Desalination and Water Treatment
www.deswater.com
doi: 10.5004/dwt.2021.26494

209 (2021) 367–378
January

Enhance the adsorption behavior of methylene blue from wastewater by using $ZnCl_2$ modified neem (*Azadirachta indica*) leaves powder

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Received 10 June 2020; Accepted 23 August 2020

ABSTRACT

Many unwanted by-products containing several hazardous dyes are found in wastewater produced from the manufacturing units, such as printing, leather, paper, textiles, cosmetics, etc. Especial attention is given to overcome this problem, using different treatment methods and adsorbents. From the tree leaves of the neem (*Azadirachta indica*), an adsorbent was developed, characterized, and used for Methylene Blue (MB) elimination from wastewater. The area of the adsorbent surface, pore volume, and average pore width were found to be 58.6 m^2/g, 0.106 cm^3/g, and 13.8 Å, respectively. The adsorption behavior of MB using the modified powder of neem leaves was investigated under different experimental conditions. The adsorption capacities for MB by chemical modified adsorbent were found to be 370, 434, and 476 mg/g at 298, 313, and 328 K, respectively. The kinetic and isotherm calculated data obeyed the models of second-order kinetic and Langmuir, correspondingly. Constants of thermodynamics like $\Delta S°$, $\Delta H°$, and $\Delta G°$ were estimated. The positive values of $\Delta H°$ recommend that this adsorption is an endothermic process. The values of $\Delta G°$ are negative at the temperatures under investigation (298–328 K), indicating that this adsorption is a spontaneous process.

Keywords: Methylene Blue; Neem *(Azadirachta indica)* leaves; Thermodynamic parameters; Isotherm parameters; Kinetic parameter

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1. Introduction

Manufacturing units like leather, textiles, cosmetology, paper, printing, plastics, etc., used different synthetic dyes to color their manufactured goods. Certainly, many synthetic dyes are brighter in color, low cost, rapid, and simple to apply to fiber. Dyes utilized in the textile-producing units are identified as: (a) anionic (direct, and acidic), (b) cationic (basic), and (c) non-ionic (dispersed dyes). Cationic or basic dyes are used very often in the textile industry, because of their reactivity, desirable distinctive of brightness in color, easily soluble in water, low-priced, and simple to use on fabrics. In general, in the production of dyes, the chemicals used are poisonous, carcinogenic, explosive as well. About 15%–20% of the total manufactured of dyes are vanished and are released as wastewater discharged in the dyeing process. Among the different chemical pollutants of the aquatic ecosystem, dyes are a major one. Methylene Blue (MB) as a basic dye commonly used in various industrial products, like in the production paint, wool and cloths dyeing, in microbiology, surgical goods, diagnostics, and as a sensor for organic hazardous wastes photo-oxidation. The industrial effluents having MB dye have always been undesirable in water, resulting in major environmental problems that require to remove before its discharge [1–3].

International environmental standards are becoming firmer, to apply a suitable treatment process before the disposal of industrial wastewaters. Different physical and chemical methods, additional to adsorption, such as coagulation, froth floatation, chemical oxidation, oxidation or ozonation, membrane separation, and solvent extraction processes have been exercised by several workers for the elimination of organics as well as inorganic pollutants from wastewater; however, these procedures are valuable and economical, only when the comparatively high amounts of the contaminants are found. For elimination of MB from the wastewater, coal, fly ash and red mud were applied as effective filters for the ultrafiltration of this dye from aqueous solutions. Nevertheless, adsorption is a better option as compared to other means of MB treatment from the wastewater in terms of the expense, efficiency, simplicity of its usage, along with uncomplicatedness of design and function. The selection of a proper adsorbent plays an essential role because adsorption is a physiochemical phenomenon where adsorbate molecules are bonded to the surface of an adsorbent by intermolecular forces. The natures of force depend upon the ionic nature of adsorbate and the ionic nature and site activity of adsorbent surface [4–8]. For the removal of MB, activated carbon is generally utilized, However, their comparatively high investment and difficulty in regeneration, limit its relevance. Therefore, neem leaves powder (potentially economical alternative adsorbent) has been applied to adsorb MB as reviewed by Bhattacharyya and Sharma [9]. The adsorption capacity of MB was found to be 8.76 mg/g [9], 60.60 mg/g [10], and 353 mg/g [11] by using the unmodified neem leaf powder. Consequently, adsorbents should be improved in their surface activity and so, increases their adsorption capability. For this, the MB adsorption capacity by H_2SO_4 modified neem (*Azadirachta indica*) leaves powder was investigate and found to be 402 mg/g [11]. Therefore, the effect of the other activation agents such as $ZnCl_2$, NaOH, H_3PO_4, and HCl on the adsorption efficiency of neem leaves powder toward MB must be examined. It was found that the $ZnCl_2$ modified neem (*A. indica*) leaves powder has superior adsorption performance toward potassium permanganate [12]. Despite, the higher adsorption efficiency of $ZnCl_2$ modified neem leaves powder toward $KMnO_4$, no attempt carried out till now to investigate the impact of $ZnCl_2$ modification on the adsorption capacity of neem leaves powder toward MB. Therefore. in the current study, aims have been caused to look at the elimination of MB from the industrial effluents by applied the $ZnCl_2$ modified neem leaves powder because it is eco-friendly, easily available, low-cost, unharmed, and simple-to-disposes.

