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A potentially low-cost adsorbent for methylene blue removal from synthetic wastewater

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ABSTRACT

Wastewaters produced from the industries contain various unwanted by-products and a large number of hazardous dyes. Several treatment processes are used for the processing of effluent waters containing dyes. Adsorbent prepared from leaves of *Nitraria retusa* was used for removing methylene blue from wastewater. The area of the adsorbent surface, the volume of the pore, the width of the average pore and pH_{ZPC} were determined as 57.8 $m^2\ g^{-1}$, 0.092 $cm^3\ g^{-1}$, 13.8 Å and 6.2, respectively. The results of kinetic data analysis confirm a chemisorption process, and the second-order model is favorable. Adsorption isotherm constants were investigated by Langmuir, Freundlich, and Temkin models. The obtained data expressed well by the model of Langmuir. The adsorption capacities of 571.43, 763.36, and 813.01 mg g^{-1} were got at 303, 323 and 333 K, correspondingly. The positive values of $\Delta H°$ and $\Delta G°$ recommend that this adsorption is an endothermic and un-spontaneous process.

Keywords: Methylene blue; *Nitraria retusa* leaves; Synthetic wastewater; Thermodynamic parameters; Kinetic parameters; Isotherm parameters

1. Introduction

Among the various chemical contaminants of waters, dyes are a key one. Methylene blue (MB) is used as a sensitizer inorganic contaminants photo-oxidation. It is also used in the production of paint and dyeing, in surgery, diagnostics, and microbiology. The waste polluted by MB dye has always been undesirable in water, resulting in major environmental problems, which considered a pollutant that needs to be treated before discharge [1,2]. It was earlier reported that exposure to those industries wastewater

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causes dyspnea, convulsions, tachycardia, methemoglobinemia, nausea, etc. [3,4].

Thus, several methods like solvent extraction, electrocoagulation, coagulation, oxidation by using UV/H_2O_2, and flotation process were applied previously for the elimination of MB from wastes of the industries related to the usage and productions [5–10]. Currently, these methods do not meet more attention due to their complicated or complex design, high cost, and low efficiency. It was stated before that the photodegradation processes using catalysts like ZnO, NiO, and TiO_2 are significant and operative methods for the elimination of MB from aqueous solutions [11–14]. The main shortcomings of these techniques are associated with their final outputs, which may have more adverse impacts than that of the original pollutant itself. It was earlier reported by the different workers that adsorption with activated carbon forms like (granular, powder, and fiber) is the most effective means for the uptake of MB from aqueous solutions, due to its efficiency, flexibility, inexpensive, and ability to eliminate all kinds of contamination present at any concentration [3,15]. Currently, the use of activated carbon in the adsorption technique becomes limited due to the higher cost of the raw materials and the methods used for its production [16,17].

Therefore, these days the residues of agricultural and industrial activities have been used as adsorbents for wastewater purifications, due to their cheapness and large availability. For example, the materials such as agricultural residue of walnut shells, sorghum stalks, Crofton weed stalks, rice hulls, mango leaf powder, agar, spent mushroom substrates, calcined corn cob powder, natural clays, and neem leaves powder have been used to remove MB from aqueous solutions [18–26].

A plant of *Nitraria retusa* is available in huge amounts in shallow sand hummocks of saline grounds of the coastal areas. This plant can grow in salty water and can also in low water availability conditions. The red fruits of this plant are used for the production of tasty and refreshing juice that is used for a long time ago in some Arab Countries as medicine. Additionally, these red fruits were also used for the extraction of medicine that can be used against nephrotoxicity and hepatotoxicity. Moreover, polysaccharides, polyphenol, and flavonoids, and alkaloids, are extracted from the leaves of this plant and used as antioxidant materials [27–34].

Despite, the valuable and vital applications of the fruit and leaves of the *Nitraria retusa* plant, no attempt has been carried out till now to examine the efficiency of this plant as an adsorbent for MB. Hence, the aim of this research is to determine parameters of kinetic, isotherm, and thermodynamic for adsorption of MB by chemically modified *Nitraria retusa* leaves powder. The impact of experimental conditions on the adsorption capacity and rate will also be considered in this work.

2. Materials and methods

2.1. Apparatuses, materials and reagents

Nitraria retusa leaves used in this research as a cheap adsorbent were collected from the area of Haql, the City of Tabuk, Saudi Arabia. Chemicals like HCl, NaOH, $ZnCl_2$, $NaNO_3$ and ethyl alcohol were obtained from Sigma-Aldrich (USA) and used in this work. Tools and instruments such as rotary vacuum evaporator, Soxhlet apparatus, surface analyzer of Brunauer–Emmett–Teller (BET) (Quantachrome NovaWin2 Ver.2.2, UK), spectroscopy of Fourier-transform infrared (FT-IR) (Perkin Elmer-2000, USA), microscopy of scanning electron (SEM) (LEO 1455 VP, England) and Jenway Model 6800 UV-Vis spectrophotometer (UK) were also applied.

2.2. Adsorbent preparation

The leaves of *Nitraria retusa* were washed several times with distilled water. After that, the clean leaves were dried at room temperature for one week and milled to powder using a blender. A 100 g of this powder was added to a Soxhlet containing 250 mL of ethyl alcohol and then the mixture was boiled for 10 h. The filtration was carried out and the residual solid was put in a 500 mL glass beaker containing 300 mL of 20% w/w of $ZnCl_2$. Then the mixture was boiled until all the amount of water almost evaporated. Finally, the powder was also washed by distilled water many times and dried overnight at 115°C using an oven. The final product was kept in desiccators for adsorption processes.

