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Magnetic Natural Coagulants for Plastic Recycling Industry Wastewater Treatability

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Abstract: The plastic recycling industry generates a high volume of wastewaters. In this study, an unprecedented use of *Moringa oleifera* and tannin (*Acacia mearnsii* bark) associated with magnetite was proposed for the treatment of these wastewaters. The response surface method (RSM) and central composite rotational design (CCRD) methodology was applied to optimize the influence of operational variables (pH, temperature, electrical conductivity, turbidity, apparent color, chemical oxygen demand (COD), and total solids) on the performance of the magnetic natural coagulants on coagulation, flocculation, and sedimentation process. The results indicated that temperature, pH, electrical conductivity, and total solids did not generate significant differences in treatments when magnetite was added to natural coagulants. Similarly, the parameters apparent color, turbidity, and COD also did not present significant differences in treatments with *Moringa oleifera* and magnetite association, although achieving high efficiencies. Finally, the addition of magnetite significantly improved tannin efficiency removal for turbidity, apparent color, and COD with the optimized treatment (21.55 mg L^{-1} of tannin concentration and 28 min of sedimentation). Thus, natural coagulants associated with magnetite are potential alternatives for the treatment of plastic recycling wastewater and could be used as an environmentally friendly coagulant.

Keywords: *Acacia mearnsii*; central composite rotational design; coagulation; magnetic nanoparticle; magnetite; *Moringa oleifera*; polymer washing effluent; real effluent; tannin

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1. Introduction

Since synthetic polymers were firstly introduced into industrial-scale production in the 1940s, they have been used in a broad range of fields. Furthermore, industries and companies from different sectors see plastic as a versatile material option that protects their products while making them aesthetic for the consumer [1].

Thus, due to the widespread use of the plastics, the global production is estimated to be 8300 million tons of plastic, out of which 6300 million tons has been discarded as waste. Wherein, 79% is directly discarded in aquatic and terrestrial lands and less than 10% is recycled [2].

The management of post-consumer discarded waste is a great challenge. It is known that plastics do not degrade and remain in the landscape for many generations [1,3]. In this way, the recovery, management, and recycling of plastic waste reaches an important dimension. Separating plastic for reuse or recycling is an alternative for not overloading landfills, in addition to reducing the extraction of raw materials. Developing plastic recycling also promotes local growth by reinternalizing local jobs. Typically, a plant producing about 50,000 metric tons of recycled plastic employs around 30 people. This is significantly more jobs than those generated by sending an equivalent amount of waste to landfill, or incinerating it, or by the petrochemical industry synthesizing an equivalent quantity of virgin resins [4]. In this context, in Brazil, the plastic recycling sector generated 17,919 direct jobs in 2019 and generated a revenue of US$454 million [5].

The plastic waste is converted to raw material and then to new plastic materials. The recycling of plastic waste is usually done through a mechanical process that includes grinding, washing, agglutination, extrusion, and quenching [1]. However, the washing step plays a fundamental role where large volumes of water are used and, consequently, produce large amounts of effluents [6]. Water washing is the conventional cleaning method. Various cleaning agents can be added to the cleaning equipment, then stirred and rinsed, and the contaminants attached to the plastic surface are able to be removed [1].

Plastic washing wastewater contains high concentrations of turbidity, chemical oxygen demand (COD), suspended solids, and oil grease that leads to an increase in the pollution load of the wastewater treatment plant. These wastewaters also have high pH values and are frequently discharged without treatment in most plastic recycling plants, increasing the municipal wastewater treatment plant and/or polluting water bodies [1].

Coagulation, flocculation, and sedimentation (C/F/S) are conventional treatments for water and wastewaters and can also be applied for plastic washing wastewater. Aluminum and ferric salts are the most used coagulants. However, a disturbing drawback is their usage in water and wastewater treatment due to the generation of a high volume of sludge, and the requirement of pH adjustment and the high concentration of residual metals in the treated water and sludge are concerning [7]. Furthermore, there has been a important remark on the possible link of the pathogenesis of Alzheimer's disease to the neurotoxicity of aluminum [8], and also multiple sclerosis [9] and central nervous system-related [10] disorders.

Following the need to compromise with the issues of chemical coagulants correlated with rising environmental and health concerns, significant interest has been shown by scientists in the research of environmentally friendly coagulants [11]. In this context, tannin (from *Acacia mearnsii* bark) [7,12] and *Moringa oleifera* seeds [13–15] have been studied to replace chemical agents as natural coagulants with satisfactory removal levels with the additional advantages such as biodegradability, low cost, lower sludge volume production, and high availability [16].

Natural coagulants can replace chemical agents, however, to achieve satisfactory removal levels, a longer sedimentation time compared to the treatment with inorganic coagulants is necessary [17,18]. In this context, magnetic nanoparticles associated with natural coagulants can be used to reduce treatment sedimentation time [19]. Magnetic nanoparticles can be associated to colloids during C/F/S process, and, with the aid of a magnet in the sedimentation, these flakes are separated more quickly by means of magnetic attraction [20]. In addition, other key aspects can impact on the separation under a magnetic field, such as magnetic nanoparticles with higher effective contact areas, like those exhibiting a rod-like shape [21], that can be efficiently isolated under the exposure of an external magnetic field.

In this context, response surface methodology (RSM) and central composite design rotatable design (CCRD) employs mathematical and statistical modelling tools to analyze issues in which numerous factors influence a response of concern, with the objective of maximizing that response with the fewest number of experiments. It provides adequate data on variable effects, as well as information on pairwise, direct interaction, and non-linear variable effects. This approach has been widely used in a variety of research to investigate the impact of operational parameters, optimize experimental variables, and also model biological, chemical, or physical interactions, and therefore, can be used to optimize wastewater processes [22,23].

