








Kinetic study of removal of the dispersed blue 124 dye from water using avocado seed Fuerte variety as adsorbent

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Abstract— Adsorption processes with biomaterials are an environmentally friendly technology that allows the removal of pollutants; on the other hand, it is known that different factors can alter the removal of pollutants. For this reason, the kinetics of removal of Disperse Blue 124 (DB-124) dye from water using Fuerte variety avocado seed waste as adsorbent was evaluated in the present research. The studies were carried out in batch adsorption systems. For this purpose, the effect of pH, adsorbent dosage, initial dye concentration and temperature on the removal kinetics were jointly evaluated. It was found that the best conditions of the adsorption process were at an initial DB-124 concentration of 200 mg/L, a dosage of 2 g/L, pH=2 and a temperature of 40 °C, achieving the removal of 87.64 % of the dye. The kinetic study was fit in all cases to a pseudo-second order model, which indicates that the adsorption process corresponds to a chemisorption. It was also found that the removal of DB-124 is favored at higher temperatures, which corresponds to an endothermic process. The present research may initiate future DB-124 adsorption studies in real environments using textile wastewater.

Keywords— Disperse blue 124, removal, water, avocado seed, kinetics.

I. INTRODUCTION

Today, water pollution is considered a global concern and is increasing rapidly due to industrialization and other human activities [1]. Among the most polluting industrial activities is the textile industry, since the dyes that are not fixed to textiles are eliminated through effluents or wastewater into the soil, but mainly into rivers [2] reaching the environment, which represents a threat to aquatic ecosystems and people's health. Textile dyes have reported several damages to human health, including dermatitis caused by textile dyes such as Disperse Blue 106 and Disperse Blue 124 (DB-124) [3].

DB-124 (Fig. 1) is a monoazo compound consisting of diazene with a 5-nitrothiazol-2-yl group attached to one nitrogen and a substituted 4-aminophenyl group attached to the other; it is used as a standard dye for testing allergy-releasing dyes in textiles [4]. Common uses include polyester blouses,

garment linings, blue underwear and pants, coveralls, socks, uniforms [5].

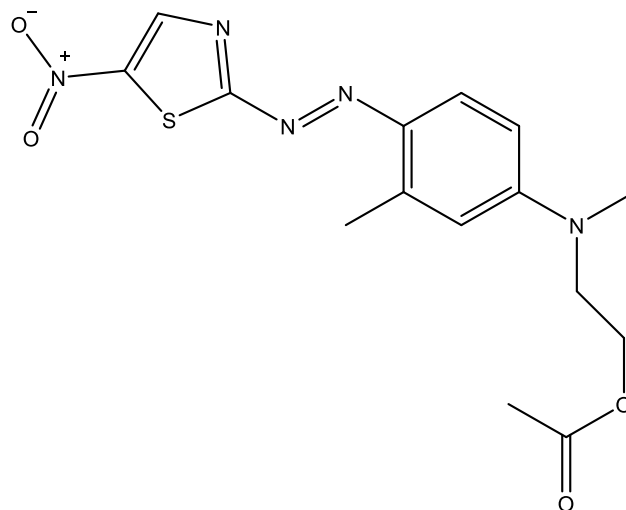


Fig. 1 Disperse Blue 124 molecule.

In the face of water pollution with dyes, there are two approaches to deal with the effluent problem; the first is the application of alternative dyeing techniques and technology and the second is the treatment of effluents after dyeing [2]. Adsorption is a technique used for the removal of pollutants from industries, in this sense, in recent decades research has been done on low-cost adsorbents and high load capacity, such as lignin, which is considered as waste, making it an interesting material in adsorption processes [6].

