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Avocado seed powder residues as a promising bio-adsorbent for color removal from textile wastewater

Residuos de polvo de semilla de aguacate como bioadsorbente prometedor para la eliminación del color de las aguas residuales textiles

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Abstract

Pollution by textile dyes is one of the most relevant environmental problems due to its significant negative effects on the environment. In response to this, several remediation processes have been developed, with adsorption being an effective process for removing these contaminants from water. In addition, the use of natural adsorbents proves to be a cost-effective alternative to remove organic pollutants. In this research, the capacity of avocado seed as a bio-adsorbent for the removal of color from textile wastewater obtained from a textile company was evaluated. Using the Response Surface Methodology and a Central Composite Design, it was found that the factor with the greatest influence on the removal process was pH. In addition, at 20 °C, the optimum conditions to achieve the greatest color removal from the textile wastewater were pH=2, dosage of 20 g/L and a 30-minute agitation time. According to these conditions, 96.35 % of the color of the wastewater was removed.

Keywords: Avocado seed, adsorption, textile wastewater, pollution, removal.

Resumen

La contaminación por colorantes textiles es uno de los problemas ambientales más relevantes debido a sus importantes efectos negativos sobre el medio ambiente. En respuesta a ello, se han desarrollado varios procesos de remediación, siendo la adsorción un proceso eficaz para eliminar estos contaminantes del agua. El uso de adsorbentes naturales resulta ser una alternativa rentable para eliminar los contaminantes orgánicos. En esta investigación se evaluó la capacidad de la semilla de aguacate como bio-adsorbente para la remoción de color de aguas residuales textiles obtenidas de una empresa textil. Utilizando la Metodología de Superficie de Respuesta y un Diseño Central Compuesto, se encontró que el factor con mayor influencia en el proceso de remoción fue el pH. A 20 °C, las condiciones óptimas para lograr la mayor remoción de color del agua residual textil fueron pH=2, dosis de 20 g/L y un tiempo de agitación de 30 minutos. Según estas condiciones, se eliminó el 96.35 % del color del agua residual.

Palabras clave: Semilla de aguacate, adsorción, agua residual textil, contaminación, remoción.

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1 Introduction

The demand for water continues to increase in recent years due to the need of the growing population (Baggio *et al*., 2021). The available water is collected and supplied according to the needs of industries, municipalities, agriculture, etc. (Belay *et al*., 2019; Maurya and Singh, 2021). After the use of the water, in most cases it is returned to the river, lake or soil without prior treatment due to the difficulty of implementing pollutant removal technologies (Marshall, 2013). The textile industry uses large quantities of water in its textile manufacturing processes (Senthil Kumar and Grace Pavithra, 2019). This industrial activity uses various chemical substances, including dyes, which generates a large amount of wastewater that represents a latent threat to the environment (Samanta *et al*., 2019). The colorants present in water affect its aesthetic quality, in addition to harming aquatic ecosystems as they interfere negatively in the photosynthesis of aquatic organisms, and can also bioaccumulate in water resources and enter the food chain (Lellis *et al*., 2019). Many of the dyes used in the textile industry have also been shown to be toxic, mutagenic, carcinogenic (Hashemi and Kaykhaii, 2022) and allergic (Jadhav and Jadhav, 2021). For this reason, removing dyes from textile wastewater before discharge to water bodies is of crucial importance.

Among the alternatives for the elimination of these dyes from water are advanced oxidation processes (Jain *et al*., 2022) whose degradation mechanism is based on the formation of hydroxyl radicals, however, the activity of these radicals is limited in complex environmental matrices (Brienza and Katsoyiannis, 2017) such as wastewater. Another alternative is the degradation of dyes using bacteria based on enzymatic activity by means of oxidases and azoreductases (Jamee and Siddique, 2019) and have proven to be effective at laboratory scale and their application to real conditions is still limited (Moyo *et al*., 2022). Another alternative is the adsorption process, which is characterized by being a cost-effective, simple, sustainable and environmentally friendly technique (Rashid *et al*., 2021). Although adsorption methods have been extensively studied, further studies are needed to understand the specific principles and mechanisms of adsorption in order to define the suitability of the use of an adsorbent for a given pollutant or wastewater (Adeleke *et al*., 2019). For this reason, the use of wastes to be used or converted into adsorbents is an alternative that is constantly being studied (Hossain *et al*., 2020).

One of the wastes generated in significant quantities by industries dedicated to avocado processing is avocado seeds, since it is estimated that 4 000 000 metric tons of avocado are produced per year, of which 13 to 18% corresponds to the seeds, which are disposed of by incineration or disposed of in the environment, generating pollution (Tesfaye *et al*., 2022). Avocado seed powder has been shown to be effective in removing some dyes at laboratory scale, such as crystal violet (Bazzo *et al*., 2016), Acid Yellow 17, Amaranth (Munagapati *et al*., 2021), Alizarin Red S (Bharath Balji and Senthil Kumar, 2022) and methylene blue (Dhaouadi *et al*., 2020). However, studies on the application of avocado seed in real textile wastewater have not been reported.

In the present research, adsorption was applied as a treatment of real textile wastewater obtained from a textile company. Avocado seed was used as a natural adsorbent. The effect of particle size was evaluated and the relevant factors in the adsorption processes were optimized. In addition, activated carbon was used as a complementary treatment to eliminate the natural impurities contributed by the avocado seed at the end of the treatment.

2 Materials and methods

2.1 *Obtaining and processing of the bio-adsorbent*

The avocado seeds Hass variety were collected from El Cural located in the district of Uchumayo, province and department of Arequipa, Perú. (-16.4354283,-71.6378974). Approximately 3 kg of seeds were collected, washed several times with distilled water and dried at 60 °C for 48 hours (Dhaouadi *et al*., 2020; Hernández-Teyssier *et al*., 2023). Subsequently, the seeds were pulverized in a grinder machine.

