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Articles

Design and validation of a hexavalent chromium adsorption system in tannery effluents using orange peel and wheat bran

Diseño y validación de un sistema de adsorción de cromo hexavalente en efluentes de curtiembre usando cáscara de naranja y salvado de trigo

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Abstract

This study has focused on proposing a pilot-scale adsorption system capable of removing the high concentrations of hexavalent chromium present in the wastewater from the tanning process that is discharged directly into the Bogotá River. Two bioadsorbents were evaluated in synthetic water using orange and wheat bioadsorbents. For this, in the laboratory and by means of the Flocculator (Jar test) and colorimetry techniques, the removal capacity of the orange and wheat with a diameter of 850 µm was validated at pH 1, pH 3 and pH 5 in synthetic water, the conditions and the most efficient adsorbent were selected to later apply it to wastewater. Finally, the pilot-scale adsorption system was designed and validated to simulate laboratory conditions. The results show that in the synthetic water the most efficient conditions of the absorbents were at pH 1 and pH 3 for the orange bioadsorbent with a removal of 68 % and wheat 33 %, respectively. At the time of applying the orange adsorbent at pH 1 in wastewater in the Flocculator, the removal was 37 % of Cr (VI), while the validation of the system yielded an average efficiency of 58 %, significant results for the implementation of the system in the tanning sector.

Keywords: Tannery, adsorption, pollutant removal, chromium compounds.

Resumen

Este estudio se ha centrado en proponer un sistema de adsorción a escala piloto capaz de remover las altas concentraciones de cromo hexavalente presentes en las aguas residuales del proceso de curtido que son vertidos directamente al río Bogotá. Se realizó la evaluación de dos bioadsorbentes en agua sintética utilizando bioadsorbentes de naranja y trigo. Para ello, en el laboratorio y mediante el floculador (test de jarras) y técnicas de colorimetría se validó la capacidad de remoción de la naranja y el trigo, con un diámetro de 850 µm a pH 1, pH 3 y pH 5 en agua sintética; de allí se seleccionaron las condiciones y el adsorbente más eficiente para posteriormente aplicarlo en aguas residuales; finalmente se diseñó y validó el sistema de adsorción a escala piloto que simulara las condiciones del laboratorio. Los resultados muestran que en el agua sintética las condiciones más eficientes de los absorbentes fueron a pH 1 y pH 3 para la naranja con una remoción del 68 % y el trigo de 33 %, respectivamente. Al momento de aplicar el adsorbente de naranja a pH 1 en aguas residuales en el floculador, la remoción fue del 37 % de Cr (VI), mientras que la validación del sistema arrojó una eficiencia media del 58 % de resultados significativos para la implementación del sistema en el sector de las curtiembres.

Palabras clave: curtiembre, adsorción, remoción de contaminantes, compuestos de cromo.

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Introduction

The tanning process is the transformation of microbiologically unstable skins into stable leather, through crosslinking and partial drying of proteins (Vilardi, Ochando, Stoller, Verdone, & Palma, 2018); using tanning agents such as chromium salts that have the potential to stabilize the protein fibers of the skin, through the formation of chelate-type complexes that prevent the decomposition and deterioration of the leather (Alcaldía Mayor de Bogotá, 2010).

According to Arias (2013), the industries in Colombia dedicated to the activity of tanning are mostly located in the north of Cundinamarca, municipalities of Chocontá and Villapinzón, where 81.3 % of the tanneries that exist throughout Colombia are concentrated (Escobar, Ubaque, & Bohórquez, 2012) an industrial sector that causes serious social, economic and environmental problems of great magnitude (Barba, Ballestero, Patiño, & Callejas, 2013). The strongest being the contamination of the water resource with highly toxic chemical substances (CAR, 2014).

The generation of Chromium occurs in the unitary tanning process, once it comes into contact with the organic matter present in the wastewater, it is oxidized from Trivalent Chromium (Cr III) to Hexavalent Chromium (Cr VI) depending on the pH of the solution, the total concentration of Cr, the presence of oxidizing and reducing compounds, (Jobby, Jha, Yadav, & Desai, 2018), a highly toxic species for the aquatic biota and the population that uses the resource downstream (Barba *et al*., 2013). Thus, the high concentrations of Cr VI in industrial effluents from tanneries (Hongrui *et al*., 2017); and the lack of efficient treatments, (Artuz, Martinez, & Morales, 2011), represent very high risks to human health and the ecosystem of the Bogotá river (Díaz & Granada, 2016; Castillo *et al*., 2004).

According to Tejada-Tovar, Villabona-Ortiz and Ruiz-Rangel (2012) among the most efficient technologies to remove heavy metals are precipitation, ultrafiltration, reverse osmosis, ion exchange, electrodialysis, oxidation, reduction, filtration, electrochemical treatment, membrane technologies, among others (Garces & Coavas, 2012), with efficiencies close to 99 %, however, and despite their efficiency, the high cost of installation and maintenance of these technologies makes implementation in small and medium-sized companies increasingly complex, a situation that entails that each day the tanneries continue to generate highly polluting discharges and the environmental authorities have to close them.

However, in recent years, viable and environmentally friendly alternatives have emerged, among them the following stand out: phytoremediation, bioremediation, thermal desorption and bioadsorption (Ocampo-Barrero, 2012) the latter being one of the simplest given this allows them to certain materials of natural origin retain and concentrate on the surface substances and compounds of diverse chemical nature present in aqueous solutions, including heavy metals (Izquierdo, 2010).

According to Jobby *et al*. (2018), Cr (VI) compounds are strong oxidants that are easily reduced to Cr (III) in the presence of organic or inorganic electron donors, which favors remediation through physical, chemical and/or biological methods. An example of this is the research using the chromium VI bioadsorption technique, including the research carried out by Singh, Hasan, Talat, Singh and Gangwar (2009), who used wheat bran. In the study carried out by González *et al*. (2010), solutions with orange peel were used, the research of Singha, Kumar, Bhattacharya and Das (2011), sought to measure the elimination of Cr (VI) ions from aqueous solutions. Finally, the research of Garces and Coavas (2012) evaluated the orange peel modified with chitosan, for the removal of Cr.

