Desalination and Water Treatment
www.deswater.com
doi: 10.5004/dwt.2019.24905

170 (2019) 101–110
December

Equilibrium, thermodynamic and kinetic study for potassium permanganate adsorption by Neem leaves powder

Hatem A. Al-Aoh

Department of Chemistry, Faculty of Science, University of Tabuk, 71474 Tabuk, Saudia Arabia, Tel. +966-537692007; emails: issa_hatem2@yahoo.com/halawah@ut.edu.sa

Received 16 May 2019; Accepted 12 September 2019

ABSTRACT

Zinc chloride ($ZnCl_2$) was used for modification of the adsorptive properties of Neem leaves powder. Fourier-transforms infrared spectroscopy, and Brunauer–Emmett–Teller surface analyzer were applied to investigate the physical and chemical properties of the prepared sample. It was found that the surface area, density, average pore width, pore volume and pH_{ZPC} of the modified adsorbent are 58.6 $m^2\ g^{-1}$, 0.7 g cc^{-1}, 13.8 Å, 0.106 $cm^3\ g^{-1}$ and 6.8, respectively. Adsorption of potassium permanganate ($KMnO_4$) by this adsorbent was also examined. The effects of pH, adsorbate initial concentration, time and temperature were also investigated. The real experimental conditions were observed to be pH of 7, $KMnO_4$ concentration of 1,000 mg L^{-1}, 120 min contact time and temperature of 55°C. Kinetic experimental data in the case of diluted and concentrated solutions were described well by the kinetic models of second-order and first-order. Langmuir, Freundlich, and Temkin isotherm models were applied. It was observed that the model of Langmuir was the best for describing the equilibrium data. 775.19, 925.93, and 1,066.79 mg g^{-1} was the adsorption capacities at 25°C, 40°C, and 55°C, respectively. Thermodynamic parameters designate that the adsorption obtained in this research is an endothermic and spontaneous process.

Keywords: Potassium permanganate ($KMnO_4$); Neem leaves powder; Adsorption; Isotherms; Kinetics; Thermodynamics

1. Introduction

Potassium permanganate ($KMnO_4$) is usually applied as an oxidizing agent to control odors, taste, disinfection byproducts, and biological growth in the case of treatment plants [1]. It is also used for the elimination of organic pollutants (dyes, phenols), cyanide, and some heavy metals (manganese, iron) from wastewaters [1–5]. Moreover, the longer chains of organic compounds can be split and oxidized by using $KMnO_4$ [4,5]. It was also reported that $KMnO_4$ is inhalation and skin irritant, swallowing of it may cause death and has a hazard effect on the eye [6]. Thus, fluidized-bed crystallization technology [7] and adsorption method using various adsorbent have been applied for the purification of water and industrial wastewaters from $KMnO_4$. Granular activated charcoal [1], activated carbon derived from corncob and bone of animal [8], coconut shells derived activated carbon [3] and modified activated carbon with sulfuric acid [9] were used for adsorption of $KMnO_4$ from aqueous solutions. The adsorption capacities of those types of activated carbon towards $KMnO_4$ are summarized in Table 1.

Azadirachta indica (Neem) has an extensive range of biological activities [10]. Therefore, this tree has been used as a traditional remedy for families in India and its neighboring countries for a long time ago [10]. The leaf extract of this tree was used as a reduction agent for the preparation of silver nanoparticles [11]. Oil and more than 135 chemical compounds were also separated by extraction processes from seeds, bark, and leaves of the Neem tree and used as inhibitors for the growth of viruses, fungi, and bacteria [12].

Table 1
Adsorbent used for removal of $KMnO_4$ from aqueous solution

Adsorbents	q_{max} (mg g^{-1})		Sources
Modified Neem leaves powder	775.19	25°C	Present study
	925.93	40°C	
	1066.79	55°C	
Granular Activated Charcoal	57.47		[1]
Animal bone derived activated carbon	28.04		[8]
Corncob derived activated carbon	26.00		[8]
Coconut shells derived activated carbon	23.25		[3]
Modified activated carbon	100.0 ± 0.5%		[9]

Moreover, Neem leaves powders have been applied as a low-cost adsorbent for the elimination of organic and inorganic hazard materials from water and industrial wastewaters. For example, the solid powders prepared from the Neem leaves were used for removal of Congo red, and Methyl orange dyes [13], Methyl red and Potassium dichromate [14], Malachite green [15], Methylene blue [16], cadmium and lead [17], chromium (VI) [18–20], chloride, hardness and total dissolved solids [21] and lead (II) [22] from contaminated wastewaters. Moreover, Neem stems charcoal has been used for removal of flurried from a stock solution of sodium flurried [23].

The adsorption achievements of Neem powder adsorbent towards organic and inorganic pollutants are listed in Table 2. It can be seen from this table that Neem steam and leaves powders have superior adsorption efficiency. Despite the higher adsorption capacities of this low or no cost adsorbent, there is no attempt has been carried out till now to evaluate the ability of Neem leaves powder for adsorption of $KMnO_4$ from aqueous solution. Thus, the main objective of this work is to investigate the isotherm, kinetic, and thermodynamic parameters for adsorption of $KMnO_4$ on the surface of Neem leaves powder. Moreover, factors affecting the adsorption rate and capacity of this adsorbent towards $KMnO_4$ were also studied.

Table 2
Adsorption capacities of organic and inorganic material on the surface of Neem leaves powder

Adsorbates	q_{max} (mg g^{-1})		References
Congo red	24.81		[13]
Methyl orange	21.23		[13]
Methyl red	1,900.00		[14]
Potassium dichromate	5,304.00		[14]
Malachite green (Neem bark)	166.00		[15]
Malachite green (acid treated Neem bark)	500.00		[15]
Methylene blue	249.25	298 K	[16]
	263.93	308 K	
	178.57	318 K	
Cadmium	8.10		[17]
Lead	3.51		[17]
Chromium (VI)	145.77		[18]
Chromium (VI)	58.82		[19]
Chromium (VI)	26.95		[20]
Lead (II)	833.30		[22]
Fluoride	1.27		[23]

2. Research experimental

2.1. Adsorbent preparation and characterization

The matured leaves of *Azadirachta indica* were collected from Al Manshiah-Al Jadida, Tabuk, Kingdom of Saudi Arabia. These leaves were washed much time using distilled water and dried at room temperature for 3–4 d. The dried leaves were powered by an electrical blender; 100 g of the powder was extracted with 300 mL of ethyl alcohol for 8 h at the boiling point ranged from 60°C to 80°C using a Soxhlet apparatus. The extract was separated using filter paper, evaporated to dryness in a rotary vacuum evaporator and used for another work. The residue was washed many times by tap water, two times by distilled water and then dried in an oven overnight at 120°C. A 65 g of the dried Neem powder was socked with 250 mL of 30% w/w Zinc chloride ($ZnCl_2$) and refluxed for 2 h. The mixture was filtered using a Buchner funnel and the residue was also washed one time by 1 M HCl solution and several times by distilled water. The produced adsorbent was dried at 120°C for 5 h in an oven and kept in desiccators for other uses.

