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Implementation of Modified *Acacia* Tannin by Mannich Reaction for Removal of Heavy Metals (Cu, Cr and Hg)

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Abstract: The modified tannin by Mannich reaction was investigated for wastewater treatment. The removal of heavy metals, such as copper, chromium and mercury, in industrial wastewater was evaluated through the coagulation–flocculation technique, using modified *Acacia* tannin (MAT) as a coagulant agent. The successful tannin modification was evaluated by infrared spectopometry (FTIR), nuclear magnetic resonance (NMR); monitoring the removal of heavy metals was performed by atomic absorption (AA) and a direct mercury analyzer (DMA). Additionally, the parameters of water quality, total suspended solids (TSS), turbidity and chemical oxygen demand (COD) were assessed. Different doses of MAT were evaluated (375 ppm, 750 ppm, 1250 ppm and 1625 ppm) and three different levels of pH (4, 7 and 10). The highest percentages of removal obtained were copper 60%, chromium 87%, mercury 50%–80%, COD 88%, TSS 86% and turbidity 94%, which were achieved with the dose of 375 ppm of MAT at pH 10. The coagulation–flocculation process with the modified *Acacia* tannin is efficient for the removal of conventional parameters and for a significant removal of the metals studied.

Keywords: coagulation–flocculation; heavy metals; tannin; wastewater treatment

1. Introduction

Heavy metals are water pollutants that generate a negative impact in the world because they are harmful in high or even low concentrations for humans and animals. It has been reported that the presence of copper, chromium and mercury causes diseases in humans (dermatitis, diarrhea, gastrointestinal sickness, liver damage and nervous system disorders) [1]. Diseases that led to the search for efficient techniques for the removal of these metals from water.

Among the traditional primary treatments of wastewater are coagulation–flocculation, sedimentation, flotation and filtration, where it is sought to decrease large quantities of organic material and suspended solids [2]. Coagulation consists of the elimination of the double electric layer that the colloidal particles have suspended in an aqueous medium and the flocculation is the process by which the particles previously destabilized in the coagulation are agglomerated [3]; these processes are widely used due to their low cost, speed and efficiency.

The most commonly used coagulants are inorganic metal salts, such as aluminum sulfate, ferric chloride and synthetic polymers. Lately, researchers are focused on the search for substances that replace those mentioned above because they have two major disadvantages: The first one is that the sludge resulting from these processes are not biodegradable, generating a serious problem at the environmental level. The second is that substances such as inorganic salts leave traces of ferric and aluminum ions in the water that are not eliminated by subsequent treatments, and that are considered as one of the possible causes of neurodegenerative diseases, such as Alzheimer's disease [4]. Therefore, bio-flocculants have been proposed as a viable alternative and in which tannins are excellent.

Tannins are biodegradable anionic polymers, which generally come from plants, specifically from leaves, fruits and bark [5]. They are structurally complex, possessing galoil esters linked to polyols, catechins and terpene nuclei. These substances have molecular weights between 500 and 3000 Daltons [3]. Besides, they can be classified as hydrolyzable (gallotannins, ellagitannins) and non-hydrolyzables. These substances are currently investigated as coagulant–flocculating agents and for cationic potentiation by the Mannich reaction as a consequence of the reaction between an aldehyde and an amine compound, generating the addition of the carboxyl groups and aminos to the tannin structure [6,7]. The objective of the present work was to determine if the modified *Acacia* tannin could remove copper, chromium and mercury metals when employing the coagulation–flocculation process in industrial wastewater. At the same time, its behavior in the removal of the conventional parameters, for instance organic material, total suspended solids and turbidity, was also determined. Finally, we evaluated if the modification of *Acacia* tannin (AT) was successful by infrared spectrometry (FTIR) and nuclear magnetic resonance (NMR).

2. Materials and Methods

2.1. Modification of Acacia Tannin (MAT)

The modification of the tannin was carried out by the Mannich reaction using ammonium chloride and formaldehyde under conditions previously standardized in the laboratory [6,8], see Figure 1. Two solutions were prepared: (i) 10.5 mL of distilled water was added to 8.66 g of the *Acacia* tannic extract at a temperature of 65 °C and with constant agitation until a homogeneous mixture was obtained. Subsequently, a solution (ii) of 30 mL of formaldehyde was gradually added to 3.8 g of ammonium chloride and this solution was brought to reflux for two hours. At the end, the two solutions were mixed and a stock solution of 50,000 ppm was prepared.

