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Adsorption of a textile dye from aqueous solution on natural and modified sawdust

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ABSTRACT

Natural and modified sawdust were used in adsorption of textile dye (acid green 4G) from aqueous solution. Several physicochemical analyses such as Fourier-transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy, Brunauer–Emmett–Teller and pH_{zpc} were performed to characterize the adsorbents. The effects of contact time, adsorbate concentration, and temperature were investigated. The equilibrium time was found to be achieved after 120 min of contact and kinetic data were best described by the pseudo-second-order rate equation. The acid green 4G is better adsorbed by modified sawdust. The adsorption isotherms were described by Langmuir and Freundlich equation and the equilibrium was better fitted by the Freundlich model. The study of thermodynamic parameters reveals that the adsorption of acid green 4G by both adsorbents was endothermic. All the obtained results show that the modified sawdust is more practical to use in purification of water which is contaminated by textile dye than natural sawdust.

Keywords: Adsorption; Sawdust; Textile dye; Acid green 4G; Kinetics

1. Introduction

Synthetic dyes are produced and used everywhere in several fields. The textile industry is the first which uses dyes for coloration of fibers [1] and consumes a large volume of water and chemical forwent processing of textiles to produce clothing (with a global production of dyes 800,000 tons y^{-1} [2]). But in parallel, dyes can be harmful to both our health and environment by water spills waste that is visible in small quantities. The control of water pollution has become of paramount importance in recent years. Actually, the textile dyeing industry is one of the most polluting sources in the world [3] due to the release of dyes into the environment which is stable and weakly biodegradable [4,5].

Several techniques have been used and developed to reduce or eliminate the emission of these dyes such as biological degradation [6,7] membrane separation [8], adsorption [9,10], advanced oxidation processes [11–13], chemical precipitation [14] and electrochemical [15]. Nowadays, the use of natural adsorbents in the adsorption of pollutants [16,17] remains the solution for economical efficient water purification with good advantages: high efficiency without secondary pollution, ease handle, and low running costs that do not require a lot of energy [18,19].

For this reason, sawdust has been chosen due to its abundance in nature as an accessible low-cost material and respectful for the environment that has proved its effectiveness in removing many pollutants from wastewater [20–22]. The adsorption capacity of sawdust toward

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pollutants can be improved by modifying the physicochemical properties of its surface using different agents [23–25].

Therefore, this present work aims at studying the effectiveness of natural and modified sawdust for the removal of textile dye (acid green 4G) from aqueous solution by adsorption. A number of physicochemical analyses were carried out with natural (NS) and modified sawdust (MS): Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET) and pH_{zpc}. The influence of parameters such as contact time, temperature, and initial concentration of dye solution was evaluated. The adsorption capacity of dye solutions was calculated using the known kinetic models. The experimental data on the equilibrium of adsorption were compared using Langmuir and Freundlich isotherm equations.

2. Equipment and methods

2.1. Dye

The dye used as a pollutant is the acid green 4G which is a textile dye with the structural formula shown in Fig. 1.

2.2. Preparation of sawdust

Sawdust of redwood which is used as an adsorbent was obtained from joinery. It was washed with distilled water several times to remove surface impurities, dried at 100°C for 24 h, crushed and then sieved. The particles with a diameter between 2 and 1 mm were selected.

Modified sawdust was obtained by putting in contact 2 L of water in a beaker with 45 g of $FeCl_3$, 20 g of $FeCl_2$, and 400 g of sawdust. After 10 min of shaking at ambient temperature, 150 mL of NH_3 (15%) was added dropwise. And then, the resulting mixture was dried for 2 h at 110°C.

2.3. Instrumental analyses

The FTIR spectra of NS and MS were received with Perkin Elmer Spectrometer Spectrum two within the range of wave number 360–40,000 cm^{-1} (Laboratory of Inorganic and Environmental Chemistry, Tlemcen University, Algeria).

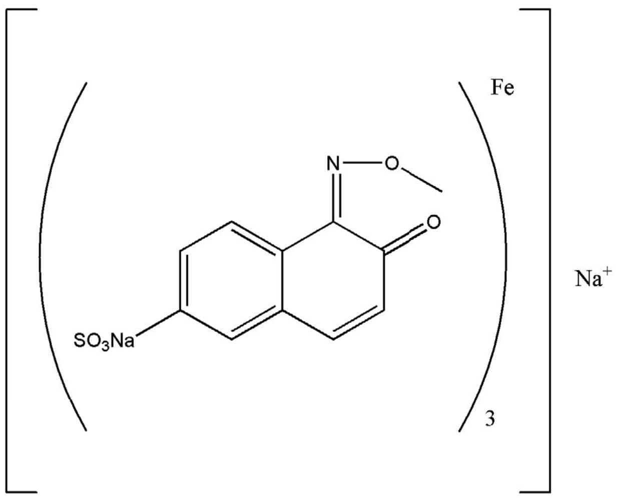

Fig. 1. General formula of acid green 4G.