The surface functional groups of the prepared sample were identified by using the Fourier-transform infrared spectroscopy (FT-IR) (Nicolet iS5 of Thermo Scientific FT-IR, USA). Whereas, the surface morphology of the raw material and adsorbent obtained were analyzed by using scanning electron microscopy (SEM) technique. The physical properties such as the density, surface area, pore volume and average pore width of the prepared adsorbent were determined by adsorption-desorption of nitrogen gas at 758.58 mm Hg and 77.35 K using Brunauer–Emmett–Teller surface analyzer (Quantachrome Nova Win2 Ver.2.2, USA). Moreover, the pH_{ZPC} of the modified adsorbent Neem produced in this work was determined by applying the method of Theydan and Ahmed [24].

2.2. Impact of pH

Experimental solutions of $KMnO_4$ with a concentration of 600 mg L^{-1} and different pH values ranged from 1.6 to 12

were prepared using 1 M of HCl or NaOH solution. A 10 mL of each solution was added to 30 mL amber bottle containing 10 mg of the adsorbent used in this research. The sealed bottles were shaken at room temperature and 150 rpm for equilibrium contact time using a shaker incubator. The mixtures were separated by filtration, and the final concentration of supernatant along with the amount of $KMnO_4$ adsorbed on the surface of this adsorbent was determined as mentioned in the equilibrium and thermodynamic section.

2.3. Kinetic experiments

10 mL of 200, 300, 400 and 600 mg L^{-1} $KMnO_4$ solutions (pH = 7) were added to amber bottles containing 10 mg of Neem leaves powder modified by $ZnCl_2$; then the bottles were placed in shaker incubator and agitated at room temperature, 200 rpm for 5 min. The components of each mixture were separated by filtration and the final concentration of $KMnO_4$ in the suspensions was measured at 525 nm using a UV-VIS spectrophotometer (Jenway, Model 6800, and the UK). Similar procedures were repeated at 15, 30, 45, 60, 120, 180, and 240 min. The amount of $KMnO_4$ adsorbed by this adsorbent at any time t (q_t) was calculated from Eq. (1):

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

V: volume of $KMnO_4$ solution (L), m: the mass of modified Neem leaves powder (g), C_0: $KMnO_4$ initial concentration (mg L^{-1}), C_t: concentration of $KMnO_4$ at any time t. The linear forms of the kinetic models listed in Table 3 have been used to investigate the kinetic parameter. The above-mentioned experiments were performed to investigate the adsorption rate, effect of agitation time, and kinetic parameters for adsorption of $KMnO_4$ on the modified Neem leaves powder.

2.4. Equilibrium and thermodynamic experiments

10 mL of each one of the eight solutions of $KMnO_4$ with different concentrations in the range of 200–1,500 mg L^{-1} was mixed with 10 mg in 30 mL amber bottles. The bottles were sealed and shaken in a shaker incubator at neutral pH (pH = 7), 200 rpm, and 25°C for 22 h. The solutions of $KMnO_4$ were separated by filtration, and the residual concentration of each solution was measured at 525 nm using a UV-VIS spectrophotometer. The similar processes were also tack placed at 40°C and 55°C. The amounts of $KMnO_4$ uptake to the surface of the modified Neem leaves powder at equilibrium were evaluated using Eq. (2):

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

C_0 (mg L^{-1}): concentration of $KMnO_4$ before adsorption, C_e: concentration of $KMnO_4$ (mg L^{-1}) after equilibrium, m: adsorbent mass (g), V: volume of adsorbate solution (L). The obtained data for adsorption at equilibrium were analyzed using the linear forms of the isotherm models summarized in Table 4.

The dimensionless factor (R_L) of the Langmuir isotherm model was computed using Eq. (3):

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

C_0: the highest initial concentration of $KMnO_4$ solution, K_L: Langmuir constant.

Eqs. (4)–(6) were applied in this work for calculation of the parameters associated with adsorption thermodynamic of 1,000; 1,200 and 1,500 mg L^{-1} $KMnO_4$ solutions by the prepared adsorbent sample.

$$\ln K_c = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{4}$$

$$K_c = \frac{q_e}{C_e} \times P \tag{5}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{6}$$

Table 3
Linear forms of kinetic models

Kinetic model name	Equations
Pseudo-first-order kinetic model	$\log\left(q_e - q_t\right) = \log(q_e) - K_1 \frac{t}{2.303}$
Pseudo-second-order kinetic model	$\frac{t}{q_t} = \frac{1}{K_2\left(q_e\right)^2} + \frac{t}{q_e}$
Intra-particle 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}) and K_{dif} (mg g^{-1} $min^{-1})^{-1/2}$: rate constants of the pseudo-first-order, pseudo-second-order and intra-particle diffusion kinetic models, respectively, C: another kinetic constant.

Table 4
Linear forms of isotherm models

Isotherm model name	Equations
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 $KMnO_4$ required for making a complete monolayer on the surface of the adsorbent, 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.

$\Delta H°$, $\Delta S°$, and $\Delta G°$: the changes in standard enthalpy, entropy, and free energy, respectively. T: the temperature of adsorption (K), P is the density of the solution (P = 1000 g L^{-1}) and R: the universal of gas constant (8.314 J K^{-1} mol^{-1}).

The obtained data in this section were also used for examining the impacts of $KMnO_4$ initial concentration and temperature on the adsorption performance of modified Neem leaves powder towards $KMnO_4$.

3. Results and discussion

3.1. Modified Neem leaves powder properties

The FT-IR spectra results of the adsorbent prepared sample were demonstrated in Fig. 1. This figure illustrates that four main absorption peaks are appearing in the regions of 1,162; 1,720; 2,928 and 3,327 cm^{-1}. These peaks represent the stretching vibration of S=O, C=O, –CH– and primary amide, respectively. Figs. 2 and 3 illustrate SEM images of the raw and modified Neem leaves powder, respectively. In comparison between these two images, it can be observed that the surface of modified adsorbent has expanded cavities and irregular macropores more than that of the raw Neem leave powder which allows the adsorbate particles to distribute easily through the micropores of the modified Neem leaves powder.