Therefore, the objective of this work was to evaluate the removal potential of orange and wheat bran in aqueous solution and in tannery wastewater in order to design and evaluate a viable implementation system in the tannery industry.

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Materials and methods

The wastewater was collected in the Rodríguez Melo tannery located at kilometer 66 in the industrial zone, between the municipality of Villapinzón and Chocontá.

The experimental design used was 2k, with this being the design that describes the most suitable experiments to know the effect that k factors have on a response and discover if they interact with each other. This is the reason why two variable factors were worked on, which were pH with three levels (1.3 and 5) and type of adsorbent with two levels (orange peel, wheat bran), with the constant factors being residual water, the diameter of the adsorbent, mixing time, and agitation speed.

The bioadsorbents used were wheat bran and orange peel, the first was commercially obtained and sieved at 850 microns, while the orange peel was obtained by collecting fruits similar in color and species, then cleaned and dried at 105°C for 12 hours in the oven and subsequently crushed and sieved at 850 microns.

The hexavalent chromium analyzes were developed in the chemistry laboratories of the Universidad Manuela Beltrán, using the diphenylcarbazide colorimetric technique.

To prepare synthetic water with a concentration of 1000 ppm ($mg*l^{-1}$) of Cr (VI) ions, it was necessary to use 0.56 g of $K_2Cr_2O_7$ that was diluted in 0.2 l of distilled water, from this solution 5 standards were prepared for each pH scale in the concentrations of 0.2 ppm, 0.5 ppm, 1 ppm, 1.5 ppm, 2 ppm, which were acidified with H2SO4 1 N to obtain pH 1 - 3 and 5, then 0.5 ml of diphenylcarbazide was added and finally it was gauged with H_2SO_4 0.2 N in a 25 ml balloon, and in this way the calibration curves of the spectrophotometer were obtained at a wavelength of 540 nanometers.

From the 1000 ppm solution, solutions of 10, 20, 30 and 50 ppm were prepared using the dissolution equations, after which the procedure of Figure 1 was performed, which was carried out 6 times for each absorbent.

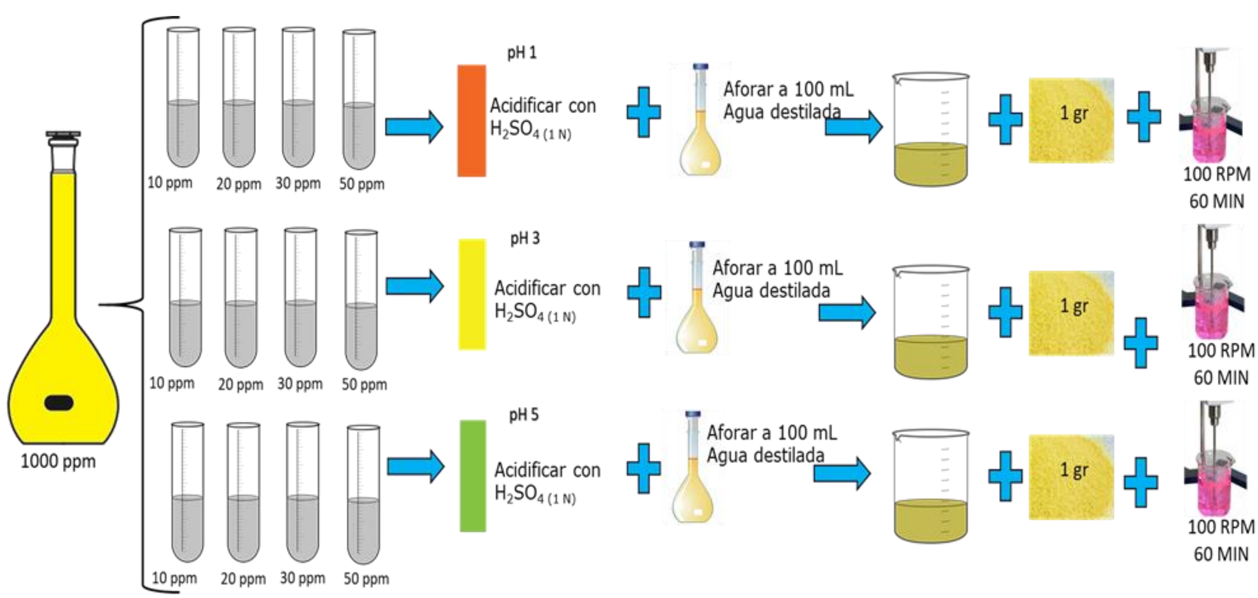

Figure 1. Research experimental diagram.

After 60 minutes of agitation, the solution was filtered, from which 5 ml aliquots were taken, to which 0.5 ml of Diphenylcarbazide, 5 ml of H2SO4 1 N and H2SO4 at 0.2 N were added to complete the gauging to 25 ml, in this way the absorbance readings were taken, and the removal percentages of Cr VI were calculated.

Once the first phase in synthetic water was completed, the pH and the most efficient adsorbent were selected, which was applied to wastewater from the Rodríguez Melo tannery. In this phase, solutions of 20, 40 and 60 ppm were prepared, gauging to 100 ml of distilled water, then it was acidified with H_2SO_4 1 N, the adsorbent was added, and the stirring process started, this procedure was carried out 8 times for each concentration.

System design and evaluation

Once the evaluation of the adsorbent in the wastewater was completed, the adsorption system was designed and evaluated on a pilot scale. For the design of the System, heuristic equations were used; for mechanical agitators the equations of inclined plates, starting from a cylindrical tank and for the bottom area of the System, the Bernoulli and Torricelli theorems were taken into account, since the bottoms of a tank are the

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most influential in the agitation and from there the liquid flows are redirected.