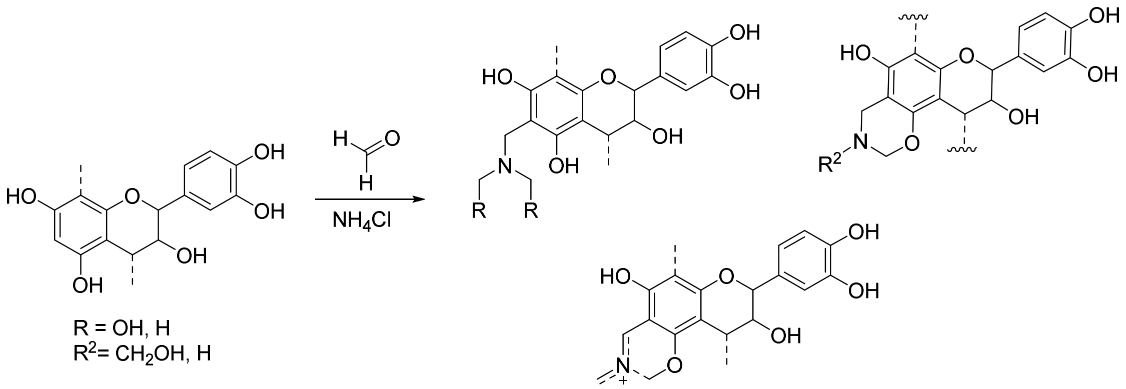

Figure 1. Possible products of the Mannich reaction with *Acacia* tannin.

2.2. Characterization

2.2.1. IR Analysis

Infrared analysis was performed using an IRTracer-100. The *Acacia* tannin (AT) and modified *Acacia* tannin (MAT) samples were deposited on the crystal. Then, those were analyzed using the module for 20 scans and where the scanning wavelength of the infrared wave was 4500–400 cm^{-1}.

2.2.2. NMR Analysis

^{13}C NMR spectra were acquired on a Bruker Avance spectrometer (75 MHz) in D_2O. For each sample, 20,000 scans were collected with an acquisition time of 0.454 s, time domine of 16 K data points and a spectral width of 240 ppm.

2.3. Application

2.3.1. The Jar Test

To evaluate the activity of the TAM a stock solution of 50,000 ppm was prepared and the dosages used were 375 ppm, 750 ppm, 1250 ppm and 1625 ppm. The jars test equipment was used (Equifar, Bogotá Colombia) and three assemblies were made, one for each pH evaluated (4, 7 and 10) and each one in triplicate, where each assembly was composed of four experiments corresponding to the different doses.

For each test, 400 mL of wastewater from a maquiladora industry was supplemented with pattern solutions (Merck) like copper, chromium and mercury. The coagulation–flocculation process was carried out in three stages: the first stage at 120 rpm for 2 min, followed by the speed of agitation at 50 rpm for 15 min and the time of repose was 30 min [9]. At the end of the process, the metals were quantified by AA and DMA, and the determination of physicochemical parameters were verified [10–12].

2.3.2. Determination of Physicochemical Parameters

The physicochemical parameters were evaluated in the wastewater untreated treatment, in order to determine the percentages of removal. The chemical oxygen demand (COD) was done using the semiautomatic colorimetric method (EPA 410.4) using the multiparameter HI 83,099 (Hanna Instruments, Inc., Woonsocket, RI, USA). The suspended solids were carried out by the drying method at 103–105 °C (APHA 2540 D) and the turbidity was determined by the nephelometric method (APHA 2130 B) using the turbidimetric HI 88713 (Hanna Instruments, Inc., Ann Arbor, MI, USA).

2.3.3. Quantification of Metals Cu, Cr and Hg

The quantification of the metals was done before and after the wastewater was treated with the MAT. Previous to the analysis of AA, microwave digestion was performed (Milestone, SK 12) using the standardized parameters for industrial wastewater to eliminate the organic matter. The quantification of heavy metals was carried out in a Variam Instrument t AA240FS (Agillent, Santa Clara, CA, USA), using the previously performed calibration curves with R^2 = 0.999 for copper and chromium. In the specific case of mercury, the quantification was direct through the direct mercury analyzer DMA-80 (Milestone-Italy). A total of 1 g of the sample was weighed and placed in a quartz cuvette, applying the previously standardized method for industrial wastewater. Moreover, all samples were made in triplicate. (EPA 3015).

