

Leachate Treatment via TiO₂/UV Heterogeneous Photocatalysis: A Multiple Polynomial Regression Model

Tratamiento de lixiviados mediante fotocatalisis heterogénea TiO₂/UV: un modelo de regresión polinomial múltiple

Dorance Becerra-Moreno¹, Fiderman Machuca-Martínez², Aymer Y. Maturana³, Salvador Villamizar⁴, Joseph Soto-Verjel⁵, and Ángelo Soto-Vergel⁶

ABSTRACT

Advanced oxidation processes such as TiO₂/UV heterogeneous photocatalysis are suitable treatment methods for wastewater with high pollutant loads such as landfill leachates. Optimizing the variables that influence the process is a fundamental aspect. However, in this regard, experimental conditions are limited in terms of resources and time, which is why modeling allows obtaining a general understanding of the phenomenon from a set of experimental data. This work sought to model the photocatalytic process via multivariate polynomial regression, considering variables such as the catalyst concentration, the pH level, and the accumulated energy concerning the percentage of degradation in terms of dissolved organic carbon (DOC). The implemented fitting method resulted in a third-degree polynomial with an R² of 0,8652, concluding that the model and its conclusions are valid. Moreover, with greater degrees, the model curve overfitted, even with better R². DOC abatement showed a negative correlation with pH and the catalyst dose, while an opposite trend was observed for the accumulated energy. The model predictions allow inferring that, at low catalyst doses and medium and high pH levels, it is possible to find maximum degradations at low cumulative energies.

Keywords: leachates, TiO₂, heterogeneous photocatalysis, model, polynomial regression

RESUMEN

Los procesos de oxidación avanzada como la fotocatalisis heterogénea TiO₂/UV son métodos de tratamiento adecuados para aguas residuales con altas cargas contaminantes como los lixiviados de rellenos sanitarios. La optimización de las variables que influyen en el proceso es un aspecto fundamental. Sin embargo, en este aspecto, las condiciones experimentales son limitadas en términos de recursos y tiempo, por lo que el modelado permite obtener una comprensión general del fenómeno a partir de un conjunto de datos experimentales. Este trabajo pretendió modelar el proceso fotocatalítico mediante regresión polinómica multivariada, teniendo en cuenta variables como la concentración del catalizador, el nivel de pH y la energía acumulada en relación con el porcentaje de degradación en términos de carbono orgánico disuelto (DOC). El método de ajuste implementado dio como resultado un polinomio de grado 3 con un R² de 0,8652, concluyendo que el modelo y sus conclusiones son válidos. Además, a mayor grado, la curva del modelo se sobreajustó, incluso con mejor R². La remoción de DOC mostró una correlación negativa con el pH y la dosis de catalizador, y se observó una tendencia opuesta para la energía acumulada. Finalmente, las predicciones del modelo permiten inferir que, a dosis bajas del catalizador y niveles medios y altos de pH, es posible encontrar degradaciones máximas con bajas energías acumuladas.

Palabras clave: lixiviado, TiO₂, fotocatalisis heterogénea, modelo, regresión polinómica

Received: March 6th, 2022

Accepted: June 1th, 2023

Introduction

Heterogeneous photocatalysis is an advanced oxidation process (AOP) that uses a semiconductor photocatalyst which, when subjected to a specific radiation, allows for oxidation-reduction processes, enabling the removal of pollutants and providing effluents with lower toxicity (Gout *et al.*, 2022). Landfill leachates contain high amounts of heavy metals, solids (suspended and settleable), and organic matter (Vahabian *et al.*, 2019). The recalcitrant characteristics of the individual pollutants and the highly variable generation rates are the leading factors that hinder their treatment (Chaturvedi and Kaushal, 2018; Müller *et al.*, 2015). It is there that AOPs, by improving

¹ Master, Universidad Francisco de Paula Santander, Cúcuta, Colombia. Affiliation: Departamento de Ciencias del Medio Ambiente, Facultad de Ciencias Agrarias y del Ambiente, dorancebm@ufps.edu.co

² PhD, Universidad del Valle, Cali, Colombia. Affiliation: Escuela de Ingeniería Química, CENM.

³ PhD, Universidad del Norte, Barranquilla, Colombia. Affiliation: Departamento de Ingeniería Civil y Ambiental – Instituto de Estudios Hidráulicos y Ambientales IDEHA.

⁴ Engineer, Universidad del Norte, Barranquilla, Colombia. Affiliation: Departamento de Ingeniería Civil y Ambiental – Instituto de Estudios Hidráulicos y Ambientales IDEHA.

⁵ Master, Universidad Francisco de Paula Santander, Cúcuta, Colombia Affiliation: Departamento de Electricidad y Electrónica.

⁶ *****



the prospects for the treatment of wastewater with high pollutant loads, accomplish their objective (Ruiz-Delgado *et al.*, 2020).

In addition, the catalyst is the main factor that directly impacts the efficiency of photocatalytic treatments. During the last few years, several kinds of these semiconductors have appeared, such as metal oxides, nanomaterials, and organic catalysts, among others. According to Al-Mamun *et al.* (2021), TiO₂ is considered one of the best photocatalytic materials due to it is non-toxicity, high photocatalytic efficiency, and photostability. Additionally, TiO₂ can be combined with other compounds such as Ag and MoO₃ (Hasan Khan Neon and Islam, 2019). This material has been used over the years for treating complex contaminants present in pharmaceutical, textile, and industrial wastewater, achieving values of more than 90% regarding the degradation of emerging pollutants (Aker *et al.*, 2022).

The complete mineralization of contaminants in any AOP requires a large amount of energy, along with chemicals such as catalysts and oxidants, which increases the cost of treatments (Thanekar *et al.*, 2018) and limits research due to the availability of resources and time. In wastewater treatment processes, the accurate modeling and optimization of the most suitable conditions is required to obtain the highest possible efficiency (Azadi *et al.*, 2018). Modeling arises, then, as an alternative to knowing the behavior of a phenomenon from actual experimental data, allowing to explain such behavior through a model and to see the prediction in measurement points that were not experimentally considered. This allows obtaining a complete knowledge of the whole phenomenon and, simultaneously, determining whether there are non-measured points or values in which the process could have behaved better (Florea, 2019).