The XRD structures of the two sawdust types were determined with an X-ray instrument (Rigaku Miniflex 300/600) operating at ambient temperature at 40 kV and 0.15 mA (Tlemcen University, Algeria).

The SEM morphologies of the adsorbents were obtained with HITACHI TM-1000 device (Tlemcen University, Algeria).

The specific surface area of each adsorbent was calculated using the BET equation and the analyses were carried with Nova 1000e Quantachrome instruments device through N_2 adsorption/desorption at 77 K for 3 h of degassing (Laboratory of Catalysis and Synthesis in Organic Chemistry, Tlemcen University, Algeria).

The pH_{zpc} is the pH value when the surface of the adsorbent is electrically neutral [26]. The pH_{zpc} was obtained using the pH drift method which consists of putting 50 mL of HNO_3 adjusted with 0.1 M HCl or 0.1 M NaOH with different initial pH (pH_i from 2 to 12) in contact with 0.5 g of sawdust in closed glass bottles [27]. After 24 h of stirring at ambient temperature, the final pH (pH_f) was measured. pH_{zpc} is the intersection of the line connecting point with the horizontal axis after drawing $pH_i - pH_f$ vs. pH. Under this value, sawdust's surface is positively charged which is means that the adsorption of the anion is favored, and the opposite happens over it [28].

2.4. Adsorption experiment

Adsorption of acid green dye onto sawdust was studied according to a batch method which consists of bringing into contact in a beaker 0.3 L of 100 mg L^{-1} dye solution with 1 g of adsorbent at constant medium shaking speed for 3 h at room temperature. After this, the samples were centrifugated at 50,000 rpm for 10 min, and then the supernatant was immediately analyzed with a UV-visible spectrometer Optizen POP device. The amount of fixed pollutant in mg g^{-1} of adsorbent (q_t) is given by Eq. (1):

$$q_t = \frac{C_0 - C_t}{m} V \tag{1}$$

where C_0 and C_t (mg L^{-1}) are respectively initial and instantaneous concentrations of pollutant, m (g) is the mass of adsorbent, and V (L) the volume of pollutant solution.

In order to determine the adsorption rate constant, kinetic models were used. For the first-order model of Lagergren, K_v is proposed by Eq. (2) [29]:

$$\log \frac{\left(q_e - q_t\right)}{q_e} = -\frac{K_v t}{2.3} \tag{2}$$

For the pseudo-second-order model of Ho and McKay, K' is given by Eq. (3) [30,31]:

$$\frac{t}{q_t} = \frac{1}{2K' q_e^2} + \frac{t}{q_e} \tag{3}$$

For the second-order model of Lagergren, K is given according to Eq. (4):

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + Kt \quad (4)$$

where q_e and q_t (mg g^{-1}) are quantities of adsorbate at equilibrium and t time respectively, t (min) is contact time, K_v, K' and K are adsorption rate constants for the first-order (min^{-1}) the pseudo-second-order (min^{-1} mg g^{-1}) and the second-order (min^{-1} g mg^{-1}) models, respectively.

2.5. Adsorption isotherms

To study the equilibrium isotherms of adsorption of acid green 4G on sawdust, a volume of 0.3 L of pollutant solution with different concentrations from 10 to 120 mg L^{-1} were put in contact with 1 g of each adsorbent. Experimental conditions are the same as those of the adsorption kinetics. Mathematical models of Langmuir and Freundlich are used to represent the adsorption isotherms.

Langmuir model is widely used for adsorption of a pollutant from liquid solution for homogenous adsorbents and can be expressed by the linearized Eq. (5) [32,33]:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (5)$$

where C_e (mg L^{-1}) is the adsorbate concentration at the equilibrium, q_m (mg g^{-1}) is the saturation adsorption capacity and b (L g^{-1}) is the characteristic equilibrium constant of adsorbent which depends on the experimental conditions.

Freundlich model is appropriate for adsorption on heterogeneous surfaces and multilayer sorption [34]. This isotherm is given by the linearized Eq. (6) [35]:

$$\text{Ln}q_e = \text{Ln}K + \frac{1}{n}\text{Ln}C_e \quad (6)$$

where K is the adsorbent capacity (g^{-1}) and n is the factor of heterogeneity.