2. Materials and methodology

2.1. Reagents, materials, and apparatuses

In the present experimental work, raw materials/chemicals such as; neem (*A. indica*) leaves, distilled water, ethyl alcohol, $ZnCl_2$, HCl, NaOH, and $NaNO_3$ have been used. The instruments were such as; Soxhlet apparatus, rotary vacuum evaporator, fully automated multi-point BET analyzer (with updated Quanta chrome & Nova Win 2 of Ver 2. 2), the spectroscopy of Fourier transform infrared (FT-IR) (Perkin–Elmer-2000 FT-IR), scanning electron microscopy (SEM) (LEO 1455 VP, England) and Jenway Model 6800 UV-VIS spectrophotometer were also used.

2.2. Adsorbent preparation

The leaves of the neem tree *(A. indica)* were obtained from Tabuk City, Saudi Arabia, and washed perfectly (1–3 times) by distilled water, after that dried at 25°C. The required quantity of dried neem leaves was converted into the powder from using an electrical blender (of power 1,200 W). By using the Soxhlet apparatus within the range of boiling point (b.p.) = 60°C–80°C up to 10 h, quantitatively 150 g of powder (neem i.e., *A. indica*) was extracted with 400 mL of ethyl alcohol. After this, the extracted powder was separated and dried perfectly by evaporation and was safely reserved for others' usage. Finally, the residues of neem, that is, *A. indica* was washed by distilled water properly (by repeating, 1–3 times) and dried in an electric oven up to 24 h at a constant temperature of 120°C. For modification and improvement, the adsorption efficiency of this sample, an 80 g of the dried powder was soaked with 300 mL of 30% w/w activation agent ($ZnCl_2$) and refluxed for 5 h. The Buchner funnel was used for the separation of the mixture components. The solid part was washed with a solution of 0.1 M HCl as well as with the distilled water, this procedure was repeated several times. The obtained modified adsorbents were dried at a constant temperature of 120°C for 15 h by using an electric oven and were kept in the desiccator for the experimental works.

2.3. Adsorbent characterization

The surface functional groups and morphology features of the neem leaves powder before and after modification were identified using the FT-IR and SEM techniques, respectively. The area of the modified adsorbent surface, pore volume, and average pore width were defined by nitrogen gas adsorption–desorption at 77.35 K and 758.58 mm Hg by means of BET surface analyzer. Additionally, the pH_{ZPC} of the modified adsorbent was established by the applied method of Theydan and Ahmed [13].

2.4. Adsorption studies

2.4.1. Kinetic studies of adsorption

In this section, fixed amounts (25 mg) of the neem leaves powder modified by $ZnCl_2$ were added to 20 mL of 60, 100, 150, and 200 mg/L MB solutions in four amber bottles; then these four bottles were sealed and put in the closed shaker incubator for 5 min at 25°C and 180 rpm. Filtration was used to isolate the mixture components from each other. The spectrophotometer of UV-VIS was then applied to measure the final concentration of MB in the suspensions at 616 nm. Then the same process was carried out at various time periods (15, 30, 45, 60, 120, 180, and 240 min). The adsorption amount for each time period (q_t) was computed using Eq. (1):

$$q_t = \frac{V}{m}\left(C_i - C_t\right) \tag{1}$$

where V is the volume of MB solution (L), m is the mass of modified powder of neem leaves (g), C_i is the MB prepared concentration (mg/L), and C_t is the concentration of MB at time t. The amounts of MB adsorbed were plotted against time to examine the impact of shaking time on the adsorption process. Furthermore, the adsorption rate and parameters of kinetics were evaluated by applying the linear forms of the three kinetic models summarized in Table 1 [14–16].

2.4.2. Impact of temperature and adsorbate concentration

Twenty milliliters from each of the 12 prepared MB solutions that have different concentrations (ranged between 10 and 800 mg/L) were put in amber bottles (30 mL) have 25 mg of the solid adsorbent. The sealed bottles were shaken in a shaker incubator for 22 h at 180 rpm, 25°C, and initial pH. The MB solutions were isolated from the solid adsorbent by filtration; and then the remaining concentration of each solution was quantified by spectrophotometer of UV-VIS at 616 nm. The same experiment was also carried out at 40°C and 55°C. The quantities of MB consumed (q_e) by the powder of the modified adsorbent at equilibrium were assessed by applying Eq. (2):

$$q_e = \frac{V}{m}\left(C_i - C_e\right) \tag{2}$$

where C_i and C_e (mg/L) are the MB concentration before and after equilibrium, respectively, m and V are the mass of adsorbent (in gram), and the volume of the adsorbate solution (in liter) correspondingly.

The relationship between q_e and C_i was plotted at three different temperatures to investigate the impact of temperature and adsorbate primary concentration on the adsorption process.

2.4.3. Adsorption isotherms parameters

Adsorption of 20 mL of seven MB solutions by using concentration ranged from 100 to 800 mg/L was carried out at three various temperatures to determine the isotherm constants by using the three linear forms models represented in Table 2.