The physical and chemical properties like density, surface area, pore-volume, average pore width and pH_{ZPC} of the prepared adsorbent were found to be 0.7 g cc^{-1}, 58.6 m^2g^{-1}, 0.106 cm^3g^{-1}, 13.8 Å, 6.8, respectively. These results indicate that the modified adsorbent has a significant surface area, pore volume and pore width that have positive effects on the adsorption capacity and rate.

3.2. Adsorption studies

3.2.1. Variation effect of pH

The value of solution pH is a very important factor affecting the adsorption process as this factor not only impacts the chemical properties of the adsorbate but also has a significant effect on the adsorbent surface charge [25]. Since the adsorbate presents in the ionic form when solution pH is higher than the pK_a of adsorbate [25]. Furthermore, the charge on the surface of the adsorbent will be positive and negative if pH less than and higher than the adsorbent pH_{ZPC}, respectively [25]. In this work, the relationship between q_e mg g^{-1} and pH was plotted as represented in Fig. 4. As shown in this figure, the amount of $KMnO_4$ adsorbed at equilibrium is increased and decreased when solution pH increased in the ranges of (1.6–7) and (7–12), respectively. This can be elucidated by the fact of the adsorbent surface (pH_{ZPC} = 6.8) is positively charged when pH values ranged from 1.6 to 7 and the adsorption process occurred due to the electrostatic attraction forces between negatively charged ions of MnO_4^- and the positively charged adsorbent surface.

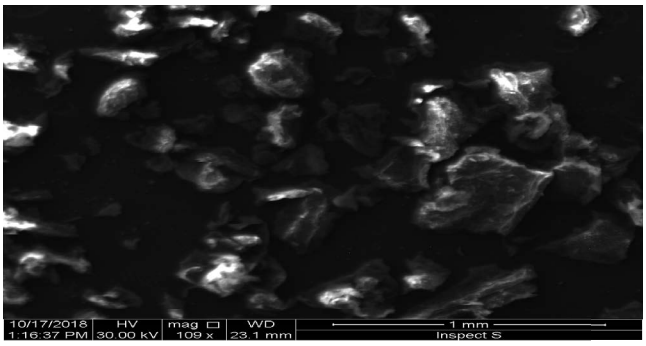

Fig. 2. SEM image of the raw Neem leaves powder.

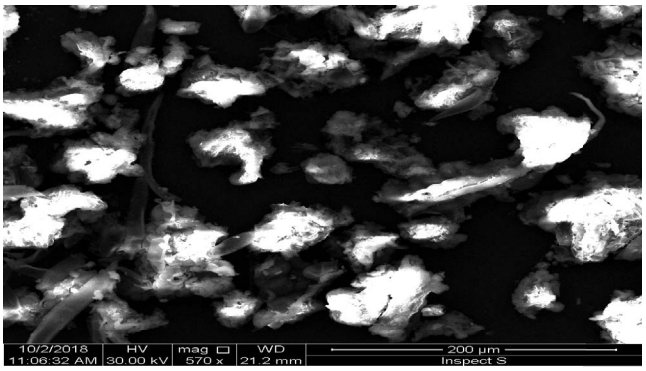

Fig. 3. SEM image of the modified Neem leaves powder.

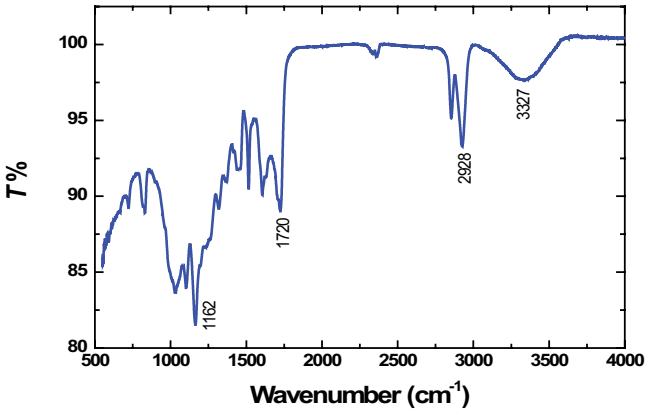

Fig. 1. FT-IR spectrum for the modified Neem leaves powder.

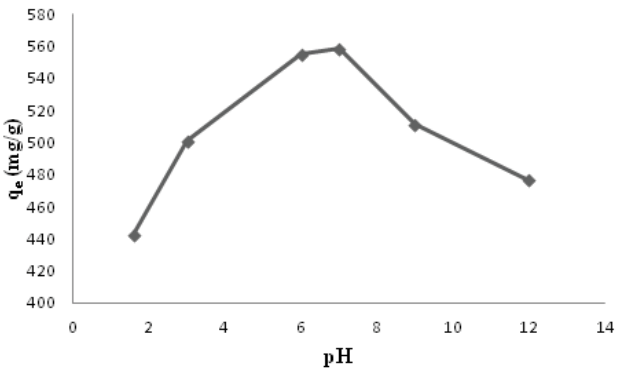

Fig. 4. Effect of pH solution on the adsorption capacity of $KMnO_4$ on modified Neem leaves powder.

Whereas, the surface of adsorbent be negatively charged when pH becomes over 7 and then the electrostatic repulsion forces between MnO_4^- ions and the negative charges of the adsorbent surface will start their negative effect on the adsorption capacity.

Similar results were reported by Ezeugo and Anadebe [8] for adsorption of $KMnO_4$ on activated carbon derived from corncob and animal bone.

3.2.2. Kinetic studies

Adsorption of 10 mL $KMnO_4$ solutions with four different initial concentrations (200, 300, 400, and 600 mg L^{-1}) and the optimal pH value (pH = 7) on the modified Neem leaves powder was carried out at various periods time (5, 15, 30, 45, 60, 120, 180, and 240 min) to investigate the impact of adsorption agitation time and adsorption kinetic parameters. The amounts of $KMnO_4$ adsorbed (q_t mg g^{-1}) were plotted against time (t min) as illustrated in Fig. 5. This figure shows that the quantity of $KMnO_4$ adsorbed onto the adsorbent surface is regularly increased with increasing agitation time and be invariable over 60 min for each concentration. Moreover, it can be seen from this figure that the initial slope related to the higher $KMnO_4$ initial concentration (600 mg L^{-1}) is higher than that of the other concentrations. This can be explained by the fact of its superior driving force of the adsorption phenomenon, which makes its adsorption fast comparing with other concentrations. The results obtained in this research are agreed well with the results reported for adsorption of chromium (IV) ion from aqueous solution using eucalyptus, Neem and mango leaves [26].