2.3. Adsorbent characterization

The surface functional groups and morphology characteristics of the prepared adsorbent were recognized by FT-IR and SEM respectively. The porosity and the area of the prepared adsorbent surface were measured by adsorption and desorption of the N_2 gas at the required experimental conditions (758.58 mm Hg, 77.35 K) using BET surface analyzer. Additionally, three solutions of 0.1, 0.01 and 0.001 M $NaNO_3$ with volume of 500 mL were prepared, series of six solutions with volume of 50 mL and different pH values ranged from 2 to 12 were prepared for each one of these three solutions by adding 0.1 M of HCl or NaOH solutions. Each one of these solutions were mixed with 0.1 g of *Nitraria retusa* leaves powder in 100 mL glass bottles. These bottles were put in shaker incubators and shaken at room temperature (30°C) and 160 rpm for 4 h. After filtration the final pH (pH_f) for each solution was measured by pH meter and then the differences between the initial and final pH values (pH_i–pH_f) were calculated and plotted against pH_i to determine the pH_{ZPC} value of the adsorbent used in this research. This method was also followed by Al-Aoh et al. [35].

2.4. Adsorption studies

2.4.1. Impact of pH

In this work, drops of 0.1 M of NaOH or HCl were added to MB solutions (80 mg L^{-1}) to prepare six solutions that differ from each other in the pH values (1–11). 10 mL of each one of the 6 prepared solutions was mixed with 0.01 g of adsorbent in amber bottles (30 mL). The sealed bottles were put in a shaker incubator and shaken at 160 rpm and 30°C for 4 h. The mixtures components were separated

by filtration. Subsequently, the MB residual concentration was measured using a spectrophotometer of UV-Vis at the wavelength of 618 nm. Eq. (1) was used for calculating the equilibrium adsorption capacities (q_e).

$$q_e = \frac{V}{m}\left(C_0 - C_e\right) \tag{1}$$

where C_0 and C_e (mg L^{-1}) are MB concentrations before and after equilibrium, respectively. V and m are the adsorbate solution volume (L) and adsorbent mass (in gram), correspondingly.

2.4.2. Initial dye concentration and temperature impacts

Adsorption of 10 mL of thirteen/different initial concentrations (10–1,000 mg L^{-1}) of MB solutions by 0.01 g of the prepared adsorbent was carried out at three various temperatures (30°C, 50°C, and 60°C), original pH solution (pH = 6) and 160 rpm for 4 h to investigate the impacts of adsorbate initial concentration and temperature on this sorption. The same procedures mentioned in section 2.4.1 (impact of pH) for the separation of MB solutions and measuring the remaining concentration of each solution were repeated. The amounts of MB consumed by the prepared adsorbent at equilibrium were evaluated by applying Eq. (1). The obtained values of q_e were plotted against C_0 to examine the temperature and adsorbate initial concentration impacts.

2.4.3. Effect of contact time and kinetic studies of adsorption

The required volume (10 mL) of 40, 60, and 100 mg L^{-1} MB solutions were mixed in amber bottles with 0.01 g of the *Nitraria retusa* leaves powder. The bottles were agitated at the original pH solution of MB (pH = 6), room temperature and 160 rpm in a shaker incubator for 5, 10, 20, 40, 60, 80, 100, 120, and 180 min. These experiments were conducted in the dark environment to avoid the photodegradation of MB and to make sure that the decrease in this adsorbate concentration was only occurred by adsorption. Then the adsorption capacity of this adsorbent towards this dye will be determined in an accuracy. Therefore, amber bottles (30 mL) and shaker incubators have been used in this work. After each period time, the filtration was performed to separate the mixture components (adsorbent, adsorbate) and the remaining concentrations of MB in the filtrates were measured as stated in section 2.4.1 (impact of pH). Then Eq. (2) was applied to compute the adsorption amount at each time (q_t):

$$q_t = \frac{V}{m}\left(C_0 - C_t\right) \tag{2}$$

where V: volume of MB solution (L), m: the mass of *Nitraria retusa* leaves powder (g), C_0: MB initial concentration (mg L^{-1}) and C_t: concentration of MB at time t.

The quantities of MB adsorbed were plotted against time to investigate the impact of experimental time on the performance of this adsorption. The kinetic models summarized in Table 1 were applied to evaluate the adsorption rate and parameters of kinetics.

2.4.4. Isotherm studies

The experimental data got in section 2.4.3 (effect of contact time and kinetic studies of adsorption) were also analyzed by the models of isotherms represented in Table 2 along with Eq. (3) to determine the isotherm parameters of this sorption.

$$R_L = \frac{1}{1 + K_L C_0} \tag{3}$$

where C_0 is the highest initial concentration of MB solution (1,000 mg L^{-1}), K_L is the Langmuir constant.

Table 1
Linear equations of kinetics

Kinetic model name	Equation
Pseudo-first-order kinetic model	$\log\left(q_e - q_t\right) = \log\left(q_e\right) - K_1 \frac{1}{2.303}$
Pseudo-second-order kinetic model	$\frac{t}{q_t} = \frac{1}{K_2\left(q_e\right)^2} + \frac{t}{q_e}$
Intraparticle diffusion kinetic model	$q_t = K_{\text{dif}}\sqrt{t} + C$

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

Table 2
Linear equations of isotherms

Isotherm model name	Equation
Langmuir isotherm model	$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}}$
Freundlich isotherm model	$\ln\left(q_e\right) = \ln\left(K_F\right) + \frac{1}{n}\ln\left(C_e\right)$
Temkin isotherm model	$q_e = B_1 \ln\left(K_T\right) + B_1 \ln\left(C_e\right)$

$q_{\max}$ (mg g^{-1}): maximum adsorption capacity related to the amount of methylene blue required for making a complete monolayer on the surface of *Nitraria retusa* leaves powder; 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.