Photocatalytic modeling has been applied from different perspectives, the oldest of which involves reaction kinetics models (Marien *et al.*, 2019; Xu *et al.*, 2020). Most recently, artificial neuronal networks (ANN) have been used to analyze the effects of operating conditions on photocatalyst performance (Ateia *et al.*, 2020) and the efficiency of the photocatalytic process (Jing *et al.*, 2017), as well as to predict temporal variations of leachate COD in photocatalytic treatment processes (Azadi *et al.*, 2018). However, these works have trained ANNs with a minimal data set, thus causing their predictions to have a high percentage of error; according to Ciresan *et al.* (2012), datasets below 50 samples per class show prediction errors of up to 30%. Another recent approach is the response surface methodology (RSM), one of the most common for these applications since it is oriented towards experimental design and the optimization of operating conditions (Ateia *et al.*, 2020; Becerra *et al.*, 2020; Colombo *et al.*, 2013). Moreover, various regression models have been applied to simulate the treatment conditions, determining the significance of variables such as treatment time, catalyst doping percentage, and catalyst dose to the linear model (Nugraha and Fatimah,

2016). Other models have been applied to a lesser extent, as is the case of Support Vector Machines (SVM), which allow optimizing the pollutants removal percentage. This was shown by Ateia *et al.* (2020), who modeled the removal of a pollutant through the least-squares method and optimized it with the Cuckoo algorithm, achieving an R² higher than 0,94 for the acid pH conditions and the medium catalyst concentration.

The objective of this research is not to describe the time-dependent relationship between the operating conditions of the system and the degradation rate of organic pollutants (Ateia *et al.*, 2020), as is the case of reaction kinetics models, but to implement a model that allows predicting values of the response variable for which no experimental validations were made. Therefore, this article presents a multiple polynomial regression model, a particular case of multiple linear regression in which the relationship between the independent and the dependent variables is an n-degree polynomial in x. To this effect, based on experimental data of a TiO₂/UV photocatalytic process used for the decontamination of landfill leachates, our work proposes to construct the process model using this polynomial regression, with the catalyst concentration (mg.L⁻¹ TiO₂), the pH, and the UV radiation level (accumulated energy in kJ.L⁻¹) as independent variables, and the degradation (mg.L⁻¹ DOC) as the dependent variable. As a result, an equation is determined which represents the process as a function of the described influential variables, predicting the degradation values in the intermediate of the accumulated energy ranges that could not be measured experimentally. This, in order to determine whether, in each photocatalytic experiment (combination of TiO₂ and pH), there was an optimal UV value different from those calculated by the RSM presented in Becerra *et al.* (2020).

Materials and methods

Our methodology consists of four stages: collection and characterization of the leachate sample, which is the input for heterogeneous photocatalysis, followed by multiple polynomial regression modeling, and finally, results analysis (Figure 1).

The leachate sample was collected from the disposal of ordinary solid waste at a landfill in Norte de Santander (Colombia). The sample was taken directly from the main collection pipe of the different disposal cells. Subsequently, the sample was transported to the Environmental Quality Laboratory of Universidad Francisco de Paula Santander, where it was characterized in terms of dissolved organic carbon (DOC), chemical oxygen demand (COD), total suspended solids (TSS), volatile suspended solids (VSS), pH, and temperature under the guidelines of the *Standard Methods for the Analysis of Water and Wastewater* (Pawlowski, 1994). As a result of this process, the input concentration of the leachate to the heterogeneous photocatalysis process was obtained.

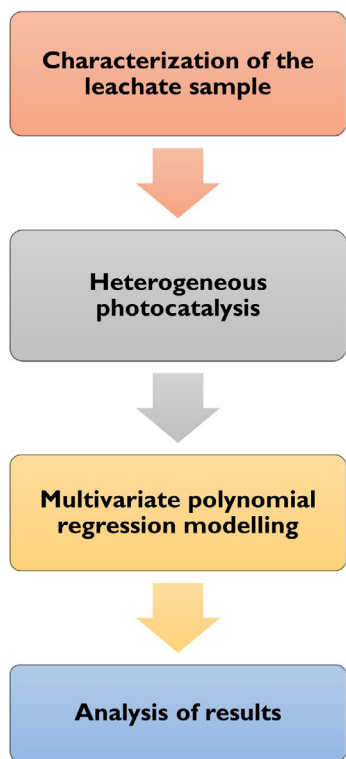


Figure 1. Research methodology
Source: Authors

The heterogeneous photocatalysis, aided by TiO_2 in the presence of UV radiation for the decontamination of leachate from a landfill, was carried out in a laboratory-scale Composite Parabolic Collector (CPC) with a surface area of $0,83 \text{ m}^2$, borosilicate tubes, and aluminum reflective material. The photocatalyst used was commercial TiO_2 P25 (Degussa-Evonik) powder with an anatase:rutile concentration proportion of 70:30, a surface area of 50 m/g ,

and an average diameter of 20 nm . The material properties of this catalyst were reported by Acosta-Herazo *et al.* (2019), Ohtani *et al.* (2010), and Satuf *et al.* (2005). Our work also employed a storage tank with a capacity of 20 L and a Humboldt pump responsible for recirculating the treatment throughout the system (Figure 2). This operation consists of adding domestic wastewater and leachate (the latter at a concentration of $500 \text{ mg.L}^{-1} \text{ COD}$) to the storage tank. The pump is turned on to recirculate the mixture for a few moments throughout the CPC. Afterwards, the amount of TiO_2 required for the experiment is added, *i.e.*, $100, 350$, or 600 mg.L^{-1} . The pH is immediately stabilized at the required level ($3, 6$, or 9) with a waterproof multiparameter, using solutions of HCl or NaOH ($0,1 \text{ N}$). At this point, the zero samples are taken, initiating the procedure described in the section devoted to calculating the accumulated energy. The experiment ends when the 60 kJ.L^{-1} are reached, according to the analysis carried out by Borges *et al.* (2016).

The StatGraphics Centurion XV statistical tool was used for the experimental design, given its capabilities for randomized testing and data visualization. Furthermore, a 3^2 factorial design with replication at the center point was developed to model the results using a response surface. The summary of the experiments is shown in Table 1. The influential variables measured for the factorial design were the catalyst dose ($100, 350$, and $600 \text{ mg.L}^{-1} \text{ TiO}_2$) and the pH ($3, 6$, and 9). These factors were considered since, when TiO_2 has been used as catalyst in the presence of UV radiation, it generates a strong oxidant radical such as OH^\cdot , in addition to the fact that it is non-toxic and anti-corrosive and it features a high pollutant removal (Al-Mamun *et al.*, 2019; Villamizar *et al.*, 2022). Fluctuations in the pH level were considered in order to understand which wastewater conditions stimulate the production of hydroxyl radicals (Balarabe and Maity, 2022; Hassan *et al.*, 2016; Yasmin *et al.*, 2020).

