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Adsorption of 1,1-dimethylhydrazine (UDMH) from aqueous solution using magnetic carbon nanocomposite: kinetic and thermodynamic study

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ABSTRACT

In this work, removal of UDMH as a pollutant with considerable toxicity is studied using activated carbon magnetic nanocomposite with fast and easy separation. To optimize the process, effective parameters, such as pH, adsorbent dosage, contact time, and temperature, have been investigated. More than 90% UDMH removal efficiency obtained within 30 min of contact time, 20 mg of adsorbent at pH 6 and room temperature. The adsorption behavior was evaluated based on equilibrium data, using both the Langmuir and Freundlich isotherm models. It was found that adsorption data were interpreted by Freundlich model better than Langmuir model with regression coefficient of 0.9971. Besides, the adsorption data were well described by the pseudo-second-order kinetic model. The adsorption thermodynamic parameters showed that the adsorption process is endothermic and spontaneous with positive standard enthalpy of 2.74 J mol^{-1} and negative standard free energy of 29.08 kJ mol^{-1}, respectively. Also standard entropy changes of 97.56 J mol^{-1} k^{-1} was calculated.

Keywords: 1,1-Dimethylhydrazine; Magnetic carbon nanocomposite; Adsorption isotherms; Kinetics; Thermodynamics

1. Introduction

Unsymetrical dimethyl hydrazine, a dialkyl hydrazine known as UDMH, is one of the hydrazine derivatives which does not have some unmeet properties of hydrazine. A colorless liquid with an ammonia or fishy odor that find application in wide variety fields including use as fundamental component of high-energy fuels in rocket and jet propellant in military applications and chemical industries and as an intermediate in the synthesis of pharmaceuticals, dyes, and other chemicals [1–3]. In spite of its significance, some identified studies and experimental carcinogenicity tests on animals revealed that this flammable and corrosive compound is suspected to be highly toxic, human carcinogenic and mutagenic [4]. UDMH is highly volatile substance, the boiling point and the solubility of UDMH in water are 64℃ at 760 mmHg and 1,000 g L^{-1}, respectively [5]. Due to its low boiling point and high solubility in water, it is very probable to permeate water sources, soil, and air during production and application. The threshold limit value (TLV) of 0.01 mg L^{-1} and LD_{50} of 155 mg kg^{-1} are reported for this toxic substance. Thus, it can certainly be a serious threat for environment and human beings by inhalation, ingestion, and dermal exposure. The

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International Agency for Research on Cancer has categorized UDMH into group B2 as a human carcinogen [6,7]. Hence, for toxicological significance of UDMH, some considerable attention should be focused in order to counteract its hazardous effects. Numerous water treatment techniques have been investigated to detoxify UDMH solution such as oxidation with air and hydrogen peroxide [8], heterogeneous Fenton system [9], reaction with gaseous chloramine [10], catalytic oxidation [11], and photocatalytic oxidation [12]. The main disadvantage of these methods is formation of a more toxic compound named N-nitrosodimethyl amine (NDMA) as an intermediate of UDMH oxidation [13]. Adsorption process was widely used to remove pollutant from aqueous media [14–19]. Among the studied methods, adsorption is considered as a promising method to remove UDMH since it is low cost and it has an easy operation; moreover, in this method, it is not probable to form some other toxic substances [20]. Also application of nanoscale materials can improve its properties and enhance removal efficiency.

In this study, removal of UDMH from aqueous solution is investigated using activated carbon magnetic nanocomposite (AC-MNC) as a reusable adsorbent. Effective parameters in the process including pH, adsorbent amount, temperature, and contact time have been optimized. Compared with other porous material, activated carbon (AC) with some significant surface properties such as large surface area and wide pore size revealed a good removal efficiency, but unfavorably the separation of sorbent will encounter some problems in large volume of sample [21], so in order to overcome this disadvantage, we prepared AC-MNC which can readily separate from the solution by a magnet. Also the adsorption isotherm models, thermodynamic parameters, and kinetic study were surveyed.

2. Experimental

2.1. Materials

AC, a stock solution of UDMH (UDMH·2HCl ≥ 99%) obtained from Fluka. Other following chemicals used in the experiments were purchased from Merck, Germany. A mixture of sodium dodecylsulfate (SDS) and p-nitrobezaldehyde (NB) was used as blank solution; also, NaOH and H_2SO_4, 96 wt%, hydrogen peroxide, 30 wt%, ($FeCl_3 \cdot 6H_2O$), and $FeSO_4 \cdot 7H_2O$ were used throughout the experiments. All the chemicals were in analytical purity and used without further purification.

