

TEXTILE DYE ADSORPTION BY NATURAL PERLITE

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Article Info	Abstract
Received: 27.12.2023 Accepted: 22.02.2024 Keywords: Adsorption, green dye FB, perlite, Adsorption Isotherm, Thermodynamic study	In today's world of industrial progress, pollution is a major concern, especially water pollution. Considered a real danger to mankind, this article looks at the treatment of water contaminated by textile dyes, which has become a danger to humans and the environment. As an example, we have chosen the green dye FB (anionic type) which is found in the rejects of a textile factory ENADITEX in the industrial zone of the wilaya of ORAN - ALGERIA, this dye is among the most used in the textile industry. The method adopted for dye removal is adsorption by natural perlite. The Experimental results showed that adsorption of the green dye FB on the porous solid studied: natural perlite, gave a removal rate of 87.51% for 60 minutes. The adsorption isotherms of the adsorbent/adsorbate systems studied are satisfactorily described by the two mathematical models Freundlich and Temkin. All the results obtained show that the adsorption kinetics of the green dye FB by the solid material is well described by the second-order model. The adsorption reaction is a physisorption, as the thermodynamic study demonstrated.

1. Introduction

Water is a precious resource but unfortunately, in recent years, it has been increasingly polluted due to ever-increasing industrial activity. The textile sector, among others, is the source of a large part of the water pollution due to the large quantity of dyes in the water [1, 2]. Therefore, these waters must be treated before they reach the natural aquatic environment.

Industrial discharges of textiles, complex and toxic mixtures are a source of a growing pollutant load [3, 4].

Difficult to biodegrade because of their complex aromatic structures [5, 6], dyes, among other things, represent an ever-increasing threat to living beings (including humans) and their natural habitats. [7, 8]. The dye limits the penetration of sunlight into the water, which disrupts biological processes and the aquatic ecosystem [9, 10]. Most of the time, they are removed by physico-chemical and biological treatment [11-13]. In contrast to the other methods used, adsorption seems to be the most successful process because it offers a wide range of advantages: simplicity of use, possibility of regeneration, recovery and recycling. Despite their effectiveness in the removal of the dye, the majority of adsorbents have certain drawbacks: low adsorption capacity.

Activated carbon is one of the most widely used adsorbents in textile wastewater treatment due to its relatively larger specific surface area. It does, however, present some cost issues [14-16].

Our study proposes the removal of the dye from the ENADITEX (SENIA ORAN) textile industry: Green FB by adsorption on an economical and more efficient adsorbent: natural perlite.

2. Materials and methods

2.1. Chemical and materials

2. 1. 1. Green dye FB

Figure 1 demonstrates the chemical structure of the anionic dye studied. It has a density of 1.2 g/L. The dye concentration in aqueous solution is determined using a UV-visible spectrometer (thermo Evolution 60 S) at an absorption wavelength of 333nm.

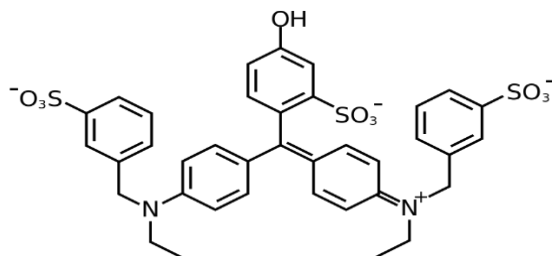


Figure 1. Chemical structure of the dye

2.2. Materials and characterization

2.2.1. Natural perlite

Natural perlite is a siliceous volcanic rock. The rock is first crushed and calibrated. In appearance, it is extracted from the Hammam Boughrara deposit in Tlemcen, Algeria. It comes in aggregate form. We used it as a powder sieved to 80 μm , in all tests with a specific surface area of 4060 cm^2/g .



Figure 2. Perlite slag before borying (a) and 80 μm powder form (b).

2.2.2. Chemical characterization

Table 1. Basic chemical composition of perlite

Components	SiO ₂	CaO	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	K ₂ O	Na ₂ O	MgO	Cl
Content (%)	76,40	3,16	13,43	2,92	0,01	4,33	0,82	0,37	0,008

Table 1 shows that perlite is a naturally occurring mineral and contains around 8.68% alkali metal oxides. The chemical composition of perlite contains mainly silica (76.40%) and Al₂O₃ (13.43%).

2.2.3. XRD characterization

Perlite is identified by X-ray diffraction (Figures 3) using a Philips PERT PRO diffractometer, equipped with a cobalt cathode at a voltage of 40 kV and a current of 50 mA.