The relationships between log ($q_e - q_t$) vs. t (pseudo-first-order kinetic model), t/q_t vs. t (pseudo-second-order kinetic model) and q_t vs. $t^{1/2}$ (intra-particle-diffusion kinetic model) were plotted as can be seen in Figs. 6a–c respectively. The kinetic parameters for $KMnO_4$ adsorption on the surface of this adsorbent were evaluated from the slopes and intercepts of these plots and listed with values of the correlation coefficient, R^2, in Tables 5 and 6. As can be noted from Table 5, the correlation coefficient values of the pseudo-second-order at lower concentrations (200, 300 mg L^{-1}) are higher than that of pseudo-first-order and the values of q_e calculated from slopes of linear plots of the second-order model almost agree well with the experimental values of q_e. This confirms that the second-order model can be applied for describing the kinetic experimental data for adsorption of $KMnO_4$ by modified Neem leaves powder in the case of diluted solutions. This also suggests that

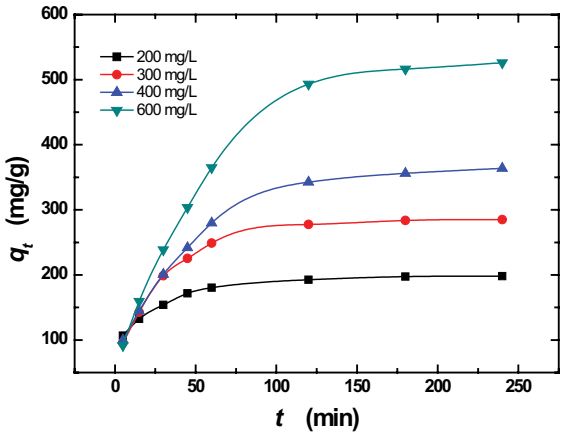

Fig. 5. Effect of the contact time on the adsorption of $KMnO_4$ by modified Neem leaves powder.

Table 6
Parameter values of the intra-particle diffusion model for $KMnO_4$ adsorption on modified Neem leave powder at different initial concentrations and 25°C ± 1°C

	Region I			Region II		
C_0	K_{dif}	C	R^2	K_{dif}	C	R^2
(mg L^{-1})	(mg $h^{-1/2}$ g^{-1})			(mg $h^{-1/2}$ g^{-1})		
200	13.58	78.21	0.993	1.18	180.41	0.841
300	28.37	34.45	0.993	1.67	259.85	0.916
400	32.86	22.22	0.997	4.74	291.29	0.988
600	49.55	–26.45	0.996	7.29	414.98	0.966

adsorption of $KMnO_4$ by this adsorbent is chemisorption at lower concentrations. The chemical adsorption occurred due to the electrostatic attraction forces between the positively charged active sites on the adsorbent surface and negatively charged ions of MnO_4^-. Similar results have been reported for adsorption of Malachite green on potato peel and Neem bark [15].

It can also be observed from Table 5 that there are significant differences between the experimental and calculated values of q_e using both first- and second-order kinetic models at higher concentrations (400 and 600 mg L^{-1}). This indicates that the adsorption of $KMnO_4$ on modified Neem leaves

Table 5
Pseudo-first and pseudo-second-order parameters and experimental q_e values for $KMnO_4$ adsorption on modified Neem leaves powder at different initial concentrations and 25°C ± 1°C

		Pseudo-first-order			Pseudo-second-order			
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
200	197.91	77.82	0.0223	0.898	204.08	0.00064	0.999	0.131
300	285.01	193.06	0.0258	0.998	303.03	0.00023	0.999	0.070
400	363.92	326.44	0.0228	0.991	400.00	0.00010	0.997	0.040
600	526.03	616.88	0.0251	0.988	625.00	0.00004	0.961	0.025

powder has been occurred by multiple mechanisms at higher concentrations.

The higher values of *C* (Table 6) indicate that the external diffusion plays a major role in the adsorption process since the value of *C* is associated with the boundary layer thickness [27]. Moreover, it can be seen from Fig. 6c that the plots were not linear over the full-time range and separated into two linear regions. This confirms that the adsorption of $KMnO_4$ on modified Neem leaves powder has been occurred by multiple steps. Similar results have been reported for adsorption of Methyl orange by cationic surfactants modified coffee waste [28].

3.2.3. Equilibrium studies

In this section, the amounts of $KMnO_4$ adsorbed at equilibrium and optimal pH value (q_e mg g^{-1}) by the prepared adsorbent were plotted against the primary concentration of $KMnO_4$ solutions (C_0 mg L^{-1}) at temperatures of 25°C, 40°C and 55°C as can be observed in Fig. 7. This figure indicates that the adsorbate initial concentration has a positive effect on the adsorption capacity of $KMnO_4$ on the surface of the adsorbent sample used in this research. This result can be explained by the fact of increasing the initial concentration leads to increasing the dynamic force that has the ability to reduce the mass movement resistances of $KMnO_4$ molecules at the liquid and solid interface [29,30]. It can also be noted from Fig. 7 that the quantities of $KMnO_4$ uptake almost be constant over 1,000 mg L^{-1} because the adsorbent surface has no empty active sites to accept additional particles of $KMnO_4$ if the adsorbate initial concentration raised up 1,000 mg L^{-1} [29,30]. Moreover, this figure demonstrates that the temperature also has a positive impact on the adsorption capacity of the modified Neem leaves powder towards $KMnO_4$, indicating that the adsorption in this work is the endothermic process. Increasing the adsorption capacity by elevating temperature from 25°C to 55°C was due to raising the kinetic energy of the $KMnO_4$ molecules and decreasing the viscosity of $KMnO_4$ solution [31]. The same results were noted in the case acid red 27 dye adsorption by activated carbon prepared from coconut husk fiber and commercial activated carbon granular [32]. The endothermic process was also reported for adsorption of Methylene blue by commercial activated carbon [33].