2.2. Instrumentation

A Hitachi model 3310 UV–vis spectrophotometer with 1-cm quartz cells was used for determination of UDMH concentration in the solutions. The λ_{max} of UDMH solution was obtained at 392 nm. Ion analyser 225 model pH meter was used for pH measurements. Transmission electron microscope (TEM), EM900 model was used for the preparation of TEM images for characterizing and detecting possible morphological changes on AC surface.

2.3. Synthesis of AC-MNC

For synthesis, first of all, the AC was modified with nitric acid (63%) for 3 h at 80°C to make it hydrophilic. Then 1.0 g of the hydrophilic AC was dispersed in 100 mL aqueous solution containing 2.98 g $FeCl_3 \cdot 6H_2O$ and 1.53 g $FeSO_4 \cdot 7H_2O$ at 70°C under N_2 condition. NaOH solution (30 mL, 0.5 mol L^{-1}) was added dropwise to precipitate iron oxides. After the addition of NaOH solution, the mixture was adjusted to pH 11 and stirred for 1 h. The mixture was aged at 70°C for 2 h and was washed 3 times with doubly distilled water. The obtained AC-MNC was dried in an oven at 100°C for 1 h.

2.4. Procedure

Adsorption experiments were performed by adding a known amount of AC-MNC in 15 ml of UDMH solution with initial concentration of 10 mg L^{-1}, in Erlenmeyer flask (25 ml capacity). Generally, all effective parameters on adsorption procedure such as contact time, pH, sorbent mass, and temperature were experimented in different range of variable. Toward testing one, other parameters were kept constant. All this optimized parameters were used for studying equilibrium adsorption isotherms. In each test after adsorption process, adsorbent was readily separated using a magnet. The concentration of UDMH in the solution was measured spectrophotometrically at 392 nm [22,23].

UV–vis spectrum analysis (Fig. 1) proved a decrease in UDMH concentration in solution after adsorption process. The removal percent of UDMH was calculated using Eq. (1):

$$\text{Removal}\,(\%) = \frac{C_0 - C_e}{C_0} \times 100 \qquad (1)$$

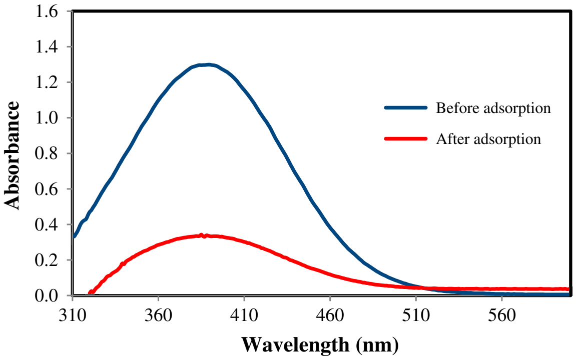

Fig. 1. The absorption spectra of UDMH, 10 mg L^{-1} concentration ([AC-MNC] = 20 mg, pH 6.0, t = 30 min, T = 25℃).

where C_0 is the initial concentration of UDMH and (C_e) is the equilibrium concentration of UDMH after adsorption process.

3. Results and discussion

3.1. Characterization of adsorbent

After the synthesis of AC-MNC, a test with the magnet showed that nanocomposite well attracted to the magnet. Fig. 2 shows the TEM image of AC-MNC.

3.2. Effect of pH

The removal efficiency varied for different pH values, presumably due to influence on adsorbent surface properties and change on adsorbate tendency to react with solid surface. The removal of UDMH was investigated using either H_2SO_4 or NaOH solution (0.01 mol L^{-1}) for pH adjustment. It was found that at low and high pH values, removal efficiency is lower than neutral state. At lower pHs, the amine group of UDMH would protonate to the form of $H_3\,N^{+}N(CH_3)_2$ and at high pHs, UDMH has partial negative charge. On the other hand, the zero point charge (ZPC) of AC-MNC was reported about 6.8 based on experimental research [24]. Below and above of pH_{ZPC}, the adsorbent exhibits a positive and negative net charges on its surface, respectively, thus in acidic and basic media, the adsorbent could not favor the adsorption of UDMH due to weak interaction and electrostatic repulsion which cause less removal efficiency [24]. As Fig. 3 shows, strong interaction and maximum adsorption capacity were found at pH 6.0.