The avocado is a fruit recognized for its beneficial characteristics for health, which has led to a great development of this industrial sector, increasing the area planted worldwide for the use of oil, pulp and/or pieces, generating large quantities of by-products, such as the seeds and peel that represents 40 % of production [7]. The avocado seed is an abundant and easily accessible waste, since the commercialization of avocado has

increased in the last years, being the seed that represents approximately 15% in weight of the fruit, then the current industrialization results in more than 3 thousand tons of seed annually, which are discarded without any use [8]. Therefore, in the present research we intend to use avocado seed to remove the dye DB-124 from water at laboratory level, for this purpose, kinetic studies were carried out to evaluate the effect of pH, adsorbent dosage, initial concentration of the dye and temperature on the efficiency and speed of adsorption of DB-124.

II. MATERIALS AND METHODS

A. Reagents and equipment

All reagents used such as Disperse Blue 124, hydrochloric acid and sodium hydroxide were obtained from Sigma Aldrich. The assays were performed in distilled water. Spectrophotometric readings were performed on the Thermo Scientific Genesys 150 UV/Vis Spectrophotometer.

B. Adsorbent collection and processing

Fuerte variety avocado seeds were obtained from waste from restaurants in the city of Arequipa, Peru. A total of 1 kg of avocado seed was collected, washed and chopped into small pieces and then dried at 40 °C for 7 days in a drying oven. Then, the avocado seed pieces were pulverized in a blade mill. The pulverized pulp was then sieved through a No. 40 sieve and stored until further use.

C. Method to quantify Disperse Blue 124

The method for DB-124 quantification consisted of preparing a calibration graph using calibration solutions of 1 to 100 mg/L DB-124. Subsequently, the absorbances were read in a spectrophotometer at 470 nm. Finally, the calibration graph was obtained and the coefficient of determination R^2 was evaluated, which should be greater than 0.995 [9]. The linear equation obtained was used to quantify DB-124 in each study sample.

D. Adsorption system

The adsorption system (Fig. 2) consisted of measuring 100 mL of DB-124 solution in jacketed beakers where established dosages of avocado pulverized (adsorbent) were added. This solution was agitated at 300 rpm for 180 minutes with controlled temperature by pumping water from a water bath into the jacketed beakers. The pH was fit with 0.1 M HCl or 0.1 M NaOH.

E. Kinetic study at different pH values

For the kinetic study at different pH values, 100 mL of a 100 mg/L DB-124 solution was measured in three jacketed beakers, which were fit to pH 2, 3, and 4. Each solution was placed in contact with a dosage of 1 g/L of avocado seed at a temperature of 20 °C. Samples of 3 mL were taken at times, 0, 5, 10, 15, 15, 20, 20, 30, 60, 90, 120, 150, and 180 minutes. These samples were centrifuged at 4000 rpm for 10 minutes and the supernatants were analyzed spectrophotometrically to calculate

the percent removal (%R) using the following formula (Equation 1):

$$\%R = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

Where " C_i " is the initial concentration of the dye in mg/L and " C_f " is the final concentration of the dye in mg/L at each time " t " [10].

Likewise, the removal capacity in mg/g (q_t) was calculated with the following formula (Equation 2):

$$q_t = \frac{C_i - C_f}{w} \times V \quad (2)$$

Where " w " is the weight of the adsorbent in g and " V " is the volume of the vessel in L.

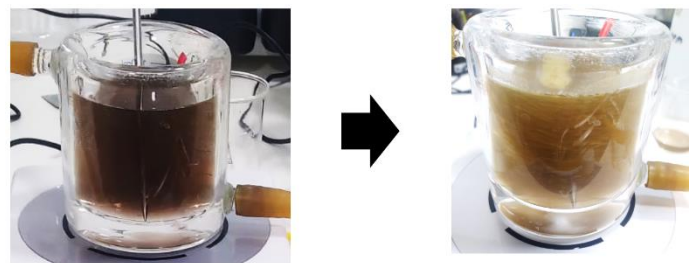


Fig. 2 Adsorption system before (left) and during (Right) the adsorption process.