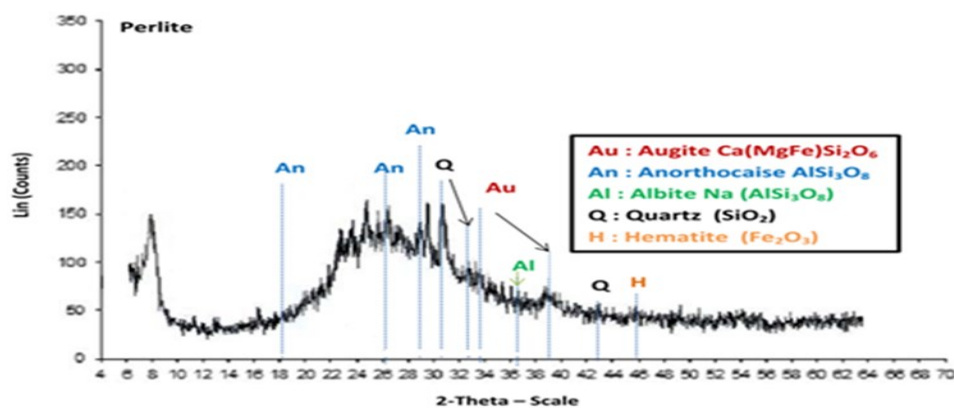


Figure 3. XRD diagram of natural perlite.

Figure 3 shows that the results of X-ray mineral analysis (XRD) of perlite reveal the strong presence of quartz at 34° , followed by alumina, then iron oxide and calcite, and a few traces of magnesium.

2.2.4. SEM-EDS characterization

SEM and EDX observations were carried out on perlite prior to grinding. These observations were carried out on polished and metallized sections of perlite dispersed in epoxy resin (same preparation method as for microprobe analysis).

The images shown in Figure 4 were taken in electron backscatter mode, which gives maximum contrast between the different phases.

SEM and EDX analysis of ground perlite yielded the results shown in the figures below. Scanning electron microscope analysis (Figure 4), at low ($G=500$) and high ($G=5000$) magnification, shows that after grinding, perlite has an angular structure with fairly sharp angles. This structure should enhance the mechanical strength of the mortars produced.

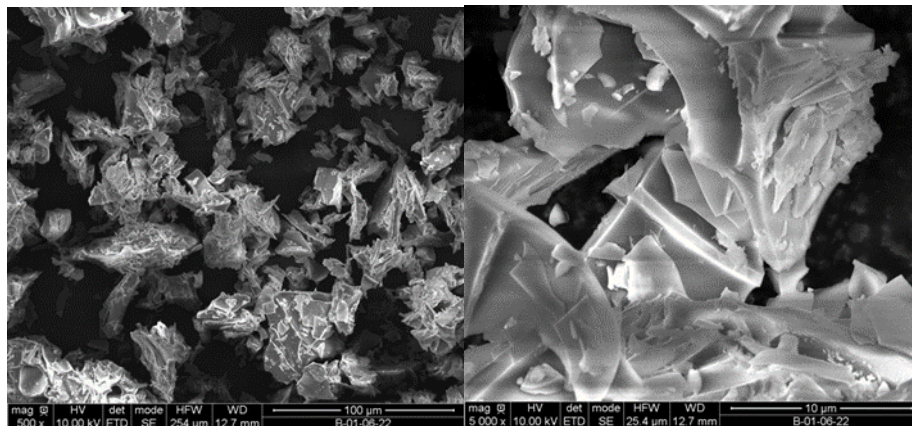


Figure 4. Scanning electron microscope analysis of perlite at low ($G=500$: left) and high ($G=5000$: right) magnification

EDX analysis of perlite, coupled with SEM analysis, figure5 shows that this species is predominantly silica like sand. This should also enable high mechanical strength to be achieved in the mortars produced.

We note that the **Si** element is higher than the other elements. This suggests that the material (perlite) has good pozzolanic activity.

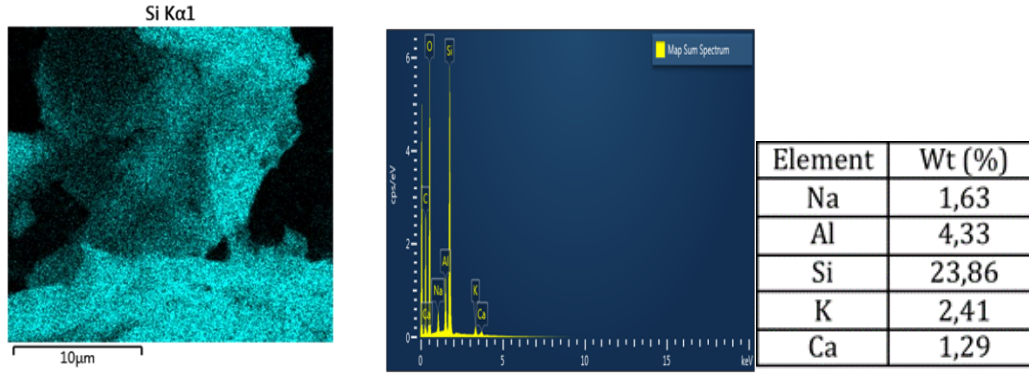


Figure 5. DX analysis, coupled with SEM observation, of perlite grit (the table on the right shows the percentages of the chemical elements Na, Al, Si, K and Ca)