The sustainable development goals proposed in Agenda 2030 include “clean water and sanitation” (SDG 6) and “life below water” (SDG 14) [24]. In this sense, the removal of contaminants from plastic recycling industry wastewater is necessary. Therefore, the main objective of this research was to demonstrate the feasibility of applying the natural coagulants tannin and *Moringa oleifera* associated with magnetite as magnetic nanoparticles in order to accelerate the sedimentation process and efficiency in the treatment of plastic recycling industry wastewater. The adsorption process treatment was optimized by RSM to obtain maximum pollutant removal through CCRD, using the optimized parameters and pH, temperature, electrical conductivity, turbidity, apparent color, COD, and total solids.

2. Materials and Methods

2.1. Chemicals and Reagents

The wastewater was kindly provided from a plastic washing company located in Londrina, Brazil. The wastewater was collected before undergoing any type of physical-chemical and biological treatment, and its characteristics are presented in Table 1. A commercial tannin-based product (Tanfloc, Tanac, Brazil) was used as a coagulant in this work. *Moringa oleifera* seeds were obtained from the campus of the Federal Technological University of Paraná (Londrina, Brazil). Analytical grade chemicals were used, namely $FeCl_3 \cdot 6H_2O$, $FeCl_2 \cdot 4H_2O$, NaOH, NaCl, and were all purchased from Synth (Diadema, Brazil) and used without further purification. Distilled water was used in all processes of aqueous solutions, suspensions, and washing processes.

Table 1. Physical–chemical parameters of the raw wastewater.

Parameters	Results
Temperature (°C)	25.3
pH	7.26
Electrical conductivity (mS m^{-1})	0.682
Turbidity (NTU)	379
Apparent color ($\times 10^3$ uH)	1.34
Chemical oxygen demand (mg L^{-1})	596
Total solids (mg L^{-1})	14.3

2.2. Synthesis of Magnetite Nanoparticles

The magnetic nanoparticle magnetite (γ-Fe_3O_4) was fabricated by a bottom-up approach, the conventional chemical co-precipitation synthesis method (Figure 1). In a typical experiment, $FeCl_2 \cdot 4H_2O$ and $FeCl_3 \cdot 6H_2O$ were dissolved into 100 mL of deionized water to obtain a molar ratio of ferric ion to ferrous ion in the solution of 0.5 and added into a 250 mL three-neck flask. The pH was adjusted to 11 with NaOH solution. The reaction solution was vigorous stirred while nitrogen gas flowed into the flask for 3 h, and the solution color changed from orange to black rapidly. After the reaction time, the solution was filtered and thoroughly washed with deionized water and dried in a vacuum desiccator at 80 °C for 24 h [25].

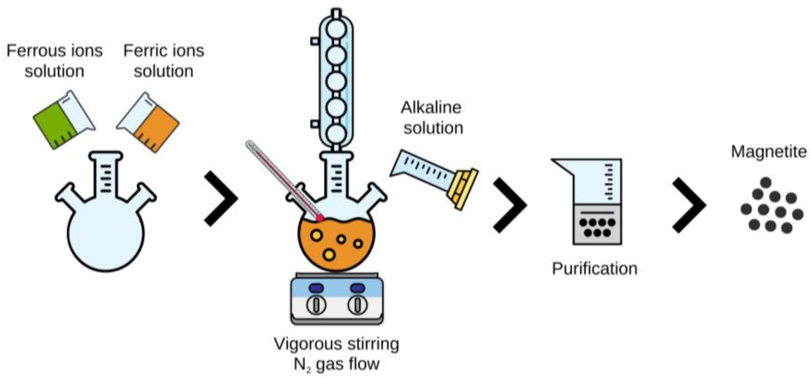

Figure 1. Schematic representation of co-precipitation chemical method for magnetite synthesis method.

2.3. Natural Coagulants Preparation

The tannin coagulant suspension was obtained from the homogenization of 1 mL of liquid tannin in 1 L of distilled water. As for the coagulant based on aqueous extract of *Moringa oleifera* seeds, a saline solution was prepared processing 50 g of *Moringa oleifera* seed without shell and 1 L of 1 M of NaCl and subsequently filtered [14]. Different amounts of coagulant solutions were used in jar tests, resulting in various concentrations.

2.4. C/F/S Experiments

C/F/S experiments were carried out in a jar test equipment (Ethik, Brazil) with 2 L of wastewater in each jar. The C/F/S conditions were adapted from previously reported methodologies [14,15] using rapid mixing gradient of 150 s^{-1} for 3 min and slow mixing gradient of 15 s^{-1} for 10 min. In order to improve sedimentation speed, neodymium magnets discs (80 mm $\times$ 15 mm) were placed under the jars in the tests with coagulants associated with magnetic nanoparticles at the moment the sedimentation process began.

2.5. Experimental Design for Parameters Optimization

The ideal range concentrations of *Moringa oleifera* and tannin solutions to be used for the CCRD and the sedimentation time for sample collection and analysis in which the behavioral analyses of the treatments could be defined were determined by pre-tests of parameters optimization (Figure 2).