F. Kinetic study at different adsorbent dosages

For the kinetic study at different adsorbent dosages, 100 mL of a 100 mg/L DB-124 solution was measured in four beakers, which were fit to the pH of the best adsorption result in the previous test. Subsequently, dosages of 0.5, 1, 1.5, and 2 g/L of avocado seed were added and stirring was started at a temperature of 20 °C. Samples of 3 mL were taken with a syringe at times, 0, 5, 10, 15, 15, 20, 20, 30, 60, 60, 90, 120, 150, and 180 minutes. These samples were centrifuged at 4000 rpm for 10 minutes and the supernatants were analyzed spectrophotometrically to calculate percent removal and removal capacity.

G. Kinetic study at different initial concentrations of DB-124

For the kinetic study at different initial concentrations of DB-124, 100 mL solutions of 50, 100, 150, and 200 mg/L of the dye were measured in four jacketed beakers. The pH and dosage in this trial correspond to those of the highest percentage of removal achieved in the previous trials. Stirring was started at a temperature of 20 °C. Samples of 3 mL were taken with a syringe at times, 0, 5, 10, 15, 15, 20, 30, 30, 60, 90, 90, 120, 150, and 180 minutes. These samples were centrifuged at 4000 rpm for 10 minutes and the supernatants were analyzed

spectrophotometrically to calculate percent removal and removal capacity.

H. Kinetic study at different temperatures

For the studies of the effect of temperature on the removal of the dye DB-124, 100 mL of the dye at a concentration of 200 mg/L were measured in jacketed beakers at pH values and dosages of the highest dye removal. Shaking was started at temperatures of 20, 30, and 40 °C.

Samples of 3 mL were taken with a syringe at times, 0, 5, 10, 15, 20, 30, 30, 60, 90, 90, 120, 150, and 180 min. These samples were centrifuged at 4000 rpm for 10 minutes and the supernatants were analyzed spectrophotometrically to calculate percent removal and removal capacity.

I. Kinetic models

The pseudo-first order and pseudo-second order kinetic equations are shown below in Equations 3 and 4 respectively:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (3)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e^2 t} \quad (4)$$

Where; " k_1 " and " k_2 " correspond to the pseudo-first order and pseudo-second order constants, respectively, " q_e " corresponds to the dye removal capacity at equilibrium in mg/g [11], [12].

III. RESULTS AND DISCUSSION

A. Spectrophotometric method to quantify Disperse Blue 124

Fig. 3 shows the calibration curve for the quantification of the DB-124 dye, where the equation of the line and the coefficient of determination can be observed.

The method developed is linear with a determination coefficient R^2 of 0.9994 (Fig. 3), which guarantees the linear correlation between the concentration of DB-124 and the absorbance given by the spectrophotometer at 470 nm. According to the United States Pharmacopoeia (USP) this coefficient must be greater than 0.995 to be considered linear. [13].

Fig. 3 also shows the equation of the line which will be used for quantifications in all the experiments developed, taking into account that " x " is the concentration of DB-124 in mg/L and " y " is the absorbance of the water samples at 470 nm.

B. Adsorption kinetics at different pH

Fig. 4 shows the graph of the effect of pH on the percentage removal of DB-124 from water contaminated by the avocado seed Fuerte variety at an initial concentration of 100 mg/L and a dosage of 1 g/L at 20 °C.

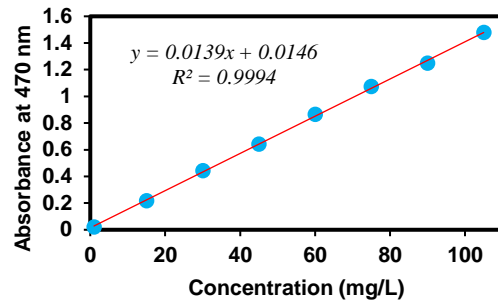


Fig. 3 Calibration curve for the quantification of Disperse Blue 124 dye in water by spectrophotometry at 470 nm.