2.2 *Textile wastewater: obtaining and analysis*

The textile wastewater was provided by a textile company in Arequipa, Peru that processes alpaca wool. The wastewater was stored under refrigeration (4-8 °C) until further use. The absorbance analysis of the textile wastewater was determined using the Thermo Scientific Genesys 150 spectrophotometer. A wavelength of 526 nm was used for the experiments since this corresponds to the wavelength of maximum absorbance registered by the equipment when performing a spectrophotometric scan. Likewise, salinity, total dissolved solids and conductivity parameters were measured with the HANNA HI9829 multiparameter. Turbidity was measured with the HANNA HI93703 turbidimeter. The pH was also measured with the HANNA HI-2002 pH-meter.

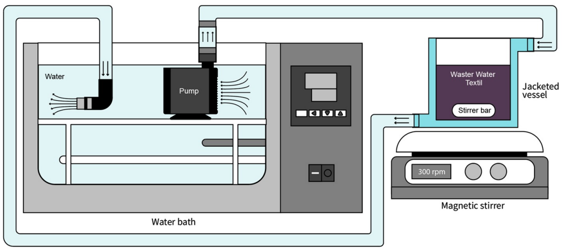

Fig. 1. Stirring system for temperature-controlled adsorption studies.

2.3 Agitation system for adsorption studies

The design of the agitation system used for adsorption studies is shown in Figure 1. This system featured a jacketed glass vessel to keep the temperature of the wastewater constant. A Tecnal thermostatic bath was used to transport the water at 10, 20 and 30 °C using a pump to the jacketed vessel. The wastewater was agitated using a magnetic stirrer and a magnetic bar. The stirring speed was 300 rpm in all experiments. The volume of wastewater used in each experiment was 100 mL.

2.4 Evaluation of particle size effect in adsorption process

The avocado seed pulverized was sieved using sieves with a mesh diameter of 75 μm, 150 μm and 300 μm. The particle sizes of the avocado seed powder obtained were <75 μm and sizes that were retained on the 75 μm and 150 μm sieves. The effect of particle size on color removal from textile wastewater was evaluated by agitating the wastewater with 20 g/L of avocado seed powder of each particle size. The pH was adjusted to 3 with 0.1 M HCl to favor the adsorption process and the stirring time was 60 minutes. At the end of this time, the suspension was centrifuged at 6000 rpm for 10 minutes. The procedure is performed in triplicate. The absorbance of the supernatant was analyzed by spectrophotometry at 526 nm.

The percentage removal rate (%R) was calculated (Dávila-Parra *et al.*, 2022) using the following equation:

$$\%R = \frac{A_0 - A_f}{A_0} \times 100 \tag{1}$$

Where A_0 and A_f correspond to the initial absorbance values of the textile wastewater and at the end of the adsorption process.

The results of the particle size effect on color removal were compared using a one-way analysis of variance (ANOVA). A value of $p<0.05$ was considered a significant difference. Once the difference was demonstrated, a Fisher's LSD *post hoc* test was applied. This statistical analysis was performed in GraphPad Prism 8 software.

Table 1. Values of the factors and levels considered in the adsorption study by the Central Composite design.

Factors	Levels				
	-2	-1	0	+1	+2
A: Dosage (g/L)	10	15	20	25	3
B: pH	2	3	4	5	6
C: Time (min)	10	20	30	40	50

2.5 Evaluation of the effect of stirring time

This test was carried out to define how time affected the color removal process of the textile wastewater using avocado seed powder. This parameter was considered because it provides information on the necessary contact time between the adsorbent and the adsorbate required for a subsequent kinetic study (Agbovi and Wilson, 2021). The particle size with the highest adsorption capacity was used. The methodology followed the same process as the particle size effect test. To evaluate the effect of time, 5 mL samples were analyzed at 5, 10, 15, 30, 60, 90 and 120 min.

2.6 Optimization of adsorption process

Having defined the particle size and the effect of agitation time most suitable for the adsorption process of the wastewater, we proceeded to define the optimum factors to achieve the greatest removal of color from the wastewater by evaluating the adsorbent dosage, pH and contact time. The experiments were carried out in the same agitation system described previously. For the optimization study of the adsorption process, we worked with the Response Surface Methodology (RSM) using a Central Composite Design. For this purpose, three factors of importance in adsorption studies were evaluated. The factors were adsorbent dosage expressed in g/L, pH and contact time in minutes (Iftekhar *et al.*, 2018). Five levels were selected (-2, -1, 0, +1 y +2), the values of which are shown in Table 1.

Design Expert software was used for the design of experiments and the RSM study. Analysis of variance (ANOVA) was used to analyze the significance of the individual terms and their interactions. Also, the value of the coefficient of determination (R-squared) was used to analyze the quality of the model (Ponnuchamy *et al.*, 2020). The optimization of the process was carried out with the "optimization tool" of the software where the objective was to achieve the maximum removal of color from the textile wastewater.

2.7 Kinetic and thermodynamic study

The kinetic and thermodynamic study was carried out taking into account the optimal values of each factor evaluated in the optimization process. The textile wastewater was agitated in the agitation system at temperatures of 10, 20 and 30 °C. Samples were taken at zero time at minute one and every 5 minutes until the appropriate removal time was obtained according to the optimized adsorption process evaluated in the previous experiment. These samples centrifuged were analyzed by spectrophotometry at 526 nm. The procedure is performed in triplicate.

For the kinetic study we used the pseudo first order model presented in equation 2 which was used in another study of dye removal using the absorbances (Giwa *et al.*, 2020).

$$\ln\left(\frac{A}{A_0}\right) = -kdt \tag{2}$$

Where; A and A_0 correspond to the absorbances at 526 nm at any time t in minutes and at zero time of the textile wastewater respectively, k_d corresponds to the removal constant of the dye from the textile wastewater in min^{-1}. To calculate k_d, t vs $\ln(A/A_0)$ was plotted.