2.4.4. Adsorption thermodynamic

Similar procedures carried out in the sections of 2.4.2 (Impact of temperature and adsorbate concentration) and 2.4.3 (Adsorption isotherms parameters) were repeated for adsorption of 60, 150, and 400 mg/L by the same fixed amount of neem leaves powder modified by $ZnCl_2$ at the different temperatures. Then the obtained results were analyzed by Van't Hoff and Gibbs Eqs. (3) and (4) [17] to calculate the thermodynamic parameters ($\Delta H°$, $\Delta S°$, and $\Delta G°$) of this adsorption:

$$\ln\left(\frac{q_e}{C_e}\right) = \frac{\Delta H°}{RT} + \frac{\Delta S°}{R} \tag{3}$$

Table 1
Models of kinetic in their linear forms

Kinetic model name	Equation	Reference
Pseudo-first-order kinetic model	$\log\left(q_e - q_t\right) = \log(q_e) - K_1 \frac{t}{2.303}$	[14]
Pseudo-first-order kinetic model	$\frac{t}{q_t} = \frac{1}{K_2\left(q_e\right)^2} + \frac{t}{q_e}$	[15]
Intra-particle diffusion kinetic model	$q_t = K_{\text{dif}}\sqrt{t} + C$	[16]

q_e (mg/g): adsorption quantity at equilibrium, q_t (mg/g): adsorption amount any time t (min), K_1 (1/min), K_2 (g/mg min), and K_{dif} (mg/g min)$^{1/2}$: rate constants of the pseudo-first-order, pseudo-second-order, and intra-particle diffusion kinetic models, respectively, and C: another kinetic constant.

Table 2
Models of isotherms in their linear forms

Isotherm model name	Equation	Reference
Langmuir isotherm model	$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}}$	[27]
Freundlich isotherm model	$\ln(q_e) = \ln(K_F) + \frac{1}{n}\ln(C_e)$	[28]
Temkin isotherm model	$q_e = B_1 \ln(K_T) + B_1 \ln(C_e)$	[29]
Dimensionless factor (R_L) equation	$R_L = \frac{1}{1 + K_L C_i}$	

$q_{\max}$ (mg/g): maximum adsorption capacity related to the amount of MB required for making a complete monolayer on the surface of the modified neem powder, C_i: MB initial concentration, K_L, K_F and K_T: constants of Langmuir, Freundlich, and Temkin, in that order. Also, n and B_1: constants related to the intensity of the adsorption and adsorption heat, respectively.

$$\Delta G° = \Delta H° - T\Delta S° \quad (4)$$

where $\Delta H°$, $\Delta S°$, and $\Delta G°$ are the changes in standard enthalpy, entropy, and free energy, correspondingly. T is the temperature of the solution (K) and R is gas constant (8.314 J/K mol).

2.4.5. Impact of pH

The same procedure mentioned in section 2.4.2 (Impact of temperature and adsorbate concentration) was repeated for adsorption of 400 mg/L of MB solution with several pH values ranged from 2 to 12 at 25°C, to investigate the impact of solution pH on this adsorption. The pH of the MB solutions was adjusted using HCl (0.1 M) or NaOH (0.1 M) solutions.

3. Results and discussion

3.1. Modified neem leaves powder characteristics

The SEM snaps of the neem leaves powder before and after modification are demonstrated in Figs. 1 and 2, on that order. It can be observed from these two images that the powder of neem leaves after modification contains numerous uneven macropores and big cavities on the surface of the adsorbent higher than of the modified neem leaves powder before modification. The existence of macropores and big cavities on the adsorbent surface has a significant impact on the adsorption efficiency. Because the diffusion of the MB cations across the adsorbent's micropores can be obtained only through of these large cavities and numerous uneven macropores at the surface of the adsorbent.

Fig. 3 exhibited FT-IR spectra of the neem leaves powder before and after modification by $ZnCl_2$. Fig. 3 shows four important absorption peaks in the spectrum related to unmodified sample. Three of these peaks are in the regions of 1,050; 2,920; and 3,330 cm^{-1}, which are related to CO–O–CO, –CH–, and primary amide stretching vibration, accordingly. The other peak in the region of 1,610 cm^{-1} is associated with $-NH_2$ deformation. Whereas, FT-IR spectrum (Fig. 3) of the modified adsorbent demonstrates five absorption bands in the regions of 1,040; 1,162; 1,720; 2,928; and 3,327 cm^{-1}. These peaks are related to CO–O–CO, C=O ester, C=O carboxylic acid, –CH– and primary amide stretching vibration, respectively. Moreover, the spectrum of the modified

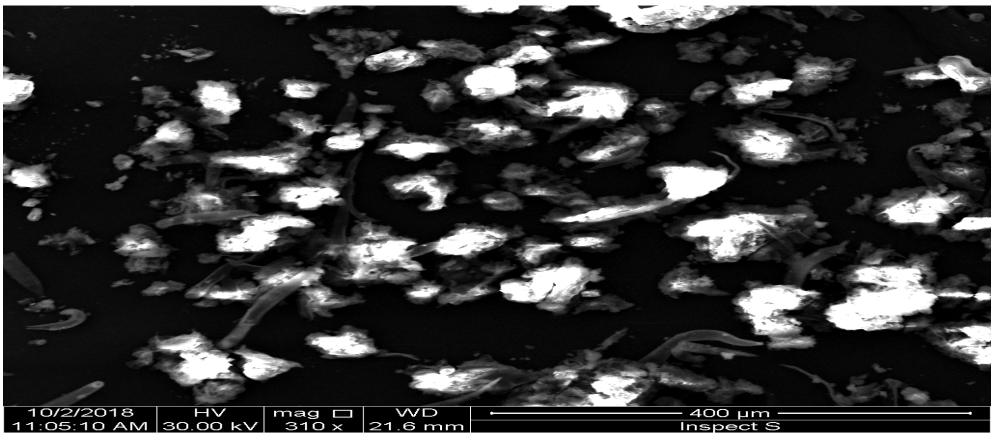

Fig. 1. SEM image of the adsorbent before modification.