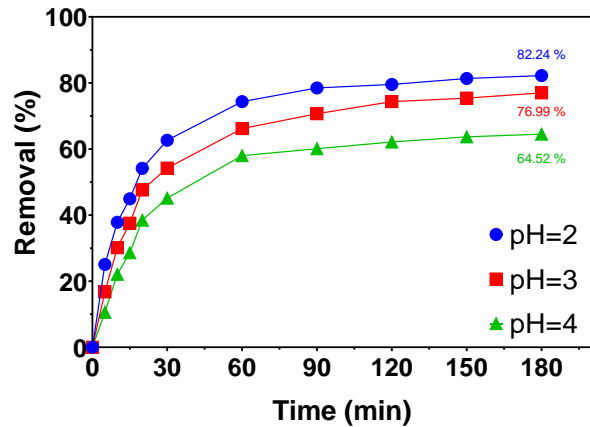


Fig. 4 Effect of pH on the percentage removal of Disperse Blue 124 dye from water.

Fig. 5 shows the kinetic fit of the two models used in the removal of the dye DB-124 where the pseudo-first and pseudo-second order kinetics are evaluated.

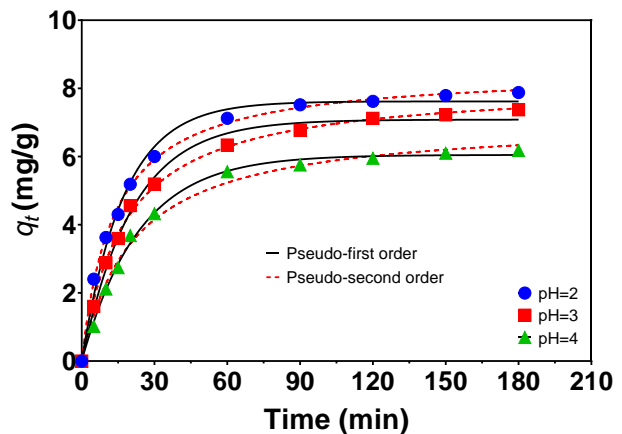


Fig. 5 Kinetic study of the removal of Disperse Blue 124 dye from water at different pH.

Table I shows the results of the kinetic analysis of DB-124 dye removal from contaminated water using Fuerte variety avocado seed at an initial concentration of 100 mg/L and a dosage of 1 g/L at different pH.

TABLE I
RESULTS OF KINETIC ANALYSIS OF THE REMOVAL OF DISPERSE BLUE 124 FROM WATER USING AVOCADO SEED FUERTE VARIETY AT DIFFERENT pH.

Model	Parameters	pH		
		2	3	4
Pseudo-first order	q_e (mg/g)	7.618	7.083	6.049
	K_1 (min^{-1})	0.0583	0.0479	0.0424
	R^2	0.9914	0.9936	0.9972
Pseudo-second order	q_e (mg/g)	8.536	8.145	7.075
	K_2 ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$)	0.0088	0.0069	0.0067
	R^2	0.9985	0.9979	0.9976

The pH does affect the adsorption process of the DB-124 dye on the pulverized avocado seed, since Fig. 4 shows that the final removal percentage after 180 minutes of agitation presents values of 82.24, 76.99 and 64.52 % for pH 2, 3 and 4, respectively. Likewise, this figure shows that as a function of time there is a difference in the percentages of removal at the different pH, since at pH=4 the adsorption process is disadvantaged, achieving better results at pH=2.

Regarding the kinetic study of the tests at different pHs, Fig. 5 and Table I show that the best fit of the experimental adsorption data corresponds to a pseudo-second order kinetic model, since the R^2 coefficients are slightly higher than the R^2 coefficients of the pseudo-first order model. Likewise, it is observed that the rate constant increases as the pH decreases with values of 0.0067, 0.0069, and 0.0088 $\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$ at pH 4, 3, and 2, respectively. Therefore, the fact that the kinetic model has a better fit to the pseudo-second order kinetics would indicate that the adsorption process follows a chemisorption mechanism and that the adsorption rate is higher at pH=2.

Cozmuta *et al.* [14], indicate that the pH of the contact solution is an important parameter controlling the adsorption process. This was demonstrated in the adsorption process of other dyes such as methylene blue (MB) as in the case of the study by Babaei *et al.* where they found different effects of pH variations on the percentage of MB adsorption, resulting in MB adsorption percentages that increased with increasing pH from 2 to 9, becoming constant at the latter pH.