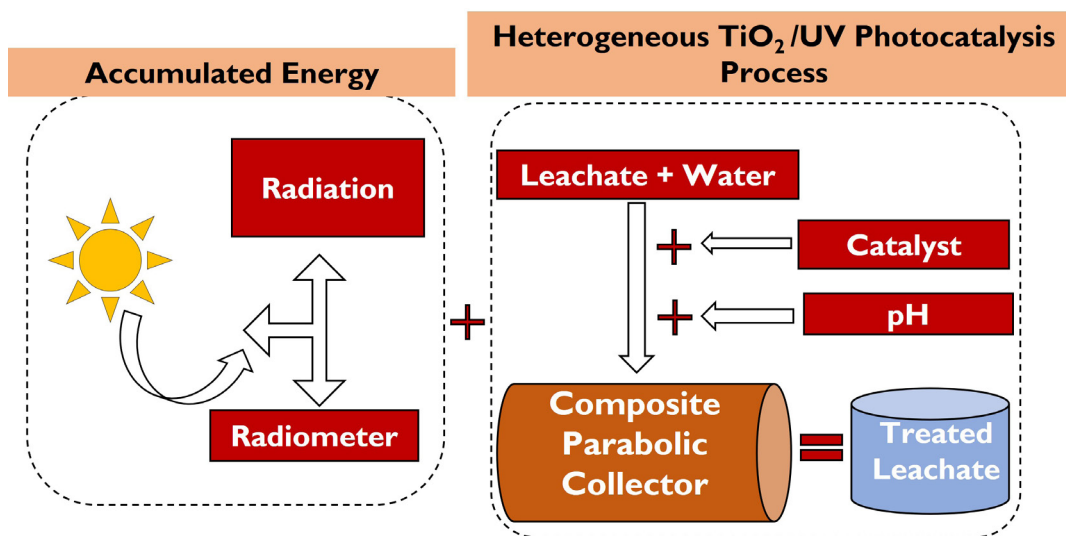


Figure 2. General model for heterogeneous TiO_2/UV photocatalysis
Source: Authors

Table 1. Photocatalysis experiments

No.	Catalyst (mg.L ⁻¹ TiO ₂)	pH	UV _{Solar} (kJ.L ⁻¹)
1	100	3	20
			40
			60
2	100	6	20
			40
			60
3	100	9	20
			40
			60
4	350	3	20
			40
			60
5	350	6	20
			40
			60
6	350	6	20
			40
			60
7	350	9	20
			40
			60
8	600	3	20
			40
			60
9	600	6	20
			40
			60
10	600	9	20
			40
			60

Note: The experiments were conveniently arranged, but StatGraphics Centurion XV randomized the experiments

Source: Authors

Taking into account that photocatalysis is carried out after combining the catalyst and UV radiation to accelerate the chemical transformation of pollutants (Moura and Picão, 2022), the accumulated energy was regarded as a blocking variable in values of 20, 40, and 60 kJ.L⁻¹ for each experiment involving the TiO₂/pH combination. Finally, a system was assembled which consisted of a multimeter (Uni-T UT71C) connected to a pyranometer (SP-110); the latter, when in contact with radiation, sequentially marks a value in millivolts (mV). Collecting precise data depends on the time lapses in which the reading is provided, which, in this case, was every 10 min (600 seconds). The next step was a mathematical conversion from mV to W.m⁻², where 1 mV represents 5 W.m⁻². Finally, Equation (1) was used to calculate the energy:

$$Q_n = Q_{(n-1)} + \Delta t_n * I_n * A_f * V_T^{(-1)} \quad (1)$$

Where:

Q_n : total accumulated energy kJ.L⁻¹

Q_{n-1} : previous accumulated energy kJ.L⁻¹

Δt_n : irradiation time (600 seconds)

I_n : average irradiation (W.m⁻² UV)

A_f : irradiated reactor surface (0,83 m²)

V_T : volume discussed (20 L)

To calculate the response variable representing the DOC, reported as a percentage (%) of degradation in each TiO₂/pH combination, a sample was taken at time zero of the treatment. This value is then calculated in comparison with the other accumulated energies via Equation (2). This sample collection process is carried out in amber containers with a 60 ml capacity. Once collected, the samples pass through membrane filters and are prepared for DOC measurements in the Teledyne Tekmar Torch Total Organic Carbon Analyzer.

$$\% \text{ DOC Degradation} = \frac{\text{mg.L}^{-1} \text{ DOC}(0) - \text{mg.L}^{-1} \text{ DOC}(kJ.L^{-1})}{\text{mg.L}^{-1} \text{ DOC}(0)} \quad (2)$$

Where:

% Degradation DOC: percent degradation in each TiO₂/pH combination for each accumulated energy at 20, 40 and 60 kJ.L⁻¹

mg.L⁻¹ DOC(0): measurement of each DOC value at time zero of treatment in each TiO₂/pH combination

mg.L⁻¹ DOC(kJ.L⁻¹): measurement of each DOC value at each accumulated energy value of 20, 40 and 60 kJ.L⁻¹

The results obtained from these experiments were the input for the multiple polynomial regression model, in order to make predictions about the intermediate of the accumulated energies in each TiO₂/pH combination, i.e., to understand the behavior of the process in the 20-40 and 40-60 kJ.L⁻¹ intervals. The accumulated energy was measured every 10 min, so that, in each experiment there was a significant amount of data to calculate the response variable. Multiple polynomial regression was carried out using the MultiPolyRegress function (Cecen, 2021), which implemented Equation (3), a matrix expression of the model. Parameter estimation was performed using the least-squares method.

$$\begin{bmatrix} y_1 \\ y_2 \\ \vdots \\ y_n \end{bmatrix} = \begin{bmatrix} 1 & x_{11} & \dots & x_{1k-1} \\ 1 & x_{21} & \dots & x_{2k-1} \\ \vdots & \vdots & \ddots & \vdots \\ 1 & x_{n1} & \dots & x_{nk-1} \end{bmatrix} \begin{bmatrix} \beta_1 \\ \beta_2 \\ \vdots \\ \beta_n \end{bmatrix} + \begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \vdots \\ \varepsilon_n \end{bmatrix} \quad (3)$$

Here,

Y is the vector of observations of the phenomenon – for this case, the percent degradation in terms of DOC.

X is the vector matrix of the independent variables: the catalyst concentration ($\text{mg.L}^{-1} \text{TiO}_2$), the pH level, and the solar UV dose applied (kJ.L^{-1}).

β is the vector of the parameters to be estimated.

\mathcal{E} is the vector of model errors.

It is essential to remember that, on many occasions, the aim is to adjust the model in order to obtain very high R^2 values, which measure the relevance of the model. Still, this research did not intend for the model to learn the data by memory, but for it to understand the influence of the independent variables on the response variable. Therefore, the selection regarding the degree of the polynomial that best represents the model was based on the R^2 value, considering that it must be higher than 0,7 if the model is appropriate and pertinent. However, the model must not be so close to 1, which would imply overfitting (Frost, 2020).

