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Effect of the pH and the Catalyst Concentration on the Removal of Hexavalent Chromium (Cr (VI)) During Photocatalysis of Wastewater from Plating on Plastics Industry

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The advancement of industrial technologies throughout history has allowed human beings to develop a great diversity of sectors and methods to satisfy their growing needs. However, various sectors use environmentally unfriendly technologies and have become a significant problem. Those sectors who use heavy metals such as mercury, nickel, cadmium, lead, chromium, among others, stand out. The hexavalent chromium (Cr (VI)) is a long-term environmental pollutant in wastewater generated in electroplating, printing, dyeing, painting, battery manufacturing, metal processing, tanning, and other industries. Chromium poisoning causes cancer, lung, and liver damage due to its multiple toxicities, so it is essential to eliminate Cr (VI) from urban and industrial wastewater before releasing it into the environment. The removal of Cr (VI) from wastewater includes various methods such as membrane separation, precipitation, adsorption, and photocatalysis. Photocatalysis is a low cost, environmentally-friendly, and efficient alternative for the removal of Cr (VI).
The present research work proposes determining the effect of catalyst concentration and pH in removing Cr (VI) through tertiary wastewater treatment known as heterogeneous photocatalysis and using titanium dioxide (TiO_2) as a catalyst. Different amounts of wastewater samples from the plating on plastics industry were collected for this study. The industry is in Bogota, Colombia. The experimental campaign was carried out on a laboratory scale, radiating the samples using UV lamps. The best conditions for decreasing the pollutant concentration were evaluated through an experimental design. The Cr (VI) concentration level in the samples was monitored using the Test Chromium Kit HI 3846 (Hanna Instruments). The photocatalyst dose and the pH of the samples were the factors evaluated. The results obtained during the work showed that the photocatalytic degradation process is beneficial since removing the pollutant for the wastewater from the plating on plastics industry was up to 98%.

1. Introduction

Water is a fundamental element for the planet and for the lives of all the organisms that inhabit it. Given its vital importance, human beings have associated its with various activities that facilitate our survival and growing needs. With the emergence of the different activities that facilitated mans survival, he gave its different uses. One of the primary uses was as a cleaning mechanism to remove the waste created from its economic activities, which led to the emergence of what is now known as wastewater (Dutt et al., 2020). However, the origin of wastewater is very diverse, and it can be classified into domestic wastewater (DWW), rainwater (RWW), industrial wastewater (IWW), and agriculture wastewater (AWW) (Ma et al., 2021). As noted above, the different needs, in turn, have brought with them the emergence of a variety of sectors that use various technologies which employ water within their methods and end up being unfriendly to the environment. Technologies include those that within their processes use heavy metals such as mercury, nickel, cadmium, lead, chromium, among

others, and that generate considerable amounts of industrial liquid waste (ILW). Some industries, such as those engaged in plating, printing, dyeing, painting, battery manufacturing, metal processing, and tanning, stand out to generate wastewater with the environmental pollutant known as hexavalent chromium (Cr (VI)). Hexavalent chromium (VI) poses a significant risk to human health. This compound can cause allergic skin reactions.
It can also cause irritation and nosebleeds when inhaled, or to a greater extent, it can weaken the immune system, cause damage to the kidneys and liver, lung cancer, and even death. Chromium hexavalent (Cr (VI)) is the toxic form of chromium metal. It is mainly generated in industrial processes such as galvanoplasty, manufacture, and welding of stainless steel, pigments, and dyes. One of the sectors that stand out for their high polluting load of industrial liquid waste corresponds to the plastic chrome plating process, where chemical baths are made with chromium that serves as a protective layer for corrosion a decorative finish. Uncontrolled chromium discharge into the environment is mainly generated because most wastewater collection systems do not allow the separation of urban and industrial effluents (Karimi-Maleh et al., 2020). Concern about the generation of wastewater and its treatments is a problem that has taken hold in this century, as there has been a sufficiently important concentration to threaten the supply of clean water. Conventional water treatment systems, composed of primary and secondary treatments, cannot efficiently remove heavy metals. Although specific technological processes have been developed to remove heavy metals from wastewater, the use of these is quite costly, and they are not well known. Therefore, heavy metals in water are a severe contamination problem, requiring companies to apply decontamination technologies. In cases that the effluent has the hexavalent chromium, a physicochemical treatment is commonly used. This treatment has two stages. In the first stage, Cr (VI) is reduced to Cr (III) by using chemical agents such as $FeSO_4$, $FeCl_2$, $NaHSO_3$, or SO_2. In the second stage, the formed Cr (III) is precipitated as Cr $(OH)_3$ or Cr_2O_3. In this sense, an exciting alternative to the chemical reduction process is the use of heterogeneous photocatalysis with titanium dioxide (Athanasekou et al., 2018). Photocatalysis is one of the essential technologies for the effective treatment of water contaminants. The method is better than the adsorption method because photocatalysis provides progressive destruction of organic pollutants (Fatimah et al., 2018). The essential benefits of treatment are low concentration operability, long-term reuse, and the absence of toxic by-products. If photocatalysis is activated by sunlight as a renewable source, it is a green solution in water treatment (Wetchakun et al., 2019). This study uses photocatalysis as a technology to decontaminate water with hexavalent chromium. Titanium dioxide (TiO_2) is used as catalyst and the effects of pH and of the catalyst concentration are analyzed during photocatalysis to remove the pollutant. This pollutant presenting large concentrations in wastewater from the plastic chrome plating industry is evaluated, as it may affect Bogotas rivers, basins, and soils.

