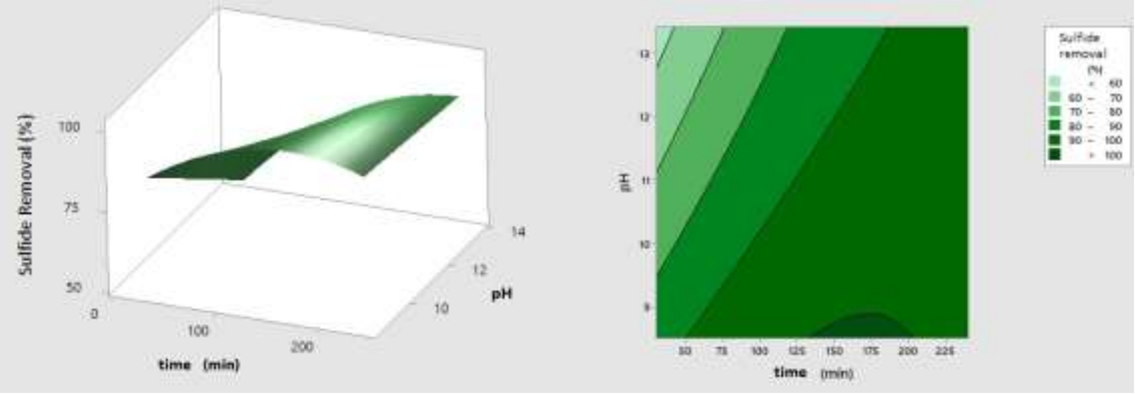

Figure 5. 3D surface and 2D contour graphics to obtain the maximum percentage of sulfide removal, with $MnSO_4$ catalyst.

Overlay of contour plots of the models obtained for MnO_2 and $MnSO_4$

EESj
Vol. 5, N° 1, 2021

Journal of Energy & Environmental Sciences

A publication of
CINCADER
Centre of Research and Training for Regional Development
Online at www.journals.cincader.org

ISSN 2523-0905
DOI: https://doi.org/10.32829/eesj.v5i1.126

Looking for the conditions of aeration time and pH that allow removal percentages from 98%, according to the superposition of contour graphs, as well as the adjusted values of the models shown in Table 1, it is proposed for the treatments with dioxide. of manganese the aeration time range of 160 - 240 min and pH between 8.5 - 9 and for the treatments with manganese sulfate an aeration time range of 110 - 240 min and pH between 8.5 - 9.8. The white area of each graph shown in Figure 6 indicates the region with the most appropriate conditions to achieve high sulfide removal.

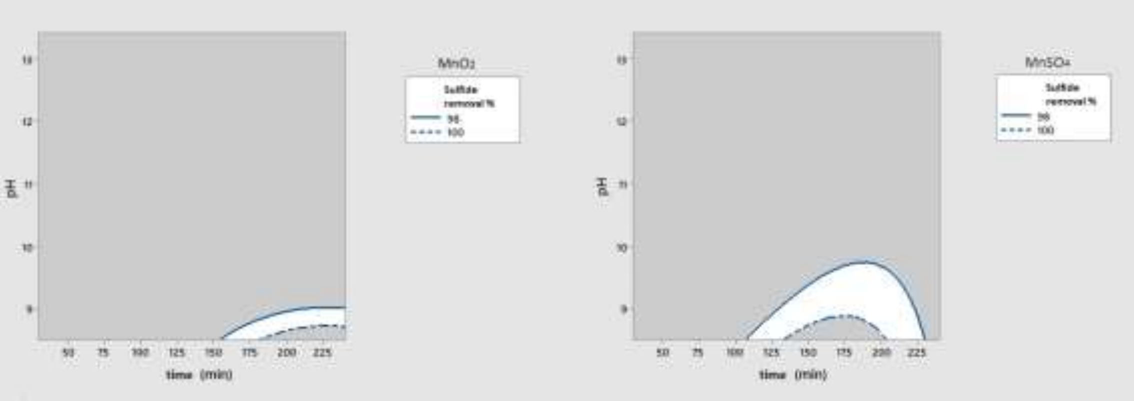

Figure 6. Overlay of contour plots for the for the models obtained with MnO_2 and $MnSO_4$