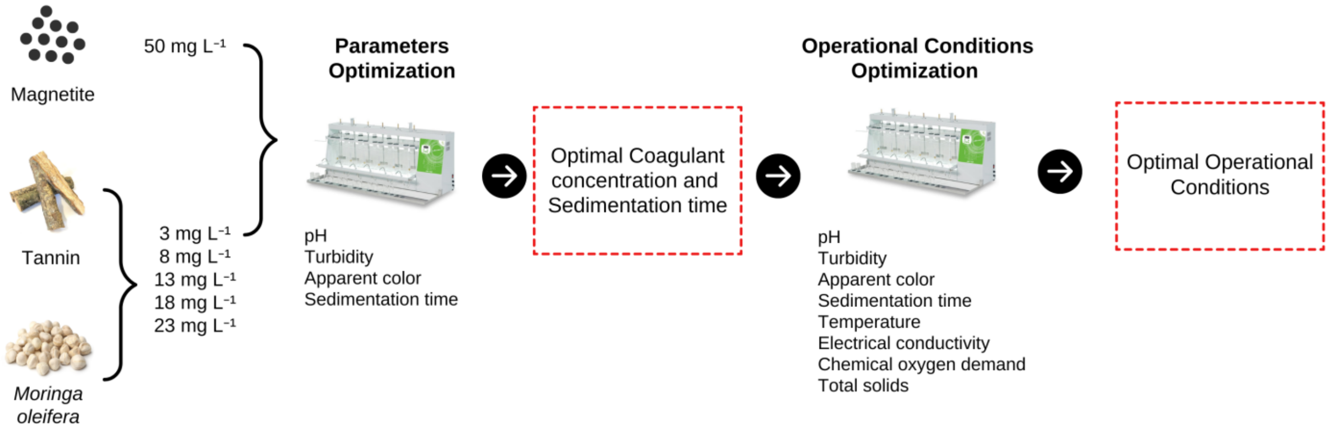

Figure 2. Scheme of experimental design for parameters and operational conditions optimization using central composite rotational design (CCRD).

The concentrations used of natural coagulant suspensions in the pre-tests were 3 mg L^{-1}, 8 mg L^{-1}, 13 mg L^{-1}, 18 mg L^{-1}, and 23 mg L^{-1} without magnetic nanoparticle and also with a fixed concentration of 50 mg L^{-1} of magnetite. In the tests with magnetite nanoparticle association, the natural coagulant suspension was added simultaneously with the magnetite suspension. From the beginning of sedimentation, the behavior of the parameters pH, turbidity, and apparent color was monitored at sedimentation times of 5, 15, and 40 min.

2.6. Optimization of Operational Conditions

After carrying out the pre-test and consequently obtaining the ideal ranges of concentration and time, the use of the CCRD was performed. A block factorial scheme was considered, whose variables were: concentration (mg L^{-1}) and sedimentation time (min), and as a block, the presence or absence of nanoparticles, including four tests in axial conditions and three repetitions at the central point, totalizing 11 tests for each coagulant within each block. The analyses were performed using the Statistica software (Version 7.0, StatSoft, Hamburg, Germany).

Initially, for each response variable, a second order model of the type was adjusted according to Equation (1),

$$\text{Answer} = \beta_0 + \beta_1 + \beta_2 C + \beta_3 T + \beta_4 C^2 + \beta_5 T^2 + \beta_6\, C \times T \tag{1}$$

where C (concentration) and T (time) are the variables, and the coefficients are associated with the intercept (β_0), block (β_1), concentration (β_2), time (β_3), quadratic concentration (β_4), quadratic time (β_5), and interaction between concentration and time (β_6). In each variable analyzed, the RSM was performed considering only the model with significant coefficients (at 5% of significance) in order obtain the optimized operational conditions.

Temperature, pH, electrical conductivity, turbidity, apparent color, COD, and total solids were collected and analyzed according to the methodologies described in the Standard Methods for the Examination of Water and Wastewater [26].

3. Results and Discussion

3.1. Parameters Optimization

The results of the pre-tests showed that the *Moringa oleifera* coagulant solution was more efficient at a concentration range from 3 mg L^{-1} to 13 mg L^{-1} and the solution based on tannin was at 13 mg L^{-1} to 23 mg L^{-1}. For the time variable, the best range for the parameters analysis obtained was between 3 and 33 min from the beginning of the sedimentation. Thus, the specific CCRD was applied with precision to determine the optimal concentrations of natural coagulants in C/F/S experiments and the sedimentation times for the optimization of the operational conditions (Table 2).

Table 2. Concentrations and sedimentation times obtained by central composite rotational design (CCRD) in experiments of optimization of operational conditions using natural coagulants.

Test	Variable			CCRD [1]	
	Time (min)	Tannin Concentration (mg L^{-1})	*Moringa oleifera* Concentration (mg L^{-1})	Time	Coagulant Concentration
1	8	14.45	4.63	−1	−1
2	8	21.55	11.37	−1	1
3	28	14.45	4.63	1	−1
4	28	21.55	11.37	1	1
5	18	13	3	0	−1.41
6	18	23	13	0	1.41
7	3	18	8	−1.41	0
8	33	18	8	1.41	0
9	18	18	8	0	0
10	18	18	8	0	0
11	18	18	8	0	0

Note: [1] Central composite rotational design.

3.2. Optimization of Operational Conditions

3.2.1. pH

Table 3 shows the results for the significant effects in the treatment with tannin and *Moringa oleifera* in terms of pH analysis.

After statistical analysis, it was possible to identify that the presence or absence of magnetite in treatment with tannin was not significant for the variable pH for the adjusted model. This also occurred for the effect of time and for the interaction between concentration and time. The effect of concentration and quadratic concentration had a significant impact on the pH. It can be observed in Figure 3A that for 18 mg L^{-1} of tannin concentration, the pH was slightly higher. However, the low value for the coefficient of determination (R^2) for adjusted data was equal to 0.321, indicating that the model is not adequate for the pH parameter.

Table 3. Significant effects for the pH parameter for coagulation, flocculation, and sedimentation (C/F/S) process using tannin and *Moringa oleifera* in the presence and absence of magnetite.