2. Materials and methods

In this study, different wastewater samples were collected from the plastic chrome plating industry in Bogotá, Colombia.
The photocatalysis process was carried out in Erlenmeyer with 250 mL volumes of wastewater, and samples were radiated with 24 mW/m^2 UV lamps.
The catalyst used during the photocatalysis process was titanium dioxide (TiO_2). Samples were arranged in magnetic stirrers to simulate the turbulent regime (Figure.1), and titanium dioxide was further pulverized to decrease particle size and surface area. The variables evaluated were pH and TiO_2 dose (g/L). The irradiation time was 30 min.
The pH values were 3.3, 5, and 7 and for TiO_2 doses were 1, 2, and 3 g/L. Definitions of these variables levels were based on the bibliographic review (Blanco et al., 2001). The pH was adjusted to the respective values using HCl (1 N). A 5 ml aliquot of the treated sample was extracted after the defined time for the test was completed to determine the contaminants removal. These tests were done in triplicate. Chromium removal in samples was quantified using the HI 3846 Chromium Test Kit from Hanna Instruments. Where Cr (VI) reacts with Diphenylcarbazide to form a purple coloration under acid buffer conditions, so the amount of coloration that develops is proportional to the concentration of chromium present in the wastewater sample (Hanna Instruments, 2012). Once the test information has been obtained, the elimination efficacy was calculated based on the difference between the initial concentrations and the one obtained after 30 min.

Figure 1: Experimental set-up

An experimental design of 2 factors and 3 levels was chosen and this is presented in table 1.

Table 1: Experimental Design

	pH	Doses (g/L)
1	3.3	1
2	5	1
3	7	1
4	3.3	2
5	5	2
6	7	2
7	3.3	3
8	5	3
9	7	3

The characterization of the contaminated sample is performed both before and after treatment.
The pH and % Cr of the initial sample was determined.
A variance analysis (ANOVA) was performed using the IBM SPSS statistical software based on the experimentation data.

3. Results and discussion

3.1 Physicochemical characterization of wastewater

Wastewater received from the company underwent the characterization of the variables related to the study which are reported in table 2

Table 2: Characterization of wastewater

Heading1	pH	Cr VI (mg/L)
Wastewater	9.1	0.92
Standar deviation (%)	0.16	0

3.2 Effectiveness of the method

At the beginning of the experimentation, a couple of tests were performed to test the methods effectiveness. The test was first performed with a catalyst dose of 1 g/L, and the pH was adjusted to neutral. During the process, aliquots were taken from the sample every 10 minutes, and contaminant removal was given within 50 minutes. A second experiment was conducted by increasing the catalyst dose to 2 g/L with neutral pH, and the time was reduced to 30 minutes, as can be seen in figure 2.

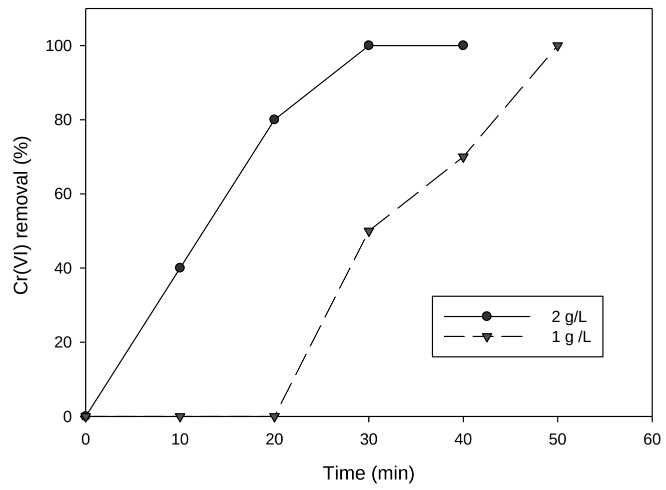

Figure 2: Removal of hexavalent chromium (catalyst doses 1 and 2 g/L; pH neutral)

The results obtained in this test show that the treatment allows removal of the contaminant; however, there are no conclusive results since the scenario of higher catalyst doses, and pH values other than neutral is not contemplated. Then, based on all the above, the experimental design was carried out.