We also evaluated the pseudo-second order model proposed by (Ho and Mckay, 1998) that used in another study using absorbances (Giwa *et al.*, 2020). The model is shown in equation 3.

$$\frac{t}{A_t} = \frac{1}{k_2 A_e^2} + \frac{t}{A_e} \tag{3}$$

where k_2 corresponds to the rate constant of removal at equilibrium in min^{-1}. A_t is the absorbance of the dye at any time and A_e is the absorbance of the dye removed at equilibrium. For the evaluation of this model, t vs t/A_t was plotted.

The thermodynamic adsorption behavior of the textile wastewater dye on avocado seed powder was evaluated by calculating thermodynamic parameters including enthalpy (ΔH^0), entropy (ΔS^0) and Gibbs free energy (ΔG^0). These parameters were calculated using the Van't Hoff equation using the equations 4 and 5 (Yang *et al.*, 2020):

$$\ln k = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R} \times \frac{1}{T} \tag{4}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{5}$$

Where T corresponds to the temperature in Kelvin and R is the ideal gas constant (8.314 J/mol.K).

2.8 Characterization of avocado seed powder

The characterization of the avocado seed powder consisted in the determination of the zero charge point (pH_{zpc}), which was performed according to (Postai *et al.*, 2016). The process consisted of adding 50 mg of avocado seed powder to 20 mL solutions of 0.1 M NaCl at pH values previously adjusted from 3 to 11 using 1 M HCl and 1 M NaOH. Subsequently, it was shaken at 150 rpm for 24 hours. The solutions were then filtered and the final pH was measured. For the calculation of the pH_{zpc} a graph was prepared relating the initial pH (pH_i) vs ΔpH. The value of ΔpH was calculated by subtracting the initial pH and the final pH (pH_i-pH_f). The value of pH_{zpc} was considered a value of ΔpH of zero.

Scanning Electron Microscopy (SEM) analysis was performed to evaluate the morphology of the avocado seed powder. ATR-FTIR analysis of avocado seed before and after the color removal process from textile wastewater was performed on the Agilent Cary 630 FTIR spectrometer.

3 Results and discussion

3.1 Particle size selection

Figure 2 shows the results of dye removal from the textile wastewater by the avocado seed powder at particle sizes of <75 μm, and the retained in the meshes of the 75 μm, and 150 μm. The analysis of variance (ANOVA) indicates that there is a significant difference ($p<0.05$) among the percentages of dye removal from the textile wastewater obtained for each particle size used. The LSD post hoc test indicates that all groups differ significantly, indicating that greater removal is achieved with the particle size retained on the 75 μm mesh. For this reason, this particle size was used in subsequent experiments. It was found that at particle sizes retained in the 150 μm mesh the adsorption of color from textile wastewater decreases because the adsorption rate is inversely proportional to the particle size making fewer adsorption sites available when the particle size is higher (Pimol *et al.*, 2008). However, it is observed that avocado seed powder smaller than 75 μm presents a lower removal percentage, this could be due to the fact that excessive pulverization of the avocado seed could be altering its physical characteristics.

3.2 Evaluation of stirring time

The results of the stirring time study are shown in Figure 3. This figure shows that the initial color is efficiently removed during the 120 minutes of the experiment. Also, it is observed that the percentage of removal becomes constant from 30 minutes, since at 60, 90 and 120 minutes there is no significant increase in the percentage of removal. (Bharath Balji and Senthil Kumar, 2022) also found that the dye Alizarin Red S adsorbs quickly on modified avocado seed, becoming constant after 30 minutes.

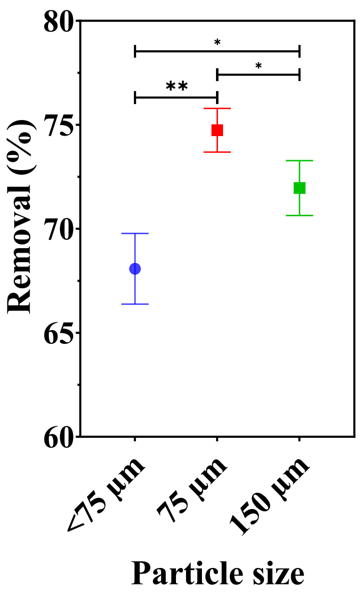

Fig. 2. Dye removal percentages from textile wastewater by different particle sizes of avocado seed powder. The statistically significant difference is expressed as *p<0.05 and **p<0.01.

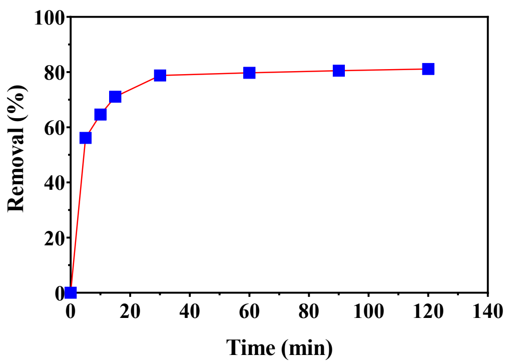

Fig. 3. Effect of time on the percentage of dye removal from a textile wastewater using avocado seed powder retained on the 75 μm mesh.

3.3 *Optimization of adsorption process*

The percentages of dye removal from the textile wastewater by the avocado seed powder using the Central Composite Design taking into account the different factors and levels are presented in Table 2. The coded values and real values studied in each experiment are shown. This table shows that at a dosage of 20 g/L, pH=2 and during 30 minutes of agitation, 91.94 % of the effluent color is removed.

Table 3 shows the R-squared value of 0.9893, which indicates that the Central Composite design model presents an adequate fit to the percentage removal values.