2.3. Adsorption tests

The equilibrium concentration was measured and the amount of green dye FB adsorbed by the three adsorbents was calculated using the following equation [17]:

$$q_e = (C_o - C_e) \cdot \frac{v}{m} \quad (1)$$

Where:

q_e is the amount of adsorbed dye per gram adsorbent at equilibrium (mg/g);

C_o is the initial concentration of the dye in solution (mg/L);

C_e is the equilibrium dye concentration (mg/L);

m is the adsorbent mass (g), and

V is the solution volume (L).

The removal rate is calculated as follows:

$$R(\%) = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

2.4. Adsorption Isotherms

To understand the phenomenon of adsorption of green dye FB on perlite, adsorption isotherms have been established at different temperatures using a thermocouple. To a volume of 100 mL of green dye solution of concentration $C=24$ mg/L are added 2g of perlite. The concentration of green dye in solution is monitored as a function of time, for temperatures 16, 45 and 60°C.

The modeling of the adsorption isotherms was established by using the Langmuir, Freundlich, and Temkin equilibrium models.

The Langmuir model is used in linear form, given by the equation [18, 19]:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{C_e q_m b} \quad (3)$$

With

q_e is the amount of solute adsorbed on 1 g of adsorbent (mg/g);

q_m is the maximum capacity of adsorption corresponding to monolayer coverage;

C_e is the equilibrium dye concentration (mg/l), and

b is the energy constant of adsorption.

The Freundlich model is used in linear form given by the equation [9, 20]:

$$\log q_e = \log K + \frac{1}{n} \log C_e \quad (4)$$

The Temkin model is used in linear form given by the following equation [21, 22]:

$$q_e = B_1 \ln A + B_1 \ln C_e \quad (5)$$

With

$$B_1 = \frac{RT}{b} \quad (6)$$

$T(K)$ is the temperature;

A (L.mg⁻¹) is the related to the equilibrium constant;

B_1 is the related to the heat of adsorption, and

R (8.314 J. mol⁻¹.k⁻¹) is the gas constant.

2.5. Adsorption Kinetics

Two models were used for kinetic studies.

2.5.1. Lagergreen first-order model

It was assumed in this model that the adsorption rate at time t is proportional to the difference between the amount adsorbed at equilibrium Q_e and the amount Q adsorbed at that time and that adsorption is reversible. The first-order adsorption rate constant is deduced from the model established by Lagergreen. The linearity of the first-order equation is expressed as follows [23, 24]:

$$\ln(1 - U(t)) = -K_1 t \quad (7)$$

With:

K_1 Rate constant (min^{-1}).

t Time of contact (min).

$$U(t) = \frac{C_0 - C_1}{C_0 - C_e} \quad (8)$$

With:

C_0 : is the concentration of the initial solution (mg/L);

C_t : is the concentration of the solution at the moment t (mg/L); and

C_e : is the concentration of the equilibrium solution (mg/L).

2.5.2. Lagergreen second-order model

The pseudo-second order equation is often successfully used to describe the kinetics of the pollutant fixation reaction on the adsorbent. The pseudo-second order model (Eq.9) characterizes the adsorption kinetics by taking into account both the case of rapid fixation of solutes on the most reactive sites and the case of slow fixation on low-energy sites, and their equation is expressed as follows [25, 26]:

$$\frac{dq}{dt} = K_2(q_e - q)^2 \quad (9)$$

The linearity of this equation is expressed as follows:

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (10)$$

q and q_e : adsorbed quantifies at times t and equilibrium.

K_2 : Rate constant (min^{-1}).

2.6. Thermodynamic study

Adsorption is a phenomenon that can be either endothermic or exothermic, depending on the adsorbent material and the nature of the adsorbed molecules. We performed adsorption experiments by varying the temperature from 16°C to 60°C . Thermodynamic

parameters such as Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were calculated [27, 28] using the following equations:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (11)$$

$$Kd = \frac{C_o - C_e}{C_e} \quad (12)$$

$$\ln Kd = \frac{\Delta S^\circ}{R} + \frac{\Delta H^\circ}{RT} \quad (13)$$

Where :

K_d is the equilibrium constant;

C_o is the concentration of the initial solution (mg/L), and

C_e is the solution equilibrium concentration in (mg/L).