Coagulant	Effects	Coefficient	Standard Error	T	*p*-Value	R^2
Tannin	Intercept	7.459	0.008	950.002	0.000	0.297
	Concentration	−0.028	0.013	−2.138	0.046	
	Quadratic concentration	−0.041	0.015	−2.709	0.014	
Moringa oleifera	Intercept	7.365	0.005	1393.791	0.000	0.321
	Block	0.025	0.011	2.409	0.026	
	Time	0.027	0.012	2.251	0.036	

Despite *p*-value < 0.05 for block and time effect in the treatment with *Moringa oleifera* (Table 3), the value of R^2 obtained was 0.297, which indicates that the model is adequate for only 29.7% of the variation in pH for *Moringa oleifera*, and thus, that the adjustment for this model was also not satisfactory. However, in Figure 3B, it is possible to observe that for *Moringa oleifera*, the higher the sedimentation time, the higher the pH. In general, the pH does not interfere in the coagulation process and does not alter the pH of the water or wastewater in studies using *Moringa oleifera* as a natural coagulant [13]. However, as the plastic recycling wastewater is very polluted (Table 1), and with increasing sedimentation time, greater amounts of contaminants were removed; this could have led to changes in pH.

The pH varied between 7.4 to 7.5 in the treatments with tannin (Figure 3A) and between 7.3 and 7.4 in the treatments with *Moringa oleifera* (Figure 3B) both in the presence and in the absence of magnetite. These results reinforce the notion that the presence of magnetite did not influence the pH. The pH values were all kept within the range required by the Brazilian regulation [27], which determines the pH at a value of 5.0 to 9.0 for the discharge of effluents into receiving water bodies.

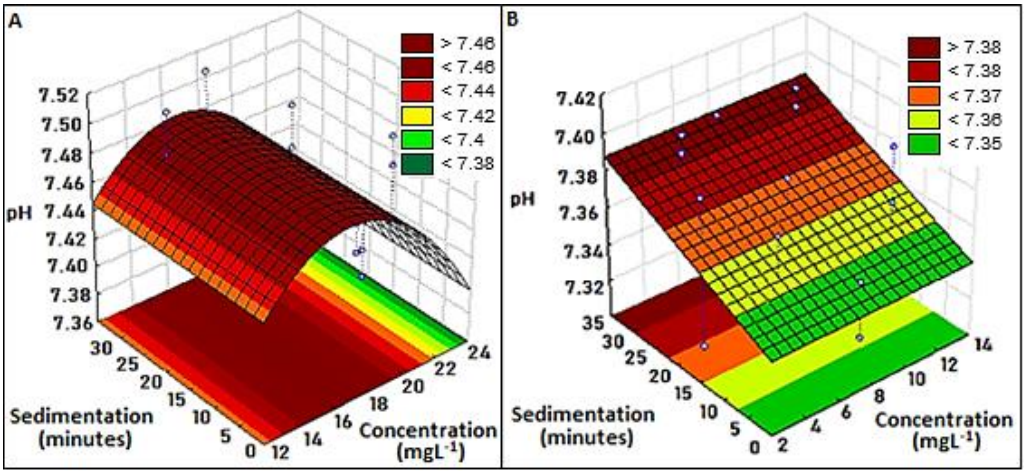

Figure 3. pH treatment surface graphs using magnetite associated with (**A**) tannin and (**B**) *Moringa oleifera*.

3.2.2. Temperature

The temperature for all tests varied between 24.0 °C and 26.0 °C. Such observed variations were due to the ambient temperature change. Statistical significance was not found in the parameters used, and, therefore, it was not possible to adjust the model, since the variation of the temperature factor was explained only by the general average of the intercept. Thus, the natural coagulants and the magnetite nanoparticles do not cause reactions capable of altering the temperature of the medium.

3.2.3. Electrical Conductivity

The values obtained for electrical conductivity were constant in all treatments with tannin for all times and concentrations tested, indicating that no variable analyzed statistically influenced the electrical conductivity parameter. Therefore, it was not possible to perform the statistical analysis and to plot the response surface graph.

A range between 0.81 mS m^{-1} and 1.51 mS m^{-1} was observed for electrical conductivity in the treatments with *Moringa oleifera* without magnetite, and with magnetite a variation between 0.91 mS m^{-1} and 1.50 mS m^{-1} was observed. The results of the statistical analysis are displayed in Table 4.

Table 4. Significant effects for the electrical conductivity parameter for coagulation, flocculation, and sedimentation (C/F/S) process using *Moringa oleifera* in the presence and absence of magnetite.

Effects	Coefficient	Standard Error	T	*p*-Value	R^2
Intercept	1.238	0.009	141.574	0.000	
Block	0.023	0.009	2.480	0.024	
Concentration	0.398	0.010	37.969	0.000	0.986
Quadratic concentration	−0.056	0.012	−4.639	0.000	
Quadratic time	−0.030	0.012	−2.518	0.022	

The effects of intercept, block, concentration, quadratic concentration, and time were significant in the treatment with *Moringa oleifera* and magnetite. For the adjusted model, the obtained R^2 statistic was equal to 0.986, indicating that this model explains 98.6% of the electrical conductivity variation. Furthermore, it was also possible to obtain the response surface graph for the treatment using *Moringa oleifera* coagulant associated with magnetite for the electrical conductivity parameter (Figure 4).