In the present research, different results than Babaei were found, since at lower pH higher removal was achieved, which could be due to the nature of the chemical structure of the dye used. This assumption is confirmed by the study of Castellar-Ortega *et al.* which found that lower pH improved the removal process of the direct blue dye 86 [15]. This could be due to the increased protonation of certain functional groups of the adsorbent at pH=2 as explained by Hidayat *et al.* [16] causing the negatively charged dye DB-124 to adsorb onto the avocado seed.

C. Kinetics at different adsorbent dosages

Fig. 6 shows the graph of the effect of the dosage of avocado seed Fuerte variety (0.5, 1, 1.5, and 2 g/L) on the percentage removal of DB-124 from contaminated water at an initial concentration of 100 mg/L and pH=2 at 20 °C.

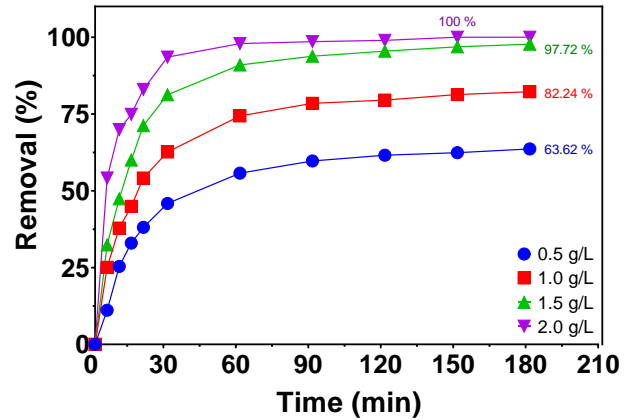


Fig. 6 Effect of adsorbent dosage on the percentage removal of Disperse Blue 124 dye from water.

Fig. 7 shows the graph of the kinetic fit of DB-124 dye removal where the pseudo-first and pseudo-second order kinetic models are evaluated.

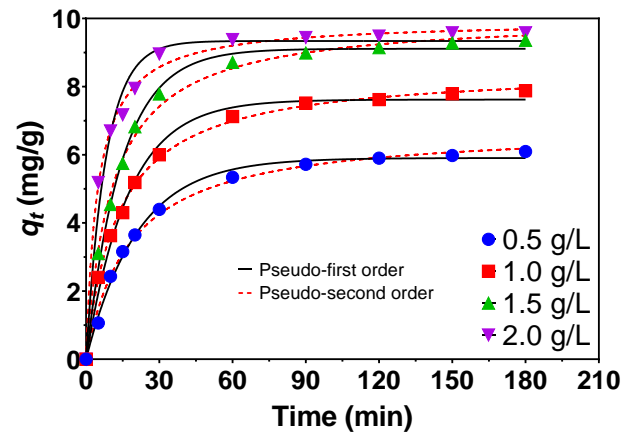


Fig. 7 Kinetic study of the removal of Disperse Blue 124 dye from water at different dosage.

Table II shows the results of the kinetic analysis of the removal of the dye DB-124 from water using avocado seed Fuerte variety at an initial concentration of 100 mg/L and pH=2 at different dosages of adsorbent.

The adsorbent dosage (avocado seed) would also affect the removal capacity of the DB-124 dye, since Fig. 6 shows that the final removal percentage after 180 minutes of agitation presents values of 63.62, 82.24, 97.72, and 100 % for the dosages of 0.5, 1.0, 1.5, and 2.0 g/L, respectively. Likewise, Fig. 6 shows that as a function of time there is a difference in the removal percentages at the different adsorbent dosages, since at all the time intervals a higher dosage would favor the removal

percentage. Regarding the kinetic study of the tests at different dosages, it is observed in Fig. 7 and Table II that the best fit of the experimental adsorption data corresponds to a pseudo-second order kinetic model since the R^2 coefficients are slightly higher than the R^2 coefficients of the pseudo-first order model. Also, it is observed that the rate constant increases with increasing dosage giving values of 0.0082, 0.0088, 0.0093, and 0.0201 $\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$ at dosages of 0.5, 1.0, 1.5, and 2.0, respectively.