3. Results and discussions

3.1. Effect of adsorbent dose green dye removal

The different masses (0.5g, 1g, 1.5g, 2g) of perlite are added to 100 ml of green dye FB solution with initial concentration: $C_i = 24$ g/L, at room temperature and stirring at 500 rpm. The suspensions are centrifugally filtered and analyzed by UV-Visible. The experimental results shown in Fig. 6 demonstrate that the retention rate as a function of time depends on the adsorbent mass.

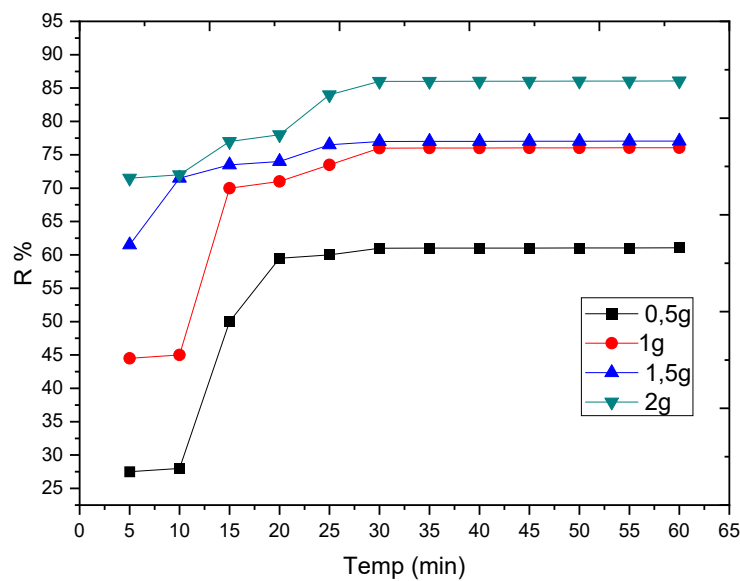


Figure 6. Percent green dye removal by perlite as a function of time for an initial concentration $C_i = 24$ mg/L.

The green dye removal rate increases as adsorbent mass increases, as can be observed in Fig. 6. This is accordant with the literature: when the mass of the solid increases, so does its specific surface area of contact with the dye, which results in an increase in dye fixation. The maximum removal rate of 87% is obtained for a mass of perlite equal to 2g and for an initial solution concentration of the green dye $C_i = 24$ mg/L.

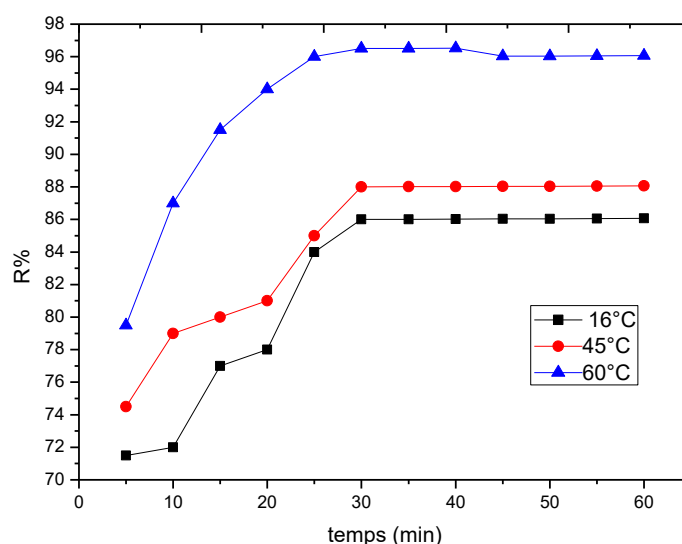


Figure 7. Effect of temperature on percent dye removal by perlite, $m_{\text{perlite}} = 2$ g.

3.2. Temperature effect on dye removal

At an initial concentration of 24 mg/L, 2 g of adsorbent are added separately to 100 ml of green dye FB solution. The mixtures are heated to different temperatures (16°C, 45°C, and 60°C) in a water bath.

Figure 7 indicates how heating the solution causes more thermal agitation, which increase the rate of removal as the temperature increases. As a result, the disturbed dye begins moving more rapidly toward of the solid surface, and is fixed to by monolayer or multilayer deposition and diffusing into the solid perlite's pores

3.3. pH effect on dye removal

To test the effect of pH on green dye removal, the following mixtures are prepared: 100 ml of dye solution with initial concentration $C=24$ mg/L is added to 2 g of perlite at 16°C.

The pH of the mixture is adjusted by adding HCl (1N). Percent removal is calculated and plotted in Fig. 8.