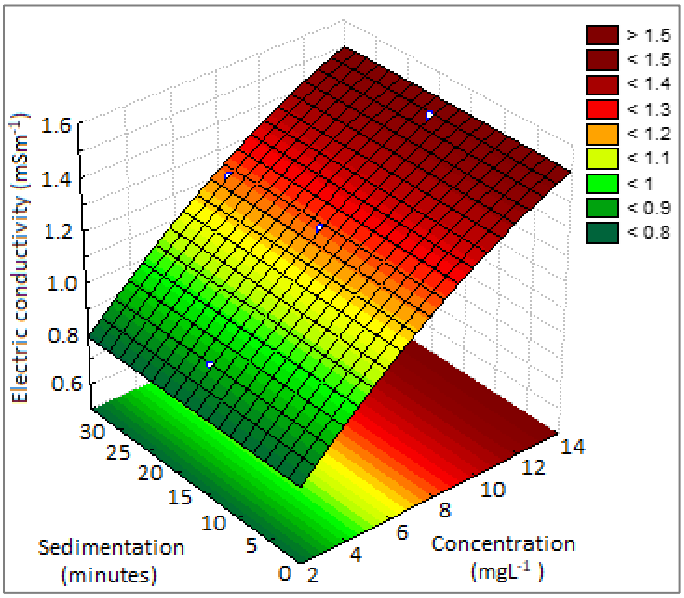

Figure 4. Electrical conductivity surface graph for the treatment with *Moringa oleifera* associated with the magnetite nanoparticle.

Analyzing the response surface graph (Figure 4), it can be seen that the electrical conductivity parameter varies mainly according to the concentration variable, as the higher the concentration of *Moringa oleifera* used, the greater the value of the electrical conductivity. This fact is due to the presence of sodium chloride in the extraction of *Moringa oleifera* coagulant.

In addition, magnetite nanoparticles association with *Moringa oleifera* treatment presented significant block effect (Table 4). However, the sedimentation time (time effect) did not influence the electrical conductivity parameter (Figure 4), and thus, the electrical conductivity parameter was not influenced by magnetite addition. Furthermore, salts are difficult to remove in water and wastewater treatments, requiring advanced treatments such as membrane processes [28].

3.2.4. Turbidity

A significant difference was observed for turbidity removal using tannin considering the effects of intercept, block, concentration, and time, indicating that the presence of magnetite positively influenced the coagulant performance (Table 5). The R^2 statistic for the adjusted model was equal to 0.827 for tannin, indicating that the model explains 82.7% of the variation in turbidity.

Table 5. Significant effects for the turbidity parameter for coagulation, flocculation, and sedimentation (C/F/S) process using tannin and *Moringa oleifera* in the presence and absence of magnetite.

Coagulant	Effects	Coefficient	Standard Error	T	*p*-Value	R^2
Tannin	Intercept	79.547	0.460	172.793	0.000	0.827
	Block	3.828	0.921	4.158	0.001	
	Concentration	8.988	1.082	8.308	0.000	
	Time	4.349	1.047	4.152	0.001	
Moringa oleifera	Intercept	88.930	0.910	97.719	0.000	0.769
	Time	15.588	1.514	10.293	0.000	
	Quadratic time	−7.475	1.606	−4.654	0.000	

For the treatment with *Moringa oleifera* (Table 5), only the effects of intercept, time, and quadratic time were significant. As the effect of the block was not significant (p-value > 0.05), the presence of the nanoparticle did not significantly influence the turbidity parameter. The same was observed with the effect of concentration. In addition, the model adjusted in the treatment with *Moringa oleifera*, and the R^2 statistic was equal to 0.769, indicating that the model explains 76.9% of the variation in turbidity. The data plotted for treatments with tannin and *Moringa oleifera* associated with magnetite are presented in Figure 5.

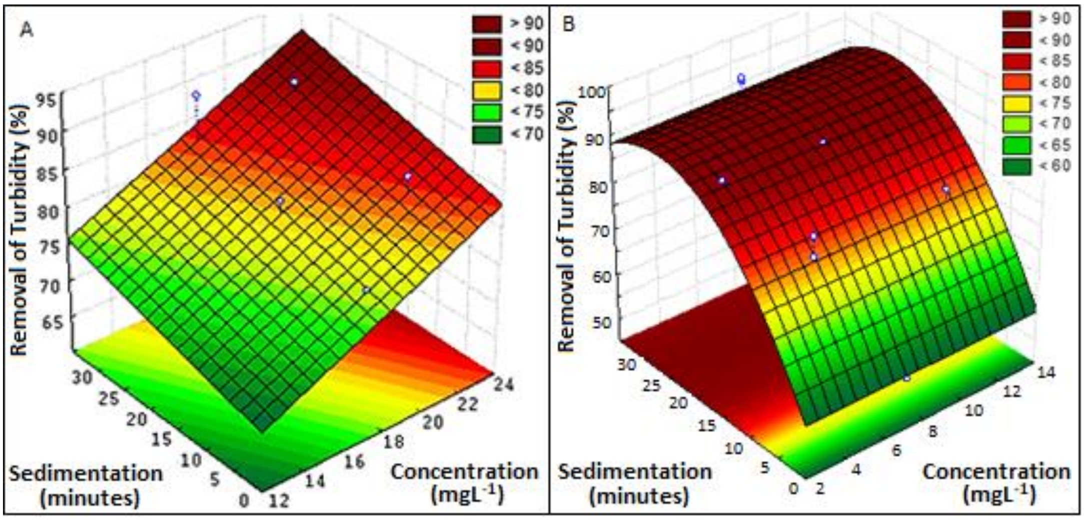

Figure 5. Turbidity treatment surface graphs using magnetite associated with (**A**) tannin and (**B**) *Moringa oleifera*.