The ANOVA of the results of the Central Composite design experiments are presented in Table 4. It is observed that the p-value of the model is significant (p<0.0001), which demonstrates the good fit of the model to the data evaluated. Likewise, no significant lack of fit was found (p>0.05), which guarantees the results of the design used. Also, it is shown that the factors of adsorbent dosage, pH and contact time also prove to have a significant effect on the dye removal process from the textile wastewater.

Composite Central Design results in surface plots with the second order polynomial model (Leonzio and Zondervan, 2019). The mathematical model obtained as a result of the analysis of the data according to the Composite Center design is presented below (equation 6):

$$\%R = 43-15+8.02A-16.29B+2.70C+0.59AB$$
$$+1.24AC+1.19BC+1.77A^2+4.50B^2-0.023C^2 \tag{6}$$

Where the dose of avocado seed powder in g/L is "A", the pH is "B" and "C" corresponds to the contact time in minutes. With this mathematical model, the theoretical "predicted" textile wastewater dye removal percentages were calculated and correlated with the "actual" experimental results, obtaining a linear dispersion between these two responses (Figure 4).

Table 2. Results of the percentages of dye removal from the textile wastewater for each experiment of the Central Composite design using avocado seed powder as bio-adsorbent.

Run	Coded values			Real values			Removal (%)
	A	B	C	A: Dosage (g/L)	B: pH	C: Time (min)	
1	0	0	0	20	4	30	43.7
2	1	-1	-1	25	3	20	72.63
3	0	-2	0	20	2	30	91.94
4	1	1	1	25	5	40	49.14
5	2	0	0	30	4	30	64.23
6	0	0	0	20	4	30	41.37
7	-1	-1	1	15	3	40	60.56
8	-1	-1	-1	15	3	20	58.79

9	0	0	0	20	4	30	43.7
10	1	1	-1	25	5	20	37.64
11	0	0	0	20	4	30	40.12
12	-1	1	1	15	5	40	27.99
13	0	0	0	20	4	30	46.19
14	1	-1	1	25	3	40	77.45
15	0	0	2	20	4	50	46.63
16	0	0	-2	20	4	10	36.39
17	-2	0	0	10	4	30	33.13
18	0	2	0	20	6	30	27.26
19	-1	1	-1	15	5	20	23.35
20	0	0	0	20	4	30	40.75

Table 3. Parameters corresponding to the Central Composite Design.

Regression parameter	Magnitude	Regression parameter	Magnitude
Std. Dev.	4.82	R^2	0.9538
Mean	49.01	Adjusted R^2	0.9365
C.V. %	9.84	Predicted R^2	0.9032
		Adeq Precision	26.6016

Table 4. Results of the percentages of dye removal from the textile wastewater for each experiment of the Cenral Composite design using avocado seed powder as bio-adsorbent.

Source	Sum of squares	df	Mean Square	F-value	p-value	
Model	5979.9	9	664.43	102.44	< 0.0001	significant
A-Dosage	1029.98	1	1029.98	158.8	< 0.0001	significant
B-pH	4246.25	1	4246.25	654.66	< 0.0001	significant
C-Time	116.83	1	116.83	18.01	0.0017	significant
AB	2.77	1	2.77	0.4274	0.528	insignificant
AC	12.28	1	12.28	1.89	0.1989	insignificant
BC	11.41	1	11.41	1.76	0.2142	insignificant
A^2	78.57	1	78.57	12.11	0.0059	significant
B^2	508.67	1	508.67	78.42	< 0.0001	significant
C^2	0.0139	1	0.0139	0.0021	0.964	insignificant
Residual	64.86	10	6.49			
Lack of Fit	38.48	5	7.7	1.46	0.3445	insignificant
Pure Error	26.38	5	5.28			
Cor Total	6044.77	19				

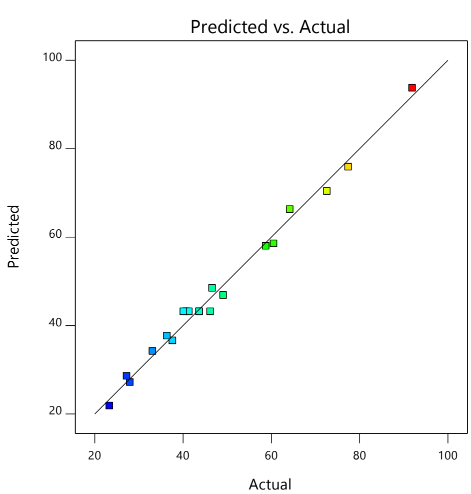

Fig. 4. Graph of the relationship between predicted values and actual values.

Figure 5 shows the response surface plots obtained from the adsorption study using the Central Composite design. It can be seen in Figure 5a that pH plays an important role in the process of dye removal from the textile wastewater because as the pH decreases the percentage of removal increases, achieving the highest response at pH=2. The dosages studied also show a significant effect, achieving higher removal percentages with higher doses of avocado seed powder used. The pH is one of the most influential factors in adsorption processes as it defines whether an adsorption process could correspond to a mechanism based on electrostatic attraction (Xiao *et al.*, 2021).

On the other hand, Figure 5b show that both time and adsorbent dose would have a significant effect on the percentage of dye removal from the textile wastewater, achieving the highest response at the highest dose of avocado seed powder and the longest time for the removal of the dye from the textile wastewater. However, it is noted that the effect of these two factors is lower when compared to pH. This is corroborated in Figure 5c where it is noted that pH offers a more marked effect compared to contact time and bio-adsorbent dosage.

For the optimization of the actual textile wastewater dye removal process, a pH value of 2 was considered, as it was the factor that most modified the percentage of removal. As for the adsorbent dosage and contact time, the default value suggested by the software was used (Figure 6). As for the response variable of the percentage of removal, the objective was to achieve the maximum percentage of dye removal from the textile wastewater. As a result, the ramps in Figure 6 showed that a dose of 20 g/L, a pH=2 and a contact time of 30 minutes are sufficient to achieve the maximum removal of 93.73 % of the dye with a desirability of 1. These values were used for the following studies.