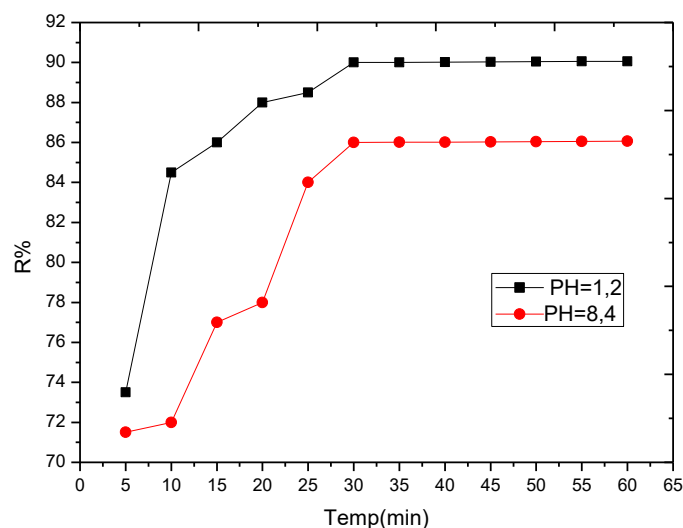


Figure 8. Effect of pH on percent dye removal by perlite, $m_{\text{perlite}} = 2\text{g}$.

Figure 8 shows that removal is much better in an acidic medium. This is because perlite contains a considerable amount of silicon oxide the lower the PH value less than 3, the higher the positive charge of the silicon oxide, which favors adsorption by attraction, which can be explained by the electrostatic interaction of the anionic species with the positively charged surface. The electrostatic attraction of the dye to the perlite surface increases with decreasing pH. Decreasing the pH above PZC=3 increases the density of positive charges favoring repulsion between adsorbent particles, which in turn increases specific surface area and adsorption capacity.

3.4. Adsorption isotherms

Isotherms at various temperatures have been determined with a 100 ml volume of solution, an initial concentration of $C_0 = 24 \text{ mg/L}$, and 2 g of perlite. The equilibrium contact time was obtained from the kinetic study. Langmuir, Freundlich and Temkin adsorption isotherm models were fitted to the experimental data.

3.4.1. Langmuir isotherm

For the three temperatures studied, the experimental results showed the isotherms in Figs. 9-11.

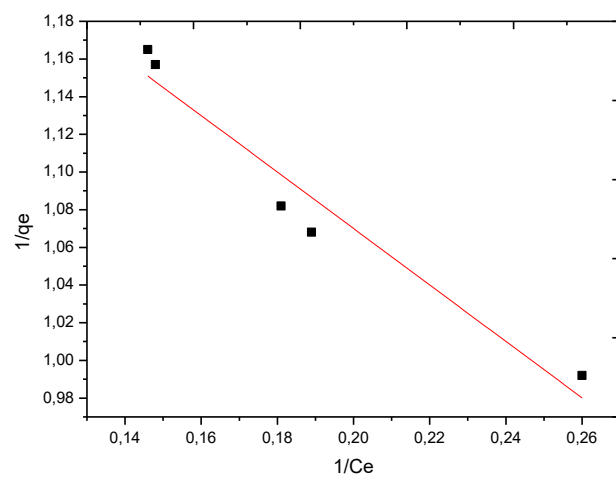


Figure 9. Adsorption isotherm of green dye FB on perlite according to the Langmuir model at 16°C.

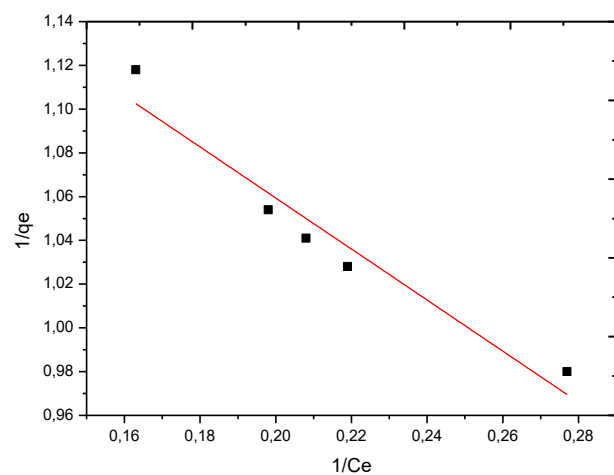


Figure 10. Adsorption isotherm of green dye FB on perlite according to the Langmuir model at 45°C.

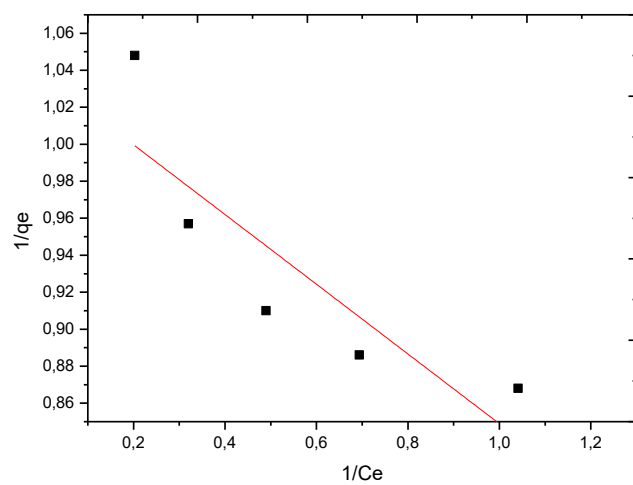


Figure 11. Adsorption isotherm of green dye FB on perlite according to the Langmuir model at 60°C.