The treatment using tannin without magnetite obtained a maximum turbidity removal of 84%, resulting in a residual turbidity of 59.4 NTU in the treatment with 21.55 mg L^{-1} of coagulant dosage and 28 min of sedimentation. The treatment with tannin and magnetite nanoparticles resulted in a maximum turbidity removal of 89% (Figure 5A), corresponding to a final effluent with turbidity of 41.0 NTU. This result was obtained in two treatments conditions, 21.55 mg L^{-1} coagulant dosage and 28 min of sedimentation, and also with 18 mg L^{-1} coagulant dosage and 33 min of sedimentation. Thus, tannin associated with magnetite nanoparticle had its performance significantly improved and could, therefore, reach better percentages of turbidity removal.

The maximum turbidity removal using *Moringa oleifera* with and without magnetite corresponded to 93%. With regard to the treatment without magnetite, the best result of turbidity removal was obtained in two treatments: with 28 min of sedimentation and 14.45 mg L^{-1} of coagulant concentration and with 33 min of sedimentation and 18 mg L^{-1} of coagulant concentration. Such turbidity removals corresponded, respectively, to a final effluent with turbidity of 27.7 NTU and 28.0 NTU (Figure 5B). *Moringa oleifera* associated with magnetite obtained the best results of turbidity removal by using 18 mg L^{-1} of concentration with 33 min of sedimentation, resulting in a final effluent with turbidity of 25.0 NTU.

Observing Figure 5B, the effect of sedimentation time was decisive in the efficiency of turbidity removal in the treatment of *Moringa oleifera* with the association of magnetite. Previous studies report the sedimentation time as a limiting factor for the use of *Moringa oleifera* as a natural coagulant for water and wastewater treatments [13,17]. However, the use of magnetite was not statistically significant in reducing the sedimentation time in the present study. This may have occurred due to the lack of a mixing step before the addition of the magnetic natural coagulant to the wastewater. According to Zhang et al., this is a crucial step prior to its use as a coagulant, as the coagulant-nanoparticle cluster is formed [29].

3.2.5. Color Removal

The results of statistical analysis for apparent color removal using tannin with magnetite showed that an enhanced behavior could be observed for all concentrations (Table 6). For this parameter, all the effects proved to be significant (p-value < 0.05), with the exception of quadratic time and concentration and time interaction. For the treatment with tannin, the adjusted R^2 statistic was equal to 0.878, indicating that the adjusted model explains 87.8% of the apparent color variation.

Table 6. Significant effects for the apparent color parameter for coagulation, flocculation, and sedimentation (C/F/S) process using tannin and *Moringa oleifera* in the presence and absence of magnetite.

Coagulant	Effects	Coefficient	Standard Error	T	p-Value	R^2
Tannin	Intercept	76.001	0.823	92.337	0.000	0.878
	Block	7.069	1.180	5.991	0.000	
	Concentration	12.622	1.387	9.103	0.000	
	Quadratic concentration	−8.647	1.585	−5.457	0.000	
	Time	3.626	1.342	2.701	0.015	
Moringa oleifera	Intercept	88.930	0.910	97.719	0.000	0.857
	Time	15.588	1.514	10.293	0.000	
	Quadratic time	−7.475	1.606	−4.654	0.000	

In the treatment with *Moringa oleifera*, only the effects of intercept, time, and quadratic time had a significant role in the treatment, and thus, the most influential factor for the removal of apparent color was the sedimentation time (Table 6). For *Moringa oleifera*, the adjusted R^2 statistic was 0.857, indicating that the adjusted model explains 85.7% of the apparent color variation. The values plotted on a surface graph for treatments with magnetite are shown in Figure 6.

The best result of apparent color removal was 78% for treatment with tannin without magnetite, with a final effluent corresponding to 299 uH, using 21.55 mg L^{-1} of coagulant and 28 min of sedimentation. When associated with the magnetite nanoparticle (Figure 6A) the apparent color removal was increased to 84% in the same concentration and time of analysis, corresponding to a final value of 221 uH. Thus, for tannin, it was concluded that the highest efficiency obtained was not necessarily the highest concentration or the longest time of sedimentation. Increased dosages of natural coagulants, beyond optimum results, can lead to a saturation and charge reversal, and subsequently to an increase in residual parameters due to the stabilization of destabilized particles [30].

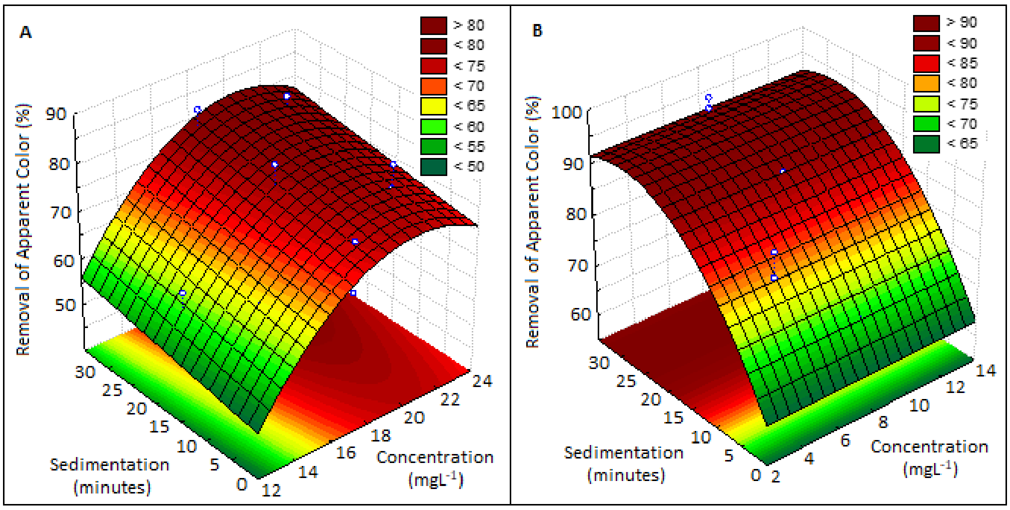

Figure 6. Surface graphics of the apparent color treatment using magnetite associated with (**A**) tannin and (**B**) *Moringa oleifera*.