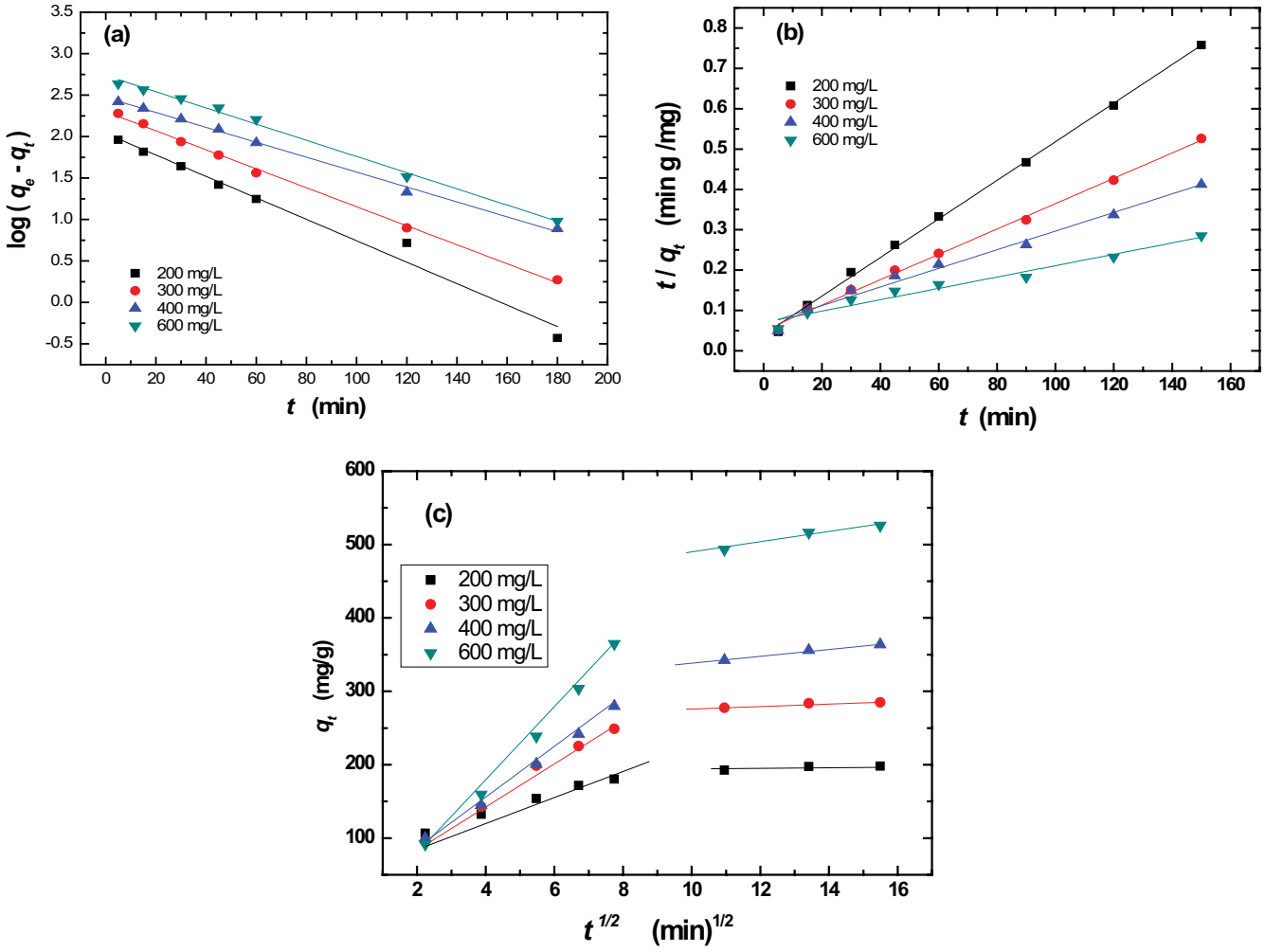

Fig. 6. Pseudo-first-order, pseudo-second-order and Intra-particle diffusion kinetic models for $KMnO_4$ adsorption on modified Neem leaves powder.

Langmuir, Freundlich, and Temkin isotherm models were applied in this research to investigate the isotherm parameters for adsorption of $KMnO_4$ on modified Neem leaves powder at 25°C, 40°C and 55°C. Figs. 8a–c demonstrate the plots of Langmuir, Freundlich, and Temkin equations, respectively. Isotherm constants of Langmuir (q_{max}, K_L), Freundlich (K_F, n) and Temkin (K_T, B_1) were calculated from the slopes and intercepts of these three models' plots. The values of these parameters are along with values of R^2 of each model are listed in Table 7. Eq. (3) was used for calculating the values of the dimensionless factor (R_L) of the Langmuir isotherm model, which are listed in Table 7. Values of R_L and $1/n$ (Table 7) are in the ranges of (0.0031–0.0314) and (0.157–0.321), respectively. This confirms that the experimental conditions applied in this work are favorable [34]. Fig. 8, along with the values of R^2, indicating that the experimental equilibrium data obtained in this research can be analyzed by Langmuir model better than the other two models. This makes sure that the adsorption of $KMnO_4$ by the adsorbent used in this work is a monolayer and the modified Neem leaves powder has homogeneous adsorption active sites [34]. It was reported in the past that equilibrium data for adsorption of Methyl orange by NiO and CuO nanoparticles [34], adsorption of 4-nitrophenol on activated carbon fiber prepared from coconut husk and commercial activated carbon granular [35] and adsorption

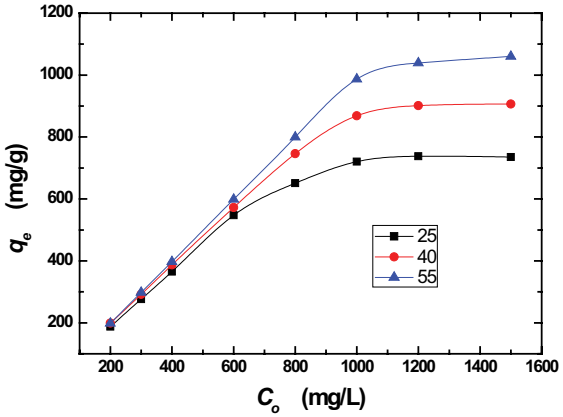

Fig. 7. Effect of the initial concentration on $KMnO_4$ adsorption by modified Neem leaves powder.