The subsequent analysis considered the results obtained by the RSM in comparison with the predictions calculated using the multivariate polynomial regression model. This allowed determining whether, among the values not measured experimentally, there were degradation percentage values higher than those calculated via the response surface. The polynomial regression model analyzes the correlation between the variables, the distribution of the response variable, and the model's fit.

Results and discussion

The leachate characterization is shown in Table 2.

Table 2. Leachate characterization

Parameter	Units	Value
COD	$\text{mg O}_2 \cdot \text{L}^{-1}$	7 920
DOC	$\text{mg C} \cdot \text{L}^{-1}$	2 767
TSS	$\text{mg TSS} \cdot \text{L}^{-1}$	19 941
VSS	$\text{mg VSS} \cdot \text{L}^{-1}$	8 587
pH	-	7,29

Source: Authors

The COD is used to calculate the inlet concentration of the photocatalytic reactor. From 7 920 mg.L^{-1} COD, an inlet concentration of 500 mg.L^{-1} COD was determined for the process.

The results obtained during the TiO_2/UV heterogeneous photocatalysis are consolidated in Table 3. Each experiment is specified in terms of TiO_2/pH concerning the degradation percentages (DOC) for each measured accumulated energy value. According to what was proposed in Table 1, the latter was set at the values of 20, 40, and 60 kJ.L^{-1} . However, since these values were measured every 10 min, they are close to the fixed values. This is why, in Table 3, this variable appears in decimal form; it depends directly on the solar irradiance on the days of the experiment, some of which were cloudy and others very sunny.

According to these results, it can be inferred that there is an influence of the TiO_2 and pH variables on the percentage of degradation in each combination. This is shown by the fact that the highest degradations are associated with low and medium catalyst doses together with low and medium pH levels. Likewise, the process is favored at low pH – in this case, level 3. For the high catalyst dose (600 $\text{mg.L}^{-1} \text{TiO}_2$), the results are not consistent with the pH levels in comparison with the other combinations, given that, in this case, the maximum degradation occurred at maximum pH. Thus, it can be concluded that high doses of this catalyst can unbalance the degradation process in the sense that they do not allow for an efficient absorption of solar radiation. This was confirmed by Yashni *et al.* (2021), who reported the best photocatalytic performance with a pH equal to 3 and concluded that this variable directly impacts the oxidative strength of the generated gap, enhancing the compound's ionization and increasing the removal percentages. Moreover, the concentrations allow stating that, in photocatalytic processes with a low catalyst dosage, hydroxyl radical generation was fostered, improving the pollutant removal efficiency and exhibiting a better light transmittance into the reactor (Rizzo *et al.*, 2014). Consequently, the lower efficiencies could be related to the fact that the aim of our studies was to transform toxic waste liquid into one with more biodegradable characteristics and suitable for biological degradation, taking into account that, when AOPs are used as the only treatment, they are usually expensive due to energy and chemical products consumption (Berberidou *et al.*, 2017; Oller *et al.*, 2011; Paździor *et al.*, 2019).

As for the accumulated energies, the highest degradations in all cases occurred at the maximum measurement of 60 kJ.L^{-1} . This can be seen as a limitation of the process since the accumulated energy is related to the duration of the treatment. Therefore, the higher the accumulated energy required, the greater the time needed for the process to reach the desired or required degradations of the evaluated pollutants. It is essential that this variable is regarded as influential in the design of experiments to determine whether there are degradation values in non-maximum accumulated

energy ranges, thus contributing not only to optimizing the photocatalytic process, but also to the efficient use of resources in wastewater treatment, an issue that has been controversial in recent years.

In this case, fluctuation was identified between the degradation percentages of each sampled accumulated energy, as is the case of experiment numbers 1, 3, 6, 9, and 10. This fluctuation is generated by the composition of the leachate since, when it is subjected to a chemical process such as photocatalysis, a partial transformation of its contaminant species (*i.e.*, trace metals, recalcitrant compounds, and organic macro- and micro-pollutants) may occur, reaching maximum removal efficiency only when the appropriate UV dose is applied (60 kJ. L⁻¹). This phenomenon was similarly reported by Amigh and Mokhtarani (2022), Çifçi and Meriç (2015), Hassan *et al.* (2017), Nomura *et al.* (2020), and Rocha *et al.* (2011).

Table 3. Photocatalysis results

No.	Catalyst (mg.L ⁻¹ TiO ₂)	pH	UV _{Solar} (kJ.L ⁻¹)	Degradation (% DOC)
1	100	3	22,66	16,04
			43,86	14,71
			63,46	57,90
2	100	6	20,65	10,11
			40,39	15,34
			62,22	23,89
3	100	9	20,34	1,30
			40,55	-0,62
			60,99	1,43
4	350	3	22,19	25,31
			40,20	27,85
			62,79	29,84
5	350	6	20,35	3,50
			40,91	6,25
			57,27	11,92
6	350	6	22,83	5,13
			39,65	2,97
			60,84	7,18
7	350	9	21,69	5,94
			42,00	8,90
			61,76	5,49
8	600	3	20,68	7,07
			39,38	8,87
			60,67	12,48
9	600	6	21,68	0,72
			40,48	0,26
			58,67	5,02
10	600	9	20,89	21,44
			43,91	2,36
			61,20	22,44

Source: Authors

Figure 3 shows the correlation between the independent variables and the response variable: degradation - pH = -0,47; degradation - UV = 0,34; and degradation - catalyst = -0,21. The highest correlation is found with pH; the higher the pH, the lower the degradation. The same happens with the catalyst, which, in higher quantities, impairs the degradation process. Finally, regarding the UV dose, which maintains a direct proportional relationship, the higher the accumulated energy, the higher the degradation. This was confirmed by Jia *et al.* (2013), who achieved the highest removal percentage in the longest UV-radiation exposure time. Thus, this analysis is consistent and reproducible with the results obtained via the RSM.