3.3. Effect of adsorbent dosage

Various amounts of adsorbent ranging from 1 to 40 mg were used. The removal efficiency of UDMH varied with the different dosage of the adsorbent as shown in Fig. 4. An increase in the adsorption efficiency with a high adsorbent dosage is due to an increase in adsorbent surface area and more available adsorption sites to interact with UDMH molecules [25]. It was found that the adsorbent amount of 20 mg is a desirable value and there is no need to extra adsorbent. Therefore, this amount was selected to do subsequent experiments.

3.4. Effect of contact time

Determination of contact time of the process was carried out within the time range of 5–60. The plot is depicted in Fig. 5 revealed fast adsorption at the initial times due to available active sites on adsorbent surface but after about 20 min, the sites would occupied

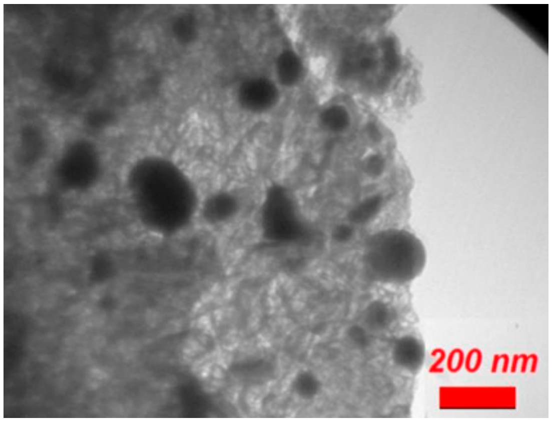

Fig. 2. TEM image of AC-MNC.

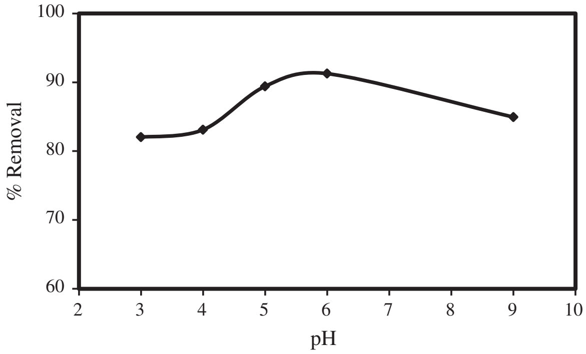

Fig. 3. The effect of pH on removal efficiency ([AC-MNC] = 20 mg, pH 6, V = 15 ml, $[UDMH]_0$ = 10 mg L^{-1}, stirring speed of 200 rpm, T = 25℃).

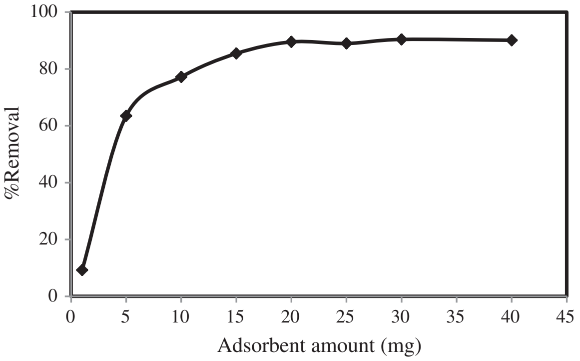

Fig. 4. The effect of adsorbent dosage on removal efficiency (pH 6, V = 15 ml, $[\text{UDMH}]_0$ = 10 mg L^{-1}, t = 30 min, stirring speed of 200 rpm, T = 25℃).

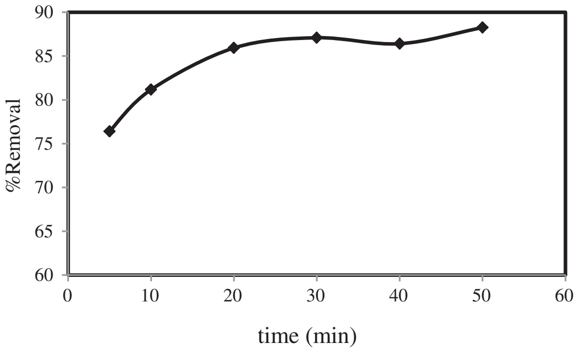

Fig. 5. The effect of contact time on removal efficiency ([AC-MNC] = 20 mg, pH 6, V = 15 ml, $[\text{UDMH}]_0$ = 10 mg L^{-1}, stirring speed of 200 rpm, T = 25℃).

which cause a very slight increase in removal efficiency. The AC-MNC showed the removal efficiency of approximately 90% within 30 min contact time. After this time, the adsorption efficiencies stayed almost steady and small differences on them could be negligible.