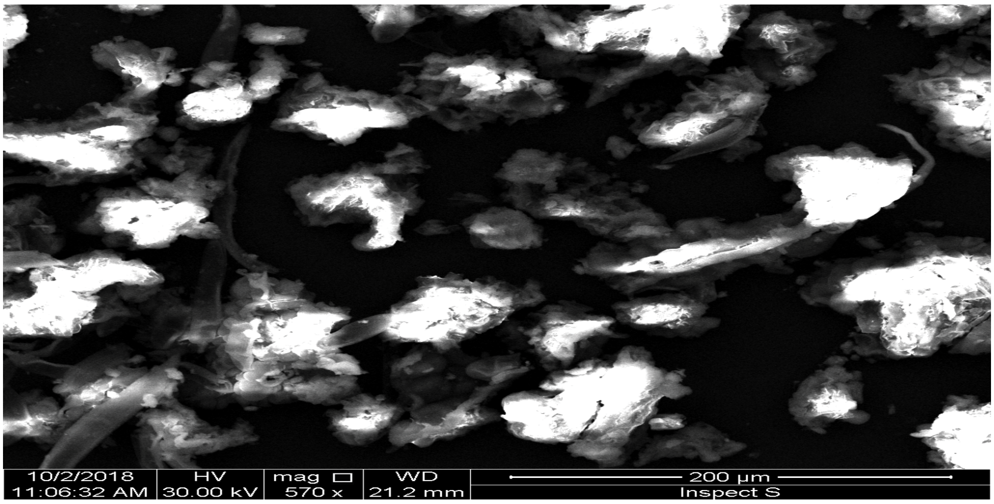

Fig. 2. SEM image of the adsorbent after modification.

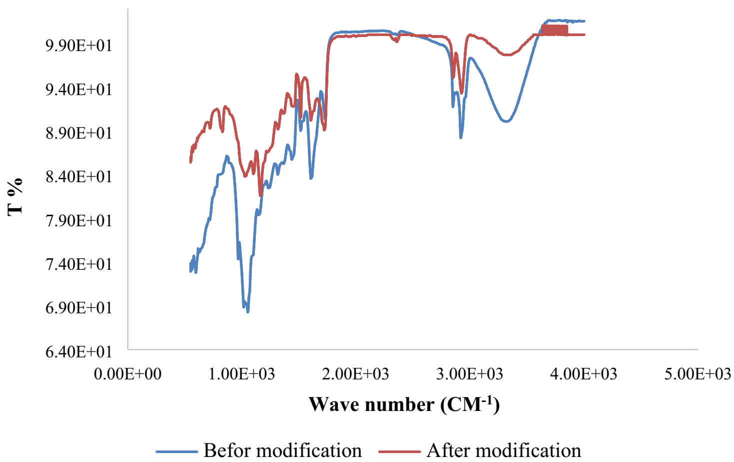

Fig. 3. Spectrum of FT-IR for the powder of neem leaves before and after modification.

adsorbent has another band at 1,600 cm^{-1} related to deformation of $-NH_2$. The results of FT-IR indicate that functional groups of C=O ester and C=O carboxylic acid have been produced due to the modification process. The absorption bands regions of 1,050; 1,610; 2,920; and 3,330 cm^{-1} were also shifted after modification to the regions of 1,040; 1,600; 2,928; and 3,327 cm^{-1}, respectively. Moreover, modification of this sample by $ZnCl_2$ caused intensity changes in the absorption peaks.

The relationship between ($pH_i - pH_f$) and pH_i is shown in Fig. 4. It is indicated that the pH_{ZPC} for the adsorbent is 6.8. The area of the adsorbent surface, pore volume, and average pore width were found to be 58.6 m^2/g, 0.106 cm^3/g, and 13.8 Å, correspondingly.

3.2. Equilibrium studies

3.2.1. Impact of pH

The relationship between pH and q_e (mg/g) was graphed as indicated in Fig. 5. The amount of MB adsorbed is gradually and acutely raised as pH of solution enhanced in the ranges of 1.6–6.8 and 6.8–12, correspondingly, as shown in Fig. 5. As MB is dissolved in water, it will be converted to its cationic form, if the solution pH > pK_a of MB (3.14). Moreover, the adsorbent surface charge will be positive and negative when the solution pH is less and higher than the adsorbent pH_{ZPC} (6.8), respectively [18]. Therefore, as the solution pH raised from its initial pH to pH_{ZPC}, the repulsion force between MB cations and the positive charges of the adsorbent surface is gradually reduced. This implies the minor rise in the adsorption of the dye on the surface of adsorbents. Whereas the surge in the quantities of adsorption, when pH > pH_{ZPC} is owing to the attraction forces among cations of MB and the negatively charged adsorbent surface. Fig. 5 also shows that this adsorption is maximized at pH = 12. Similar findings were stated previously for the MB adsorption by activated carbon prepared from jute fiber [19].