Table 1. Prediction of sulfide removal percentage for proposed aeration times and pH according to quadratic models

Time (min)	pH	MnO_2 catalyst % sulfide removal	EE* adjustment	$MnSO_4$ catalyst % sulfide removal	EE adjustment
120	8,5	94,2395	1,8323	99,1785	0,8415
120	9	91,0540	1,3969	97,2472	0,7746
150	8,5	94,4881	1,3969	100,752	0,8415
150	9	99,9901	1,7607	99,1971	0,7746
180	8,5	96,8046	1,3016	100,895	0,8450
180	9	99,9901	1,7607	99,7165	0,7526
210	8,5	101,1890	1,8323	99,6074	0,9831
210	9	98,0034	1,3969	98,8054	0,8604

* EE: Standard error

Statistical analysis of the models obtained for manganese dioxide and manganese sulfate

According to the analysis of variance in Table 2, the model obtained for the response surface graph in its linear and quadratic part shows that all the independent variables present a test statistic of p less than 0.05, demonstrating statistical significance. Likewise, it is observed that there are no interactions between the pH factors and aeration time.

Table 2. Analysis of Variance for the total quadratic model using MnO_2 catalyst

Source	DF*	SS* Ajust.	MS* Ajust.	Value F	Value p
Model	4	22813,70	5703,40	264,03	0,0000
Lineal	2	19389,90	9694,90	448,81	0,0000
time (min)	1	1981,20	1981,20	91,72	0,0000
pH	1	17408,60	17408,60	805,90	0,0000
Square	2	619,40	309,70	14,34	0,0000
time (min)*time (min)	1	209,80	209,80	9,71	0,0040
pH*pH	1	409,60	409,60	18,96	0,0000
Error	27	583,20	21,60		
Total	31	23397,00			

* DF: Degrees of freedom, SS Adj .: Adjusted sum of squares, MS Adj .: Adjusted mean squares

In Table 3, all the statistics of test b are less than 0.05 indicating significant differences in the treatments, with the exception of the quadratic term of the pH. In this case, for the $MnSO_4$ catalyst, if there is an interaction of the pH factors and aeration time; therefore, they are considered in the model.

Table 3. Analysis of Variance for the total quadratic model using $MnSO_4$ catalyst

Source	DF*	SS* Ajust.	MS* Ajust.	Value F	Value p
Model	5	3491,71	698,34	101,45	0,0000
Lineal	2	3051,92	1525,96	221,69	0,0000
time (min)	1	1800,69	1800,69	261,6	0,0000
pH	1	1251,23	1251,23	181,78	0,0000
Square	2	346,82	173,41	25,19	0,0000
time (min)*time (min)	1	343,79	343,79	49,94	0,0000
pH*pH	1	3,03	3,03	0,44	0,5130
Interaction of 2 factors	1	320,38	320,38	46,54	0,0000
time (min)*pH	1	320,38	320,38	46,54	0,0000
Error	24	178,97	6,88		
Total	29	3670,68			

Table 4 shows that the model for the manganese dioxide catalyst explains 97.51% of the variation of the sulfide removal percentage and that the model for the manganese sulfate catalyst explains 95.12% of the variation of the sulphide removal percentage.