2.6. Thermodynamic parameters

The adsorption phenomenon is always accompanied by a thermal process either exothermic (if $\Delta H < 0$) or endothermic (if $\Delta H > 0$) [36]. The measurement of adsorption heat allows to differentiate the chemisorption and the physisorption which is given by Gibbs–Helmholtz relation represented by Eqs. (7)–(10) [37,38]:

$$\Delta G = -RT\text{Ln}K_c \quad (7)$$

$$\Delta G = \Delta H - T\Delta S \quad (8)$$

$$\text{Ln}K_C = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (9)$$

$$K_c = \frac{C_e}{C_0 - C_e} \quad (10)$$

where ΔG (J mol^{-1}) is the free enthalpy, ΔH (J mol^{-1}) is the enthalpy, ΔS (J mol^{-1} K^{-1}) is entropy, R is the universal perfect gas constant (3.14J mol^{-1} K^{-1}), K_c is the equilibrium constant and T (K) is the absolute temperature.

3. Results and discussion

3.1. Characteristic results of sawdust

3.1.1. FTIR analyses

The infrared spectrograms of NS and MS are shown in Figs. 2 and 3, respectively.

The two spectra reveal the presence of broadband at 3,380 cm^{-1} for NS and 3,386 cm^{-1} for MS which may be

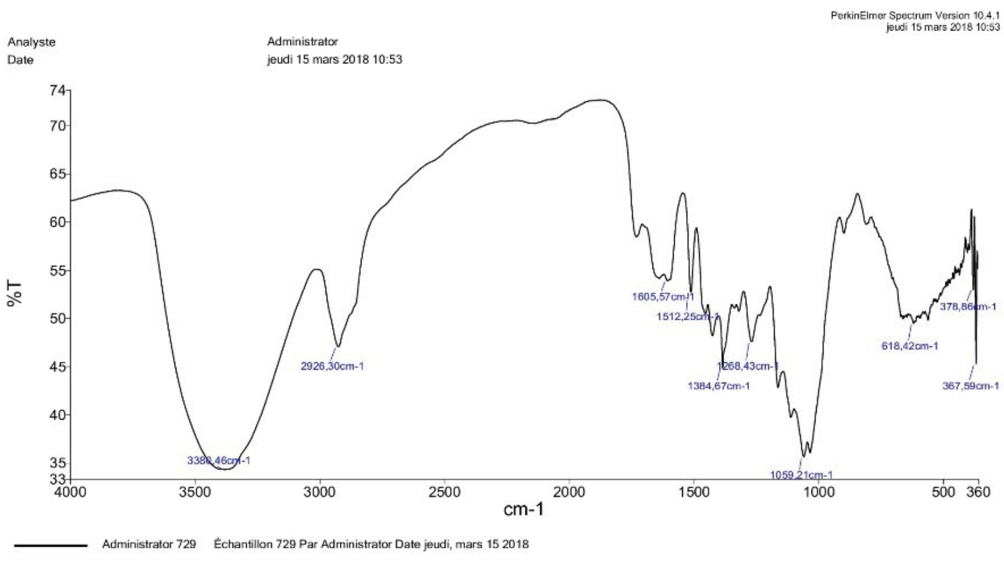

Fig. 2. FTIR spectra of NS.

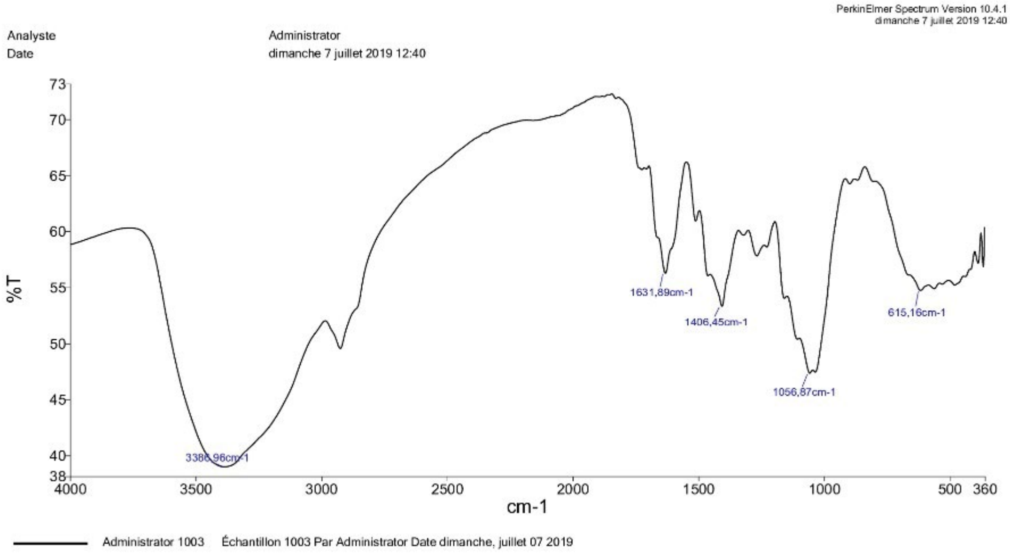

Fig. 3. FTIR spectra of MS.