3.3 Experimental design

The results of the experimental design are presented in Figure 3.

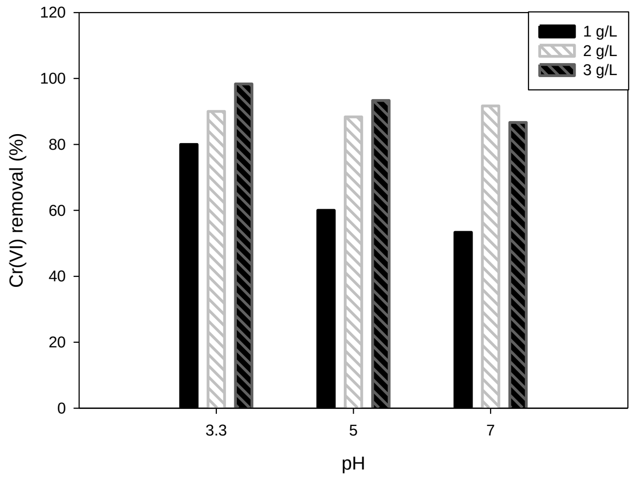

Figure 3: Experimental design of hexavalent chromium removal

As presented in figure 3, it could be observed that the pH variable could have an essential effect on Cr (VI) degradation since photocatalytic processes are more efficient in acidic media where the pH values correspond to 3 < pH < 5 (Blanco et al., 2001). Higher removal values can be observed to occur at a pH of 3 and 5. pH also affects the catalysts photocatalytic activity, allowing for better adsorption of the contaminant. Besides, for catalyst doses, it is observed that the most significant degradations of the contaminant occur at the highest doses. The best condition for photocatalytic degradation was observed for a value of pH of 3.3 and of the TiO_2 dose of 3 g/L.

3.4 Variance Analysis (ANOVA)

The analysis was performed to approximate the most appropriate factorial combination with the experimental design data (2 fixed factors each with 3 levels). The results obtained with the SPSS tool are presented in table 3.

Table 3. Variance Analysis -ANOVA

Origin of variations	Sum of squares	Degrees of freedom	Average squares	F	Probability (p)	Critical value for F
Doses	4390.7407	2	2195.3704	11.9747	0.0005	3.5546
pH	718.5185	2	359.2593	1.9596	0.1698	3.5546
Interaction	659.2593	4	164.8148	0.8990	0.4851	2.9277
Within the group	3300	18	183.3333			
Total	9068.519	26				

According to the results presented in Table 3, the value of p is 0.0005. This value is less than the level of significance that in the analysis is 0.05 %. From this, it can be inferred that there is a significant difference in catalyst doses, which significantly affects chromium removal. On the other hand, if the pH case data are contrasted, it shows that this factor does not significantly affect removal (1,960 < 3,555). There is no statistically significant interaction effect between the two variables. Therefore, the removal does not affect (0.899 < 2.928).

3.5 Fishers Lead Significant Difference (LSD).

The LSD test was performed to determine the simple effects of each factor studied on Cr (VI) removal. Table 4 presents LSD for catalyst dose effects, and Table 5 presents LSD for pH effects.

Table 4. LSD test for simple effect of doses

Doses (g/L)	Amount	Media
1	9	64
2	9	90
3	9	93
Contrast	Difference	LSD
1-2	26	13.4
1-3	28	13.4
2-3	3	13.4

When comparing the mean catalyst doses (1 and 2 g/L) and (1 and 3 g/L), the values are 26 > 13.4 and 28 > 13.4, respectively. These values imply that there are statistical differences between the two doses. Comparing the mean doses 2 g/L with 3 g/L has 3 < 13.4; therefore, there are no differences between the two doses. During experimentation, the most extensive removal of Cr (VI) was presented when the dose was 3 g/L, and it can be corroborated at the value of the highest mean presented in Table 4. This behavior was previously reported by Wang (Wang *et al.*, 2016) and it was found a direct relationship between the amount of catalyst disposed of in the samples and the pollutant removal from the wastewater.