When using *Moringa oleifera*-based coagulant, the maximum removal of apparent color was 93% (89 uH) obtained at two different conditions, the first with a concentration of 14.45 mg L^{-1} (28 min) and the second with 18 mg L^{-1} (33 min). In tests associated with magnetite, the greatest removal obtained was 95% (65 uH) using 8 mg L^{-1} of coagulant and 33 min of sedimentation (Figure 6B). Despite the concentration and the use of magnetite not being significant in statistical analysis for apparent color removal, the settling time was again shown to be a determinant in obtaining greater efficiency removals.

3.2.6. COD

COD removals using tannin without magnetite ranged from 57 to 70% and with magnetite from 51 to 76%. In contrast, the treatments with *Moringa oleifera* varied from 43 to 64% without magnetite and from 47 to 76% with magnetite. The significant effects obtained after performing a statistical analysis of COD data for all treatments are shown in Table 7.

Table 7. Significant effects for the chemical oxygen demand (COD) parameter for coagulation, flocculation, and sedimentation (C/F/S) process using tannin and *Moringa oleifera* in the presence and absence of magnetite.

Coagulant	Effects	Coefficient	Standard Error	T	*p*-Value	R^2
Tannin	Intercept	68.252	0.847	80.588	0.000	0.786
	Block	4.348	1.214	3.581	0.002	
	Concentration	5.708	1.427	4.001	0.001	
	Quadratic concentration	−5.917	1.631	−3.629	0.002	
	Time	8.330	1.381	6.031	0.000	
	Concentration and time interaction	−3.956	2.014	−1.965	0.067	
Moringa oleifera	Intercept	59.433	1.313	45.257	0.000	0.347
	Time	10.417	2.988	3.487	0.002	

Although the effect of the interaction of concentration and time in the use of tannin was not significant (*p*-value > 0.05), this effect was included as its value is near 0.05 and its inclusion improved the quality of adjusted model. Thus, R^2 corresponded to 0.786, indicating that the model explains 78.6% of the COD variation. Both the time and concentration variables were significant for greater efficiency in the wastewater treatment using tannin and magnetite (Figure 7A). The best result using tannin without magnetite was 70% of COD removal, using a concentration of 21.55 mg L^{-1} and 28 min of sedimentation, and with magnetite association, 76% of COD removal with 18 mg L^{-1} of tannin and 33 min of sedimentation. Thus, tannin associated with magnetite improved the efficiency in removing the COD parameter. This result is not surprising since magnetic nanoparticles can induce free radicals [31] that are responsible for enhancing antioxidant properties in tannin and other coniferyl alcohol polymers with similar chemistry [32].

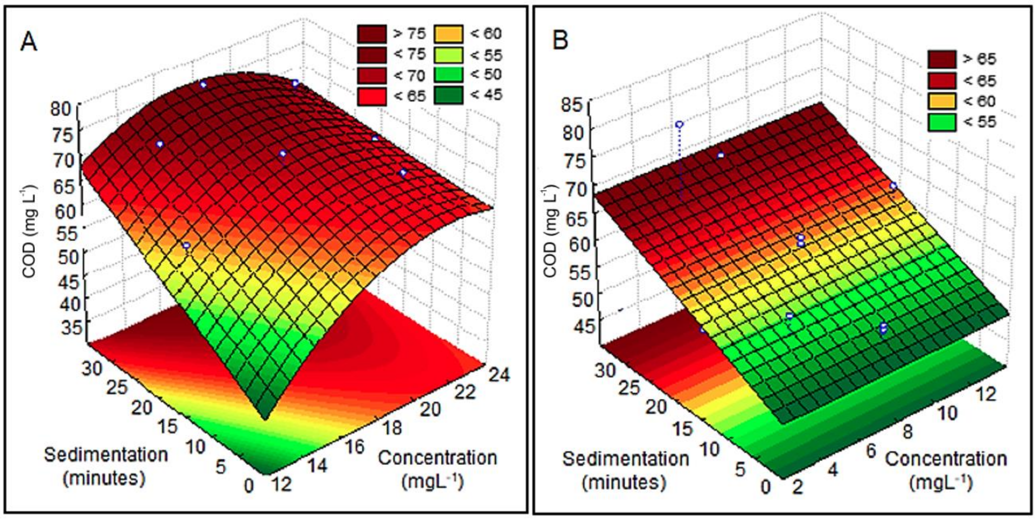

Figure 7. Surface graphics of COD treatment using magnetite associated with (**A**) tannin and (**B**) *Moringa oleifera*.

For the treatment with *Moringa oleifera* and magnetite, both intercept and time factors were significant for the model adjustment. However, the presence of magnetite was not significant in the treatment with *Moringa oleifera*. The model adjustment resulted in R^2 being equal to 0.347, and thus, indicating that the model was not adequate for COD variation in relation to the treatment with *Moringa oleifera*. In addition, the treatment with *Moringa oleifera* and magnetite is evidently influenced by sedimentation time (Figure 7B), as the higher the sedimentation time, the higher the COD removal. The best result obtained for COD removal using *Moringa oleifera* was using 8 mg L^{-1} of coagulant and 33 min of sedimentation in the treatment without magnetite (64%), and 4.63 mg L^{-1} of coagulant and 28 min of sedimentation with magnetite (76%).