assigned to the intramolecular bonds of OH [39]. The absorption peak observed at 2,926 cm^{-1} for both NS and MS is due to the presence of the CH group. The absorption peak of C=O bound observed at 1,700 cm^{-1} for NS may be attributed to lignin aromatic groups and disappeared for MS which indicated the break of C=O bound after modification of sawdust [40]. Absorption at 1,605 cm^{-1} for NS and 1,631 cm^{-1} for MS and 1,512 cm^{-1} for both may correspond to the C=C fragment of an aromatic group of lignin [41]. The peak of absorption at 1,406 cm^{-1} may be attributed to the methoxy group of lignin in sawdust [42]. The peak at 1,384 cm^{-1} for NS can be a symbol of the hemicellulose which disappeared for MS because it was dissolved after treatment [43]. The O–CH_3 group that was found at 1,059 cm^{-1} for NS and 1,056 cm^{-1} for MS can confirm the presence of cellulose in wood structure [43].

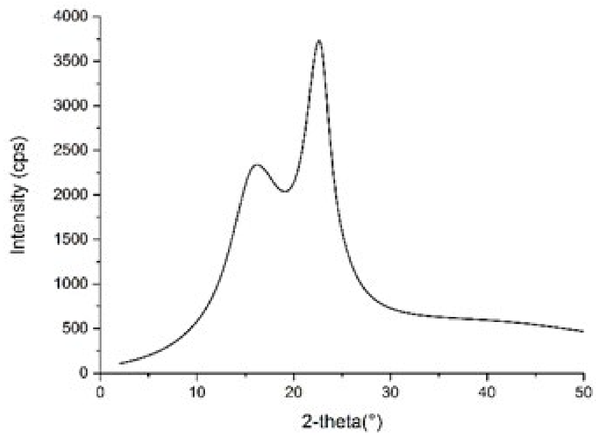

Fig. 4. XRD pattern of NS.

3.1.2. XRD analysis

Figs. 4 and 5 illustrate the XRD pattern of sawdust before and after modification.

Both adsorbents present the same curves showing the amorphous properties of our two materials. According to the data provided by the device, curves appearing at 2θ values of 16.23° and 22.63° with the intensity of 2339CPS and 3728CPS, respectively for NS and 16.19° and 22.3° with the intensity of 335CPS and 703CPS, respectively for MS correspond to the characteristic form of native cellulose of lignocellulosic compounds. The two other curves which appear in MS DRX at 2θ = 32.95° and 35.13° with intensity values of 126CPS and 159CPS, respectively correspond to hematite.

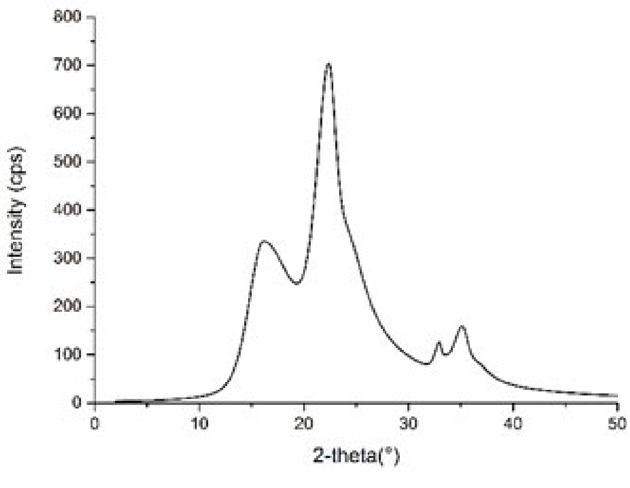

Fig. 5. XRD pattern of MS.

3.1.3. SEM morphology

The microstructure of the sawdust surface before and after treatment has been described using the SEM. The different captured pictures are as shown in Fig. 6.

SEM morphological examination gives two different structures of NS and MS. Figs. 6a–c reveal the presence of

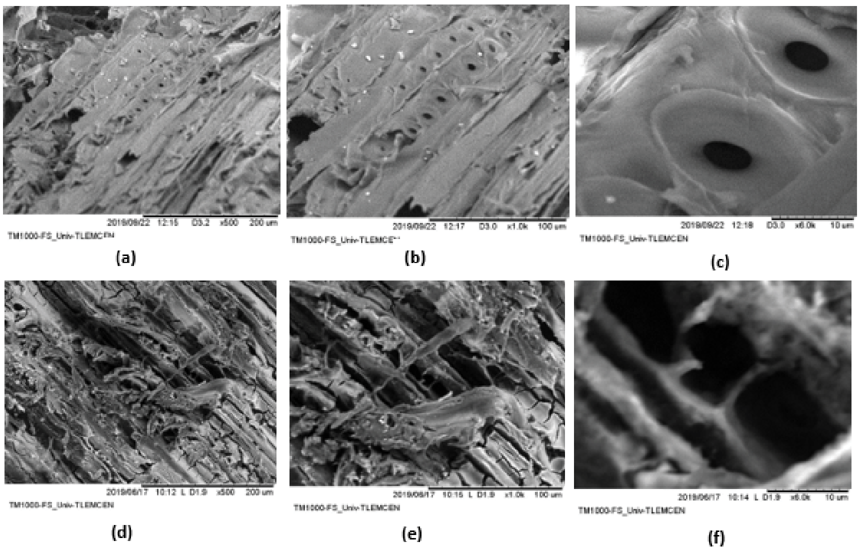

Fig. 6. SEM morphology of (a–c) NS and (d–f) MS.

pores in the external surface. The enlarged picture is shown in Fig. 6f reveals an increase in pore volume caused by the removal of hemicelluloses due to the modification of sawdust [44].