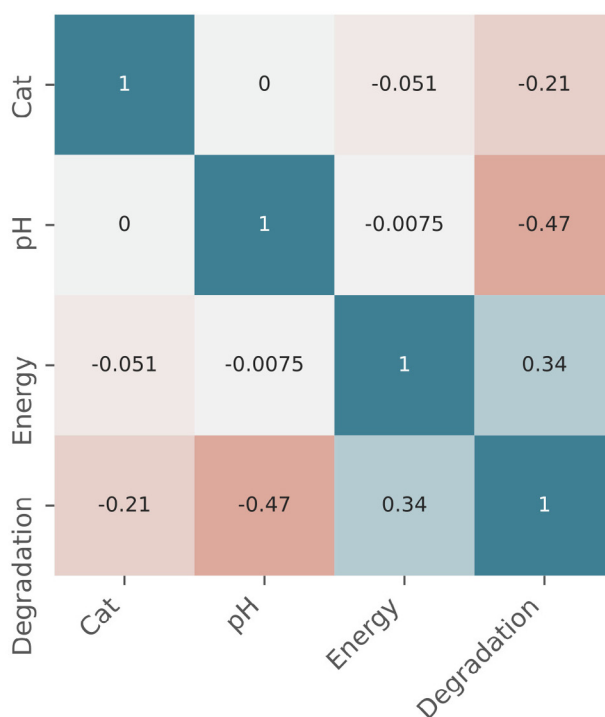


Figure 3. Correlation of variables

Source: Authors

With the dataset in Table 3, a multivariate polynomial regression model was developed in the MATLAB Online R2020b software. The degree of the polynomial was set at $n = 3$, obtaining an $R^2 = 0,8652$. For lower degrees, the model did not fit correctly, and, for higher degrees, it showed overfitting. Some researchers state that an $R^2 = 0,8$ clearly indicates a very good regression model performance and explains a significant amount of the variance in the data (Chicco *et al.*, 2021). In our case, other models were tested with a fourth-degree polynomial, obtaining an R^2 of around 0,9. However, we noticed that the model's curve was overfitted to the experimental data. Therefore, the reported R^2 was considered to be more adequate in explaining the variance of our experimental data.

Equation (4) models the heterogeneous photocatalysis in the decontamination of landfill leachate.

$$\begin{aligned}
 Y = & 7,4903X_3 - 0,18517X_3^2 + 0,0082063X_2X_3 - \\
 & 0,00032472X_2X_3^2 + 0,039433X_2^2 - 0,01116X_2^2X_3 - \\
 & 0,94587X_1 - 0,0030433X_1X_3 - 7,7654e-06X_1X_3^2 - \\
 & 0,044475X_1X_2 + 0,00025262X_1X_2X_3 + 0,0022061X_1X_2^2 + \\
 & 0,0038557X_1^2 + 2,3428e-06X_1^2X_3 + 2,6147e-05X_1^2X_2 - \\
 & 3,9225e-06X_1^3 + 0,013281X_2^3 + 0,0016262 * X_3^3
 \end{aligned}
 \tag{4}$$

Figure 4 reports the accuracy and precision of the model, and it identifies the type of bias in it. Figure 5 demonstrates that the residuals follow a random pattern, i.e., no trend and no non-constant variance. Figure 6 shows that the residuals fit a normal distribution, i.e., Figures 5 and 6 confirm that the ordinary least-squares assumptions are valid for the model.

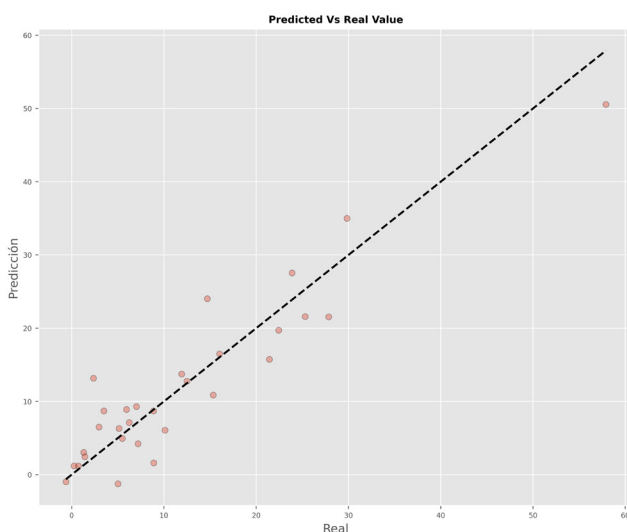


Figure 4. Graph of predicted vs. real values
Source: Authors

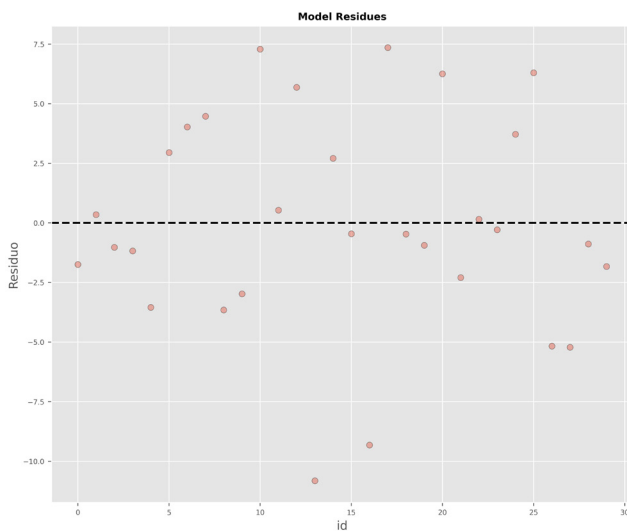


Figure 5. Graph of model residuals
Source: Authors

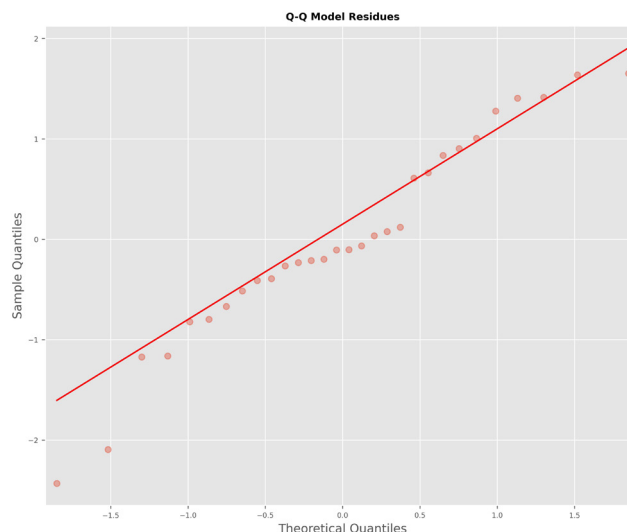


Figure 6. Graph of Q-Q model residues
Source: Authors

Conclusions

This paper modeled the TiO₂/UV heterogeneous photocatalysis process for the decontamination of landfill leachate using experimental data as the input. The fitting method implemented was a multivariate polynomial regression, resulting in a third-degree polynomial with an R² of 0,8652. This model was validated using residual analysis, indicating that the errors are independent, follow a normal distribution, and have a constant variance. Therefore, the model and the conclusions derived from it are valid.