3.2.7. Total Solids

For the treatment with tannin with and without magnetite, the removal of total solids varied from 93% to 96%. *Moringa oleifera*, with and without magnetite, presented removal of total solids percentages ranging from 96% to 97%. After carrying out the statistical analyses, it was concluded that the efficiencies in the removal of total solids were similar for all the treatments with tannin whether or not it was associated with the magnetite nanoparticles. The same was observed for *Moringa oleifera*.

3.3. Other Natural Coagulants Associated with Magnetite Nanoparticles

The results obtained in the present study can be compared with the results obtained by other several studies that used magnetite nanoparticles associated with natural coagulants (Table 8). A great differential of the present study was the use of much lower concentrations of coagulants (3–22 mg L^{-1}) when compared to other similar works (100–16,000 mg L^{-1}). This is a very important issue, because even when dealing with waste, or an abundant natural material, often of low cost, it can present transport, storage, and processing costs, which can make a large-scale process unfeasible. The same comparison can be observed for the concentration of magnetite nanoparticles, which becomes even more important, since there is a cost for magnetite nanoparticles production. In addition, few studies used real effluents. Thus, although the results found were not those of greater parameters removal or shorter sedimentation time, the results are relevant as they present the treatment of a real effluent with low coagulant and magnetite dosages.

Table 8. Natural coagulants associated with magnetite nanoparticles.

Coagulant	Wastewater	Coagulant Dosage (mg L^{-1})	Magnetite Dosage (mg L^{-1})	Raw Water Parameters	Sedimentation Time (min)	Removal (%)	Reference
Moringa oleifera seeds	Surface water	400	10	Turbidity: 79 NTU [a], color: 265 uH [b]	30	90 (turbidity), 85 (color)	[20]
Moringa oleifera seeds	Surface water	200	67	Turbidity: 143 NTU, Color: 509 uH	10	97 (color), 97 (turbidity)	[19]
Moringa oleifera seeds	Palm oil wastewater	1000	~10	TSS [c]: 120 mg L^{-1}, color: 4 uH, turbidity: 65 NTU, COD [d]: 16,405 mg L^{-1}	15	83 (TSS), 28 (color), 85 (COD)	[33]
Moringa oleifera seeds	Synthetic dairy effluent	16,000	1000	Color: 1336 uH, turbidity: 200 NTU, bacterial load 10^3 CFU ml^{-1}	30	82 (color), 50 (turbidity), 99 (*S aureus*)	[34]
Moringa oleifera seeds	Synthetic textile wastewater	100	-	10 mg L^{-1} RB5 [e], color: 162 uH	20	94 (color), 96 (RB5)	[35]
Banana extract	Synthetic turbid water	2600	144	150 NTU	25	93 (turbidity)	[36]
Rice starch	Real wastewater	4000	4000	Color: 315 uH, turbidity: 46 NTU, COD: 352 mg L^{-1}	20	85 (turbidity), 85 (color), 54 (COD)	[37]
Leucaena seeds	Synthetic textile wastewater	-	3	50 mg L^{-1} CR [f]	30	90 (CR, pH 3)	[38]
Leucaena seeds	Synthetic wastewater	100	-	10 mg L^{-1} CR	5	89 (CR, pH 2)	[39]
Acacia mearnsii bark	Plastic recycling industry wastewater	22	50	Turbidity: 379 NTU, color: 1340 uH, COD: 596, TS [g]: 14 mg L^{-1}	28	89 (turbidity), 84 (color), 74 (COD), 94 (TS)	This study
Moringa oleifera seeds		5			28	92 (turbidity), 92 (color), 76 (COD), 96 (TS)	

Note: [a] Turbidity unit, [b] Hazen unit (mg Pt-Co L^{-1}), [c] Total suspended solids, [d] Chemical oxygen demand (mg L^{-1}), [e] Reactive black 5 dye, [f] Congo red dye, [g] Total solids.

4. Conclusions and Future Perspectives

The results demonstrated that natural coagulants can be efficiently combined with nanoparticle magnetite for plastic recycling industry wastewater treatment. However, the presence of magnetite nanoparticles was not significative on parameters such as pH, temperature, electrical conductivity, and total solids for treatments with both natural coagulants. *Moringa oleifera* presented higher removals of apparent color (91%), turbidity (92%), COD (76%), and TS (96%) in its optimal concentration (5 mg L^{-1}) and sedimentation time (28 min), although the magnetite addition was not significant for those variables and the sedimentation time was the determining efficiency factor for treatments with *Moringa oleifera*. The addition of magnetite significantly improved tannin efficiency removal for turbidity (89%), apparent color (84%), and COD (74%) with the optimized treatment (21.55 mg L^{-1} of tannin concentration and 28 min of sedimentation). Thus, although *Moringa oleifera* showed higher removals when compared to tannin for the studied parameters, *Moringa oleifera* showed no significant difference when associated with magnetic nanoparticles. Therefore, it is concluded that magnetite associated with tannin has the potential to become an environmentally friendly alternative for the treatment of wastewater, replacing the inorganic coagulants widely used today. Furthermore, based on this study, further research is still needed to be carried out from the following aspects:

- Different magnetic nanoparticles can be tested, especially with *Moringa oleifera*, which obtained the best removals efficiencies.
- The adsorption mechanism and interaction with magnetic nanoparticles can be further studied.
- Other real effluents, pilot, and large-scale experiments are necessary.
- Leaching and loss experiments related to the stability of the nanoparticles.
- Ecotoxicity analysis caused by magnetite nanoparticles and by-products.

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