3. Results and Discussion

3.1. IR Analysis

Figure 2 shows the spectra of *Acacia* tannin (AT) and the modified *Acacia* tannin (MAT). The broad band between 3000 cm^{-1} and 3600 cm^{-1} was associated with the -OH vibration, indicating that MAT had more hydroxyl groups than AT due to the use of formaldehyde in the Mannich reaction [13]. The small shoulder at 1720 cm^{-1} is associated with the C–N link due to the ammonium chloride incorporated into the synthesis of MAT [14]. In addition, the peak at 1635 cm^{-1} is a characteristic band of the stretching vibration of the C=C bond in the aromatic ring. MAT seems to have more intensity than AT because the aromatic ring is more exposed when the structure is opened for the modification. [15–17]. The weak band observed around 1477 cm^{-1} is related also to the aromatic rings stretching vibration that is absent in MAT [18]. Further, the absorption band at 1454 cm^{-1} belonged to the aliphatic C–H deformation in methyl groups, indicating overlapping with absorption coming from the asymmetric bending of the CH3 groups [19,20]. The band 1300 cm^{-1} in MAT is attributed to a C–O stretching vibration that is absence in raw tannin [21]. The 1022 cm^{-1} absorption band in tannin was broader and shifted in MAT compared to the tannin sample, showing a significant increase in intensity due to C–N linkages. This, as a result of the use of ammonium chloride, where the amine links to the tannin by Mannich reaction, indicated that the amine group was successfully added to the tannin [17,22]. Finally, the wide and intense band 700 cm^{-1} is related to the C–H vibration of the benzene rings and the O–H of alcohol vibration due to the formaldehyde [15,23].

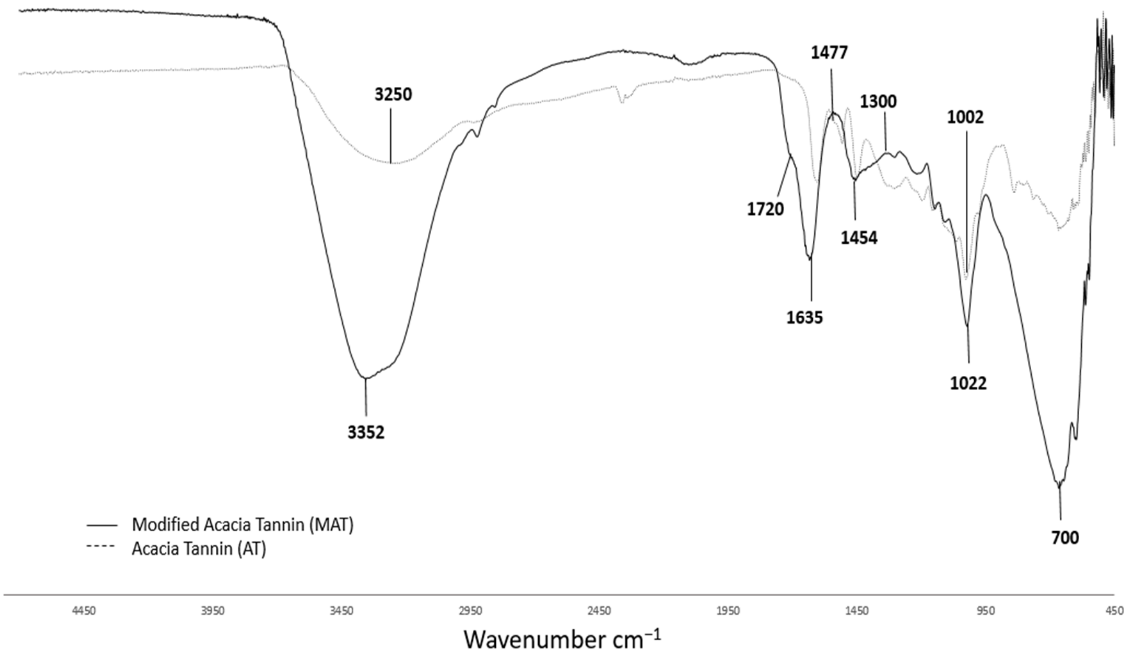

Figure 2. The spectra of *Acacia* tannin (AT) and the modified *Acacia* tannin (MAT).