2.4.5. Isotherm studies

The experiments performed in section 2.4.3 (effect of contact time and kinetic studies of adsorption) were repeated for sorption of 80, 120, and 200 mg L^{-1} MB solutions by the adsorbent used in this research. Then Eqs. (4) and (5) were used for calculating the parameters associated with this sorption thermodynamic ($\Delta H°$ kJ mol^{-1}, $\Delta S°$ kJ mol^{-1} K^{-1}, and $\Delta G°$ kJ mol^{-1}).

$$\ln\left(q_e / C_e\right) = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R} \quad (4)$$

$$\Delta G° = \Delta H° - T\Delta S° \quad (5)$$

where T and R related to adsorption temperature and universal gas constant (8.314 J K^{-1} mol^{-1}), in that order $\Delta G°$ (kJ mol^{-1}), $\Delta S°$ (kJ mol^{-1} K^{-1}) and $\Delta H°$ (kJ mol^{-1}) are the changes in standard free energy, entropy, and enthalpy, correspondingly.

3. Results and discussion

3.1. Characteristics of the modified Nitraria retusa leaves powder

The image of SEM for the modified powder of *Nitraria retusa* leaves is shown in Fig. 1. It can be observed from this figure that the adsorbent surface contains irregular large holes and uneven macropores. The presence of the big holes and macropores on the surface of any adsorbent enact a significant role in the effectiveness of adsorption. Because the cations of MB can diffuse across the micropores of the adsorbent only during these big holes and macropores. BET surface analyzer results indicate that the adsorbent has 57.8 m^2 g^{-1} surface area, 0.092 cm^3 g^{-1} pore volume, and average pore width of 13.8 Å. A plot pH_i–pH_f vs. pH_i (Fig. 2) demonstrates that the value of pH_i–pH_f be zero only when the pH of the solution is 6.2 in the case of the three concentrations of sodium nitrate solution. This means that the pH_{ZPC} of adsorbent used in this research is 6.2 similar was reported by Al-Aoh et al. [35] for commercial activated carbon. The spectrum of FT-IR (Fig. 3) demonstrates that there are four absorption bands at 3,313; 2,922; 1,611 and 1,047 cm^{-1}. These bands are associated with –OH alcohols or phenols, $–CH_2–$, distortion of $–NH_2$ and S=O stretching vibration, respectively. The type of functional groups on the adsorbent's surface has a significant effect on the adsorption efficiency. Because in some cases, chemisorption takes place between the adsorbate particles and the adsorbent functional groups.

3.2. Results of adsorption

3.2.1. Effect of pH

Fig. 4 demonstrates the relationship between solution pH and q_e. It can be seen from this figure, that the q_e of this adsorption is higher at solution pH = 1. Then q_e is decreased and increased as pH raised from 1 to 7 and from 7 to 11, correspondingly. As MB is dissolved in water, it is converted into anions and cations in the solution when the pH of the solution is higher than MB pK_a (pK_a of MB

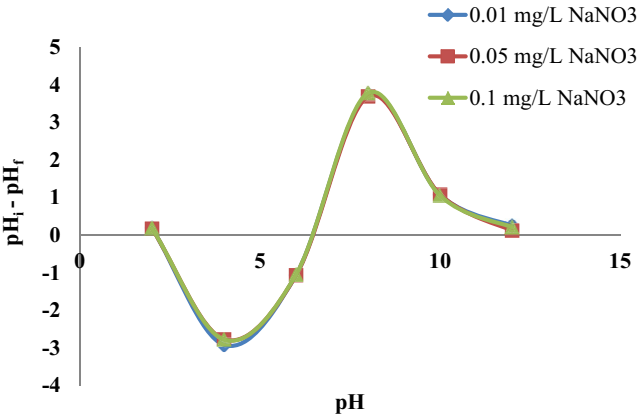

Fig. 2. pH_{ZPC} for the $ZnCl_2$ modified leaves powder of *Nitraria retusa*.

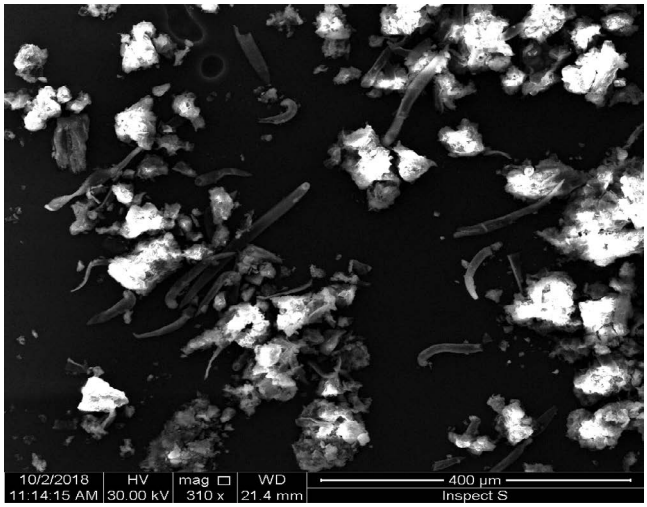

Fig. 1. Scanning electron microscopy for the $ZnCl_2$ modified leaves powder of *Nitraria retusa*.