Table 4. Standard deviations and coefficients of determination R2 for the models obtained with MnO_2 and $MnSO_4$

Catalyst	Standard Deviation (S)	Determination coefficient of R^2	R^2 adjusted	R^2 pronosticated
MnO_2	4,64774	97,51%	97,14%	96,29%
$MnSO_4$	2,62361	95,12%	94,19%	91,98%

Copyright © 2021, CINCADER.
ISSN 2523-0905
DOI: https://doi.org/10.32829/eesj.v5i1.126

4. Conclusions

According to the results obtained, the $MnSO_4$ catalyst achieves the highest removal percentages with a shorter aeration time compared to the MnO_2 catalyst. To obtain removal percentages of 98% or more, according to mathematical modeling, for manganese dioxide it is required to work in the aeration time range of 160 - 240 min and pH between 8.5 - 9 and for sulfate treatments manganese, aeration time range of 110 - 240 min and pH between 8.5 - 9.8. Experimentally, at a pH of 8.5, sulphide removal percentages greater than 95% are obtained for both catalysts.

5. Acknowledgments

The authors thanks to the Water Research Laboratory from the School of Environmental Engineering at the National University of Trujillo.

References

Ahmad, N. W. 2009. Remediation of sulfidic wastewater by catalytic oxidation with hydrogen peroxide. Journal of Environmental Science. 21(12): 1735-1740. doi: https://doi.org/10.1016/S1001-0742(08)62481-X

Caliari, P.C., Pacheco, M. J., Ciríaco, L., Lopes, A. 2019. Tannery wastewater: Organic load and sulfide removal dynamics by electrochemical oxidation at different anode materials. Environmental Technology & Innovative. 14. doi:https://doi.org/10.1016/j.eti.2019.100345.

Cunha, I. T., Teixeira, I. F., Albuquerque, A. S., Ardisson, J. D., Macedo, W. A., Oliveira, H. S., et al. 2016. Catalytic oxidation of aqueous sulfide in the presence of ferrites (MFe_2O_4, M = Fe, Cu, Co). Catalysis Today, 259(1); 222-227. https://doi.org/10.1016/j.cattod.2015.07.023

Guzmán, K., Luján, M. 2010. Reducción de emisiones de la etapa de pelambre en el proceso de curtido de pieles. Acta Nova, 4 (4), pp. 464-492.

Herszage, J., Dos Santos Alfonso, M. 2003. Mechanism of Hydrogen Sulfide Oxidation by Manganese (IV) Oxide in Aqueous Solutions. Langmuir. 19(23): 9684–9692. https://doi.org/10.1021/la034016p.

Hong Le, N, Han, Y., Jung, H., Cho, J. 2019. Catalytic reaction system for rapid selective oxidation of alkyl sulphide. Journal of Hazardous Materials. 379. https://doi.org/10.1016/j.jhazmat.2019.120830.

Kothiyal, M., Kaur, M., Dhiman, A. A., 2016. Compartive Study on Removal Efficiency of Sulphide and Cod from the Tannery Effluents by Using Oxygen. International Journal of Environmental Research. 10(4): 525-530. 10.22059/IJER.2016.59681

Miao, L. W. 2018. Review on manganese dioxide for catalytic oxidation of airborne formaldehyde. Applied Surface Science. 441-453. https://doi.org/10.1016/j.apsusc.2018.10.031

Qiu. G. L. 2011. Oxidation behavior and kinetics of sulfide by synthesized manganese oxide minerals. Journal of Soils and Sediments. 11(8): 1323-1333.

Salas, G. 2005. Eliminación de sulfuros por oxidación en el tratamiento del agua residual de una curtiembre. Revista Peruana de Química e Ingeniería Química, 8(1): 49-54.

Selvaraj, H., Aravind, P., Sindhuja, H., Sundaram, M. 2019. Removal of sulfide and recycling of recovered product from tannery lime wastewater using photoassisted-electrochemical oxidation process. Journal of Industrial and Engineering Chemistry. https://doi.org/10.1016/j.jiec.2019.11.024.

Wilk, L. J., Ciechanowska, A., Kociolek, E. 2020. Removal of sulfides from water using a hybrid ion exchanger containing manganese(IV) oxide. Separation and Purification Technology. 231. https://doi.org/10.1016/j.seppur.2019.115882.