The electronics were programmed using Arduino 1.8.5 software searching for automatic and standardized operating commands on the digital dashboard. Finally, the statistical analyzes were performed with the Arena software package using the Input Analyzer tool.

After designing and building the system, simulations were carried out with residual water from the tannery, taking a volume of 30 l, to which 300 g of adsorbent (10 g/l) and 300 ml of 1N sulfuric acid were added to acidify the solution at pH at 1. After 60 minutes of constant agitation at 100 RPM, the colorimetry analyzes, and absorbance readings were carried out.

Results

According to Figure 2, the mean removal of Cr VI using wheat bran in synthetic water was 28 %, at pH 1 the maximum removal was 67 % in the 10 ppm standard and the minimum removal was 5 % with 95 % confidence in the 50 ppm standard, with the mean removal of this pH being 31 %.

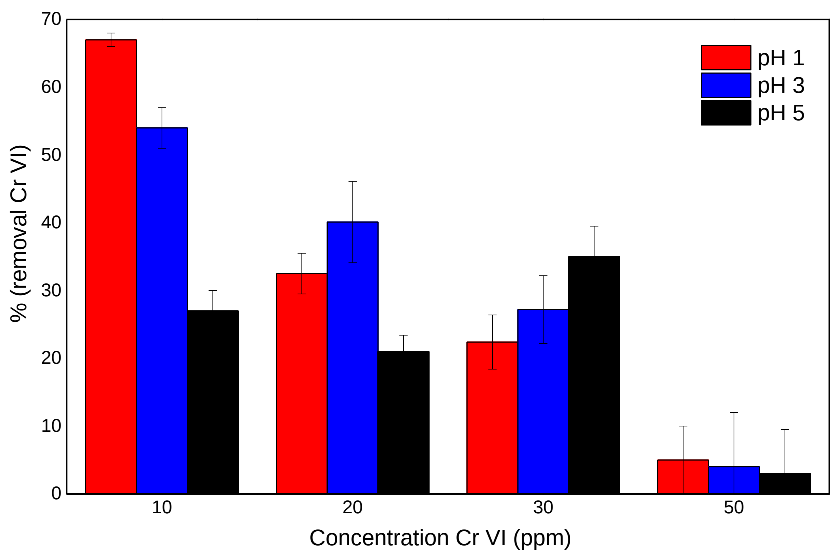

Figure 2. Chromium VI removal ranges with wheat bran.

For pH 3, the mean removal of chromium VI was 34 % fluctuating between 54 % (10 ppm) and 4 % (50 ppm), at pH 5 it was found that the mean removal of chromium VI ions was 19 %, at said pH the maximum removal was 35 % at 30 ppm and the minimum of 3 % at 50 ppm, efficiencies that are not significant in the removal of chromium VI. Finally, it was found that the highest removal as a function of pH using wheat bran was at pH 3.

The results for the orange adsorbent presented a mean removal of 42 %, in Figure 3 it is evidenced that the maximum removal of Cr VI at pH 1 was 88 % in the 10 ppm standard and the lowest 31 % in the standard 50 ppm, the mean removal being 68 % with a 95 % confidence level.

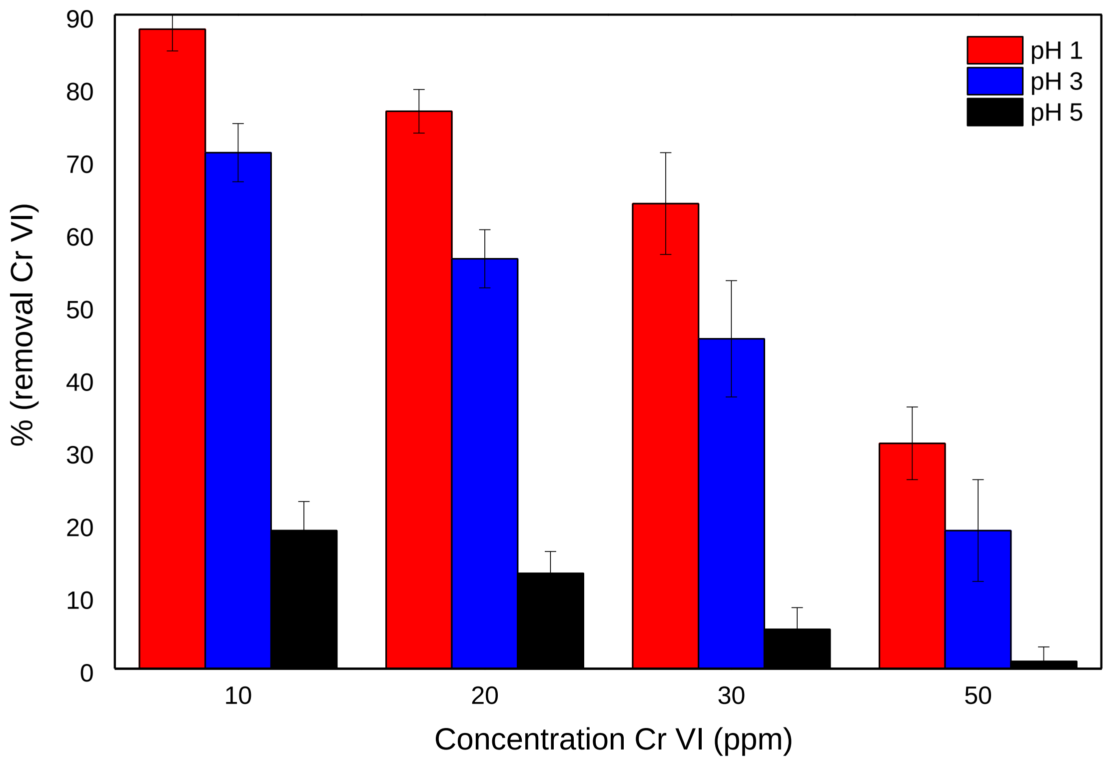

Figure 3. Chrome VI removal ranges with orange peel.