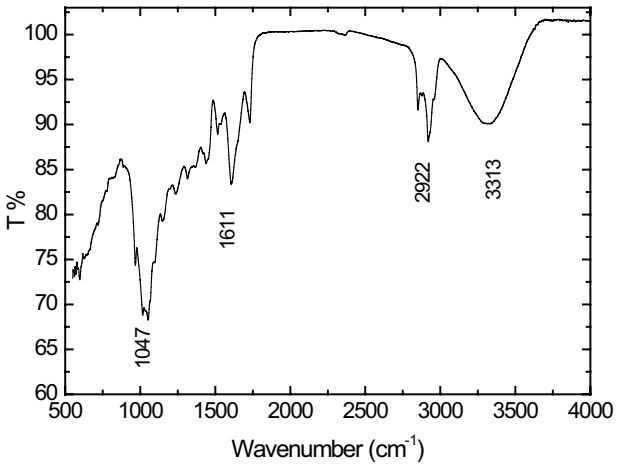

Fig. 3. Fourier-transform infrared spectroscopy for the $ZnCl_2$ modified leaves powder of *Nitraria retusa*.

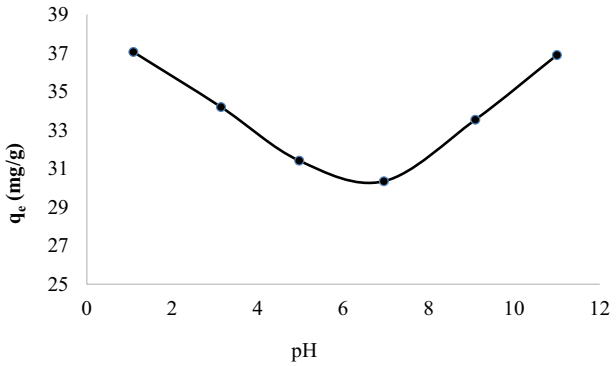

Fig. 4. Solution pH impact on methylene blue adsorption by $ZnCl_2$ modified leaves powder of *Nitraria retusa* at room temperature.

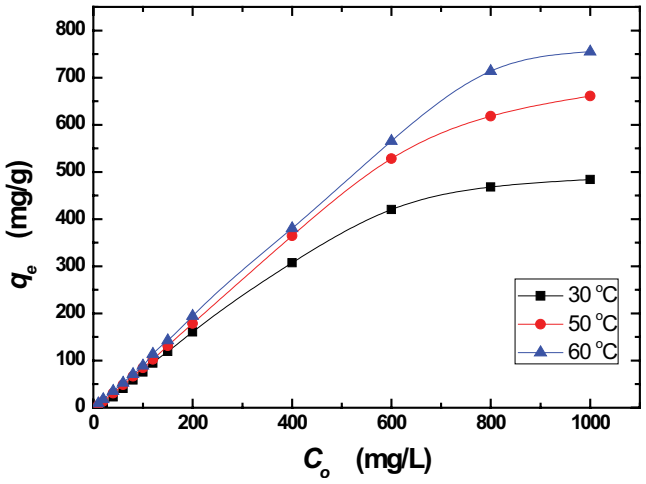

Fig. 5. Temperature and adsorbate initial concentration impacts on methylene blue adsorption by $ZnCl_2$ modified leaves powder of *Nitraria retusa* at solution pH of 6.

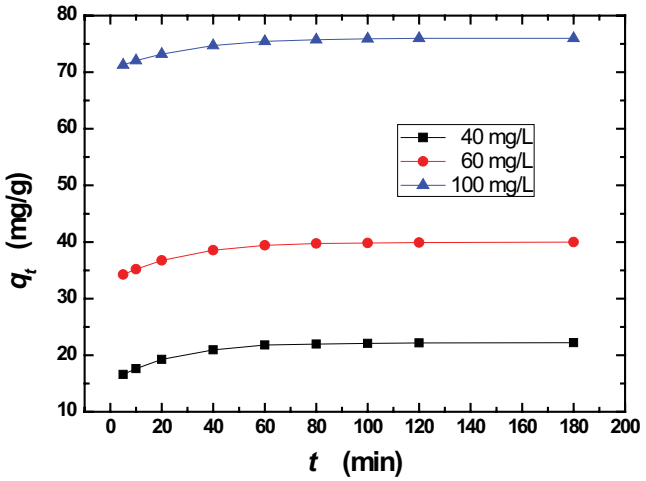

Fig. 6. Impact of the contact time on methylene blue adsorption by $ZnCl_2$ modified leaves powder of *Nitraria retusa* at room temperature and solution pH of 6.

is 3.8). Moreover, MB cations adsorption is largely affected by the density and type of charges that exist on the adsorbent surface [3]. The type and density of the adsorbent surface charge are also affected by solution pH [3]. Since, the charge will be negative and positive when the solution pH is higher and less than pH_{ZPC}, respectively. Therefore, the adsorption capacity obtained at pH 1 (pH < MB pK_a) is higher because MB adsorbed on the adsorbent surface in its molecular form. The decreasing of q_e when the solution pH increased from 1 to almost 7 (pH_{ZPC} = 6.2) is due to the repulsion forces between cations of MB and the positively charged adsorbents surface because MB molecules start to convert to its ionic form when pH increased in the range of (1–7). Whereas, the positive effect observed when pH increased over 7 is a result of the electrostatic attractions among MB cations and the negatively charged adsorbent surface. Related outcomes were reported for MB adsorption by jute fiber carbon [4]. Despite the highest adsorption capacity in this work was obtained at pH 1 and 11, all the other adsorption experiments were performed at the original pH of MB solution (pH = 6) at which the capacity of sorption was very low as can be seen in Fig. 4.