3.4.2. Freundlich isotherm

The experimental results for the three temperatures in study are shown in Figs. 12-14.

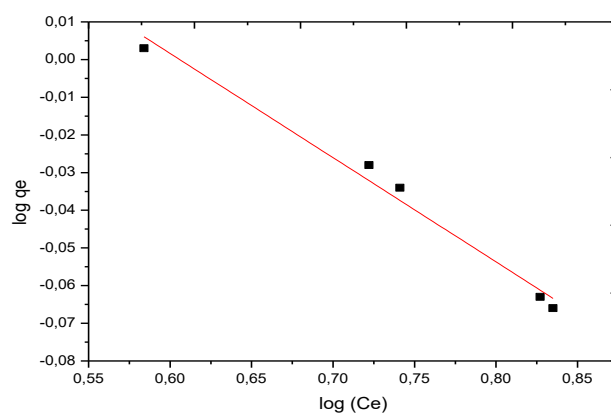


Figure 12. Adsorption isotherm of green dye FB on perlite according to the Freundlich model at 16°C.

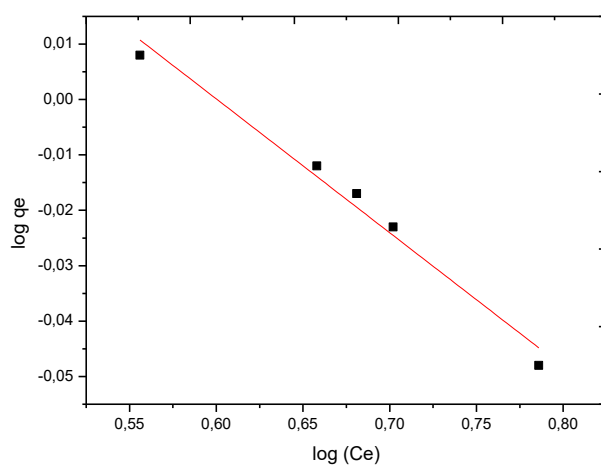


Figure 13. Adsorption isotherm of green dye FB on perlite according to the Freundlich model at 45°C.

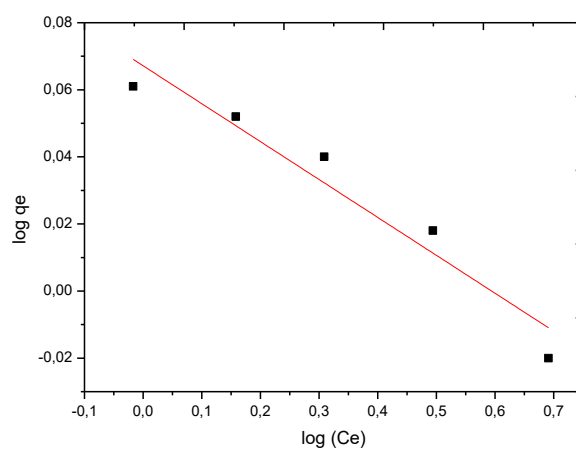


Figure 14. Adsorption isotherm of the green dye FB on perlite according to the Freundlich model at 60°C.

3.4.3. Temkin isotherm

Temkin model adsorption isotherms for the green dye FB are displayed in Figs. 15–17.

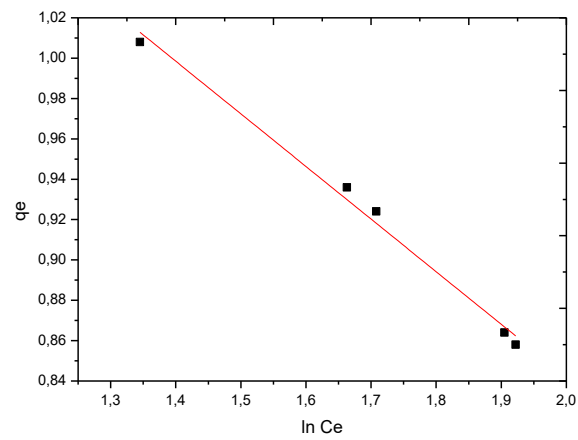


Figure 15. Adsorption isotherm of green dye FB on perlite according to the Temkin model at 16°C.