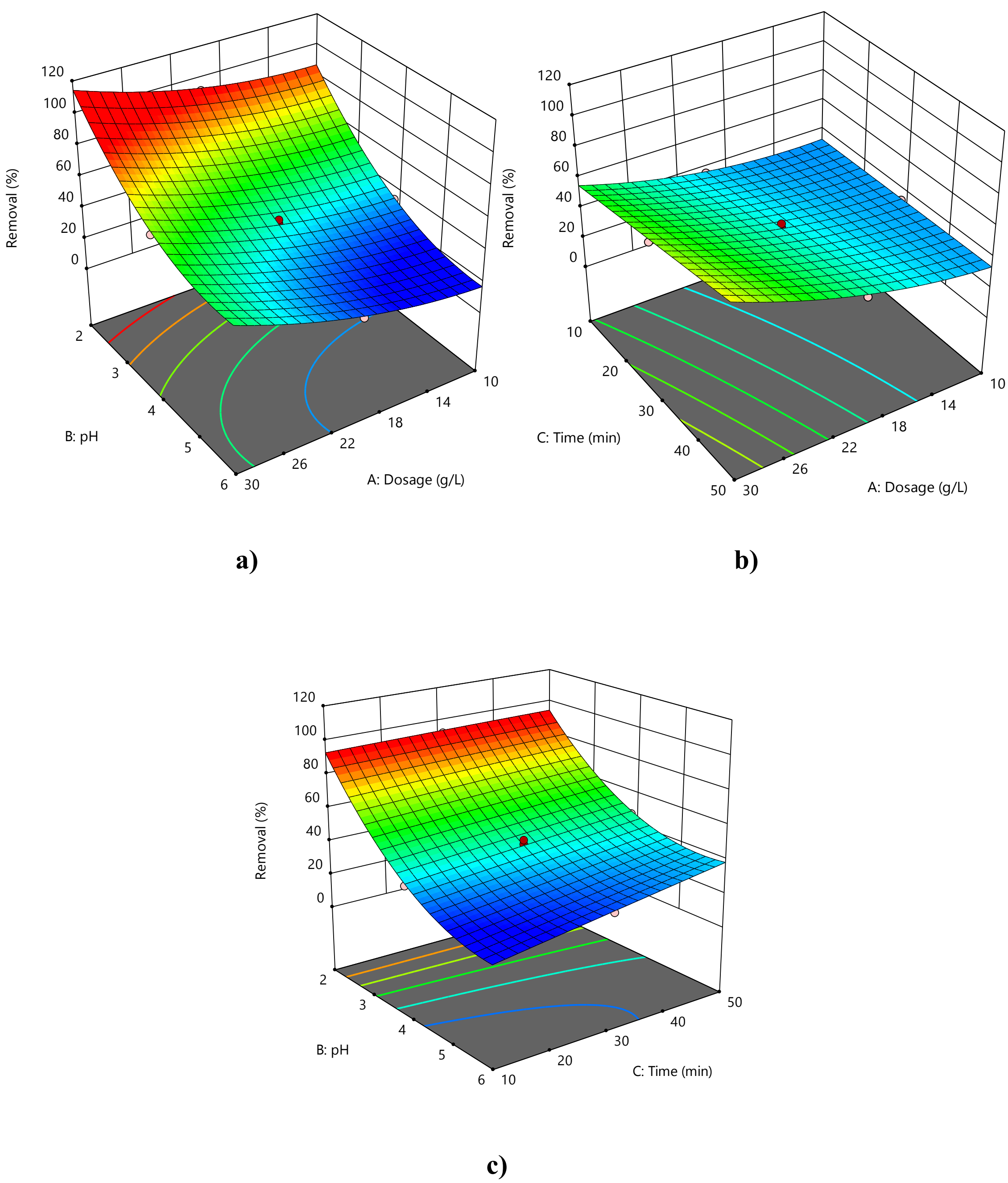

Fig. 5. Response surface plots corresponding to the study of the interaction between the factors evaluated in the Central Composite design.

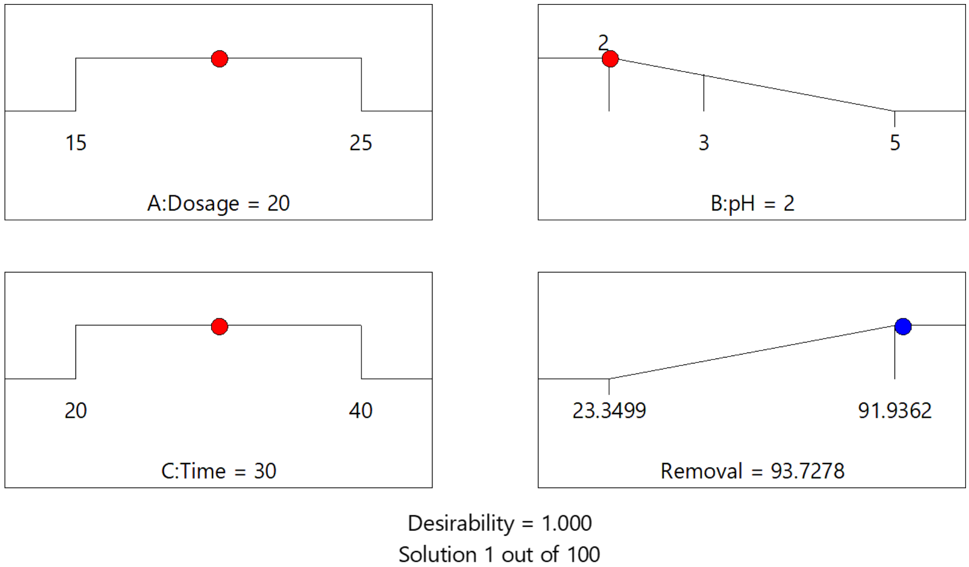

Fig. 6. Optimization ramps of the dye removal process from the textile wastewater taking into account pH, time and avocado seed powder dosage factors.