3.2.2. Temperature and adsorbate initial concentration effects

The amounts of MB adsorbed at equilibrium (q_e) by the experimental adsorbent were plotted vs. the MB primary concentration (C_0) at 30°C, 50°C, and 60°C and pH solution of 6 (Fig. 5). It can be seen from Fig. 6, that the temperature has a positive impact on this adsorption. Because increasing the temperature will increase the mobility of MB cations and reduce the solution viscosity. It can also be noticed from the plotted graphs that the quantities of MB uptake are increased with increasing MB initial concentration. Moreover, any change in the quantities of MB uptake can be observed at a concentration of 800 mg L^{-1}. This is because there are no vacant active sites on the adsorbent surface to receive extra MB cations if the MB concentration elevated up 800 mg L^{-1} [36,37]. The results of this part indicate that MB primary concentrations of 800 mg L^{-1} and 60°C is the ideal condition for MB adsorption by this adsorbent. Related results were viewed for MB adsorption by commercial activated carbon [35].

3.2.3. Contact time effect

The relationship between q_t (mg g^{-1}) and contact time (t) for adsorption of 10 mL MB solution at concentrations of 40, 60, and 100 mg L^{-1} is demonstrated in Fig. 6. It is established that the capacity of adsorption increases as agitation time is increased and reached to a straight line at 60 min for the taken experimental concentrations (room temperature, original pH solution, and 160 rpm). This increase in the capacity of adsorption was due to most of the adsorption active sites were empty before 60 min but after this time, the majority of adsorption sites were filled by MB molecules. Therefore, the adsorption capacities are constant after 60 min which indicates that the equilibrium contact

time in this work is 60 min. Similar works are reported prior to the MB adsorption by graphene [38].

3.2.4. Kinetic constants

Kinetic models summarized in Table 1 have been applied to analyze the experimental data for MB adsorption at concentrations of 40, 60, and 100 mg L^{-1} on a fixed amount of the adsorbent at room temperature, 160 rpm and the original MB pH solution of 6. The linear forms of first-order, second-order, and intraparticle diffusion kinetic models have been plotted as demonstrated in Figs. 7a–c, correspondingly. The values of slopes and intercepts of these plots have been used to estimate the parameters related to these three kinetic models (Table 3). As shown in Fig. 7a, a linear relationship was only noticed for the second-order model. In comparison, between experimental q_e values and the values of q_e calculated by both first and second-order models (Table 3), it will be noticed that experimental values of q_e are similar to q_e computed using the second-order model. Moreover, the values of the correlation coefficient (R^2) of the first-order are less than that of the second-order. These results approve that the second-order model is favorable for describing the kinetic experimental data for MB adsorption by *Nitraria retusa* leaves powder. This established that this adsorption is chemisorption. Tan et al. [17] and Liu et al. [38] in their works observed similar results.

Fig. 7c demonstrates that the plot of q_t against $t^{1/2}$ no pass through the origin indicating that the intraparticle diffusion is not the rate-controlling step. Moreover, the parameters C and R^2 of this model have smaller values (Table 3) which designate that the intraparticle diffusion cannot contribute to the adsorption of MB on the adsorbent used in this study. A large number of unequal macropores and holes on the surface of the adsorbent are responsible for the distribution of the adsorbate particles that can be seen in the adsorbent SEM image (Fig. 1). Related results were viewed for methylene blue adsorption by granular and fiber activated carbon [35] and for methylene blue adsorption by Fe_3O_4-graphene@mesoporous SiO_2 nanocomposites [39].

3.2.5. Adsorption isotherms parameters

The isotherm models listed in Table 2 have been used to analyze the equilibrium experimental data for MB adsorption by the modified leaves powder of *Nitraria retusa* at 30°C,