3.5. Adsorption isotherms

In adsorption technique, some equilibrium experiments should be done to study the relationship between adsorbate molecules and adsorbent sites. This relationship described by isotherm models [26]. The isotherm plot is q_e vs. C_e which carried out by varying the initial concentration of adsorbate from 5 to 70 mg L^{-1} at the optimum conditions. As identified in Eq. (1), C_e (mg L^{-1}) is the equilibrium concentration of UDMH in the solution and q_e (mg g^{-1}) is the amount of UDMH adsorbed per unit mass of adsorbent. As q_e *vs.* C_e plot in Fig. 6 shows, q_e values keep increasing with the adsorbate concentration increment. The adsorption data were modeled using two most commonly applied models, Freundlich and Langmuir models, to determine adsorption behavior.

3.5.1. Langmuir isotherm

The Langmuir isotherm is widely used for monolayer adsorption onto a homogeneous adsorbent surface containing finite number of identical sites. Also, the interaction between adsorbed molecules is negligible [27]. The Langmuir isotherm shows that the amount of adsorbed molecules (q_e) would increase as the adsorbate concentration increases up to a saturation point. As long as there are available surface sites, adsorption would increase by increasing adsorbate concentrations, but as soon as all of the first layer sites occupied, a further increase in adsorbate concentrations does not increase q_e value [28,29]. Therefore, in the plot of q_e vs. C_e, the value of q_e remains constant from a certain adsorbate concentration. The linear form of the Langmuir adsorption isotherm could be expressed as Eq. (2):

$$\frac{C_e}{q_e} = C_e\left(\frac{a_L}{K_L}\right) + \frac{1}{K_L} \tag{2}$$

where C_e (mg L^{-1}) is the equilibrium concentration of UDMH in the solution, q_e (mg g^{-1})is the amount of UDMH adsorbed per unit mass of adsorbent that could be calculated based on a mass balance equation as given in Eq. (3), $q_{max} = [K_L/a_L]$ signifies theoretical maximum adsorption capacity of an adsorbent (mg g^{-1}) which depends on the number of available surface sites, a_L (L mg^{-1}) and K_L (L g^{-1}) are the Langmuir constants that relate to energy of adsorption [30,31]. Langmuir isotherm obtained from plotting C_e/q_e vs. C_e and the values of q_{max} and K_L could be estimated from the slope and intercept of the given equation:

$$q_e = \frac{V(C_0 - C_e)}{m} \tag{3}$$

where the C_0 (mg L^{-1}) is the initial concentration of UDMH, V is the volume of experimental solution in liter, and m is the dry weight of adsorbent in gram. The regression coefficient of Langmuir isotherm and q_{max} value were calculated as 0.949 and 64.93, respectively.

3.5.2. Freundlich isotherm

The Freundlich equation is more widely used but provides no information on the monolayer adsorption capacity in contrast to the Langmuir model [32]. This model is an equation which assumes a heterogeneous adsorption surface in which adsorbent sites have different energies. It considers multilayer adsorption, accompanied by interactions between adsorbed molecules [28]. The linearized form of the Freundlich adsorption isotherm can be determined by the following equation:

$$\ln q_{\mathrm{e}} = \ln K_{\mathrm{f}} + \left(\frac{1}{n}\right) \ln C_{\mathrm{e}} \tag{4}$$

where C_e is the equilibrium concentration (mg L^{-1}), q_e is the amount adsorbed at equilibrium (mg g^{-1}), and K_f ($mg^{(1-1/n)}$ $L^{1/n}$ g^{-1}) and $1/n$ are empirical Freundlich constants related to sorption and are as a relative indicator of adsorption capacity, $1/n$ is indicative of the intensity of the energy reaction as well as the favorability and capacity of the adsorbent/adsorbate system [13]. These values were calculated from the intercept and slope of the plot of $\ln q_e$ vs. $\ln C_e$. The two isotherm constants and regression coefficients are presented in Table 1. As Fig. 7 shows, correlation coefficients represent that adsorption behavior could be fit with the Freundlich adsorption equation better than Langmuir model. Also in Freundlich model, increase in initial adsorbate concentration would increase the q_e value but due to adsorbent multilayer behavior, this value does not remain constant from a certain adsorbate concentration, compared with explained adsorbent behavior for Langmuir isotherm. Because as soon as the available surface sites of the first layer occupied, the active sites of other layers could be occupied with the adsorbate molecules.