3.2. NMR Analysis

Figure 3a shows the ^{13}C-NMR spectrum of AT. Signals at 116 ppm (C2′, C5′), 120 ppm (C6′) and 145 ppm (C3′, C4′) show the presence of procyanidin (PC) units, besides the signal at 96 ppm corresponds to C8, which is linked to C4 [24]. On the other hand, Figure 3b shows the ^{13}C-NMR spectrum of MAT, where the signals between 65 and 90 are commonly observed in hemiaminals from the Mannich reaction. The variety of signals are due to the reaction that can occur in carbons 6, 2′, 3′ and 6′. In addition, the second condensation between the amine and formaldehyde lead to capture of the iminium group by a phenolic OH, giving rise to 1, 3-oxazines rings. Finally, signals at 166 ppm, 173 ppm and 23–40 ppm appear due to hemiaminal–iminium equilibria and N-CH_3 or Ar-CH_3, respectively.

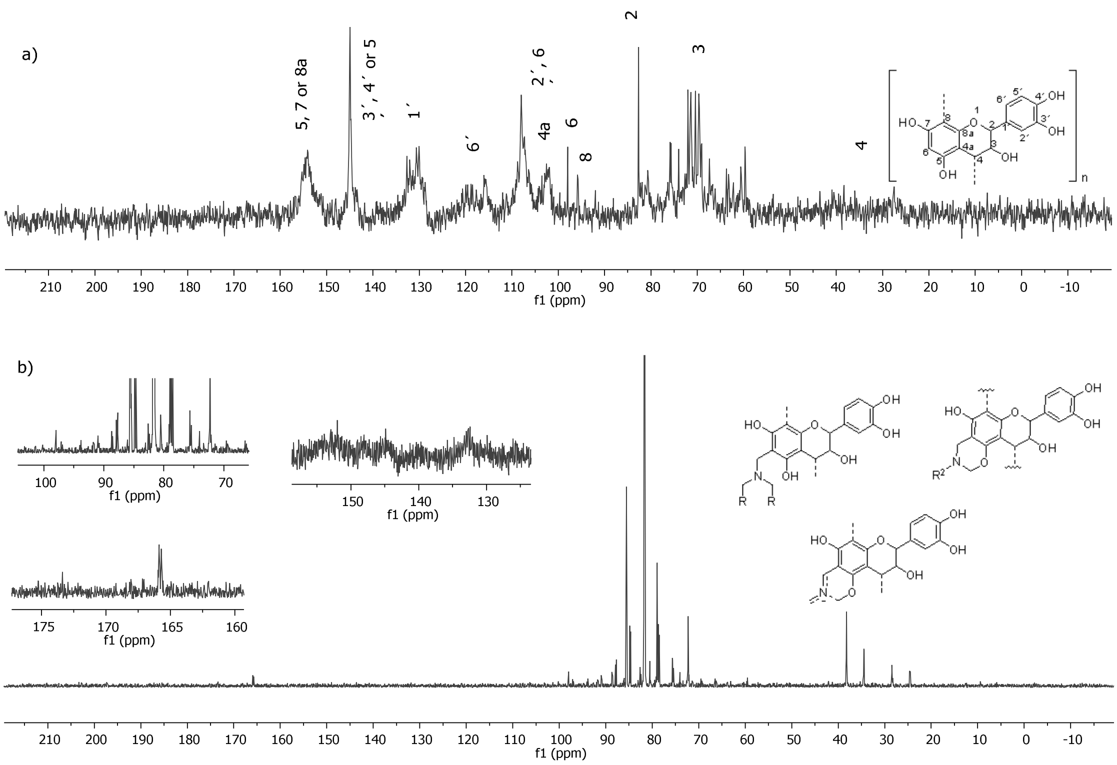

Figure 3. [13]C-NMR spectra of *Acacia* tannin (AT) and the modified *Acacia* tannin (MAT).

3.3. Removal of Heavy Metals

Two variables must be considered to determine the efficiency of the process: the pH and the doses of the coagulant–flocculant. On one hand, it is important to determine the optimal pH of treatment because being out of range would lead to the use of larger amounts of MAT to generate an effective process. On the other hand, the dose of coagulant–flocculant should be evaluated since it has a direct effect on the efficiency of the process because a low amount of MAT will not neutralize the charges and there would be no microfloccles formation and, in the case of there being saturation of the coagulant, generate an inversion of the charges.