Table 5. LSD test for simple effect of pH

pH	Amount	Media
3.3	9	89
5	9	81
7	9	77
Contrast	Difference	LSD
3.3-5	9	13.4
3.3-7	12	13.4
5-7	3	13.4

It comparing the information presented in Table 5, it was observed that in the mean pH 3.3 and 5, it has 9 < 13.4; therefore, there are no differences between the two values. Similar behavior occurs between mean comparisons for pH 3.3 and 7 (12 < 13.4) and pH 5 and 7 (3 < 13.4). However, for experimentation, the highest observed mean was that corresponding to pH 3.3. The importance of the medium being acidic is confirmed since there is the most effective removal of Cr (VI). Some studies such as that of Ghorab et al (Ghorab et al., 2013) and Zhao et al (Zhao *et al.*, 2019) have reported a similar pollutant removal behavior in acidic media. From the above, it can be inferred that with the LSD test, that the catalyst doses correspond to 3 g/L, and the to pH of 3.3 for achieving the largest removal.

4. Conclusions

The photocatalysis applied to wastewater treatment from plating on the plastics industry for hexavalent chromium removal performs better in acidic media since the contaminants largest removals in the experimentation were at pH 3.3 and 5. On the other hand, it was also possible to establish that catalyst doses play an essential role in pollutant removal because, with higher doses of catalyst, the removal of the contaminant was carried out in less time.
Consequently, during the study, the maximum removal of contaminant (98.3 %) is reached when the dose of TiO_2 is 3 g/L and the pH is 3.3.
Tests shall be carried out on the conditions obtained to determine the rate of degradation and the influence of radiation intensity.

References

Athanasekou, C. P., Likodimos, V. Falaras, P., 2018, Recent developments of TiO2 photocatalysis involving advanced oxidation and reduction reactions in water, *Journal of Environmental Chemical Engineering*, 6(6), pp. 7386–7394.

Blanco Gálvez Julián, Malato Rodríguez Sixto, Estrada Gasca Claudio A., Bandala Erick R., Gelover Silvia y Leal Teresa; Purificación de aguas por fotocatálisis heterogénea: Estado del arte. En: Eliminación de contaminantes por fotocatálisis heterogénea. M. B., editor. CYTED, 2002. p. 51-75.

Dutt, M. A., Hannif. M. A. Nadem, F. Bhatti, H. N., 2020, A review of advances in engineered composite materials popular for wastewater treatment, *Journal of Environmental Chemical Engineering*, 8(5), p. 104073.

Fatimah, I., Fadillah, S. Yulan., 2018, TiO2 supported on brick waste as low cost photocatalyst for dye photodegradation, *Chemical Engineering Transactions*, 63, pp. 733–738.

Ghorab, M. F., Djellabi, R. and Messadi, R., 2013, Photo-reduction of Hexavalent Chromium in Aqueous Solution in the Presence of TiO2 as Semiconductor Catalyst, *E3S Web of Conferences*, 1, p. 23000.

Karimi-Maleh, Ayati, A., Ganbari, S. Orooji, Y., Tanhaei, B., Karimi, F., Alizadeh, M., Rouhi, J. Fu, L., Sillanpaa; L., 2020, Recent advances in removal techniques of Cr(VI) toxic ion from aqueous solution: A comprehensive review, *Journal of Molecular Liquids*, 329, p. 115062.

Ma, D. Yi, H., Lai, C., Liu,X., Huo,X., An, Z., Li, L., Fu,Y., Li, B., Zhang, M., Qin,L., Liu,S., Yang, L., 2021, Critical review of advanced oxidation processes in organic wastewater treatment, *Chemosphere*, 275, p. 130104.

Wang, L. Kang, S., Li, X., Qin, L. Yan, H., Mu, J., 2016, Rapid and efficient photocatalytic reduction of hexavalent chromium by using “water dispersible” TiO2 nanoparticles, *Materials Chemistry and Physics*, 178, pp. 190–195.

Wetchakun, K., Wetchakun, N. Sakulsermsuk, S., 2019, An overview of solar/visible light-driven heterogeneous photocatalysis for water purification: TiO2- and ZnO-based photocatalysts used in suspension photoreactors, *Journal of Industrial and Engineering Chemistry*, 71, pp. 19–49.

Zhao, Z. An, H., Lin, J., Feng, M., Murugados, V., Ding, T., Liu, H., Shao, Q., Mai, X., Wang, N., Gu,H., Angaiah, S., Guo, Z., 2019, Progress on the Photocatalytic Reduction Removal of Chromium Contamination, *Chemical Record*, 19(5), pp. 873–882.