3.6. Adsorption kinetics

Kinetic models are employed to evaluate the mechanism of the adsorption process and the rate at which the adsorbate is removed from aqueous solutions. In order to find out the kinetic behavior, the effect of contact time on the adsorbed amount of UDMH (q_t) at any time was carried out for two concentrations of 10 and 30 mg L^{-1} of UDMH which are presented in Fig. 8. The figure shows that in the first minutes of contacting adsorbate and adsorbent, UDMH molecules rapidly interacted with the adsorbent surface due to high concentration gradient between the absorbent and solution. But after about 20 min, the adsorption rate is reduced until the system reaches equilibrium state in 30 min. By increasing the contact time of 30 min to 1 h, there was no change in the absorption rate. Kinetic study shows that the data were well fitted by pseudo-second-order kinetic model which was investigated as follows.

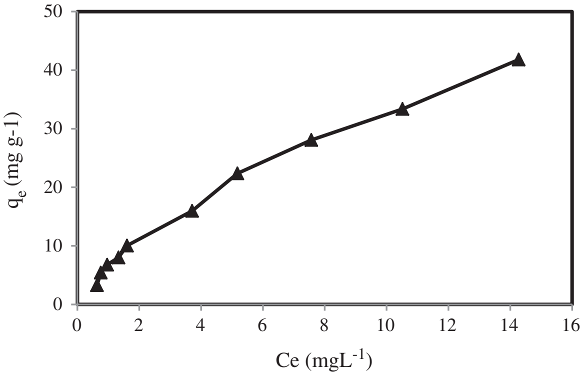

Fig. 6. Adsorption isotherm of UDMH on AC-MNC (pH 6, V = 15 ml, t = 30 min, stirring speed of 200 rpm, temperature of 25 ± 1°C).

The pseudo-second-order adsorption kinetic model consists of all the steps of adsorption including external film diffusion, adsorption, and internal particle diffusion. The equation can be expressed as [33]:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_2 (q_{\mathrm{e}} - q_t)^2 \tag{5}$$

where k_2 (g/mg h) is the pseudo-second-order rate constant for the adsorption. Eq. (5) can be changed linearly into Eq. (6):

Table 1
Langmuir and Freundlich parameters and their regression coefficients

Langmuir	a_L (L mg^{-1})	k_L (L g^{-1})	$q_{max} = [k_L/a_L]$ (mg g^{-1})	R^2
	0.107	6.963	64.93	0.949
Freundlich	$1/n$	K_f ($mg^{(1-1/n)}$ $L^{-1/n}$ g^{-1})		R^2
	0.687	6.82		0.9967

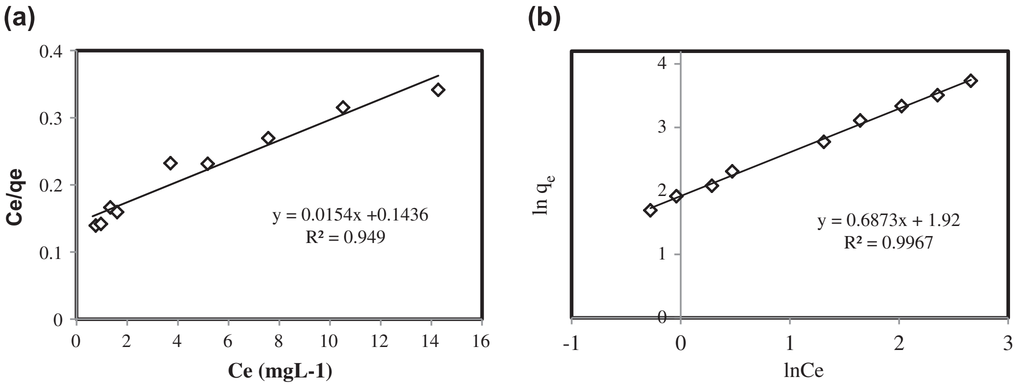

Fig. 7. Adsorption isotherm plots of UDMH on AC-MNC: (a) Langmuir isotherm and (b) Freundlich isotherm.