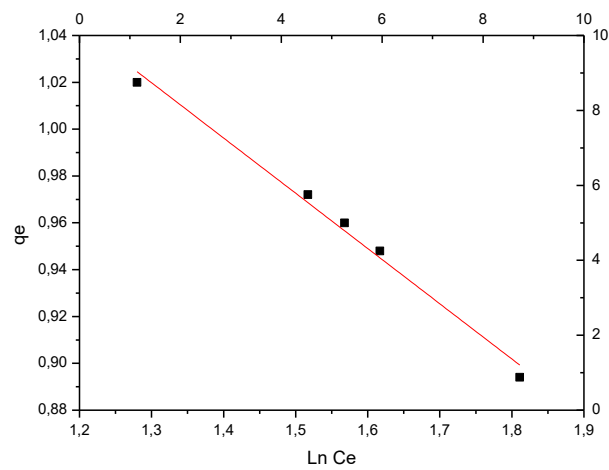


Figure 16. Adsorption isotherm of green dye FB on perlite according to the Temkin model at 45°C.

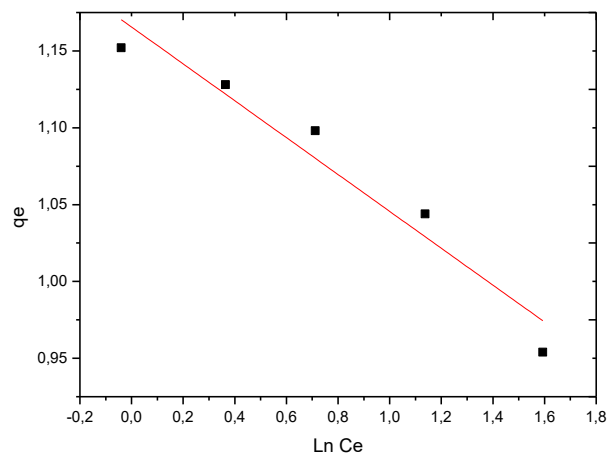


Figure 17. Adsorption isotherm of green dye FB on perlite according to Temkin model at 60°C.

Parameter values for the Freundlich, Langmuir and Temkin models are summarized in Table 2.

Table 2. Isotherms parameters values from isotherm models fitting to purple dye adsorption.

T(°C)	Langmuir			Freundlich			Temkin		
	B	q _m	R ²	n	K	R ²	B ₁	A (L.mg ⁻¹)	R ²
16	0.913	0.730	0.931	3.623	1.468	0.980	0.260	189.105	0.989
45	1.109	0.773	0.922	4.149	1.396	0.975	0.235	282.182	0.987
60	5.517	0.964	0.668	8.849	1.166	0.917	0.119	17852.805	0.928

The Temkin and Freundlich models have high correlation coefficients close to unity, making them the two most suitable for the green dye adsorption process.

3.5. Kinetic study

The adsorption of the green dye FB by perlite has been studied using both first- and second-order models, and the experimental results are shown in Table 3.

a. First-order Lagergreen model

Figure 18 shows the adsorption kinetics of green dye according to the first-order kinetic model.

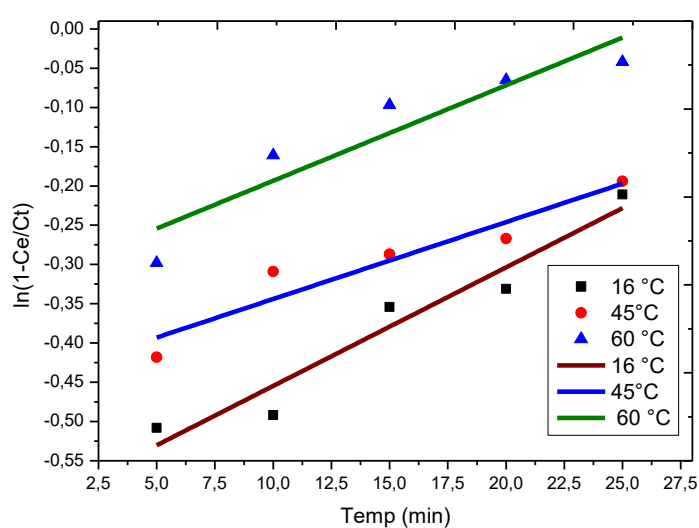


Figure 18. Graphical representation of the results of the first-order kinetic model for the adsorption of the green dye F.B on perlite at (16 ,45, 60°C).