3.1.4. Brunauer–Emmett–Teller

Figs. 7 and 8 correspond to isotherm of NS and MS respectively according to the BET method.

As seen, both isotherms represented in Figs. 7 and 8 can be classified in type IV BET isotherm which is characteristic for mesoporous compounds.

The specific surface area of NS is about 175.19 $m^2 g^{-1}$ with a total mesopore volume of 0.15 $cm^3 g^{-1}$. After modification of sawdust, the surface area and total volume of pores increase to 296.08 $m^2 g^{-1}$ and 0.27 $cm^3 g^{-1}$, respectively.

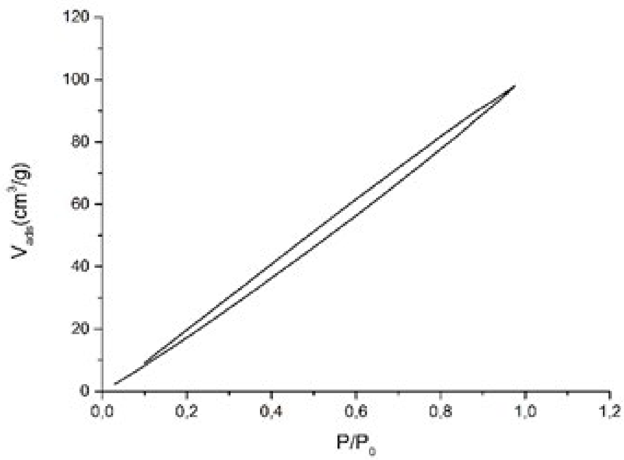

Fig. 7. Isotherm of NS according to BET.

3.1.5. pH_{zpc}

The pH_{zpc} of sawdust before and after treatment is shown in Fig. 9.

The value decreases from 4.2 for NS to 2.2 for MS which means that the number of acidic groups increased after modification of sawdust which is good for adsorption of an ionic organic compound.

3.2. Effect of contact time

The evolution of adsorption of acid green by different sawdust is represented in Fig. 10.

As shown, the retention plots of the dye by the two materials have the same forms characterized by higher adsorption from the first min of acid green 4G/sawdust contact after which there is no considerable change in adsorption capacity until the equilibrium is reached. The strong adsorption during the first minutes is probably due to the greater number of vacant sites available on adsorbents surface then after a certain time [45]. The rate of dye removal on different adsorbents was evaluated after 2 h of stirring and

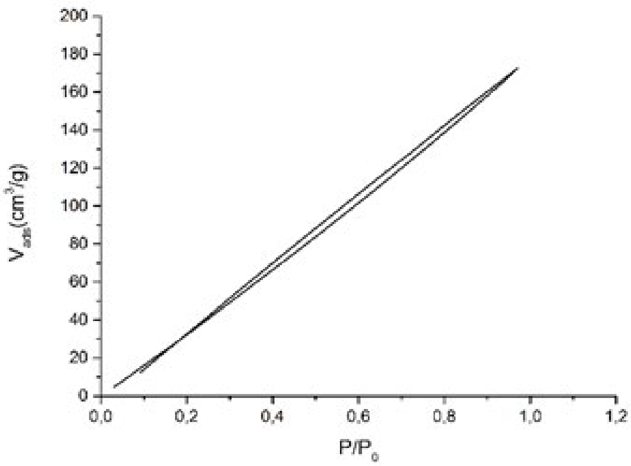

Fig. 8. Isotherm of MS according to BET.

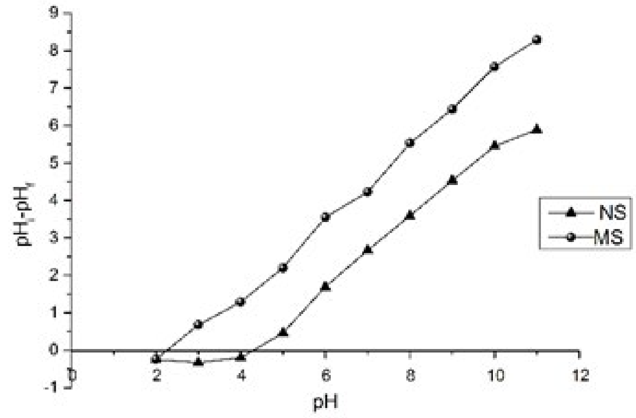

Fig. 9. pH_{zpc} of NS and MS.