The catalyst dose and the pH have a negative influence on the percentage of degradation. This agrees with the RSM analysis, which showed that the maximum degradations occurred at low catalyst levels and acid pH values, so they have a negative correlation, i.e., if either of the two increases, the degradation will decrease, which will affect the treatment process. Based on a similar analysis, it was inferred that the influence of the accumulated energy is positive on the percentage of degradation, and this is coherent with that obtained via the RSM, as the maximum degradations occurred at the highest levels evaluated. This means that, as the UV levels increase, the degradation will also increase, which is the purpose of all wastewater treatments – to obtain the highest possible pollutant removals.

Based on the predictions of the model at intermediate accumulated energy values that were not measured experimentally, it can be concluded that, in the case of low catalyst doses (100 mg.L⁻¹) both the polynomial regression model and the RSM agreed that the highest degradation in terms of DOC was achieved at the maximum cumulative energy of 60 kJ.L⁻¹ and at a pH = 3. However, at this same low dose, the model predicted higher degradation values at much lower accumulated energies for pH levels of 6 and 9. Thus, for a range between 25 and 30 kJ.L⁻¹ the model predicted degradations of 6% (pH=9) and 28% (pH=6), while similar degradation values were obtained in the RSM,

but at the maximum accumulated energy. Therefore, it can be inferred that, at low catalyst doses and medium and high pH levels, it is possible to find maximum degradations at low cumulative energies. This phenomenon occurred in a similar way for the other pH and catalyst combinations.

It is important to remember that leachates naturally have a pH close to neutrality (7,29), so evaluating their degradation at a low catalyst dose and their natural pH can provide promising results regarding the inferences made via modeling. This would allow for a decrease in the use of reagents to acidify the pH, thus optimizing not only the influential variables, but also the use of resources.

This work intends to be a partial conclusion concerning leachate treatment via heterogeneous photocatalysis, as well as to contribute to the modeling of this phenomenon given the amount of available data – please note that all the possible combinations that could occur in the treatment were not evaluated.

Acknowledgements

This work was supported by the Universidad Francisco de Paula Santander and Universidad del Valle, to which we would like to express our gratitude.