Figure 4 shows the percentages of removal of copper, chromium and mercury obtained after wastewater treatment by means of the coagulation–flocculation process with MAT under different pH (4, 7 and 10) and different doses (375 ppm, 739 ppm, 1220 ppm and 1573 ppm). The highest percentages of removal of each metal evaluated were achieved under the same conditions of pH (10) and dose (375 ppm) of MAT. These removal percentages are possibly due to the fact that increasing the pH of the solution increases the degree of ionization of the phenolic hydroxyl groups found in the tannin structure [25]. In addition, in turn the protonation effect becomes weaker, which leads to an increase in the negative charges, which generates an increase in the electrostatic adsorption of the negatively charged surface of the polymer and the metal [26]. One of the possible mechanisms of removal is chelation, where the phenolic hydroxyl of tannin can be strong donors and this generates a high affinity for the metal ion. The process can be generated in two steps, the first one is that the phenolic hydroxyls present in the molecule are negatively charged through a process of deprotonation and this is accompanied by a release of protons to the solution. Followed by this, the chelation reaction is generated where the hydroxyl charged above act as a ligand and this generates the bond with the ion, resulting in a chelating ring [26].

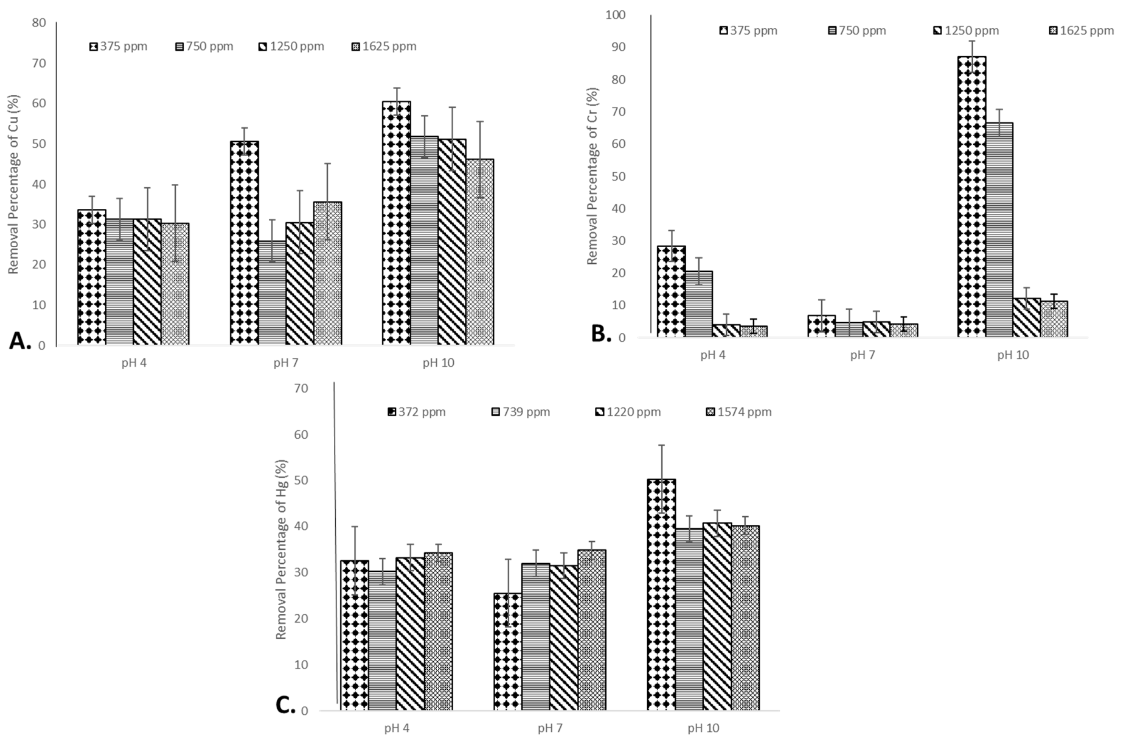

Figure 4. Removal percentage of copper (**A**), chrome (**B**) and mercury (**C**) after the coagulation–floculation process with MAT.