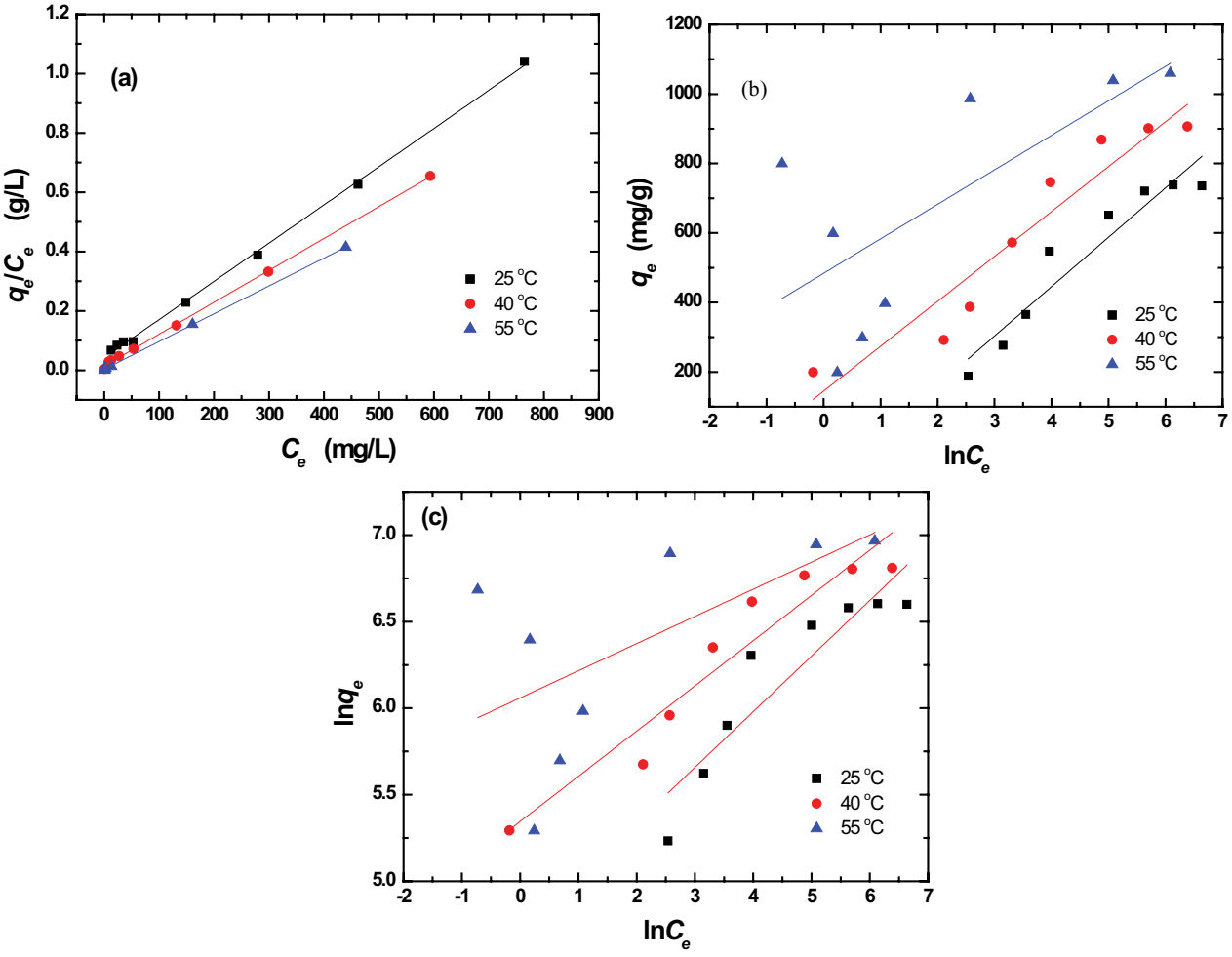

Fig. 8. Langmuir, Freundlich and Temkin isotherm models for the adsorption of $KMnO_4$ by modified Neem leaves powder at three different temperatures.

Table 7
Langmuir, Freundlich and Temkin parameters for adsorption of $KMnO_4$ on modified Neem leaves powder at three different temperatures

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})$^{-1/n}$	$1/n$	n	R^2	K_T (L mg^{-1})	B_1 (J mol^{-1})	R^2
25	775.19	0.0309	0.0314	0.999	109.36	0.321	3.11	0.819	142.19	0.4203	0.899
40	925.93	0.0778	0.0127	0.999	209.57	0.261	3.83	0.906	129.31	3.0569	0.898
55	1,066.79	0.3232	0.0031	0.999	428.08	0.157	6.37	0.270	99.36	130.1074	0.418

of Bromophenol blue on nickel oxide nanoparticles [36] give an excellent fit of the Langmuir isotherm. It can also be seen from Table 7 that the adsorption capacities obtained in this work are 775.19, 925.93, and 1066.79 mg g^{-1} for temperatures of 25°C, 40°C, and 55°C respectively. This confirms that temperature has a positive effect and this adsorption is an endothermic process. In comparison with the other adsorbents that have been previously used for removal of $KMnO_4$ (Table 1) from aqueous solutions, the modified Neem leaves powder used in this research has adsorption capacities higher than the highest one by 7–10 times. This indicates that modified Neem leaves powder will meet attentions highly in water and wastewater's purifications.

3.2.4. Temperature effect and thermodynamic studies

The relationships between the amounts adsorbed at equilibrium (q_e, mg g^{-1}) and temperature (T °C) (Fig. 9) as well $\ln(q_e/C_e)$ with $1/T$ (K^{-1}) (Fig. 9) for adsorption of three different $KMnO_4$ solutions (1,000; 1,200; and 1,500 mg L^{-1}) by the prepared adsorbent sample were plotted to investigate the temperature effect and thermodynamic parameters, in that order. Fig. 9 shows that the equilibrium adsorption amount is gradually elevated by raising the temperature and confirms that this type of adsorption is an endothermic process. These results agree well with that obtained in the sections of 3.2.2 and 3.2.3.

The intercepts and slopes of the plots of $\ln K_c$ and $1/T$ (Fig. 10) have been used for computing $\Delta S°$ and $\Delta H°$ values, respectively. The values of these two thermodynamic parameters were used for calculating the values of $\Delta G°$ by applying Eq. (6) at three different temperatures. The values of these three parameters are also listed in Table 8.

The positive values of $\Delta H°$ and $\Delta S°$ (Table 8) propose that the adsorption of $KMnO_4$ by the adsorbent used in this work is endothermic [37] and decreasing the randomness at the interface between the sold (adsorbent surface) and liquid (adsorbate solution) during adsorption process [38]. Moreover, it can be seen from this table that the randomness is decreased from 0.310 to 0.081 when the adsorbate initial concentration increased in the range of 1,000–1,500 mg L^{-1}. This designates that the most important factor affecting the adsorption performance in this work is the adsorbate initial concentration.

The negative values of $\Delta G°$ (Table 8) indicate that the adsorption procedures obtained in this research are a spontaneous process in nature. Furthermore, it can be observed from Table 8 that the growing temperature from 25°C to

Table 8
Thermodynamic parameters for adsorption of $KMnO_4$ on modified Neem leave powder

C_0 (mg L^{-1})	$\Delta H°$	$\Delta S°$	$\Delta G°$ (kJ mol^{-1})			R^2
			25°C	40°C	55°C	
1,000	90.68	0.310	–1.697	–6.347	–10.997	0.850
1,200	37.76	0.130	–1.084	–3.039	–4.994	0.987
1,500	24.91	0.083	0.113	–1.135	–2.383	0.999

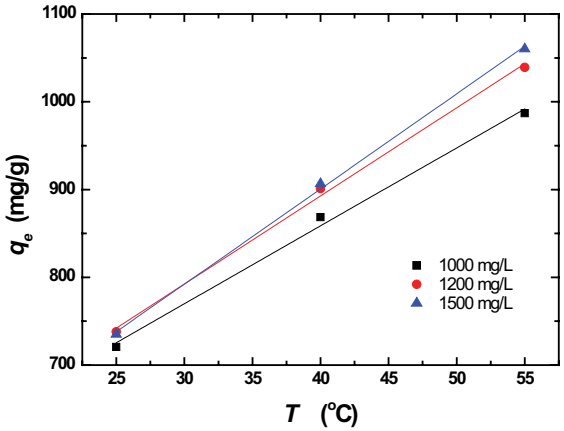

Fig. 9. Effect of temperature on the adsorption of $KMnO_4$ by modified Neem leaves powder at three different concentrations.