3.2.2. Effect of agitation time

Fig. 6 illustrates the adsorption uptakes of 20 mL MB solution at different concentrations (from 60 to 200 mg/L)

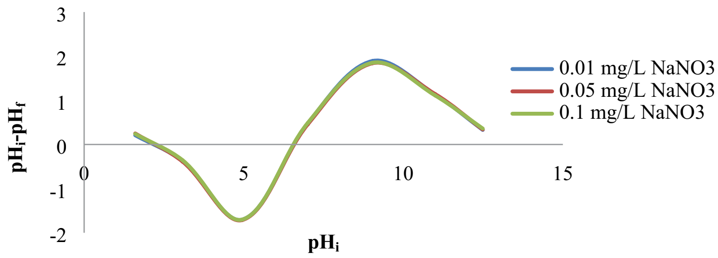

Fig. 4. pH_{ZPC} of the chemical modified powder of neem leaves.

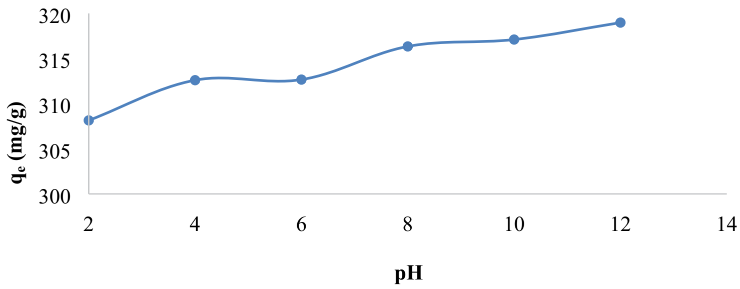

Fig. 5. pH solution impact on the adsorption performance of MB by $ZnCl_2$ modified powder of neem leaves.

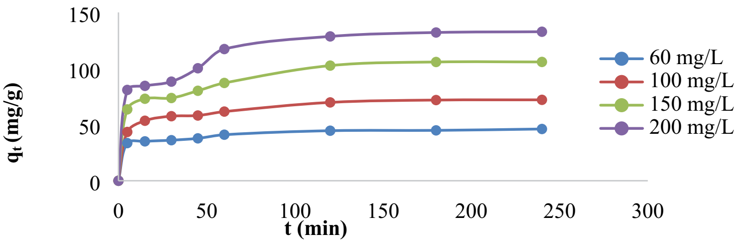

Fig. 6. Contact time impact on the MB adsorption by $ZnCl_2$ modified powder of neem leaves.

vs the adsorption contact periods (5, 15, 30, 45, 60, 120, 180, 240 min) for the modified neem leaves powder. It was found that the adsorption ability of the adsorbent improved by elevating agitation time and reached a plateau at 60 min for each concentration. This increase in the adsorption capacity is due to the development of a significant percentage (%) of cavities, elevated average pore diameter, and a strong attractive force between adsorbate and adsorbent. Similar works are reported earlier for the MB adsorption by graphene [20].

3.2.3. Kinetic studies

To study the mechanism of MB adsorption by the adsorbent, the parameters of kinetics at four different concentrations (60, 100, 150, and 200 mg/L) were examined by the kinetic models of first-order, second-order, and diffusion of intra-particle, which are briefed in Table 1. The relationship among the values of $\log(q_e - q_t)$ against t (first-order), t/q_t against t (second-order), and q_t against $t^{1/2}$ (intra-particle-diffusion) have been graphed (Figs. 7–9, accordingly). The constants of these three models were estimated from intercepts and slopes of their plots and listed in Tables 3a and 3b. From Table 3a, it can be observed that the correlation coefficient (R^2) values of the second-order are bigger than that of the first-order and the values of q_e that calculated by using the pseudo-second-order are roughly the same to experimental q_e. These results designated that the second-order model was useful in describing the adsorption of MB from dilute solution by the modified powder of neem leaves. This confirms that valence forces by exchange or sharing of electrons are involved in the adsorption process, which indicates that this adsorption is chemisorption. Related results were found by Liu et al. [20] and Lim et al. [21]. The significant values of C represented the boundary layer thickness, illustrated in (Table 3b) stated that external diffusion has a key function in the adsorption mechanism [22]. Additionally, it can be noticed in Fig. 9 that the plotted graphs are not linear in all-time range and parted into two linear sections. This establishes that this adsorption has been taken place in multiple steps. Related outcomes were observed for methyl orange adsorption by the modified waste of coffee [23].

3.2.4. Effect of temperature and adsorbate initial concentration

Temperature is a significant factor to explain any physio-chemical process, as the increasing temperature can

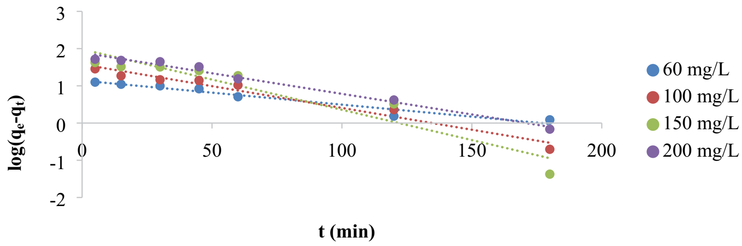

Fig. 7. Pseudo-first-order kinetic model for MB adsorption by $ZnCl_2$ modified powder of neem leaves.