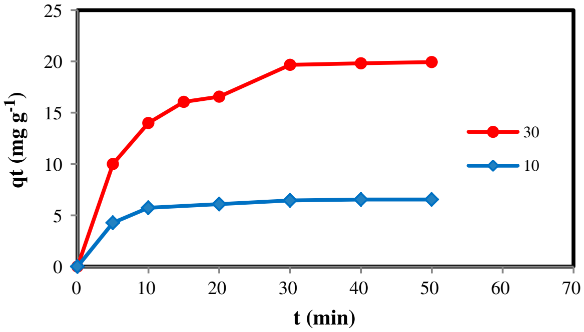

Fig. 8. Adsorption kinetics of UDMH on AC-MNC (pH 6, $V = 15$ ml, stirring speed of 200 rpm, $T = 25$°C).

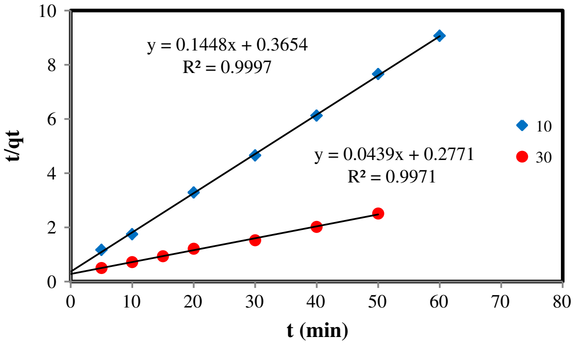

Fig. 9. Pseudo-second-order kinetic model plot for the adsorption of UDMH on AC-MNC (pH 6, $V = 15$ ml, stirring speed of 200 rpm, $T = 25$°C).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{6}$$

According to the regression coefficient obtained from the plot of t/q_t vs. t showed in Fig. 9, adsorption kinetic was fitted well with pseudo-second-order kinetic model. Also the values of q_e from kinetic model and experiment given in Table 2 are close and this further showed the good fit of this mode.

3.7. Adsorption thermodynamics

Thermodynamic parameters provide additional in-depth information regarding the energetic changes involved during adsorption [34]. The thermodynamic parameters such as standard enthalpy change (ΔH°), the Gibbs free energy change (ΔG°), and entropy change (ΔS°) for the adsorption of UDMH on AC-MNC were calculated from the following equations:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{7}$$

$$K_d = \frac{q_e}{C_e} \tag{8}$$

where K_d is the adsorption coefficient, R is the ideal gas constant (8.314 J mol^{-1} K^{-1}), and T is absolute temperature (K). The values of enthalpy change (ΔH°) and entropy change (ΔS°) were obtained from the slope and the intercept of van't Hoff plot of $\ln K_d$ vs. $1/T$ as presented in Fig. 10(a). The positive values of ΔH° confirm endothermic nature of the adsorption process. In such condition, an increase in the temperature leads to increase in adsorption efficiency as shown in Fig. 10(b). Positive ΔS° values imply good affinity of the UDMH molecules toward the adsorbent [35]. Moreover, the positive ΔS° values indicate the increase in randomness at the solid–liquid interface during adsorption which might be due to following reason.

Table 2
Pseudo-second-order kinetic parameters and regression coefficients

$[UDMH]_0$ (mg L^{-1})	$q_{e,cal}$	$q_{e,exp}$	$K_2 \times 10^{-2}$ (g mg^{-1} h^{-1})	R^2
10	6.88	6.61	1.29	0.9997
30	22.07	19.93	0.74	0.9971

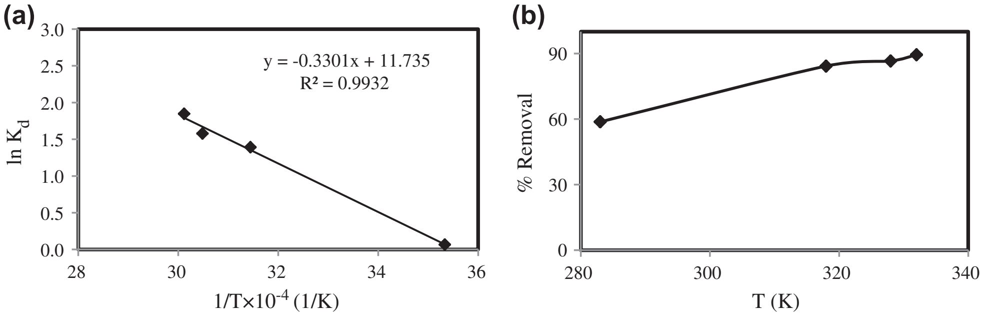

Fig. 10. The plot of van’t Hoff equation (a) and temperature effect on adsorption efficiency (b) of UDMH onto AC-MNC.