Table 1 shows the initial concentrations of the metals studied and the final concentrations obtained after the treatment processes with MAT under pH 10 and at doses of 375 ppm. The best percentage of removal was chromium metal with the highest percentage of removal (87%), followed by copper (60%) and finally mercury (50%).

Table 1. Concentration before and after treatment of wastewater with MAT, as well as the removal percentage.

Metal	Initial Concentration (ppm)	Final Concentration (ppm)	Removal Percentage (%)
Copper	80	32.5	60
Chromium	30	4	87
Mercury	0.07	0.049	50

Taking into consideration the results obtained, three additional trials were chosen. The first was to determine if there was any effect on the removal of the metals when two of them will be in solution, for which the water supplemented with copper–chromium was analyzed and the results are shown in Table 2. With the second test, we wanted to determine if the metal was really being removed by a metal–TAM interaction and not by a drag effect generated by the union of the organic material with the biopolymer. Finally, considering that the initial concentrations of mercury that were removed were in parts per billion (ppb), it was decided to determine the behavior of the modified tannin at higher concentrations; that is, parts per million (ppm), and obtained results are shown later.

As is shown in Table 2, there was a higher removal percentage when the two metals are simultaneously in solution and in addition it is observed that the percentages of chromium are higher than those of copper metal. The explanation for this phenomenon is that chromium has more coordination states (+6) than copper (+2) and the interaction with tannin will be faster with copper, which causes the active sites of TAM to decrease; this generating lower percentages of copper removal [27]. Under the best conditions of pH (10) and coagulant dose (375 ppm) it can be evidenced that the highest percentages of removal are when the metal is unitary in the solution when it is mixed, which is due to a competitiveness that is related to the stability constant (pKa) that in the case of chromium is 4 and for copper 4.68, and that the smaller the constant, the ligands of the metals with the OH- groups are stronger [28].

Table 2. Removal percentage when the solution only have a metal (A) and when the two metals are simultaneously in solution (Cu + Cr).

pH/Metal	A Metal		Cu + Cr	
	% Cr	% Cu	% Cr	% Cu
4	28.47	33.66	69.86	38.54
7	6.76	50.59	69.55	38.59
10	87.11	57.57	52.25	29.28

Figure 5 shows the difference in the percentages of removal of the metals in the presence and absence of organic material (OM), noting that most of the removal percentages are higher in the absence of organic material, which indicates that the removal of the metal is due to an interaction between the metal and the tannin and does not have a drag effect generated by the micro flocs formed between the organic material and MAT.

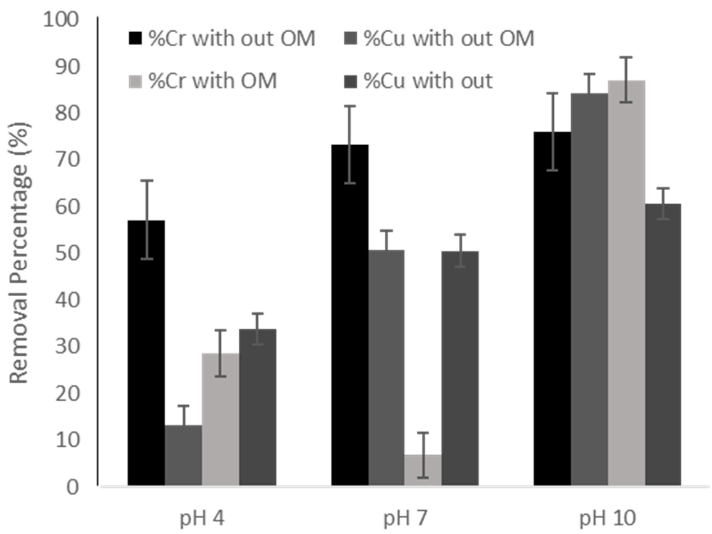

Figure 5. Removal percentages of the metals copper and chrome in the presence and absence of organic material.

Figure 6 shows the removal percentages of mercury when the initial ion concentrations were increased. Here it is evident that there is a directly proportional relationship between the initial concentration and the percentage of removal, as the concentration of the metal increases the percentage of removal. This behavior is a result of the fact that the more ions there are in a solution, the easier is the interaction with the polymer. Therefore, removal percentages higher than 90% can be observed—percentages that were not observed in the first test (Figure 4C)—where the maximum percentage of removal was 50% for the few ions that were in the solution (ppb).