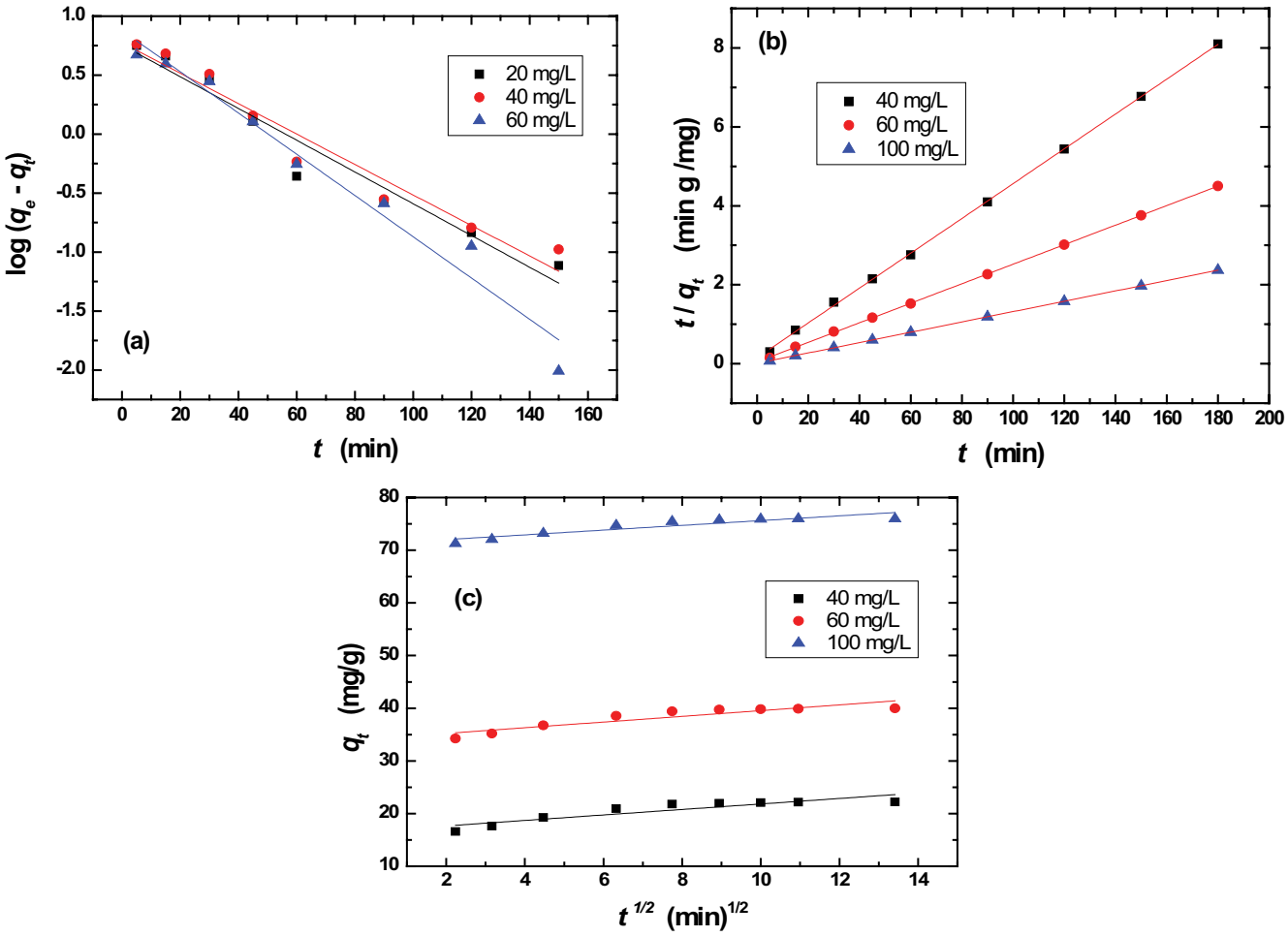

Fig. 7. (a) Pseudo-first-order, (b) Pseudo-second-order, and (c) diffusion of intra-particle kinetic models for methylene blue adsorption by $ZnCl_2$ modified leaves powder of *Nitraria retusa* at room temperature and solution pH of 6.

Table 3
Kinetic parameters for methylene blue adsorption by $ZnCl_2$ modified leaves powder of *Nitraria retusa*

	Pseudo-first-order				Pseudo-second-order				Intraparticle diffusion		
C_0 (mg L^{-1})	$q_{e,exp}$ (mg g^{-1})	$q_{e,cal}$ (mg g^{-1})	K_1 (h^{-1})	R^2	$q_{e,cal}$ (mg g^{-1})	K_2 (g mg^{-1} min^{-1})	R^2	Rate	K_{dif} (mg $h^{-1/2}$ g^{-1})	C	R^2
40	22.22	5.69	0.031	0.946	22.68	0.0128	0.999	0.289	0.521	16.616	0.793
60	39.99	5.96	0.030	0.947	40.44	0.0129	0.999	0.523	0.542	34.126	0.811
100	75.99	7.55	0.040	0.963	76.39	0.0158	0.999	1.209	0.451	71.109	0.830

50°C, and 60°C. The plots of these isotherm models are illustrated in Figs. 8a–c, correspondingly. The values of slopes and intercepts of these three models' plots were used for calculation the isotherm parameters of this sorption. The values of these isothermal parameters and the values of R^2 of each model were reported in Table 4. Moreover, the dimensionless factor (R_L) values of the Langmuir model were computed using Eq. (3) and listed in Table 4. $1/n$ and R_L values (Table 4) ranged from 0.367 to 0.424 and from 0.017 to 0.076, respectively. This confirms that the conditions of this adsorption experiment are suitable [40]. Figs. 8a–c are along with values of R^2 (Table 4) for each isotherm