The removal ranges for pH 3 correspond to 71 % in a pattern of 10 ppm and 19 % for 50 ppm, the average removal being 49 %, while at pH 5 the orange peel adsorbent presented a variable behavior, where the maximum removal value was 19 % (10 ppm) and the minimum 1 % (50 ppm), which leads to the average removal of the orange peel at pH 5 being 9 %.

Once the concentrations and removal ranges of the two adsorbents had been evaluated, the most appropriate pH conditions were selected for the removal of hexavalent chromium in wastewater, according to Figure 4 in which the results of each pH are interposed and each adsorbent is finds that orange peel at pH 1 is the most efficient.

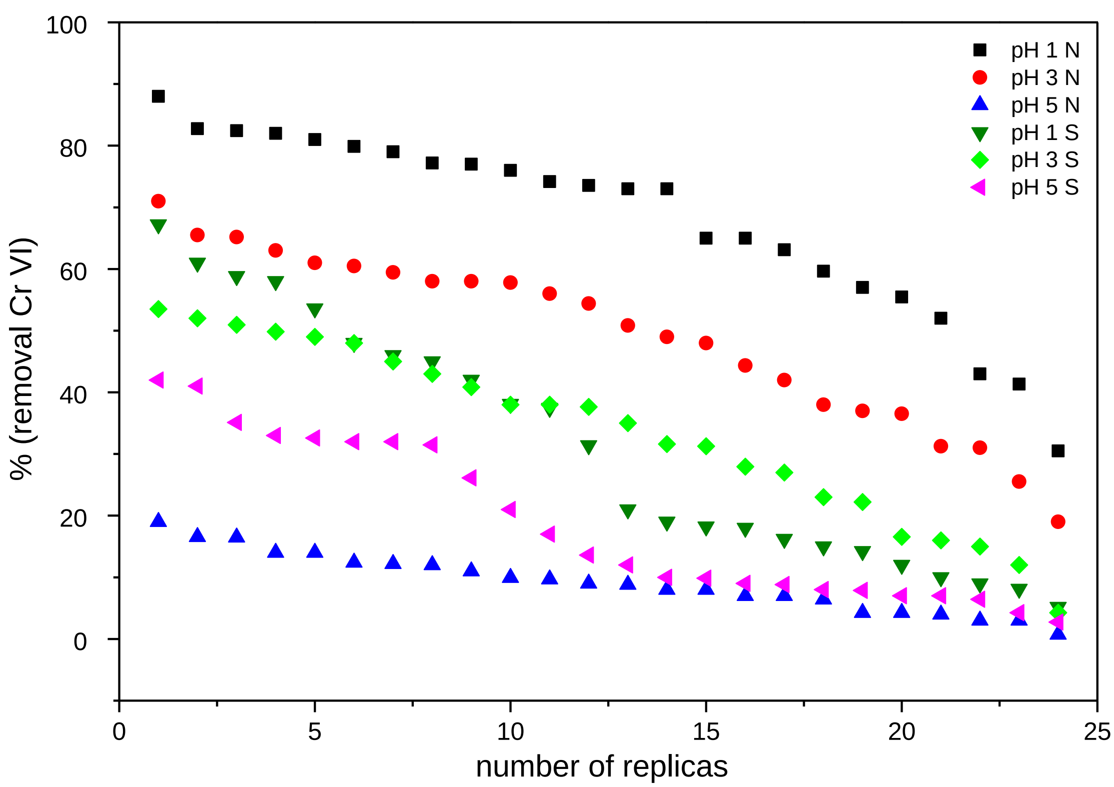

Figure 4. Adsorbent removal ranges as a function of pH.

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With the Sand Input Analyzer, the type of non-normal distribution and the Kruskal-Wails test were determined, a test that was applied for the two adsorbents (orange and wheat bran) depending on the pH (pH 1 and pH 3, pH 5). The hypothesis allowed it to be evaluated if the orange and wheat bran were efficient for the removal of hexavalent chromium in tannery waters, from which it is concluded that wheat bran is the adsorbent that does not have similar removal ranges, given that there are statistically significant differences.

Table 1 shows the chemical characterization of the water in the Rodríguez Melo tannery, where it was identified that high levels of chromium VI are generated in the unit tanning process.

Table 1. Results of the characterization of wastewater.

Parameters	Deliming	Fleece	Tanning	Dying
pH	9.32	12.07	4.81	3.95
Conductivity µS/cm	18.25	6.22	10.36	12.33
DQO $(mg*l^{-1})$	-----	2 946.8	2 964.4	1 715.3
Total chromium $(mg*l^{-1})$	1.24	8.81	1 363.4	13.96
Chromium (VI) $(mg*l^{-1})$	-----	-------	112.8	7.2

The residual water problem presented an initial concentration of 1363.4 ppm of Total Chromium and 112.8 ppm of Cr VI, which was acidified with H_2SO_4 1 N until obtaining pH 1, conditions in which the orange adsorbent was then added.

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According to Figure 5, the adsorption of Cr VI metal ions at pH 1 in wastewater with orange peel in different concentration patterns allowed it to be found that there are no statistically significant differences between the different chromium concentrations since for the standard for 20 ppm the mean removal was 39 %, for 40 ppm it was 38 % and for the 60 ppm scale it was 34 %.