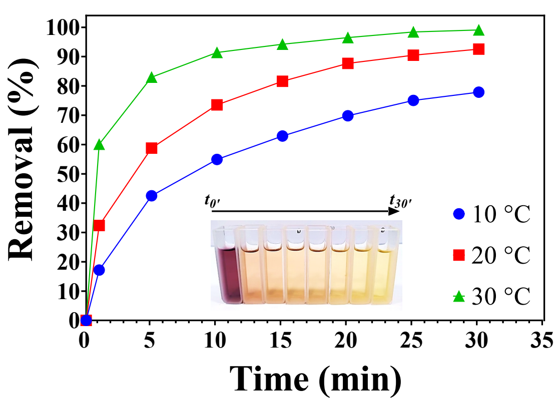

Fig. 7. Effect of temperature on dye removal from textile wastewater during 30 minutes of treatment with avocado seed powder.

3.4 Kinetics

The kinetic study was carried out at different temperatures (10, 20 and 30 °C) taking into account the optimum values of pH, dose and contact time obtained in the previous experiment. Removal percentages were calculated at times 0, 1, 5, 10, 15, 20, 25 and 30 minutes. The results are shown in Figure 7, where it is observed that the percentage of removal at ten minutes of the experiment exceeds 90 % when 30 °C is used and is lower than this when 20 and 10 °C are used. Also, it can be deduced that the higher the temperature, the higher the removal capacity of the dye by the avocado seed. This figure shows the textile wastewater before and after the bio-adsorption process with avocado seed, thus demonstrating that this waste has a high capacity to remediate the color of textile wastewater. Regarding the effect of temperature it is known that adsorption can be endothermic or exothermic and according to what was found in this study the process could be endothermic since the increase in temperature, then the increased temperature would cause an increase in the solubility of the adsorption medium, this makes the dye (adsorbate) can easily reach the surface of the adsorbent regardless of its hydrophilic or hydrophobic character (Zango *et al.*, 2021).

Figure 8 shows the results of the kinetic study. Figure 8a shows the fit of the data to the pseudo first-order model, finding a better fit of this model compared to the pseudo second-order model (Figure 8b) when comparing the R^2 coefficient of each trial. Then it can be said that the pseudo first order model best fits the process of dye removal from the textile wastewater by the avocado seed powder. The results found are consistent with the research carried out by (Bharath Balji and Senthil Kumar, 2022) where they removed Alizarin Red S using avocado seed modified with sulfuric acid and found that the pseudo-first order model best fit the adsorption process being adsorption on the pores of the adsorbent.

Table 5 shows the values of the color removal rate constant k_d of the textile wastewater, which increases with temperature. This would indicate that the higher the temperature, the faster the removal process.

3.5 Thermodynamics

Table 6 shows the values of the thermodynamic parameters. The positive value of ΔG^0 indicates the process is not spontaneous. A similar study carried out by (Munagapati *et al.*, 2021) where they evaluated the ability of avocado seed to remove acid yellow 17 and amaranth dyes, they found that the process is not spontaneous.

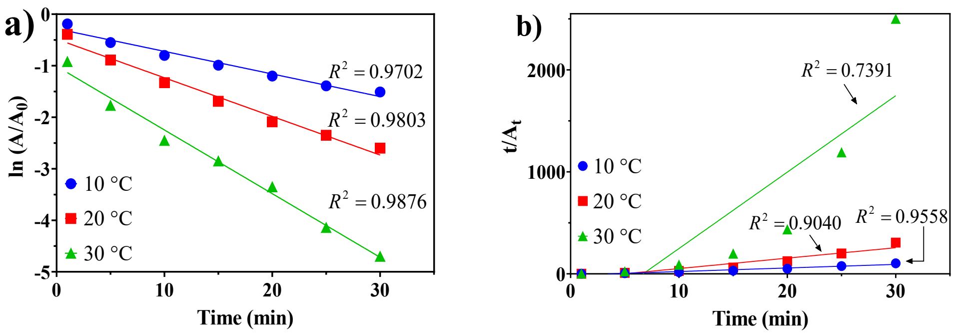

Fig. 8. Plots of kinetic models of (a) pseudo first-order (b) pseudo-second-order for the removal of dye from textile wastewater using avocado seed powder.

Table 5. Adsorption parameters of the textile wastewater dye described by the pseudo first order model.

Temperature (K)	k (min^{-1})	R^2
283	0.0438	0.9702
293	0.0750	0.9803
303	0.1235	0.9876

Table 6. Thermodynamic parameters for color adsorption of textile wastewater with avocado seed powder.

Temperature (K)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol)	ΔG^0 (kJ/mol)
283	36.95	104.58	7.36
293			6.31
303			5.27

As in the present investigation, the value of ΔG^0 decreases with temperature, therefore, an external agent is required for the process to take place (Guerrero-Coronilla *et al.*, 2015). The value of ΔS^0 resulted in a positive value. A positive entropy value indicates an increase in the randomness at the solid-liquid interface, which results in an increase in the randomness of the interaction between adsorbate and adsorbent (Bazzo *et al.*, 2016). In relation to the ΔH^0 it resulted in a positive value which indicates the endothermic nature of the color removal process of the textile wastewater. Values of ΔH^0 between 80-200 kJ/mol indicate a chemisorption and between 2.1-20.9 kJ/mol indicate a physisorption process (Cho *et al.*, 2015). With the results obtained, it could be said that the process could correspond to physisorption.

3.6 Wastewater analysis before and after treatment with avocado seed powder

Figure 9a shows the spectrophotometric scan of the textile wastewater, with maximum absorbance peaks at 526 nm and 623 nm. After the treatment of this wastewater with avocado seed powder at optimum conditions at 20 °C, it is observed that the color is efficiently removed (Figure 9b), however, it is observed that the natural color of the avocado seed leaves the water with an opaque yellow color (Figure 9b). The yellow color of the avocado seed could correspond to the perseorangin which is a yellow to orange color present in the seeds of avocado seed (Hatzakis *et al.*, 2019).