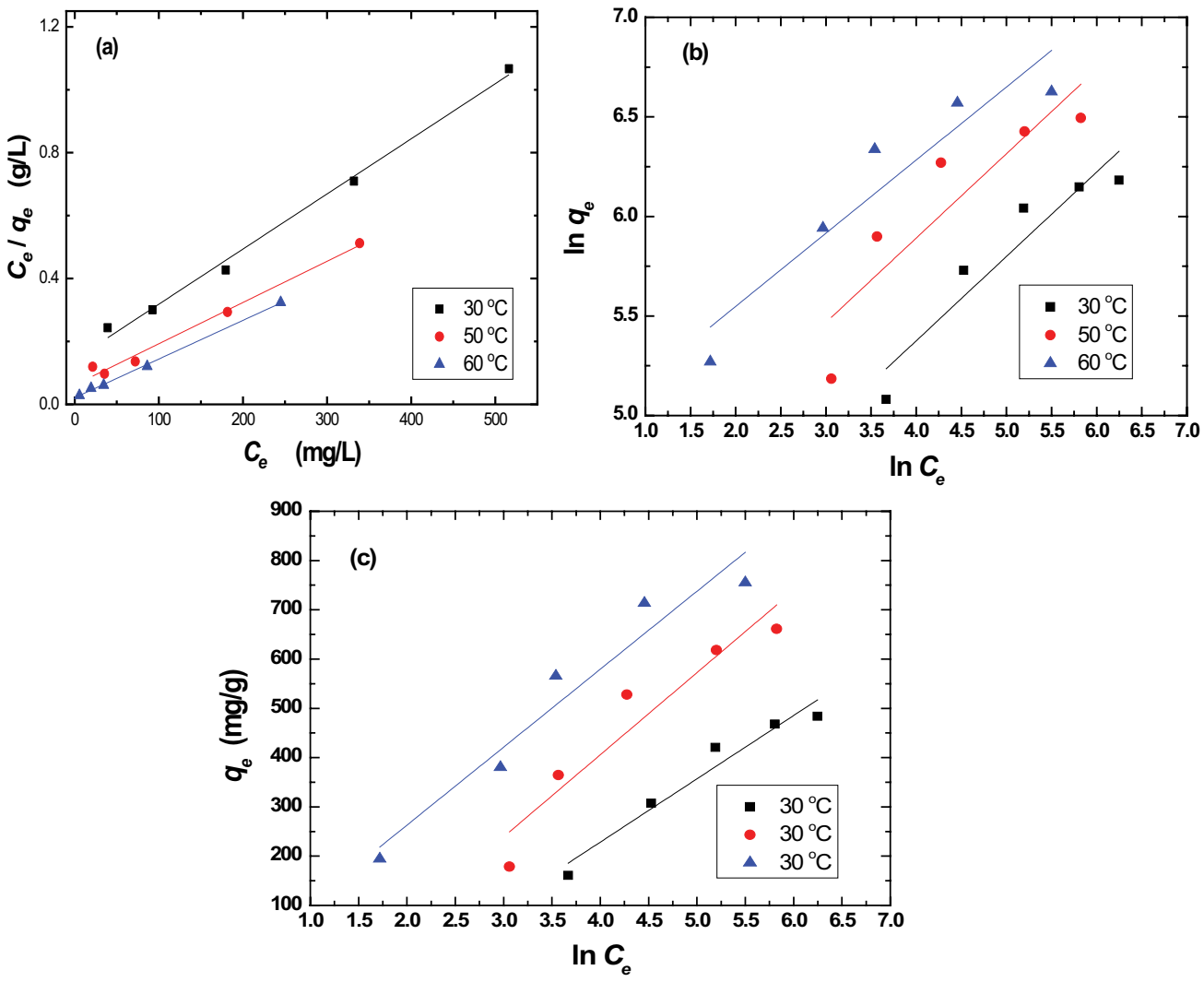

Fig. 8. (a) Langmuir, (b) Freundlich, and (c) Temkin isotherms for methylene blue adsorption by $ZnCl_2$ modified leaves powder *Nitraria retusa* at three different temperature and solution pH of 6.

Table 4
Isotherm parameters for methylene blue adsorption by $ZnCl_2$ modified leaves powder of *Nitraria retusa*

T (°C)	Langmuir model				Freundlich model				Temkin model		
	q_{max} (mg g^{-1})	K_L (L mg^{-1})	R_L	R^2	K_F (mg g^{-1}) (L mg)$^{-1/n}$	$1/n$	n	R^2	K_T (L mg^{-1})	B_1 (J mol^{-1})	R^2
30	571.43	0.012	0.076	0.993	39.66	0.424	2.359	0.860	0.108	128.4814	0.937
50	763.36	0.021	0.045	0.984	66.49	0.423	2.360	0.736	0.209	166.6083	0.879
60	813.01	0.058	0.017	0.998	123.17	0.367	2.722	0.852	0.713	158.2252	0.922

model indicate that the experimental data obtained in this work follow the isotherm model of Langmuir more than the other two models (Freundlich, Temkin). This established that MB adsorption by the modified leaves powder of *Nitraria retusa* is a monolayer and the adsorption active sites on the surface of adsorbent are homogeneous [40].

It was reported previously that the isotherm experimental data for 4-nitrophenol adsorption by palm oil fuel ash modified by amino silane coupling agent [40], fiber and granular activated carbon [41], methylene blue sorption on activated carbon fiber prepared from coconut husk [35], adsorption of MnO_4^- by *Nitraria retusa* leaves powder [42] and $KMnO_4$ adsorption by neem leaves powder [43] were excellently described by Langmuir isotherm model. The capacities obtained in this adsorption are 571.43, 763.36 and 813.01 mg g^{-1} at 30°C, 50°C and 60°C, in that order. These capacities (571.43, 763.36 and 813.01 mg g^{-1}) are higher and significant compared with the capacities of the other adsorbents. Moreover, these higher capacities were obtained at the original pH solution of this dye (pH = 6) at which the sorbent used in this work has the lowest sorption efficiency towards MB as noted in section 3.2.1 (Fig. 4). Therefore, it can be suggested that the adsorption capacity will be higher than the capacities obtained in this work (571.43, 763.36 and 813.01 mg g^{-1}) if the same procedures are achieved at solution pH 1 or 11. This indicates that the adsorbent used in this work will meet significant attention in the coming future in the field of water purification from MB.