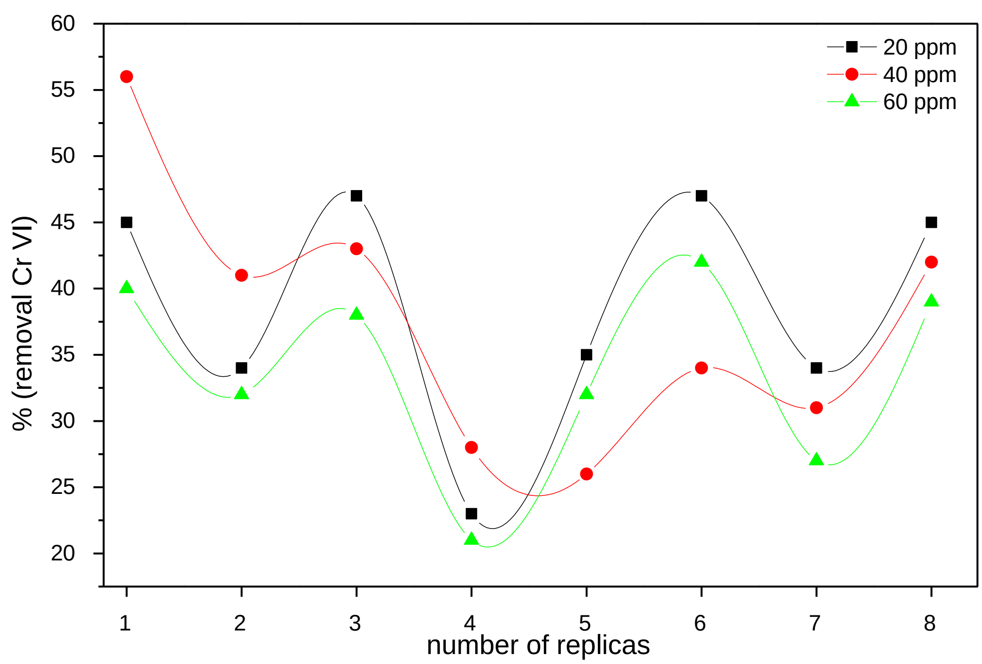

Figure 5. Chrome VI removal ranges with Orange peel.

Once it was found that the metal concentration does not affect the removal of Cr VI in the selected conditions for the wastewater, 24 experimental runs were carried out which are displayed in Figure 6, where it is found that the maximum removal of the peel of orange in tannery wastewater was 56 % and the minimum was 21 %, with the average removal being 3 7 %.

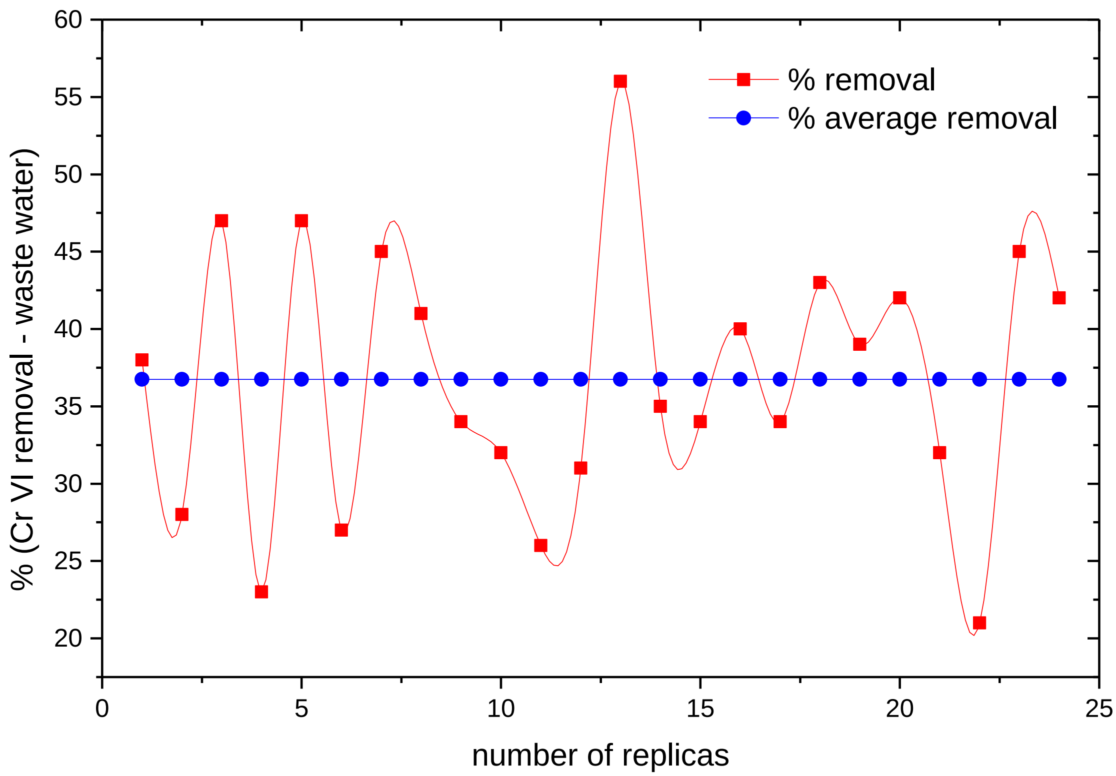

Figure 6. Removal of Cr VI with orange peel in wastewater pH 1.

The average removal of hexavalent chromium, with orange peel in synthetic water was 68 %, while in wastewater the average removal was 37 %, a decrease caused by the chemicals that are added to the tanning process which change the composition water chemistry under more complex conditions.

According to the heuristic equations for the Design of mechanical agitators, an inclined plate agitator was designed (Figure 7), and the powers required to keep the adsorbent solids in suspension for 60 minutes at 100 RPM was calculated. The Klopper bottom was designed with spherical radius in order to extract the clarified water through the lateral outlet and after a sedimentation time to extract the sludge with the adsorbed chromium.