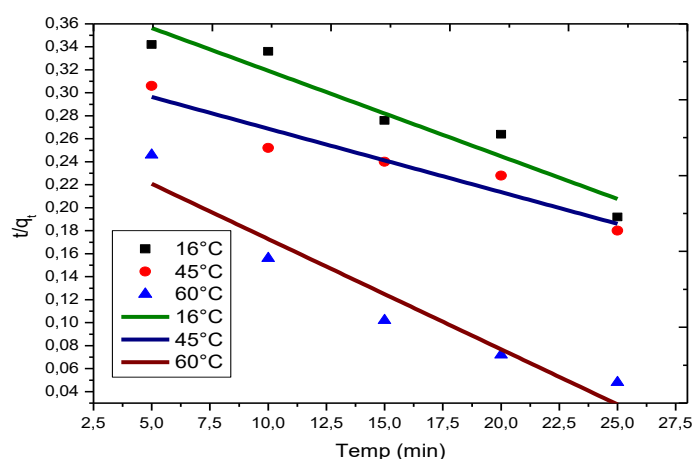


Figure 19. Graphical representation of the results of the second-order kinetic model for the adsorption of the green dye FB on perlite at (16, 45, 60°C).

Table 3. Kinetic parameters of the Lagergreen models

T(°C)	First Order		SecondOrdre			
	K	R ²	K ₁	q _e ex	q _e cal	R ²
16	0.031	0.522	1.389	0.180	0.192	0.919
45	0.009	0.880	1.829	0.170	0.180	0.952
60	0.012	0.834	3.755	0.041	0.048	0.878

b. Second-order Lagergreen model

Figure 19 shows the adsorption kinetics of the green dye FB according to the second-order kinetic model.

The results show that the adsorption kinetics is better described by the second order model as indicated by the high determination coefficient.

Table 3 shows the equilibrium adsorbed quantity of the pseudo-second-order model and that calculated by the dye-removal experiments, which reveals an agreement between the theory and the experiment.

3.6. Thermodynamic study

To study the thermodynamics of green dye adsorption on perlite, a 2g quantity of adsorbent is brought into contact with 100 mL of an aqueous solution of the dye with an initial concentration of 24 mg/L and at temperatures of 16°C, 45°C and 60°C. Table 4 summarizes the experimental results.

The plot of $\ln K_d$ as a function of $1/T$ shown in Fig. 20 enables the calculation of ΔH° and ΔS° .

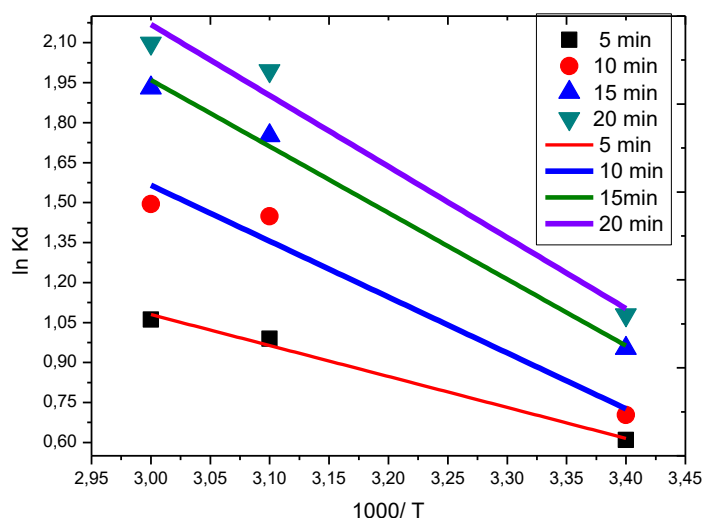


Figure 20. Determination of the thermodynamic parameter

Table 4. Thermodynamic parameters of green dye adsorption

Adsorbent	ΔS° (J.mol ⁻¹ .K ⁻¹)	ΔH° (Kj.mol ⁻¹)	ΔG° (Kj.mol ⁻¹)	T (°C)
perlite	66.5615	16.736	-2.7665	16
			-3.4481	45
			-5.4289	60

Negative values of ΔG° at different temperatures indicate the spontaneous nature of the adsorption process.

The negative values of ΔG° at different temperatures indicate the spontaneous nature of the adsorption process.

The positive value of ΔS° indicate that there is an increase in disorder in the solid interface solution system / solute during the adsorption process.

The positive value of ΔH° indicate that the adsorption is endothermic.

The value of ΔH° , which is less than 80 kJ/mol reveals that the adsorption of the dye investigated was physical.

4. Conclusions

We studied the factors influencing the adsorption of green dye by the perlite solid: adsorbent quantity, pH and temperature, The maximum removal rate (87.51%) for perlite mass of 2g and initial concentration of 24mg/L at room temperature and (99%) at pH= 8.32. for a temperature equal to 60°C, perlite mass (2 g) and initial concentration 24 mg/L the removal rate is maximum (99%).

Adsorption isotherms studies revealed that the Freundlich and Temkin models adequately described the investigated dye adsorption while the second order model better described its adsorption kinetics.

The thermodynamic study showed that green dye adsorption on perlite is a spontaneous, physical, and endothermic process.

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