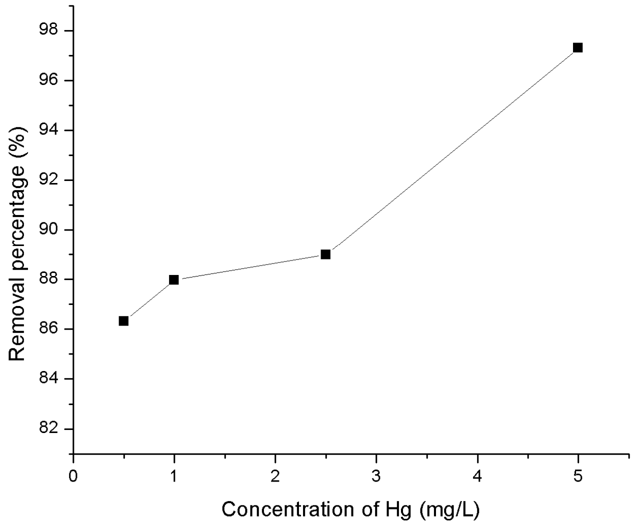

Figure 6. The removal percentages of mercury when the concentration increases from ppb to ppm.

3.4. Physicochemical Parameters

Coagulation–flocculation is a primary treatment, whose objective is to decrease the parameters such as the chemical demand of oxygen, total solids, turbidity and color, among others [29]. It is a widely used method due to its low cost and ease of operation, but its efficiency can vary depending on the type of coagulant–flocculant and the water to be treated. Considering the aforementioned, in this work, we evaluated the behavior of modified tannin (MAT) for the removal of conventional parameters in the same industrial wastewater that are sought to be reduced through this process. Table 3 shows the initial physicochemical parameters of wastewater from the maquiladora industry.

Table 3. The physicochemical parameters of the wastewater before the coagulation–floculation processs with MAT.

Physicochemical Parameters	Results
Dissolved oxygen (ppm)	0.15
pH	9.4
Temperature °C	19
Conductivity µS	0.53
Chemical oxygen demand (COD) (mg/L)	22,957
Turbidity (NTU)	435.33
Real color (PCU)	1094
Apparent color (PCU)	2160
Total suspended solids (mg/L)	867.851

Figure 7 shows the percentages of organic material removal (COD), turbidity and total suspended solids (TSS) after treating the wastewater by means of the coagulation–flocculation process with MAT under different pH (4, 7 and 10) and doses (375 ppm, 750 ppm, 1250 ppm and 1625 ppm). It can be seen that the highest percentages of removal of these parameters were under the same conditions through which the highest percentages of removal of the evaluated metals were obtained; that is to say, at a basic pH (10) and a dose of 375 ppm of MAT. At the same time, it can be observed how the tannin is efficient for the removal of all these parameters, giving it an advantage over the commercial coagulants which tend to work under a certain pH.