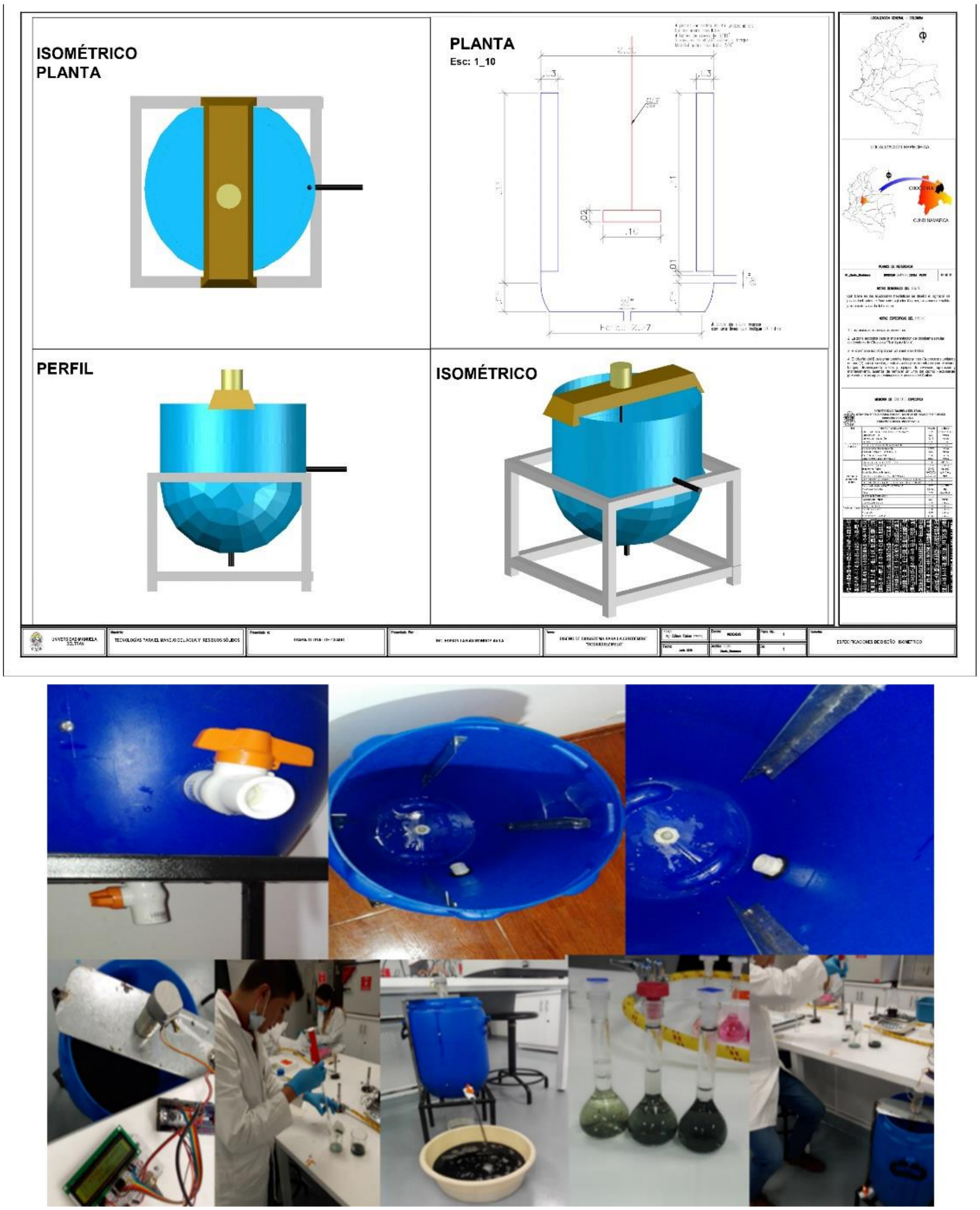

Figure 7. Design and Construction of the Adsorption System.

For the design of the outlet orifice, sedimentation tests were carried out, where it was found that the height in the agitator occupied by the sediment is between 11.4 % and 11.7 % of the total height of the water sheet in the system. In order to prevent the sediment from leaking through said outlet, it was considered to increase a 3 % (safety factor), which allows it to be analyzed that for the design of the outlet orifice the range varied between 14.4 % and 14.7 %.

After designing and building the adsorption system, the 24 simulations with residual water of the tanning unitary process were started at pH 5 and concentration of 112.8 ppm of Cr VI, every 5 minutes removal samples were taken in order to know the behavior of the same as a function of time.

In Figure 8, the behavior of hexavalent chromium removal in the System is observed, where it was found that the maximum removal was 64 %, the minimum 45 % and the mean removal value 54 %.

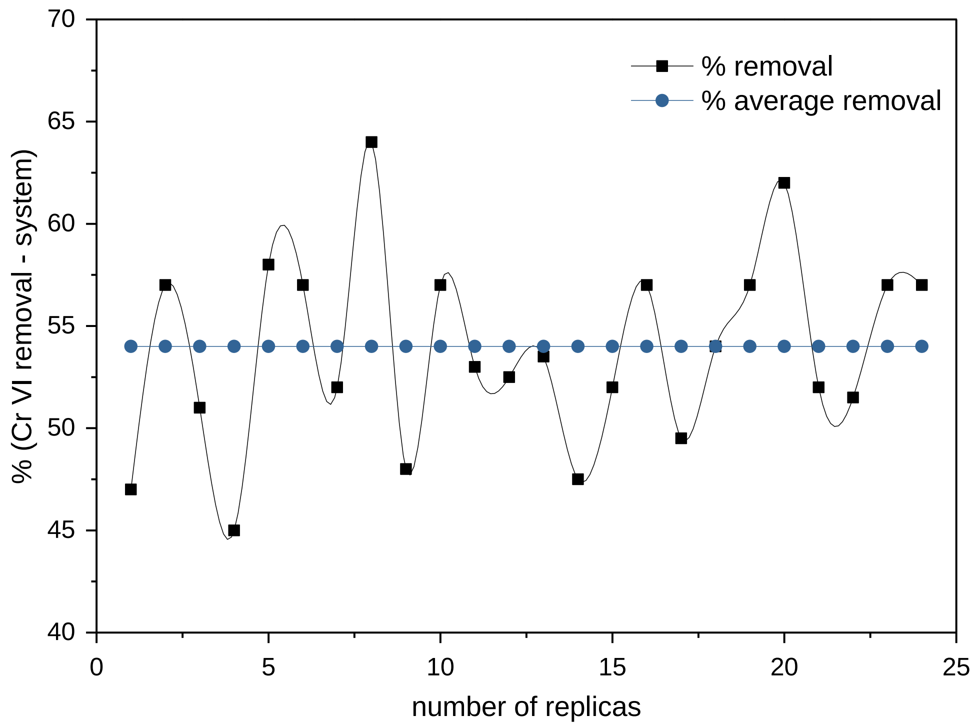

Figure 8. Removal of the orange peel in the System.