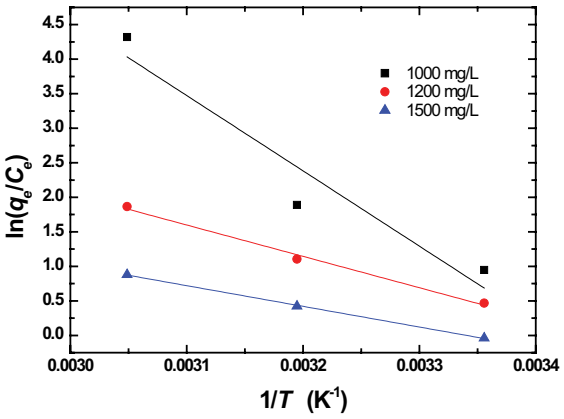

Fig. 10. Plots of $\ln K_c$ vs. $1/T$ for the adsorption of $KMnO_4$ by modified Neem leaves powder at three different concentrations.

55°C increases the negative values of $\Delta G°$. This confirms that raising temperature increases the spontaneity degree for adsorption of $KMnO_4$ on the surface of modified Neem leaves powder. Similar trends were reported for adsorption of some selected dyes by polymer nanocomposite modified with methylamine and copper (II) chloride [39].

4. Conclusions

In this work, Neem leaves powder was chemical modified by $ZnCl_2$ and characterized in terms of its surface functional groups, surface morphology, pH_{ZPC}, surface area, density, and porosity. The prepared adsorbent has been used for adsorption of $KMnO_4$ from aqueous solution. Factors affection the adsorption efficiency, kinetic, isotherm and thermodynamic parameters were investigated. It was found that a temperature of 55°C, pH solution of 7 and 1,000 mg L^{-1} of $KMnO_4$ primary concentration represent the optimal conditions of this adsorption. The obtained Kinetic results indicate that the second-order kinetic model describes well the experimental kinetic data in the case of diluted. Moreover, the parameters of the intra-particle diffusion kinetic model confirm that this adsorption occurred by multiple steps. Equilibrium data were analyzed well by the Langmuir isotherm model and found that the adsorption capacities of 775.19, 925.93 and 1,066.79 mg g^{-1} are obtained at 25°C, 40°C and 55°C, respectively. Parameters of thermodynamic studies indicate that the adsorption of $KMnO_4$ by this adsorbent is a spontaneous and endothermic process. The higher adsorption capacities resulting in this research authenticate that the modified Neem leaves powder as low or no-cost materials will meet significant interesting in the case of water and wastewaters purification.

Acknowledgments

The author extends his appreciation to the Deanship of Scientific Research at Tabuk University for funding the work through the research project no. S-90-1437.