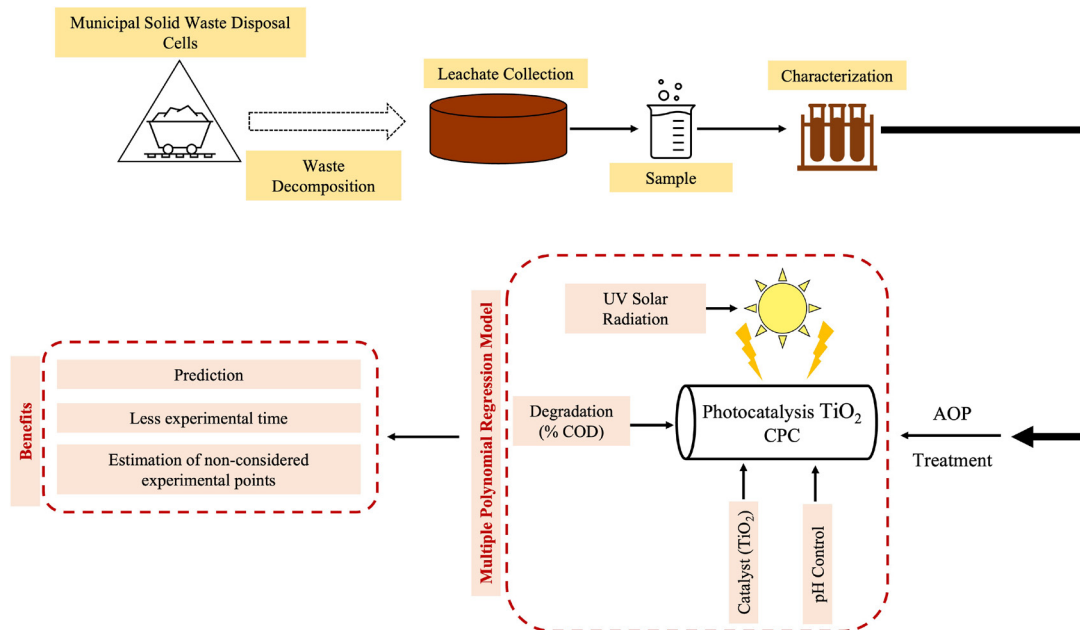
References

- Acosta-Herazo, R., Mueses, M. Á., Puma, G. L., and Machuca-Martínez, F. (2019). Impact of photocatalyst optical properties on the efficiency of solar photocatalytic reactors rationalized by the concepts of initial rate of photon absorption (IRPA) dimensionless boundary layer of photon absorption and apparent optical thickness. *Chemical Engineering Journal*, 356, 839–849. <https://doi.org/10.1016/j.cej.2018.09.085>
- Akter, S., Islam, M. S., Kabir, M. H., Shaikh, M. A. A., and Gafur, M. A. (2022). UV/TiO₂ photodegradation of metronidazole, ciprofloxacin and sulfamethoxazole in aqueous solution: An optimization and kinetic study. *Arabian Journal of Chemistry*, 15(7), 103900. <https://doi.org/10.1016/j.arabjc.2022.103900>
- Al-Mamun, M.R., Kader, S., Islam, M. S., and Khan, M. Z. H. (2019). Photocatalytic activity improvement and application of UV-TiO₂ photocatalysis in textile wastewater treatment: A review. *Journal of Environmental Chemical Engineering*, 7(5), 103248. <https://doi.org/10.1016/j.jece.2019.103248>
- Al-Mamun, M. R., Kader, S., and Islam, M. S. (2021). Solar-TiO₂ immobilized photocatalytic reactors performance assessment in the degradation of methyl orange dye in aqueous solution. *Environmental Nanotechnology, Monitoring & Management*, 16, 100514. <https://doi.org/10.1016/j.enmm.2021.100514>
- Amigh, P., and Mokhtarani, N. (2022). Leachate post treatment, using Ag-TiO₂ nanoparticles immobilized on rotating vanes. *Journal of Water Process Engineering*, 47, 102842. <https://doi.org/10.1016/j.jwpe.2022.102842>
- Ateia, M., Alalm, M. G., Awfa, D., Johnson, M. S., and Yoshimura, C. (2020). Modeling the degradation and disinfection of water pollutants by photocatalysts and composites: A critical review. *Science of The Total Environment*, 698, 134197. <https://doi.org/10.1016/j.scitotenv.2019.134197>
- Azadi, S., Karimi-Jashni, A., and Javadpour, S. (2018). Modeling and optimization of photocatalytic treatment of landfill leachate using tungsten-doped TiO₂ nano-photocatalysts: Application of artificial neural network and genetic algorithm. *Process Safety and Environmental Protection*, 117, 267–277. <https://doi.org/10.1016/j.psep.2018.03.038>
- Balarabe, B. Y., and Maity, P. (2022). Visible light-driven complete photocatalytic oxidation of organic dye by plasmonic Au-TiO₂ nanocatalyst under batch and continuous flow condition. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 655, 130247. <https://doi.org/10.1016/j.colsurfa.2022.130247>
- Becerra, D., Soto, J., Villamizar, S., Machuca-Martínez, F., and Ramírez, L. (2020). Alternative for the treatment of leachates generated in a landfill of Norte de Santander – Colombia, by Means of the coupling of a photocatalytic and biological aerobic process. *Topics in Catalysis*, 63, 1336-1349. <https://doi.org/10.1007/s11244-020-01284-1>
- Berberidou, C., Kitsiou, V., Lambropoulou, D. A., Antoniadis, A., Ntonou, E., Zalidis, G. C., and Poullos, I. (2017). Evaluation of an alternative method for wastewater treatment containing pesticides using solar photocatalytic oxidation and constructed wetlands. *Journal of Environmental Management*, 195, 133-139. <https://doi.org/10.1016/j.jenvman.2016.06.010>
- Borges, M. E., Sierra, M., Cuevas, E., García, R. D., and Esparza, P. (2016). Photocatalysis with solar energy: Sunlight-responsive photocatalyst based on TiO₂ loaded on a natural material for wastewater treatment. *Solar Energy*, 135, 527-535. <https://doi.org/10.1016/j.solener.2016.06.022>
- Cecen, A. (2021). *Multivariate polynomial regression - File exchange - MATLAB central*. <https://github.com/ahmetcecen/MultiPolyRegress-MatlabCentral>
- Chaturvedi, H., and Kaushal, P. (2018). Comparative study of different Biological Processes for non-segregated Municipal Solid Waste (MSW) leachate treatment. *Environmental Technology and Innovation*, 9, 134–139. <https://doi.org/10.1016/j.eti.2017.11.008>
- Chicco, D., Warrens, M. J., and Jurman, G. (2021). The coefficient of determination R-squared is more informative than SMAPE, MAE, MAPE, MSE and RMSE in regression analysis evaluation. *PeerJ Computer Science*, 7, e623. <https://doi.org/10.7717/peerj-cs.623>
- Çifçi, D. I., and Meriç, S. (2015). Optimization of suspended photocatalytic treatment of two biologically treated textile effluents using TiO₂ and ZnO catalysts. *Global Nest Journal*, 17(4), 653–663. <https://doi.org/10.30955/GNJ.001715>
- Ciresan, D. C., Meier, U., and Schmidhuber, J. (2012, June 10-15). *Transfer learning for Latin and Chinese characters with Deep Neural Networks* [Conference presentation]. 2012 International Joint Conference on Neural Networks (IJCNN), Brisbane, QLD, Australia. <https://doi.org/10.1109/IJCNN.2012.6252544>