After knowing the mean efficiency of the validated system, the three mean removal curves were crossed, in Figure 9 the mean removal of Chromium (VI) in the three scenarios was compared synthetic water (68 %) wastewater in laboratories (37 %) and wastewater in the System (54 %) with it being found that the efficiency of the designed system is greater than the efficiency obtained in laboratory-scale wastewater.

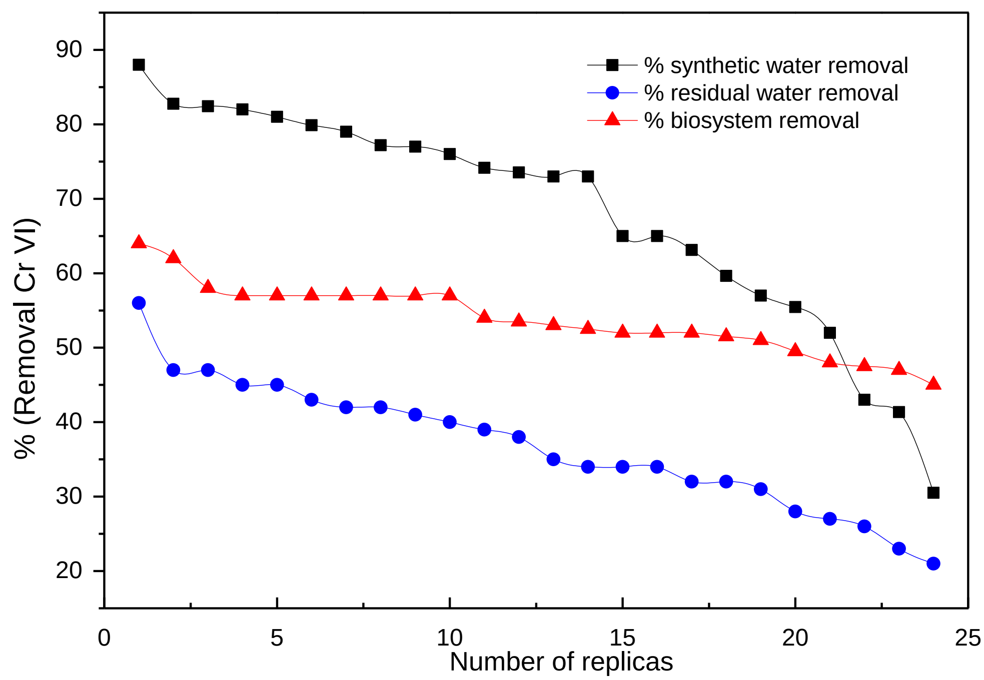

Figure 9. Removal curves in the (3) evaluated scenarios.

During the simulations and every 2.5 minutes, removal readings were taken in order to identify the moment in which the greatest removal occurs and to identify an optimal time. In Figure 10, the behavior of Cr VI removal is found, identifying that at 10 minutes the highest removal percentage is presented with an average value of 68 %, from 40 to 60 minutes the variation of the curve it is not very significant since the removal rates vary between 55 and 57 %.

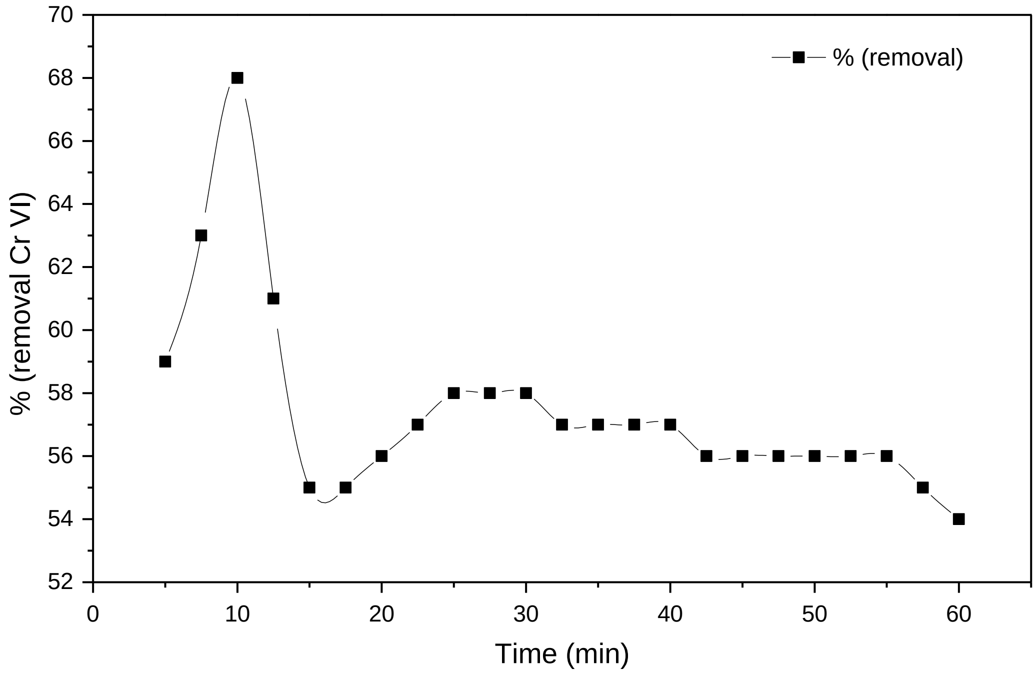

Figure 10. Cr VI removal *vs*. contact time.