The fit to the pseudo-second order kinetic model indicates that the adsorption corresponds to chemisorption. Similar results were found by Kara *et al.* [17] who studied the adsorption of three reactive dyes, Remazole Red, Remazole Blue and Rifation Yellow, from aqueous solutions using fly ash as adsorbent in a stirred batch system to investigate the influence of two parameters, namely, adsorbent dosage and particle size finding that the adsorption of the reagents increased with increasing adsorbent dosage, and increased with decreasing particle size. In this respect Rápó and Tonk [18] explain that, increasing the adsorbent dosage is positively correlated with dye removal efficiency and performance since, with increasing adsorbent dosage, more active surface area is available for adsorption and more active adsorption sites are available.

TABLE II

RESULTS OF THE KINETIC ANALYSIS OF THE REMOVAL OF THE DISPERSED BLUE DYE 124 USING FUERTE VARIETY AVOCADO SEED AS ADSORBENT AT DIFFERENT DOSAGES.

Model	Parameter	Dosage (g/L)			
		0.5	1	1.5	2
Pseudo first order	q_e (mg/g)	5.905	7.618	9.11	9.339
	K_1 (min^{-1})	0.0477	0.0583	0.069	0.1226
	R^2	0.9954	0.9914	0.9956	0.9786
Pseudo second order	q_e (mg/g)	6.8	8.536	10.06	9.939
	K_2 ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$)	0.0082	0.0088	0.0093	0.0201
	R^2	0.9958	0.9985	0.9957	0.9959

D. Adsorption kinetics at initial dye concentrations

Fig. 8 shows the percent removal rates of avocado seed at a dosage of 2 g/L and pH=2, at 20 °C and at dye concentrations of 50, 100, 150, and 200 mg/L.

Fig. 9 shows the graph of the kinetic fit of DB-124 dye removal from waters where the pseudo-first and pseudo-second order kinetics are evaluated.

Table III shows the results of the kinetic analysis of the removal of the dye DB-124 from contaminated water using avocado seed Fuerte variety at a dosage of 2 g/L and pH=2 at different concentrations of the dye.

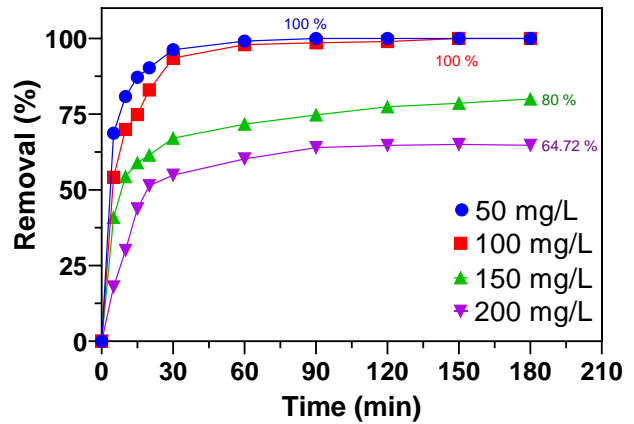


Fig. 8 Effect of initial dye concentration on the percentage removal of Disperse Blue 124 dye from water.

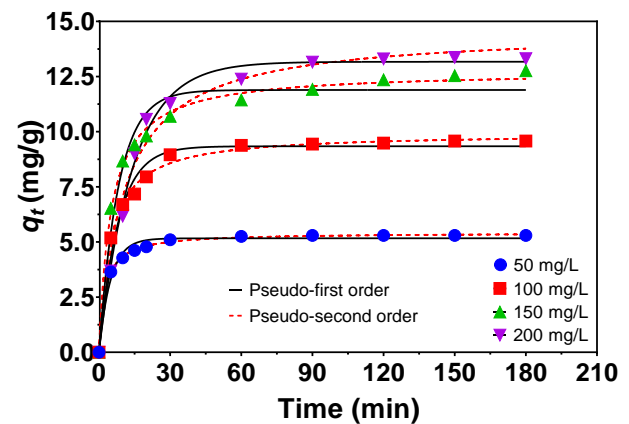


Fig. 9 Kinetic study of the removal of Disperse Blue 124 dye from water at different concentrations of the dye.