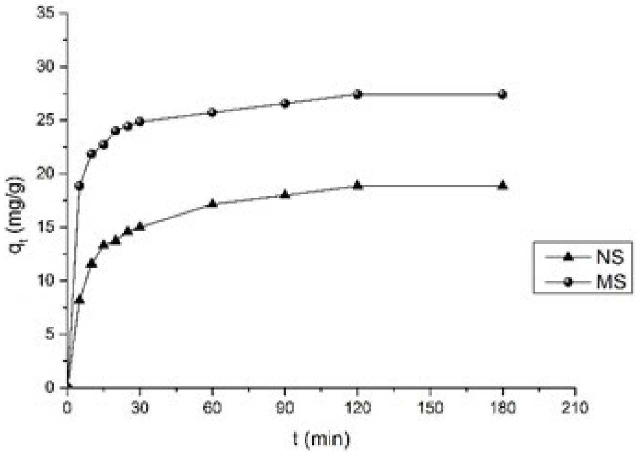

Fig. 10. Effect of contact time.

the adsorption capacity obtained was equal to 18.86 mg g^{-1} for NS and 27.43 mg g^{-1} for MS.

To evaluate the effectiveness of the two materials, a comparison with industrial activated carbon (AC) (Supelco) was made with the same conditions. The obtained results are regrouped in Table 1.

The results show that the MS gives better results than NS and AC with a higher percentage of purification.

In order to determine the model that could properly describe the adsorption kinetics of green dye onto natural and modified sawdust, adsorption rates constants for the first, pseudo-second, and second-order models were determined graphically as shown in Figs. 11–13, respectively.

The rate constants were calculated from the obtained lines and the results are represented in Tables 2–4.

The obtained results show that the value of the correlation coefficient for the pair dye/NS and dye/MS is higher in the pseudo-second-order (R^2 = 0.99). According to the experimental values listed in Table 5, adsorption capacities are in very close agreement with that calculated with the pseudo-second-order. Both parameters indicate that the kinetics of adsorption of acid green 4G by NS and MS obey to the pseudo-second-order model.

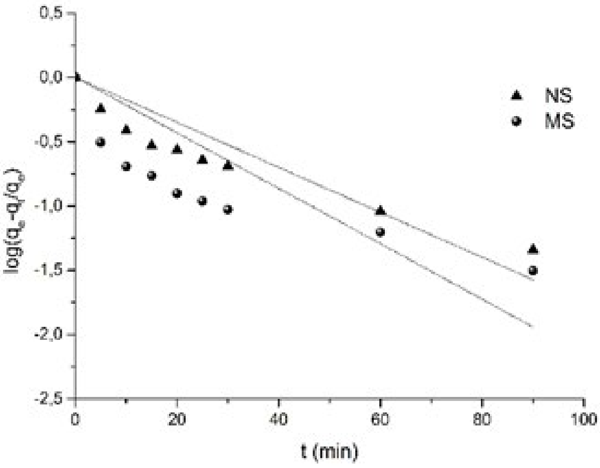

Fig. 11. First-rate model.

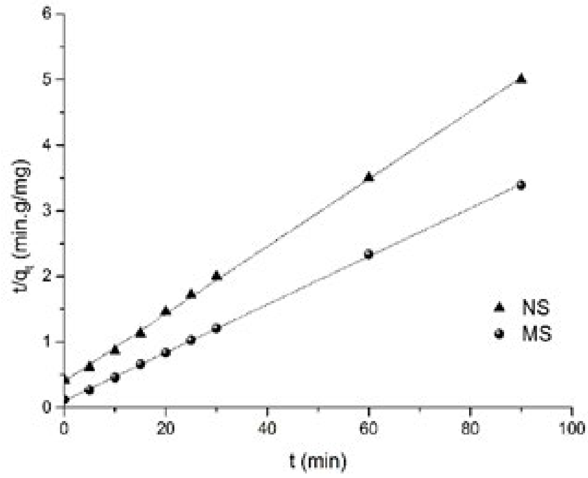

Fig. 12. Pseudo-second-rate model.

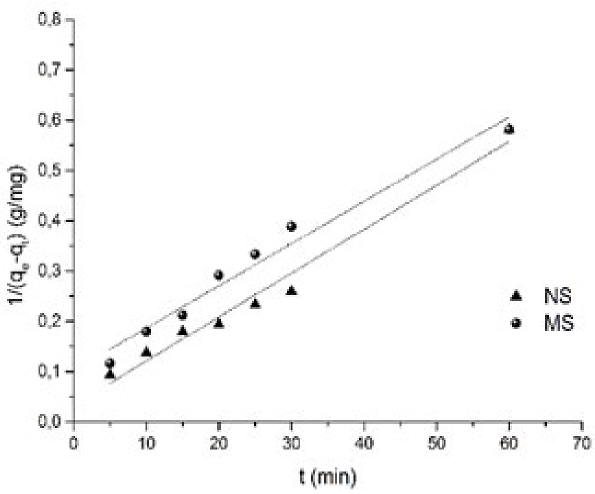

Fig. 13. Second-rate model.