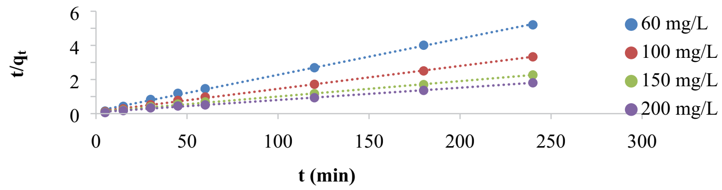

Fig. 8. Pseudo-second-order kinetic model for MB adsorption by $ZnCl_2$ modified powder neem leaves.

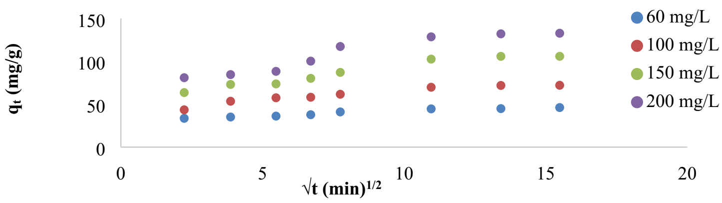

Fig. 9. Intra-particle diffusion model for MB adsorption by $ZnCl_2$ modified powder of neem leaves.

Table 3A
Parameters of the pseudo-first and pseudo-second-order for MB adsorption by $ZnCl_2$ modified powder of neem leaves

C_i (mg/L)	$q_{e,exp}$(mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model			
		$q_{e,cal}$ (mg/g)	K_1 (1/h)	R^2	$q_{e,cal}$ (mg/g)	K_2 (g/mg h)	R^2	Rate
60	46.116	13.775	0.0147	0.948	46.948	0.0031	0.999	0.143531
100	72.088	37.705	0.0269	0.965	74.627	0.0016	0.999	0.121157
150	105.804	95.830	0.0375	0.909	111.111	0.0008	0.997	0.088583
200	132.758	77.857	0.0256	0.984	138.889	0.0006	0.997	0.088670

affect the adsorbents adsorption potential. If increasing temperature caused an increase in the adsorption capacity, this designates that this process is an endothermic, as the temperature increases the kinetic energy of the dye's particles. While if the opposite happened by increasing the temperature (caused decreasing in the capacity of the adsorption process) this means that the process is exothermic. This might be related to the decreasing in the forces of adsorption among the adsorbate and the adsorbent active centers. The experimental adsorption amounts at equilibrium (q_e (mg/g)) were graphed vs. the initial concentration of MB solutions (C_i (mg/L)), at 25°C, 40°C, and 55°C (Fig. 10). Fig. 10 demonstrates that the temperature has a positive effect on the adsorption of MB by the modified powder of neem leaves, indicating the endothermic process. Moreover, MB uptake is also increased with increasing the adsorbate initial concentration and then nearly getting stable at 600 mg/L (Fig. 10) as the adsorbent surface bears no further vacant active sites to reconcile novel MB molecules [24,25]. A related study for MB endothermic adsorption on commercial activated carbon was also reported by Al-Aoh et al. [26].

Table 3B
Parameter values of the intra-particle-diffusion kinetic model for MB adsorption by $ZnCl_2$ modified powder of neem leaves

C_i (mg/L)	Region I			Region II		
	K_{dif} (mg/h$^{1/2}$g)	C	R^2	K_{dif} (mg/h$^{1/2}$g)	C	R^2
60	1.2370	30.278	0.906	0.3311	40.798	0.862
100	3.0209	39.112	0.905	0.5152	64.414	0.851
150	3.8571	55.443	0.935	0.7393	94.921	0.800
200	6.1198	62.399	0.828	0.9338	118.730	0.901

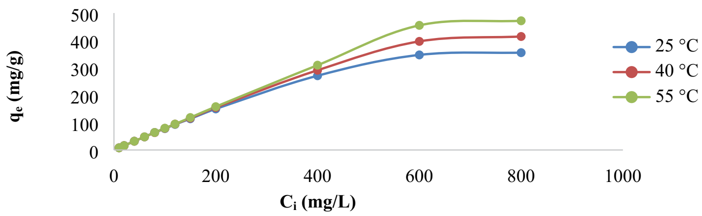

Fig. 10. Temperature and initial concentration impact on MB adsorption capacity by $ZnCl_2$ modified powder of neem leaves.