References

[1] R.K. Verma, R. Kapoor, S.K. Gupta, R.R. Chaudhari, An efficient technique for removal of K^+ and MnO_4-ions through adsorption in aqueous solution by using activated charcoal, Pharm. Chem. J., 1 (2014) 20–25.
[2] A. Hendratna, The Application of MnO_2 and $KMnO_4$ for Persistent Organic Compounds and COD Removals in Wastewater Treatment Process, TRITA-LWR Degree Project, Digitala Vetenskapliga Arkivet, 2011, p. 2.
[3] F. Aprilliani, E. Warsiki, A. Iskandar, Kinetic studies of potassium permanganate adsorption by activated carbon and its ability as ethylene oxidation material, IOP Conf. Ser.: Earth Environ. Sci., 141 (2018) 012003.
[4] M. Ordiales, D. Fernández, L.F. Verdeja, J. Sancho, Potassium permanganate as an alternative for gold mining wastewater treatment, JOM-US, 67 (2015) 1975–1985.
[5] P.B. Fayad, A. Zamyadi, R. Broseus, M. Prévost, S. Sauvé, Degradation of progestagens by oxidation with potassium permanganate in wastewater effluents, Chem. Cent. J., 7 (2013) 2–11.
[6] *D.M. Ruthven, Principle of Adsorption and Adsorption Processes*, Chapters 2 and 3, John *Wiley* & Sons, New York, *1984*, pp. 1–7.
[7] G.-X. Li, Y.-H. Huaug, T.-C. Chen, Y.-J. Shih, H. Zhang, Reduction and immobilization of potassium permanganate on iron oxide catalyst by fluidized-bed crystallization technology, Appl. Sci., 2 (2012) 166–174.
[8] J.N.O. Ezeugo, C.V. Anadebe, Removal of potassium permanganate from aqueous solution by adsorption onto activated carbon prepared from animal bone and corn cob, Equations J. Eng., 1 (2018) 29–36.
[9] M.E. Mahmoud, A.A. Yakout, S.R. Saad, M.M. Osman, Removal of potassium permanganate from water by modified carbonaceous materials, Desal. Wat. Treat., 57 (2015) 1–11.
[10] R.N. Chopra, S.L. Nayer, I.C. Chopra, Glossary of Indian Medicinal Plants, 5th ed., New Delhi, CSIR, 1956, p. 220.
[11] S.R. Kuchekar, M.P. Patil, V.B. Gaikwad, S.-H. Han, Synthesis and characterization of silver nanoparticles using *Azadirachta indica* (Neem) leaf extract, Int. J. Eng. Sci. Invention Res. Dev., 6 (2017) 47–55.
[12] S. Susmitha, K.K. Vidyamol, P. Ranganayaki, R. Vijayaragavan, Phytochemical extraction and antimicrobial properties of *Azadirachta indica* (Neem), Global J. Pharmacol., 7 (2013) 316–320.
[13] M.B. Ibrahim, S. Sani, Neem (*Azadirachta indica*) leaves for removal of organic pollutants, J. Geosci. Environ. Prot., 3 (2015) 1–9.
[14] G.G. Pandhare, N. Trivedi, S.D. Dawande, Adsorption of color from a stock solution using Neem leaves powder as a low-cost adsorbent, Int. J. Eng. Sci. Emerging Technol., 5 (2013) 97–103.
[15] N. Sharma, D.P. Tiwari, S.K. Singh, The efficiency appraisal for removal of Malachite green by potato peel and Neem bark: isotherm and kinetic studies, Int. J. Chem. Envion. Eng., 5 (2014) 82–88.
[16] M.A.K.M. Hanafiah, M. Ismail, W.S.W. Ngah, W.K.A.W.M. Khalir, H. Zakaria, Adsorption behavior of Methylene blue on ethylenediaminetetraacetic dianhydride modified Neem (*Azadirachta indica*) leaf powder, Key Eng. Mater., 594–595 (2014) 270–274.
[17] G.G. Pandhare, N. Trivedi, R. Pathrabe, S.D. Dawande, Adsorption of cadmium (II) and lead (II) from a stock solution using Neem leaves powder as a low-cost adsorbent, Int. J. Innovative Res. Sci. Eng. Technol., 2 (2013) 5752–5761.
[18] A. Sharma, K.G. Bhattacharyya, Adsorption of chromium (VI) on *Azadirachta indica* (Neem) leaf powder, Adsorption, 10 (2004) 327–338.
[19] V. Vinodhini, N. Das, Relevant approach to assess the performance of sawdust as adsorbent of chromium (VI) ions from aqueous solutions, Int. J. Environ. Sci. Technol., 7 (2010) 85–92.
[20] M. Utkarsh, G. Suresh, Kinetic and equilibrium studies of Cr (VI) removal from aqueous solutions using activated Neem bark, Res. J. Chem. Environ., 5 (2011) 939–943.
[21] Y.S. Tomar, D. Rastogi, Removal of chloride, hardness and TDS from water using different adsorbents, Int. J. Res. Appl. Sci. Eng. Technol., 6 (2018) 5111–5117.
[22] K.G. Bhattacharyya, A. Sharma, Adsorption of Pb(II) from aqueous solution by *Azadirachta indica* (Neem) leaf powder, J. Hazard. Mater., B113 (2004) 97–109.
[23] S. Chakrabarty, H.P. Sarma, Defluoridation of contaminated drinking water using Neem charcoal adsorbent: kinetics and equilibrium studies, Int. J. ChemTech Res., 4 (2012) 511–516.
[24] S.K. Theydan, M.J. Ahmed, Adsorption of Methylene blue onto biomass-based activated carbon by $FeCl_3$ activation: equilibrium, kinetics, and thermodynamic studies, J. Anal. Appl. Pyrolysis, 97 (2012) 116–122.
[25] X.-L. Wu, Y.P. Shi, S.X. Zhong, H.J. Lin, J.-R. Chen, Facile synthesis of Fe_3O_4-graphene@mesoporous SiO_2 nanocomposites for efficient removal of Methylene blue, Appl. Surf. Sci., 378 (2016) 80–86.
[26] S.V. Kumar, R. Narayanaswamy, M. Sripathy, K.V. Pai, Comparative study of removal of chromium-IV ion from aqueous solution using eucalyptus, Neem and mango leaves, Int. J. Eng. Res. Dev., 8 (2013) 56–61.
[27] J.W. Lin, Y.H. Zhan, Z.L. Zhu, Adsorption characteristics of copper (II) ions from aqueous solution onto humic acid-immobilized surfactant-modified zeolite, Colloids Surf., A, 384 (2011) 9–16.

[28] R. Lafi, A. Hafiane, Removal of Methyl orange (MO) from aqueous solution using cationic surfactants modified coffee waste (MCWs), J. Taiwan Inst. Chem. Eng., 58 (2016) 424–433.
[29] B.C. Qu, J. Zhou, X.M. Xiang, C.L. Zheng, H.X. Zhao, X.B. Zhou, Adsorption behavior of Azo Dye C. I. Acid Red 14 in aqueous solution on surface soils, J. Environ. Sci., 20 (2008) 704–709.
[30] V.K. Gupta, B. Gupta, A. Rastogi, S. Agarwal, A. Nayak, A comparative investigation on adsorption performances of mesoporous activated carbon prepared from waste rubber tire and activated carbon for a hazardous azo dye—Acid Blue 113, J. Hazard. Mater., 186 (2011) 891–901.
[31] B.H. Hameed, A.A. Ahmad, Batch adsorption of Methylene blue from aqueous solution by garlic peel, an agricultural waste biomass, J. Hazard. Mater., 164 (2009) 870–875.
[32] H.A. AL-Aoh, M.J. Maah, R. Yahya, M.R. Bin Abas, A comparative investigation on adsorption performances of activated carbon prepared from coconut husk fiber and commercial activated carbon for acid red 27 dye, Asian J. Chem., 25 (2013) 9582–9590.
[33] H.A. AL-Aoh, R. Yahya, M.J. Maah, M.R. Bin Abas, Adsorption of Methylene blue on activated carbon fiber prepared from coconut husk: isotherm, kinetics and thermodynamics studies, Desal. Wat. Treat., 52 (2014) 6720–6732.
[34] A.A.A. Darwish, M. Rashad, H.A. AL-Aoh, Methyl orange adsorption comparison on nanoparticles: isotherm, kinetics, and thermodynamic studies, Dyes Pigm., 160 (2019) 563–571.
[35] H.A. AL-Aoh, M.J. Maah, R. Yahya, M.R. Bin Abas, Isotherms, Kinetics and thermodynamics of 4-nitrophenol adsorption on fiber-based activated carbon from coconut husks prepared under optimized conditions, Asian J. Chem., 25 (2013) 9573–9581.
[36] H.A. Al-Aoh, Adsorption performances of nickel oxide nanoparticles (NiO NPs) towards bromophenol blue dye (BB), Desal. Wat. Treat., 110 (2018) 229–238.
[37] M. Ceglowski, G. Schroeder, Removal of heavy metal ions with the use of chelating polymers obtained by grafting pyridine–pyrazole ligands onto polymethylhydrosiloxane, Chem. Eng. J., 259 (2015) 885–893.
[38] W. Song, B. Gao, X. Xu, L. Xing, S. Han, P. Duan, W. Song, R. Jia, Adsorption-desorption behavior of magnetic amine/Fe_3O_4 functionalized biopolymer resin towards anionic dyes from wastewater, Bioresour. Technol., 210 (2016) 123–130.
[39] M. Ptaszkowska-Koniarz, J. Goscianska, R. Pietrzak, Adsorption of dyes on the surface of polymer nanocomposites modified with methylamine and copper (II) chloride, J. Colloid Interface Sci., 504 (2017) 549–560.