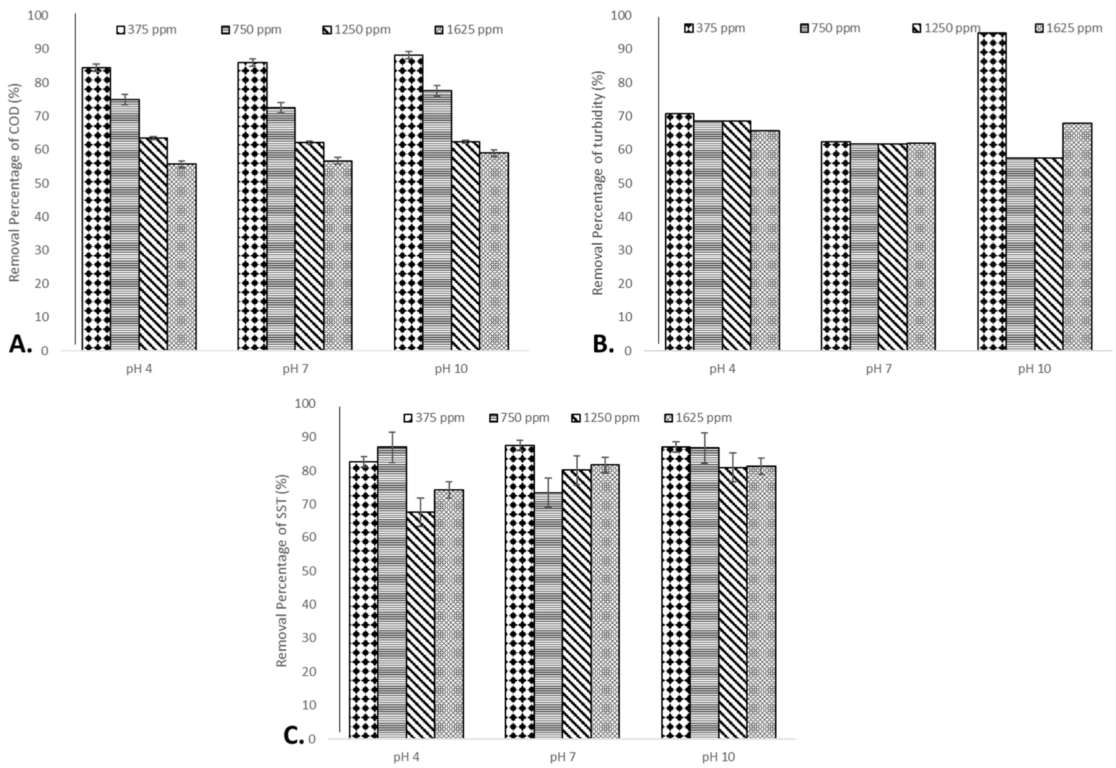

Figure 7. Removal percentages of organic material (COD), turbidity and total suspended solids (TSS) after the coagulation–flocculation process with MAT.

Figure 7A shows the percentages of organic material removal at different pH and with the different doses of MAT, where the maximum percentages of removal at different pH levels were evidenced by the lower dose of modified tannin (375 ppm) and the percentages of removal ranged between 80% and 90%. It can be observed that as the dose of the coagulant increases, the percentages of removal of the organic material decrease from the industrial wastewater. That can be explained by the phenomenon of overdose, where the excess of flocculant–coagulant leads to re-stabilization, and the abundance of positive charges between the aggregates and the flocs undergo a repulsion interaction, generating a decrease in the removal [30].

Figure 7B shows the percentages of turbidity removal and at the same time that there was homogeneity between the percentages obtained under an acid pH and neutral pH. However, the highest efficiency is observed at a basic pH (10) and with the lowest dose of MAT (375 ppm) due to the interaction of the colloidal particles that generate the formation of flocs due to weak interactions with the polymer. Moreover, the amount of interactions depends on the hydrodynamic volume of the flocculant and considering the high percentage of removal of this parameter, it can be inferred that *Acacia*-modified tannin has a high hydrodynamic volume [31].

Figure 7C shows the percentages of removal of the suspended solids. It can be observed that there was a removal under all the conditions studied, which is due to the fact that the negatively charged colloidal particles were neutralized by MAT, destabilized and aggregated in small micro flocs, which generated a large floccule as a result of adsorption bridges between the tannin and the colloidal particles that subsequently precipitated [32]. The bridge mechanism is due to the fact that different segments of the polymer chain formed during the modification of the tannin can adsorb to the surfaces of different particles and form bridges between adjacent particles, which indicates that an aggregate of particles–polymer is formed—the polymer being the bridge [33].

4. Conclusions

The coagulation–flocculation process with the modified *Acacia* tannin is very efficient both for the removal of heavy metals and for the removal of organic material, turbidity and total suspended solids. If the objective is the removal of heavy metals, the ideal conditions are at a basic pH and with a dose of 375 ppm of the stock solution of 50,000 ppm of the modified *Acacia* tannin.

In case you only want to remove the conventional parameters, such as COD, TSS and turbidity, it is not necessary to adjust pH because MAT is effective in the removal of these parameters under any pH condition.

The coagulation–flocculation process with MAT is highly efficient. Copper, chromium and mercury were successfully removed, generating an economical and easy solution for an environmental problem. The results are very promising for the removal of mercury, which is considered one of the most toxic metals.

Author Contributions: C.C. and A.P.-F. conceived the presented idea and planned the experiments; L.L. and A.M. carried out the experiments; J.D. contributed to the interpretation of NMR and IR spectra. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare that there is no any personal circumstances or interest that may be perceived as inappropriately influencing the representation or interpretation of reported research results. The authors declare no conflict of interest.

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