- Colombo, R., Ferreira, T. C. R., Alves, S. A., Carneiro, R. L., and Lanza, M. R. V. (2013). Application of the response surface and desirability design to the Lambda-cyhalothrin degradation using photo-Fenton reaction. *Journal of Environmental Management*, 118, 32–39. <https://doi.org/10.1016/j.jenvman.2012.12.035>
- Florea, O. A. (2019). *Mathematical modeling of some physical phenomena through dynamical systems*. In C. Flaut, Š. Hošková-Mayerová, and D. Flaut (Eds.), *Models and Theories in Social Systems. Studies in Systems, Decision and Control* (vol. 179, pp. 77-93). https://doi.org/10.1007/978-3-030-00084-4_4
- Frost, J. (2020). *Introduction to statistics: An intuitive guide for analyzing data and unlocking discoveries*. Statistics By Jim Publishing.
- Gout, E., Monnot, M., Boutin, O., Vanloot, P., Claeys-Bruno, M., and Moulin, P. (2022). Assessment and optimization of wet air oxidation for treatment of landfill leachate concentrated with reverse osmosis. *Process Safety and Environmental Protection*, 162, 765-774. <https://doi.org/10.1016/j.psep.2022.04.046>
- Hasan Khan Neon, M., and Islam, M. S. (2019). MoO₃ and Ag co-synthesized TiO₂ as a novel heterogeneous photocatalyst with enhanced visible-light-driven photocatalytic activity for methyl orange dye degradation. *Environmental Nanotechnology, Monitoring & Management*, 12, 100244. <https://doi.org/10.1016/j.enmm.2019.100244>
- Hassan, M., Wang, X., Wang, F., Wu, D., Hussain, A., and Xie, B. (2017). Coupling ARB-based biological and photochemical (UV/TiO₂ and UV/S₂O₈²⁻) techniques to deal with sanitary landfill leachate. *Waste Management*, 63, 292-298. <https://doi.org/10.1016/j.wasman.2016.09.003>
- Hassan, M., Zhao, Y., and Xie, B. (2016). Employing TiO₂ photocatalysis to deal with landfill leachate: Current status and development. *Chemical Engineering Journal*, 285, 264-275. <https://doi.org/10.1016/j.cej.2015.09.093>
- Jia, C.-Z., Zhu, J.-Q., and Qin, Q.-Y. (2013, January 16-18). *Variation characteristics of different fractions of dissolved organic matter in landfill leachate during UV-TiO₂ photocatalytic degradation* [Conference presentation]. 2013 Third International Conference on Intelligent System Design and Engineering Applications, Hong Kong, China. <https://doi.org/10.1109/ISDEA.2012.383>
- Jing, L., Chen, B., Wen, D., Zheng, J., and Zhang, B. (2017). Pilot-scale treatment of atrazine production wastewater by UV/O₃/ultrasound: Factor effects and system optimization. *Journal of Environmental Management*, 203, 182-190. <https://doi.org/10.1016/j.jenvman.2017.07.027>
- Marien, C. B. D., Le Pivert, M., Azaïs, A., M'Bra, I. C., Drogui, P., Dirany, A., and Robert, D. (2019). Kinetics and mechanism of Paraquat's degradation: UV-C photolysis vs. UV-C photocatalysis with TiO₂/SiC foams. *Journal of Hazardous Materials*, 370, 164-171. <https://doi.org/10.1016/j.jhazmat.2018.06.009>
- Moura, L., and Picão, R. C. (2022). Removal of antimicrobial resistance determinants from wastewater: A risk perspective on conventional and emerging technologies. In H. Sarma, D. C. Domínguez, and W.-Y. Lee (Eds.), *Emerging Contaminants in the Environment* (pp. 603-642). Elsevier. <https://doi.org/10.1016/B978-0-323-85160-2.00023-8>
- Müller, G. T., Giacobbo, A., dos Santos Chiamonte, E. A., Rodrigues, M. A. S., Meneguzzi, A., and Bernardes, A. M. (2015). The effect of sanitary landfill leachate aging on the biological treatment and assessment of photoelectrooxidation as a pre-treatment process. *Waste Management*, 36, 177-183. <https://doi.org/10.1016/j.wasman.2014.10.024>
- Nomura, Y., Fukahori, S., and Fujiwara, T. (2020). Removal of 1,4-dioxane from landfill leachate by a rotating advanced oxidation contactor equipped with activated carbon/TiO₂ composite sheets. *Journal of Hazardous Materials*, 383, 121005. <https://doi.org/10.1016/j.jhazmat.2019.121005>
- Nugraha, J., and Fatimah, I. (2016). Modeling of photocatalytic activity of ZnO/AC by using linear probability model, logit and complementary log transformation. *Procedia Engineering*, 148, 1112-1120. <https://doi.org/10.1016/j.proeng.2016.06.613>
- Ohtani, B., Prieto-Mahaney, O. O., Li, D., and Abe, R. (2010). What is Degussa (Evonik) P25? Crystalline composition analysis, reconstruction from isolated pure particles and photocatalytic activity test. *Journal of Photochemistry and Photobiology A: Chemistry*, 216(2-3), 179-182. <https://doi.org/10.1016/j.jphotochem.2010.07.024>
- Oller, I., Malato, S., and Sánchez-Pérez, J. A. (2011). *Combination of advanced oxidation processes and biological treatments for wastewater decontamination – A review*. <https://doi.org/10.1016/j.scitotenv.2010.08.061>
- Pawlowski, L. (1994). Standard methods for the examination of water and wastewater, 18th edition: Arnold E. Greenberg, Lenore S. Clesceri, Andrew D. Eaton (Editors) Water Environment Federation, Alexandria, USA, 1992; 1025 pp; US\$120 (Hardcover); ISBN 0-87553-207-1. *Science of The Total Environment*, 142(3), 227-228. [https://doi.org/10.1016/0048-9697\(94\)90332-8](https://doi.org/10.1016/0048-9697(94)90332-8)
- Paździor, K., Bilińska, L., and Ledakowicz, S. (2019). A review of the existing and emerging technologies in the combination of AOPs and biological processes in industrial textile wastewater treatment. *Chemical Engineering Journal*, 376, 120597. <https://doi.org/10.1016/j.cej.2018.12.057>
- Rizzo, L., Della Sala, A., Fiorentino, A., and Li Puma, G. (2014). Disinfection of urban wastewater by solar driven and UV lamp – TiO₂ photocatalysis: Effect on a multi drug resistant Escherichia coli strain. *Water Research*, 53, 145-152. <https://doi.org/10.1016/j.watres.2014.01.020>
- Rocha, E. M. R., Vilar, V. J. P., Fonseca, A., Saraiva, I., and Boaventura, R. A. R. (2011). Landfill leachate treatment by solar-driven AOPs. *Solar Energy*, 85(1), 46-56. <https://doi.org/10.1016/j.solener.2010.11.001>
- Ruiz-Delgado, A., Plaza-Bolaños, P., Oller, I., Malato, S., and Agüera, A. (2020). Advanced evaluation of landfill leachate treatments by low and high-resolution mass spectrometry focusing on microcontaminant removal. *Journal of Hazardous Materials*, 384, 121372. <https://doi.org/10.1016/j.jhazmat.2019.121372>
- Satuf, M. L., Brandi, R. J., Cassano, A. E., and Alfano, O. M. (2005). Experimental method to evaluate the optical properties of aqueous titanium dioxide suspensions. *Industrial & Engineering Chemistry Research*, 44(17), 6643-6649. <https://doi.org/10.1021/ie050365y>

- Thanekar, P., Murugesan, P., and Gogate, P. R. (2018). Improvement in biological oxidation process for the removal of dichlorvos from aqueous solutions using pretreatment based on Hydrodynamic Cavitation. *Journal of Water Process Engineering*, 23, 20-26. <https://doi.org/10.1016/j.jwpe.2018.03.004>
- Vahabian, M., Hassanzadeh, Y., and Marofi, S. (2019). Assessment of landfill leachate in semi-arid climate and its impact on the groundwater quality case study: Hamedan, Iran. *Environmental Monitoring and Assessment*, 191, 109. <https://doi.org/10.1007/s10661-019-7215-8>
- Villamizar, S., Maturana Cordoba, A., and Soto, J. (2022). Leachate decontamination through biological processes coupled to advanced oxidation: A review. *Journal of the Air & Waste Management Association*, 72(12), 1341-1365. <https://doi.org/10.1080/10962247.2021.1985012>
- Xu, B., Ahmed, M. B., Zhou, J. L., and Altaee, A. (2020). Visible and UV photocatalysis of aqueous perfluorooctanoic acid by TiO₂ and peroxymonosulfate: Process kinetics and mechanistic insights. *Chemosphere*, 243, 125366. <https://doi.org/10.1016/j.chemosphere.2019.125366>
- Yashni, G., Al-Gheethi, A., Radin Mohamed, R. M. S., Dai-Viet, N. V., Al-Kahtani, A. A., Al-Sahari, M., Nor Hazhar, N. J., Noman, E., and Alkhadher, S. (2021). Bio-inspired ZnO NPs synthesized from *Citrus sinensis* peels extract for Congo red removal from textile wastewater via photocatalysis: Optimization, mechanisms, techno-economic analysis. *Chemosphere*, 281, 130661. <https://doi.org/10.1016/j.chemosphere.2021.130661>
- Yasmin, C., Lobna, E., Mouna, M., Kais, D., Mariam, K., Rached, S., Abdelwaheb, C., and Ismail, T. (2020). New trend of Jebel Chakir landfill leachate pre-treatment by photocatalytic TiO₂/Ag nanocomposite prior to fermentation using *Candida tropicalis* strain. *International Biodeterioration & Biodegradation*, 146, 104829. <https://doi.org/10.1016/j.ibiod.2019.104829>

Graphical abstract



Highlights

- Multivariate polynomial regression can be used for reducing the number of experiments, making predictions, and analyzing values outside of the DoE.
- A third-degree polynomial with an R^2 of 0,8652 was considered to be the best-fitting method in this work.
- Polynomial degrees greater than 3 overfit the model's curves, even if a better R^2 is obtained.
- The catalyst dose and the pH had a negative influence on the percentage of DOC degradation.
- Model predictions allow inferring that, at low catalyst doses and medium and high pH levels, it is possible to find maximum degradations at low cumulative energies.