3.2.6. Thermodynamic studies

The relationships between $\ln(q_e/C_e)$ and $1/T$ (Fig. 9) for this adsorption at adsorbate concentrations of 80, 120, 200 mg L^{-1} were graphed to study the parameters of thermodynamic. The intercepts and slopes of plots represented in Fig. 9 have been applied for calculating the values of $\Delta S°$ (kJ mol^{-1} K^{-1}) and $\Delta H°$ (kJ mol^{-1}), respectively. Furthermore, Eq. (5) was applied for computing $\Delta G°$ (kJ mol^{-1}) parameter from values of $\Delta S°$ (kJ mol^{-1} K^{-1}) and $\Delta H°$ (kJ mol^{-1}). The values of thermodynamic constants were recorded in Table 5.

The obtained $\Delta H°$ (kJ mol^{-1}) values (Table 5) are positive, indicating that this adsorption is endothermic [44]. Whereas, the values of $\Delta S°$ (kJ mol^{-1} K^{-1}) are negative and decreased by increasing the adsorbate initial concentration (Table 5). This means, that the randomness at the interface is increased through processes of adsorption and the initial concentration of the adsorbate has a significant impact on the adsorption performance [45].

The calculated $\Delta G°$ (kJ mol^{-1}) values (Table 5) are positive and increased by rising temperatures. This verifies that this adsorption is an un-spontaneous process and the degree of the spontaneity of this adsorption is decreased by increasing temperature. Related results were observed for selected dyes adsorption by modified metallic nanocomposite polymer [46].

4. Comparison between the adsorption capacities of adsorbents

Table 6 contains the adsorption capacity values for MB adsorption by the modified leaves powder of *Nitraria retusa* and some selected low-cost-adsorbents previously used. The results in this table indicate that the adsorbent used in this research has the highest capacities for MB adsorption. This makes the world's attention to use *Nitraria retusa* leaves powder in water and wastewaters purifications.

5. Conclusion

The leaves powder of *Nitraria retusa* was modified by $ZnCl_2$ and used as adsorbent material for the treatment of aqueous solution samples from MB dye. Fully characterization of synthesized adsorbent was done in terms of the determination of its porosity, surface area, FT-IR and

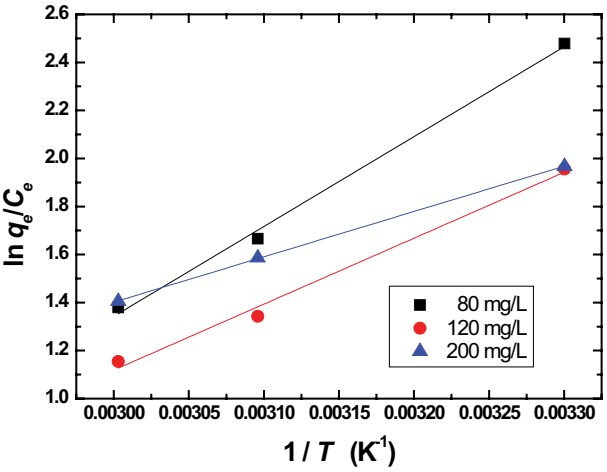

Fig. 9. $\ln(q_e/C_e)$ against $1/T$ graph for methylene blue adsorption by $ZnCl_2$ modified leaves powder of *Nitraria retusa* at three different temperatures and solution pH of 6.

Table 5
Thermodynamic parameters for methylene blue adsorption by $ZnCl_2$ modified leaves powder of *Nitraria retusa*

C_0 (mg L^{-1})	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (kJ mol^{-1} K^{-1})	$\Delta G°$ (kJ mol^{-1})			R^2
			303 K	323 K	333 K	
80	31.10	–0.08	55.99	57.63	58.45	0.994
120	22.82	–0.06	40.74	41.93	42.52	0.986
200	15.69	–0.04	26.42	27.13	27.48	0.999

Table 6
Adsorption capacities of low-cost adsorbents used for methylene blue elimination from polluted waters

Adsorbents	q_{max} (mg g^{-1})		Sources
Nitraria retusa leaves powder	571.43	30°C	Present work
	763.36	50°C	
	813.01	60°C	
Orange peel-modified phosphoric acid	307.63		[47]
Neem (*Azadirachta indica*) leaves	60.60		[48]
Teak tree bark	333		[49]
Hazelnut shell	76.9		[50]

pH_{ZPC}. Three kinetic models were applied to the analysis of experimental data obtained from this work. The obtained results confirm that the data of the kinetic experiments are described well by the model of second-order. Parameters of kinetics also strongly confirmed that external diffusion cannot be the rate-determining step or contribute to the adsorption of MB on the adsorbent used in this study. Three isotherm models (Langmuir, Freundlich, and Temkin) were practical to figure out the isotherm constants, the model of Langmuir was the best model represented for data of isotherm experiments. This recognized that MB adsorption by the adsorbent is a monolayer and the active sites of the modified leaves powder of *Nitraria retusa* are homogeneous sites. The capacities of this adsorption were found to be 571.43, 763.36, and 813.01 mg g^{-1} at 30°C, 50°C, and 60°C, respectively. The calculated thermodynamic parameters designate that this adsorption is endothermic where $\Delta H°$ values are positive. The $\Delta G°$ positive values show that the adsorption procedures obtained in this work are un-spontaneous processes. Moreover, the increasing temperature from 30°C to 60°C rises the $\Delta G°$ positive values. This verifies that increasing temperature decreases the degree of spontaneity for MB adsorption by the modified leaves powder of *Nitraria retusa*. All these findings call on those interested to give *Nitraria retusa* powder more attention in the field of purifying polluted water from MB dye.

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