3.2.5. Isotherms constants

The correlation between the experimental adsorption results with three isotherm models (Langmuir, Freundlich, and Temkin) [27–29] was undertaken in this research, to realize the adsorption process and determine the isotherm constants for this adsorption at 25°C, 40°C, and 55°C. The plots of Langmuir, Freundlich, and Temkin equations are illustrated in Figs. 11–13, in that order. The three models' parameters values and the R^2 values of each model were reported in Table 4. Parameters of Langmuir, Freundlich, and Temkin were obtained from the slopes and intercepts. The values of the Langmuir isotherm model factor (R_L) were calculated by using the fourth equation in Table 2 and recorded in Table 4. The calculated $1/n$ and R_L values (Table 4) are in the ranges of (0.323–0.346) and (0.0181–0.0063), correspondingly. These results support the favorability of the experimental conditions applied in the present study [30]. Based on the isotherm's parameters and the R^2 values, it can be suggested that the data of these experiments are well evaluated by the model of Langmuir over the other two models (Freundlich, Temkin). This established the homogeneity of the adsorbent surface and the formation of the monolayer of adsorbate [17]. Works reported by the earlier workers for Methylene blue adsorption by coconut husk fiber based-activated carbon [31], Casuarina equisetifolia needle [32] and bread fruit (*Artocarpus altilis*) peel and core [33], also confirmed that the Langmuir isotherm is

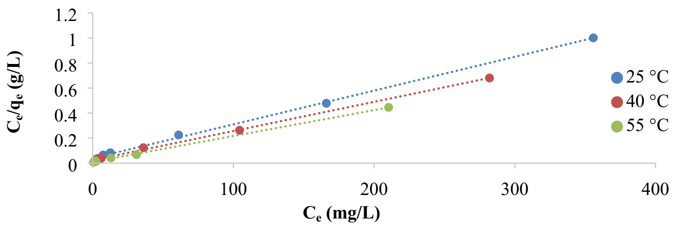

Fig. 11. Isotherm model of Langmuir for MB adsorption by $ZnCl_2$ modified powder of neem leaves.

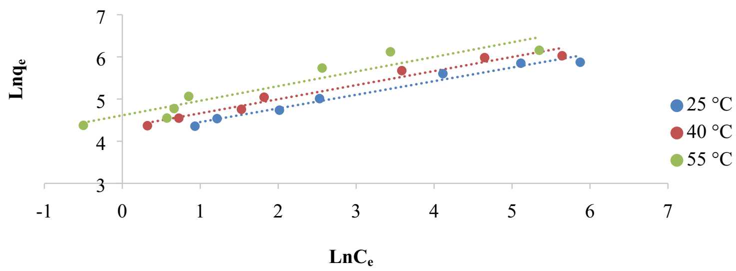

Fig. 12. Isotherm model of Freundlich for MB adsorption by $ZnCl_2$ modified powder of neem leaves.

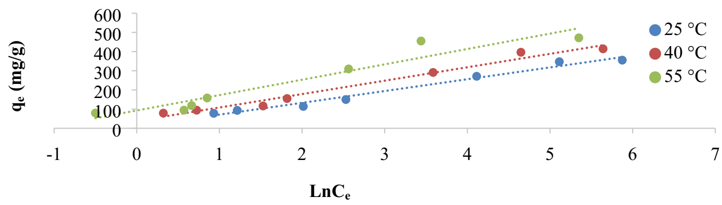

Fig. 13. Isotherm model of Temkin isotherm for MB adsorption by $ZnCl_2$ modified powder of neem leaves.

Table 4
Parameters values of isotherms and factors of separation (R_L) for MB adsorption by $ZnCl_2$ modified powder of neem leaves

Temperature	Langmuir isotherm				Freundlich isotherm				Temkin isotherm		
	q_{max} (mg/g)	K_L (L/mg)	R_L	R^2	K_F (mg/g) (L/mg)$^{1/n}$	1/n	n	R^2	K_T (L/mg)	B_1	R^2
25°C	370.37	0.0677	0.0181	0.999	62.271	0.323	3.094	0.975	1.1696	61.550	0.981
40°C	434.78	0.0950	0.0130	0.999	75.876	0.334	2.998	0.968	1.7280	69.993	0.978
55°C	476.19	0.1981	0.0063	0.999	100.836	0.346	2.888	0.894	3.1827	80.174	0.922

excellently well. The adsorption capacities of applied adsorbent received in this study are 370.37, 434.78, and 476.19 mg/g for temperatures of 25°C, 40°C, and 55°C, respectively (Table 4). These significant adsorption capacities attract the world's attention to use the modified powder of neem leaves in water and wastewaters' purifications. This also verifies the temperature has a positive effect and confirms that the adsorption resulted in this research is endothermic.

3.2.6. Thermodynamic studies

The quantitative determined values of adsorption at equilibrium (q_e (mg/g)) and the correlation with temperature (T (°C)) using different concentrations of MB solutions (60, 150, and 400 mg/L) are shown in Fig. 14. This correlation indicated that the adsorption quantities at equilibrium are constantly increased by elevating the temperature, which proves that this adsorption is an endothermic process. This result is in agreement with the collected outcomes in the previous parts of section 3.2.4 (Effect of temperature and adsorbate initial concentration) and 3.2.5 (Isotherms constants).

The plotted graphs of ln(q_e/C_e) and 1/T (Fig. 15) have been applied for calculating thermodynamic parameters $\Delta S°$ (from intercepts) and $\Delta H°$ (from slops), accordingly. These two thermodynamic parameters values were used for computing the values of $\Delta G°$ by applied Eq. (4) at the experimental temperatures (25°C–55°C). The constants of thermodynamic are recorded in Table 5.

The values of $\Delta H°$ and $\Delta S°$ (Table 5) are positive, which recommends that this adsorption is an endothermic [34] and there is an increase in the randomness at the interface of adsorbent surface and liquid adsorbate [35].