TABLE III

RESULTS OF THE KINETIC ANALYSIS OF THE REMOVAL OF THE DISPERSED BLUE DYE 124 FROM WATER USING FUERTE VARIETY AVOCADO SEED AT DIFFERENT CONCENTRATIONS OF THE DYE.

Model	Parameter	Concentration (mg/L)			
		50	100	150	200
Pseudo first order	q_e (mg/g)	5.166	9.339	11.89	13.17
	K_1 (min^{-1})	0.2045	0.1226	0.1216	0.0707
	R^2	0.983	0.9786	0.9632	0.9934
Pseudo second order	q_e (mg/g)	5.42	9.939	12.75	14.59
	K_2 ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$)	0.0736	0.0201	0.0153	0.0064
	R^2	0.9991	0.9959	0.9958	0.9944

The initial concentration of the dye would also affect the adsorption process of the DB-124 dye on the avocado seed used, since Fig. 8 shows that the final removal percentage after 180 minutes of agitation presents values of 100, 100, 80, and 64.52 % for initial DB-124 concentrations of 50, 100, 150, and 200 mg/L.

200 mg/L, respectively. Likewise, Fig. 8 shows that as a function of time there is a difference in the removal percentages at different initial concentrations of DB-124, since the removal percentages decrease as the dye concentration increases. Regarding the kinetic study of the tests at different pH, Fig. 9 and Table III show that the best fit of the experimental adsorption data corresponds to a pseudo-second order kinetic model since the R^2 coefficients are slightly higher than the R^2 coefficients of the pseudo-first order model.

Likewise, it is observed that the rate constant decreases with increasing initial concentration with values of 0.0736, 0.0201, 0.0153, and 0.0064 $\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$ at dosages of 5, 100, 150, and 200 mg/L, so that the higher the concentration of the dye, the lower the percentage of removal. This is explained by Wang *et al.* [19], which indicates that at a low initial concentration of the solution, the surface area and availability of adsorption sites are relatively high so that adsorbates are easily adsorbed and removed, on the contrary, at higher initial concentration of the solution, the total available adsorption sites are limited, resulting in a decrease in the percentage of removal.

E. Adsorption kinetics at different temperatures

Fig. 10 shows the removal percentages of the dye DB-124 using avocado seed as adsorbent at an initial concentration of 200 mg/L, dosage of 2 g/L and pH=2 at temperatures of 20, 30, and 40 °C.

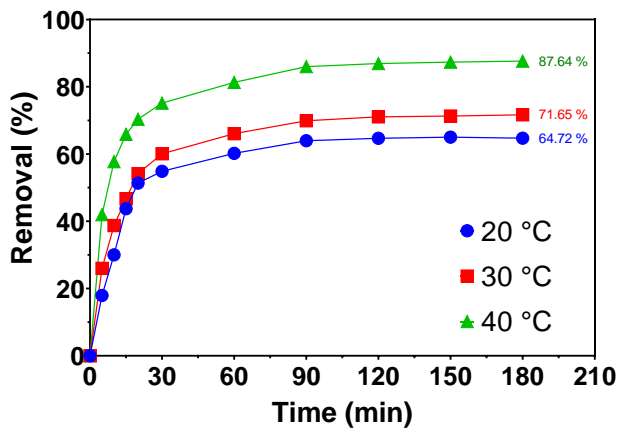


Fig. 10 Effect of temperature on the percentage removal of Disperse Blue 124 dye from water.

Fig. 11 shows the kinetic fit graph of the DB-124 dye removal where the pseudo-first and pseudo-second order kinetics are evaluated.