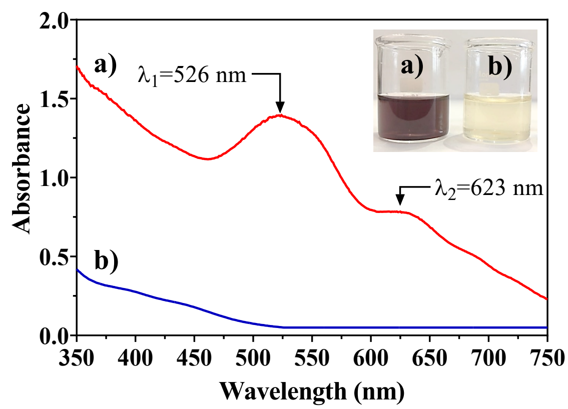

Fig. 9. Absorption spectra of the textile wastewater a) before and b) after treatment with avocado seed powder.

Table 7 shows the results corresponding to the analysis of the textile wastewater before treatment, where it is observed that the maximum absorbance at 526 nm is 1.315, which was removed to 0.048 after treatment with avocado seed powder (96.35 % of color removal), achieving an almost total elimination of the color of this textile wastewater. In a similar study carried out by (Bazzo *et al.*, 2016) , they simulated two dyehouse wastewater with a composition of crystal violet, reactive red, reactive orange, cibracron brillant yellow, remazol brilliant blue, Vilmafix red RR-2B,

Table 7. Comparison of the composition of textile wastewater textile treated with avocado seed powder.

Analysis	Wastewater textile before treatment	Wastewater textile after treatment
Absorbance (λ_{526} nm)	1.315	0.048 (20 °C)
Salinity (PSU)	3.23	2.78
Total dissolved solids (ppm)	2373	2215
Turbidity (NTU)	17.2	3.5
Conductivity (μS/cm)	4697	4824

Na_2SO_4, NaCl, Na_2CO_3, sodium acetate and sodium dodecyl sulfate (SDS) achieving 84.4 to 92.9 % removal using a dose of 4 g/L at 55 °C in 90 minutes of treatment. The present research complements the study of Bazo *et al.* as the effectiveness of avocado seed powder for color removal from real textile wastewater has been demonstrated.

With respect to other parameters such as salinity, total dissolved solids and turbidity, there was a slight decrease in their values when treated with avocado seed powder. It is also observed that the conductivity increases after treatment with avocado seed from 4697 to 4824 μS/cm.

The avocado seed powder eliminates 96.35 % of the color according to Table 7, and the turbidity is eliminated by 79.65 % (from 17.2 to 3.5 NTU). Our results demonstrate that the process used is effective and compares to the results of other studies where different forms of treatment are proposed, such as the research of Badawi y Zaher (Badawi and Zaher, 2021) who used a hybrid treatment using different processes such as coagulation with $FeCl_3$, adsorption with zero-valent nano-iron, filtration with micro zeolite were able to remove the tubidity, eliminating the color and a turbidity of 87 NTU, subsequently, the treatment was complemented by the photo-Fenton process, achieving a decrease in turbidity from 57 to 25 NTU, however, the color was not completely eliminated. Bezerra de Araujo *et al.*, 2019 used graphene oxide to treat a sample of real textile wastewater achieving 85 % removal of tubidity (from 105 to 16.1 NTU) and 60 % of color. In contrast to these reported processes, the present research would show a certain advantage since it is easy to handle and apply.

3.7 Characterization of avocado seed powder

Figure 10 shows that the value of the zero charge point (pH_{zpc}) of avocado seed powder is 5.5. This indicates that at pH 5.5 the charge of the avocado seed powder is zero, above this pH it would be negatively charged and below this pH it would be positively charged due to the concentration of hydrogen protons in the medium. Considering that the adsorption process was favored at pH lower than 5.5, which would indicate that one of the mechanisms of adsorption of the dye from the textile wastewater would be electrostatic attraction.

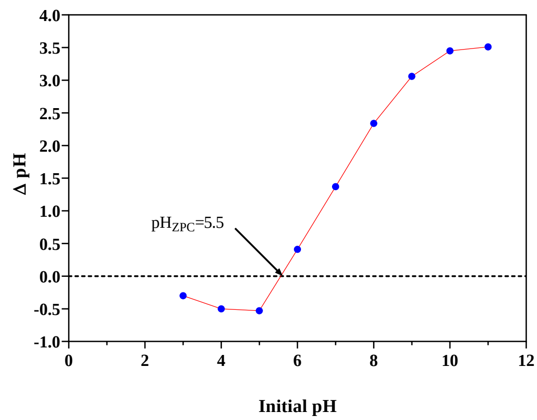

Fig. 10. Zero charge point of avocado seed powder.

The results found are consistent with the study carried out by Munagapati *et al.* (2021) where they used avocado seed as adsorbent of two anionic dyes and found a pH_{zpc} value of 5.8 where it was also concluded that the highest removal of anionic dyes is achieved at pH 2.

Figure 11 shows the SEM analysis of the avocado seed powder used in the adsorption study. Figure 11a shows the image of the avocado seed powder where a material that does not include pores is observed. This is confirmed in Figure 11b where the absence of pores is observed.