Moreover, values of $\Delta S°$ are increased from 0.1277 to 0.1637 KJ/mol as the adsorbate concentration raised from 60 to 400 mg/L. this proves that the taken initial concentration of adsorbate has an important impact on the performance of adsorption. The negative values of $\Delta G°$ recorded in Table 5 indicated that this adsorption is a spontaneous process. It also noticed that the temperature raising from 25°C to 55°C elevates the $\Delta G°$ negative values. This verifies the increasing temperature raises the spontaneity degree for this adsorption. Related results being observed for adsorption of other dyes using polymer nanocomposite [36].

4. Comparison study

Recently a lot of low-cost materials were used for adsorption of MB from aqueous solutions. $ZnCl_2$ modified powder of neem leaves that utilized in this study as MB adsorbent showed very acceptable results comparing with other unmodified and modified bio-adsorbents that used

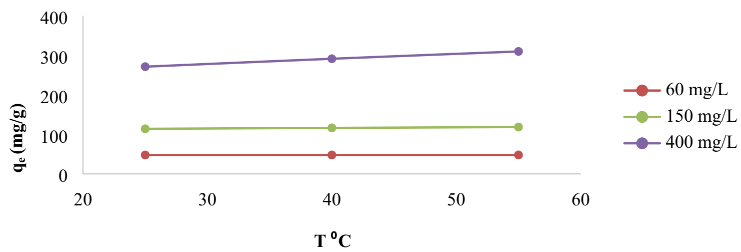

Fig. 14. Solution temperature impact on the MB adsorption by $ZnCl_2$ modified powder of neem leaves at different initial concentrations.

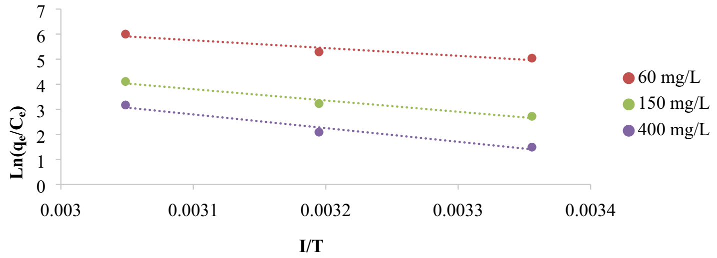

Fig. 15. Plots of $\ln(q_e/C_e)$ against $1/T$ for MB adsorption by $ZnCl_2$ modified powder of neem leaves.

Table 5
Thermodynamic parameters for MB adsorption by $ZnCl_2$ modified powder of neem leaves

Initial concentration (mg/L)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (KJ/mol)	$\Delta G°$ (KJ/mol)			R^2
			298 K	313 K	328 K	
60	25.7526	0.1277	–12.293	–14.208	–16.123	0.913
150	37.4479	0.1477	–6.569	–8.784	–11.000	0.967
400	45.3121	0.1637	–3.469	–5.924	–8.380	0.963

Table 6
Adsorbents applied for the elimination of MB from aqueous solutions

Adsorbents	q_{max} (mg/g)		Sources
$ZnCl_2$ neem leaves powder	370.37	25°C	Present study
	434.78	40°C	
	476.19	55°C	
Unmodified neem leaf powder	8.76		[9]
Neem (*Azadirachta indica*) leaves	60.60		[10]
Unmodified neem leaf powder	353.00		[11]
H_2SO_4 modified leaves powder	402.00		[11]
Artocarpus odoratissimus skin	184.6		[21]
Orange peel-modified phosphoric acid	307.63		[37]
Teak tree bark	333.00		[38]
Sun flower seed husk	045.25		[39]
Hazelnut shell	076.90		[40]
Artocarpus camansi Blanco (Breadnut) core	369.00		[41]
Peat of Brunei Darussalam	143.90		[42]
Breadnut peel	409.00		[43]
Dragon fruit skin	640.00		[44]

for water purification from MB day. Table 6 presents the adsorption capacities for MB adsorption by $ZnCl_2$ modified powder of neem leaves and the other bio-adsorbents that used recently toward MB removal. Following results from Table 6, $ZnCl_2$ modified powder of neem leaves prepared and used in this work have very satisfactory maximum adsorption capacity against the MB purification. This attracts the world's attention to use modified powder of neem leaves in water and wastewater purifications.

5. Conclusions

Neem *(A. indica)* leaves were modified by $ZnCl_2$ and used as an adsorbent for MB removal from wastewater. The physical features like the area of the adsorbent surface, pore volume, and average pore width were determined as 58.6 m²/g, 0.106 cm³/g, and 13.8 Å, respectively. The experimental kinetic data were evaluated by kinetic models of first-order, second-order, and diffusion of intra-particle. The calculated data obeyed the second-order model, which concluded the chemisorption. Langmuir model showed a higher correlation with the experimental adsorption data compared to Freundlich and Temkin models. This established that this adsorption is a monolayer and the modified neem leaves powder has homogeneous adsorption usable sites. The temperature has a positive impact on the adsorption process. Thermodynamic parameters like $\Delta S°$, $\Delta H°$, and $\Delta G°$ were studied. The positive values of $\Delta H°$ recommend that this adsorption is an endothermic process. Adsorption of MB was found to be spontaneous at the temperature range used in this study, as indicated by the negative values of $\Delta G°$. The higher adsorption performance observed from this work attracts the world's attention to use modified powder of neem leaves in water and wastewaters treatment.

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