Discussion

According to the results obtained in synthetic water, it was determined that by increasing the concentration of chromium the adsorption capacity of the bioadsorbent decreases, according to Altun and Pehlivan (2012), who established that this decrease is due to the decrease in electrostatic attraction, where a High concentration of H + ions facilitates adsorption, while high concentration of OH- ions suppresses the adsorption reaction.

When comparing the efficiency of the adsorbents, the orange removed 68 % of Cr VI while the wheat bran 34 %, a difference, according to Wen, Jiangshui, Yinjia, Xiao and Zhengqing (2015); Marshall and Champagne (1995), cited by Tejeda, Tejada, Marimón and Villabona (2014), that is due to the fact that the Orange peel in its chemical structure contains a higher proportion of hydroxyl and carboxyl groups belonging to the cellulose, pectin, hemicellulose and lignin bonds, these being the active sites for the union of the metal ion already than Cr VI.

The most optimal pH for the removal of Cr VI in synthetic water were pH 1 and pH 3, results that support the theories of González *et al*. (2010); Tejada, Montiel and Acevedo (2016); Garces and Coavas (2012), and Eggs, Salvarezza, Azario, Fernández and García (2012), who stated that the highest adsorption of Cr (VI) occurs between pH 1 and 3 due to the chemical activation of the functional groups present in the adsorbent material since the surface of the biomaterial is positively charged and the functional groups are become protonated groups that release the oxygen responsible for oxidation.

In the wastewater, it was found that the adsorption of Cr VI at pH 1 with orange peel at different concentrations does not affect the removal in the conditions selected for the wastewater since there are no statistically significant differences in the removal percentages obtained.

Based on Figure 3, it was evidenced that the removal of the orange at pH 1 decreased from 68 % in synthetic water to 37 % in wastewater, a decrease that is due to the fact that the wastewater from the tanning process consists of a complex matrix, with high levels of harmful inorganic and organic compounds (Schrank, José, Moreira, & Schröder, 2005), product of the chemicals that are added to the tanning process, which transform the chemical composition of water to more complex conditions that directly affect the adsorbent, reducing the useful surface area of adsorption.

Taking into account that studies on the removal of heavy metals by adsorption, including the one published by Izquierdo (2010) Schrank *et al*. (2005), it is recommended that fixed-bed columns can be used in wastewater with low organic load, while in high values the most advisable is to use systems in which constant agitation is maintained and thus be able to guarantee contact between the contaminant and the bioadsorbent.

After designing, building and validating the removal of Cr VI in wastewater in the system, it was found that the removal capacity increased by 17 % over the value obtained in the laboratory. This increase is due to the axial flow agitators for the mixing and suspension of solids (Arrieta, 2012), aided by the baffles installed inside the system, which are in charge of improving turbulence, fluid mixing and avoiding the formation of Vortexes (Valencia, 2010), during the operating time, these parameters increase the removal efficiency of Chromium (VI) due to the increase in its contact area, this being one of the advantages of the system over filtration systems.

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The efficiencies of the validated system do not comply with national regulations, which establish limits of less than 1.5 ppm Cr VI, which is why it is recommended that when implementing bioadsorption, two tanks be evaluated in series to achieve greater efficiencies, and to be able to comply with water quality standards.

In Figure 9, it is observed that the removal curve of the System does not exceed the removal curve in synthetic water, so that the above is affirmed meaning that the synthetic water only contained potassium and chromium ions, while in the wastewater organic matter content, residual salts from the fleece and the presence of other chemicals directly affect the surface area of the adsorbent.

According to Figure 10, the greatest removal capacity as a function of time occurred in times less than 15 minutes, results similar to those reported by González *et al*. (2010), who concluded that, at low concentrations of the metal, the biomass studied adsorbs 100 % at 10 minutes. After 35 minutes the removal behavior does not show significant variations.

Finally, the residual chromium from the tanning process is in the trivalent oxidation state, which is easily oxidized to hexavalent chromium, due to the high concentrations of organic matter and variations in pH, with these being the variables that most influence the adsorption process.

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Conclusions

In synthetic water, the orange peel showed the most optimal removal point of Cr (VI) at pH 1 with an average efficiency of 68 %, while the most optimal removal of wheat bran was at pH 3 with a mean value of 33 %, which is due to the presence of the hydroxyl and carboxyl groups active sites for the union of the metal ion and that of Cr (VI).

The orange peel applied to the wastewater removed 37 %, a value that decreased, due to the presence of multiple substances that are present in the tanning waters and that also adhere to the surface of the adsorbent, reducing the useful area for adsorption of the Cr (VI) ions.

When simulating the adsorption of Chromium VI in the system, the average removal was 54 %, a significant increase that is mainly due to the agitation system and the baffles installed inside the tank, elements that guarantee the constant suspension of the bioadsorbent.

The designed adsorption system has two advantages over a biofiltration system, the first corresponds to the ability to increase the useful area of the adsorbent generated by the agitation and suspension system, the second is due to the organic matter present in the wastewater clogging the filter surface, making it difficult to filter in depth, a situation that does not occur in the system, designed, built and validated.

The optimal time for the adsorption of the metal in the system can be between 10 and 35 minutes, time in which it can be removed between 55 and 68 % of the initial concentration of Cr VI.

The design of the adsorption system constitutes a great contribution to the implementation of bioadsorption, with it being considered feasible to implement the bioadsorption system in the unitary processes of leather tanning due to its technical efficiency that allows solutions to the reality of the artisanal industrial sector that takes place in the northern region of Cundinamarca and in the Capital District.

The removal of Cr VI in the upper and middle basin of the Bogotá River produced by the tanning industry will contribute to the compliance of the ruling issued by the State Council as well as to the project for the hydraulic adaptation and environmental recovery of the Bogotá River.

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