Figure 12a shows the appearance of the avocado seed before and after the process of adsorption of the dye from the textile wastewater, showing the change in color of the avocado seed powder, which takes on a darker appearance that corresponds to the color of the textile wastewater. This is corroborated by looking at Figure 9, which shows the effectiveness of the avocado seed powder in removing apparently all the color from the textile wastewater. Figure 12b shows the ATR-FTIR analysis of avocado seed powder before and after the process of removal of the dye from the textile wastewater. The spectrum before the adsorption process is mainly characterized by peaks at 1000 cm^{-1} corresponding to aromatic =C-H deformation vibrations in benzene rings. At 1616 cm^{-1} there is another peak that could correspond to the C=C stretching vibration. Between 2860 and 2921 cm^{-1} there is a peak corresponding to C-H stretching. At 3267 cm^{-1} there is a peak characteristic of the O-H stretching vibration.

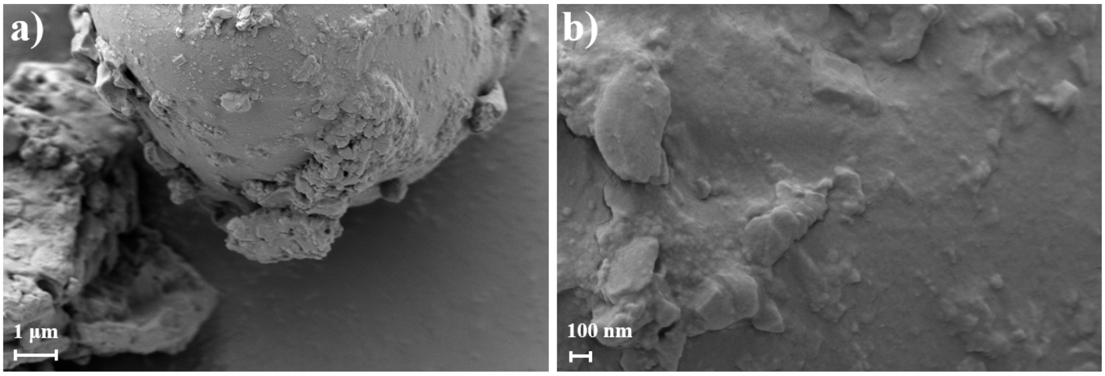

Fig. 11. Scanning Electron Microscopy (SEM) image of avocado seed powder.

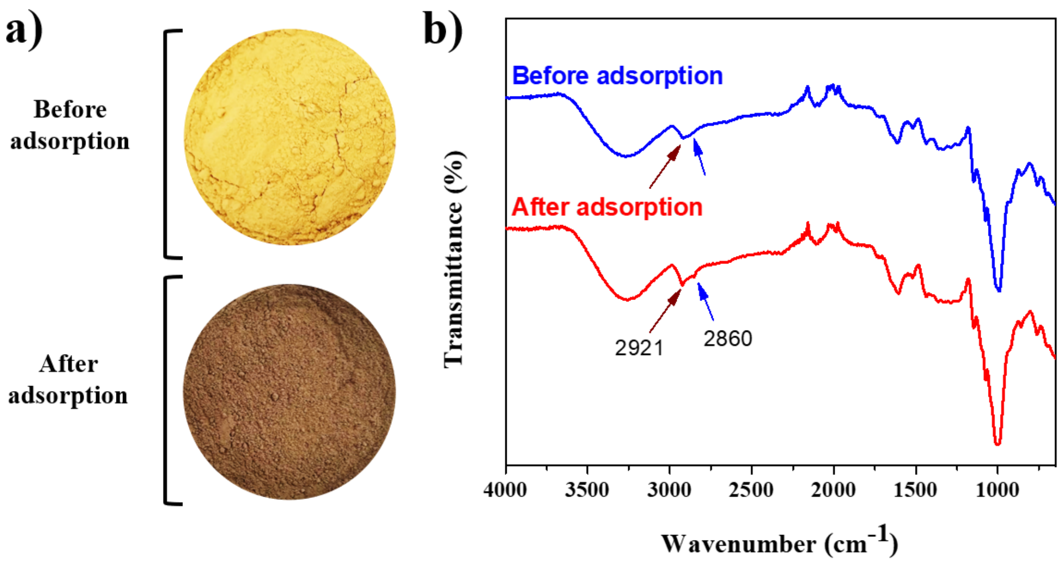

Fig. 12. a) Avocado seed powder before and after adsorption and b) ATR-FTIR spectra of avocado seed powder before and after adsorption.

The spectrum would be characteristic of the lignin present in this type of natural adsorbents. After adsorption, it is observed that there is no significant alteration in the spectrum in most of the peaks, however, an increase in the vibration at 2860 and 2921 cm^{-1} is evidenced, on the other hand, the vibration peak of the O-H groups decreases in intensity. This is due to the fact that the dye in the textile wastewater slightly alters the spectrum of the avocado seed with its structural characteristics, which corroborates the adsorption of the dye on this bio-adsorbent. The same peak modifications were found by (Munagapati *et al.*, 2021) at 2850 cm^{-1} after adsorption of anionic dyes on avocado seed.

Conclusions

A process for color adsorption of textile wastewater using avocado seed powder was proposed. It was shown that a particle size retained on the 75 μm mesh of the pulverized material achieves the highest removal compared to sizes smaller and larger than this. At optimum conditions, 96.35 % of the dye was removed from the textile wastewater in 30 minutes at 20 °C with an adsorbent dosage of 20 g/L and a pH adjusted to 2, the latter being the most important parameter in the process. Avocado seed has proven to be a waste with the capacity to remediate real textile wastewater. The adsorption kinetics follows a pseudo first order model. The thermodynamic study indicates that the adsorption process is not spontaneous and requires an external agent to occur. The characterization of the material shows that one of the probable mechanisms of adsorption would be electrostatic attraction since the removal of the color from the textile wastewater occurred at a pH lower than the zero charge point (pH_{zpc}=5.5). ATR-FTIR analysis shows increased vibrational intensity at 2860 and 2921 cm^{-1} in the spectra after adsorption. Finally, as a complementary treatment with activated carbon, it is possible to eliminate almost all the turbidity of the textile wastewater used, as well as the natural color of the avocado kernel that remains after adsorption.

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