Table 1
Results of adsorption kinetics of NS, MS and AC

Adsorbent	q_e (mg g^{-1})	% adsorption	C_f (mg L^{-1})	t_{eq} (min)
NS	18.86	62.86	37.14	120
MS	27.43	91.43	8.57	120
AC	24.28	75.72	24.28	120

Table 2
Rate constants of first-order model

Adsorbent	K_v (min^{-1})	R^2
NS	0.040	0.75
MS	0.049	0.96

Table 3
Rate constants of the pseudo-second-order model

Adsorbent	q_e (mg g^{-1})	K_v (min^{-1} mg g^{-1})	R^2
NS	18.79	4.71×10^{-3}	0.99
MS	26.88	9.12×10^{-3}	0.99

Table 4
Rate constants of the second-order model

Adsorbent	q_e (mg g^{-1})	K (min^{-1} g mg^{-1})	R^2
NS	29.67	8.7×10^{-3}	0.97
MS	9.78	8.4×10^{-3}	0.97

Table 5
Experimental and calculated adsorbed amount dye

	q_e (mg g^{-1})		
Adsorbent	Experimental	Calculated from the pseudo-second-order model	Calculated from the second-order model
NS	18.86	18.79	29.67
MS	27.43	26.88	9.78

3.3. Adsorption equilibrium

It is essential to describe how pollutants will interact with adsorbent and gives an approach to the adsorption capacity of adsorbent using adsorption isotherm [46].

Isotherms of adsorption for dye onto sawdust are represented in Fig. 14 by plotting q_e vs. C_e.

The adsorption isotherm indicates a linear distribution for dye/MS. Both adsorption plots show the increase of adsorption with increasing in initial solutions concentration.

Freundlich and Langmuir's models were used to describe the adsorption isotherms of acid green onto natural and modified sawdust by plotting C_e/q_e vs. C_e for Langmuir model and lnq_e vs. lnC_e for Freundlich model which are represented in Figs. 15 and 16, respectively.

All the calculated data are regrouped in Table 6.

According to the correlation coefficients, it can be stated that the Langmuir model did not fit the data well contrary to the Freundlich isotherm model that provides a better fit for both dye/NS and dye/MS. The high values for $n > 1$ indicate the favorable nature of adsorption [47] and supply a rational description of the experimental data. According to the results obtained, the Freundlich model is more adequate for representing the adsorption isotherms of acid green 4G by natural and modified sawdust that was proved by a higher R^2 value.

3.4. Thermodynamics parameters

The determination of thermodynamics parameters of adsorption of acid green on sawdust in the temperature

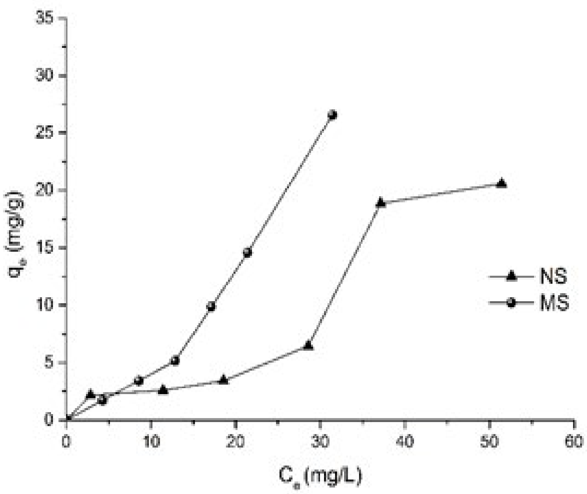

Fig. 14. Adsorption isotherms.

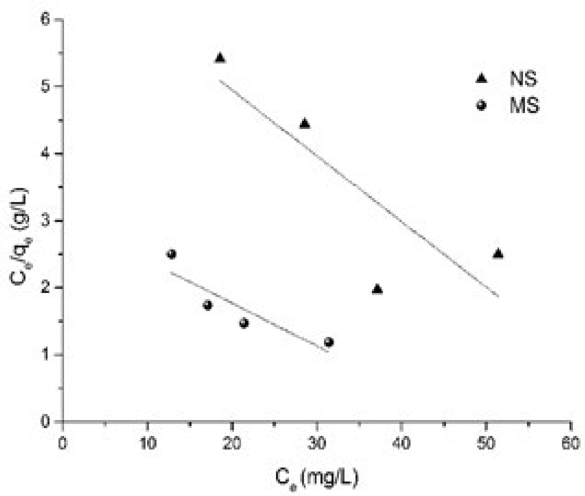

Fig. 15. Langmuir model plots.