Table IV shows the results of the kinetic analysis of the removal of the dye DB-124 from water using Fuerte variety avocado seed under conditions of an initial concentration of 200 mg/L, dosage of 2 g/L and pH=2 at different temperatures.

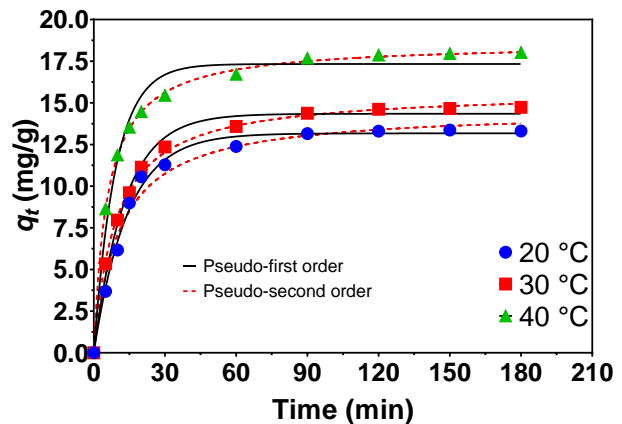


Fig. 11 Kinetic study of the removal of Disperse Blue 124 dye from water at different temperatures.

Finally, the temperature would also affect the adsorption process of the DB-124 dye on the avocado seed because it was found in Fig. 10 that the final removal percentage after 180 minutes of agitation presents values of 64.72, 71.65, and 87.64 % for temperatures of 20, 30, and 40, respectively. Likewise, this figure also shows that as a function of time there is a difference in the removal percentages at the different temperatures studied, since the higher the temperature, the higher the removal percentage.

TABLE IV
RESULTS OF THE KINETIC ANALYSIS OF THE REMOVAL OF THE DISPERSED BLUE DYE 124 FROM WATER USING AVOCADO SEED FUERTE VARIETY AS ADSORBENT AT DIFFERENT TEMPERATURES.

Model	Parameter	Temperature (°C)		
		20	30	40
Pseudo first order	q_e (mg/g)	13.17	14.34	17.33
	K_1 (min^{-1})	0.0707	0.0771	0.1099
	R^2	0.9934	0.9922	0.9798
Pseudo second order	q_e (mg/g)	14.59	15.71	18.62
	K_2 ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$)	0.0064	0.0069	0.0093
	R^2	0.9944	0.9981	0.9995

Regarding the kinetic study of the tests at different temperatures, it is observed in Fig. 11 and Table IV that the best fit of the experimental adsorption data corresponds to a pseudo-second order kinetic model since the R^2 coefficients are slightly higher than the R^2 coefficients of the pseudo-first order model. Also, it is observed that the rate constant increases as the temperature increases with values of 0.0064, 0.0069, and 0.0093 $\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$ for the temperatures of 20, 30, and 40 °C. Therefore, the adsorption process of the dye DB-124 would correspond to a chemisorption and the process would be endothermic since the removal increases with temperature.

This is explained by Chen *et al.* [20] who demonstrated that adsorption corresponds to an exothermic process. On the other hand, Jiang *et al.* [21] explains that when the removal increases with decreasing temperature it corresponds to an exothermic process and when the opposite happens the process would be endothermic. On the other hand, results similar to those of the present study were obtained by Geng *et al.* [22], who studied the adsorption of methylene blue by a new material composed of alum sludge, achieving an endothermic process since the adsorption percentage improved as the temperature increased.

IV. CONCLUSIONS

It was possible to demonstrate that the avocado seed Fuerte variety is an excellent biomaterial to be used in the removal of the dye DB-124 from water. The process would be influenced by pH, adsorbent dosage, initial concentration and temperature. The best conditions of the adsorption process were at an initial DB-124 concentration of 200 mg/L, a dosage of 2 g/L, pH=2 and a temperature of 40 °C. The kinetic study showed that the adsorption process corresponds to a chemisorption and that the removal of DB-124 is favored at higher temperatures, which corresponds to an endothermic process. With the present study, we can begin to scale up the use of avocado seed in textile wastewater where DB-124 is used.

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