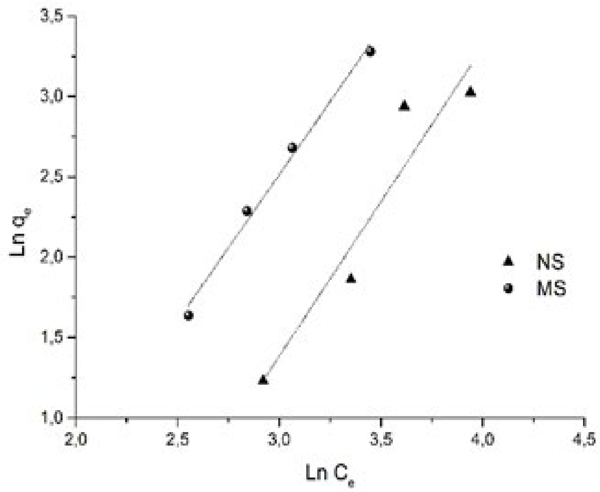

Fig. 16. Freundlich model plots.

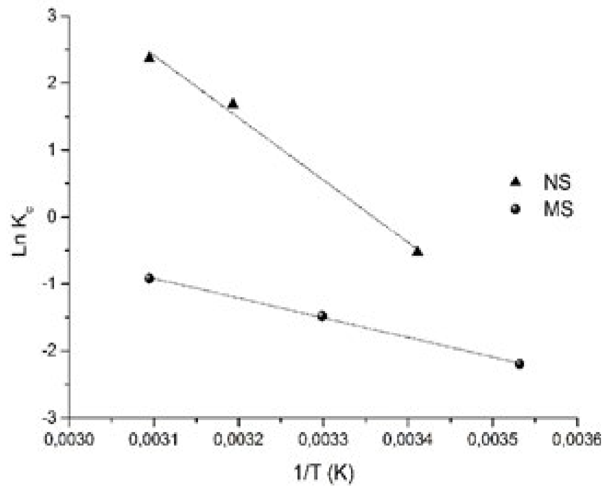

Fig. 17. Thermodynamic parameters.

Table 6
Langmuir and Freundlich parameters

	Langmuir parameters			Freundlich parameters		
Adsorbent	q_m (mg g^{-1})	b (L g^{-1})	R^2	K	n	R^2
NS	–10.21	–0.014	0.71	0.013	1.92	0.91
MS	–15.65	–0.021	0.80	0.053	1.82	0.99

range of 10°C to 50°C were obtained graphically from the slope and intercept by plotting lnK_c vs. (1/T) shown in Fig. 17.

Tables 7 and 8 listed all those thermodynamics parameters.

The positive values of ΔH suggest that the process of adsorption of green dye by the sawdust is endothermic. The absolute value of enthalpy for the couple dye/NS is greater than 40 kJ mol^{-1} that indicates that it is chemical adsorption but for the couple dye/MS this value is less than 40 kJ mol^{-1} which means that the adsorption is physical [48]. The positive values of entropy show that during the adsorption process the randomness increases at the solid/liquid interface [49]. The free enthalpy values decrease from 3.77 to –6.61 kJ mol^{-1} for dye/NS and from 5.14 to 2.43 for dye/MS in the temperature range of 283.15 to 323.15 K that indicates that the spontaneous nature of adsorption is inversely proportional to the temperature which means that the driving forces become less and hence result in lesser adsorption capacity at higher temperatures [50].

Table 7
Thermodynamic parameters (ΔH and ΔS)

Adsorbent	ΔH (kJ mol^{-1})	ΔS (kJ mol^{-1} K^{-1})	R^2
NS	77.32	0.26	0.99
MS	24.39	0.07	0.99

Table 8
Free enthalpy

	Adsorbent	Temperature (°C)				
		10	20	30	40	50
ΔG (kJ mol^{-1})	NS	3.77	1.18	–1.41	–4.01	–6.61
	MS	5.14	4.46	3.78	3.10	2.43

4. Conclusion

The results obtained in the present investigation show the effectiveness of natural and modified sawdust in removing acid green 4G dye by adsorption. The experiments reveal that this textile dye is better adsorbed by modified sawdust which proves its effectiveness by better adsorption compared to industrial AC. The equilibrium setting times for both adsorption experiments was found to be 120 min of contact under constant stirring. The extraction kinetics of adsorbate by both adsorbents obey to the pseudo-second-order rate model. The adsorption isotherms are better described by the Freundlich model than Langmuir in the range of the concentration studied. The thermodynamic parameters show that the adsorption of acid green 4G by natural and modified sawdust is exothermic.

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