UDMH in solution is surrounded by a tightly bound hydration layer where water molecules are more highly ordered than in the bulk water. When UDMH molecule comes closer to interact with the hydration surface of adsorbent, the ordered water molecules in these two hydration layers get disturbed that increase the entropy of water molecules. Although the adsorption process cause the decrease in freedom degree of UDMH molecules, it seems likely that because the entropy increase in water molecules is greater than entropy decrease in UDMH molecules, so the entropy change of this system is positive [36]. Gibbs free energy change (ΔG°) could be determined from the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{9}$$

The negative value of ΔG° indicates spontaneous adsorption which is thermodynamically favorable [33].

The values of activation energy (E_a) and sticking probability (S^*) were calculated using experimental data based on a modified Arrhenius-type equation related to surface coverage (θ) as Eq. (10) shows:

$$S^* = (1 - \theta\,)\, e^{-E_a/RT} \tag{10}$$

$$\theta = \left[1 - \frac{C_e}{C_0}\right] \tag{11}$$

The parameter S^* indicates the potential of an adsorbate to remain on the adsorbent and its value lies in the range $0 < S^* < 1$ and is dependent on the temperature of the system. The activation energy and sticking probability were estimated from the plot of ln $(1 - \theta)$ vs. $1/T$ as shown in Fig. 11 and the value of parameters are given in Table 3.

4. Comparison of various adsorbents

To compare capability of various adsorbents on the removal of UDMH, AC and multiwall carbon nanotube magnetic composite (MWCNT-MC) were assessed that their results were demonstrated in Table 4. As showed in the table, all of the adsorbents

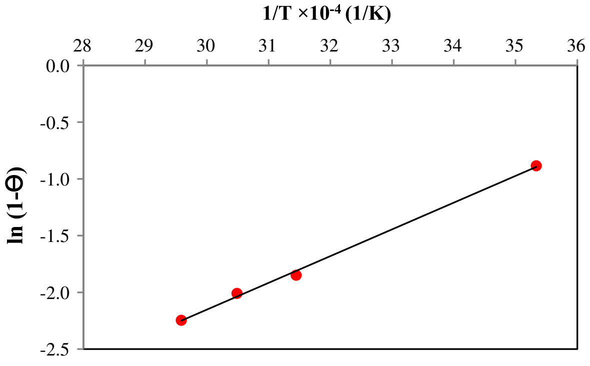

Fig. 11. Plot of ln $(1 - \theta)$ vs. $1/T$ for adsorption of UDMH onto AC-MNC.

Table 3
Thermodynamic parameters and regression coefficients of van't Hoff plot for adsorption of UDMH of 10 mg L^{-1} onto AC-MNC

Temperature (K)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} k^{-1})	E_a (kJ mol^{-1})	S^*	R^2
283	−27.61	2.74	97.56	1.96×10^{-3}	9.9×10^{-5}	0.9932
318	−31.02					
328	−31.99					
338	−32.38					

Table 4
Summary of UDMH adsorption of various adsorbents

		Adsorption isotherm					
		Langmuir			Freundlich		
Adsorbent	Removal (%)	q_{max} (mg g^{-1})	k	R^2	$1/n$	k	R^2
AC	88.24	58.47	0.091	0.929	0.665	1.21	0.991
AC-MNC	91.36	64.93	0.107	0.949	0.687	6.82	0.997
MWCNT-MC	87.73	99.14	0.027	0.986	0.804	3.25	0.993

used for UDMH adsorption have lower removal efficiency than AC-MNC. Since AC separation encounter difficulties and MWCNT-MC is not cost effective, so AC-MNC is preferable due to its fast and easy separation by a magnet and lower price.

5. Conclusion

The adsorption results elucidate that UDMH can be efficiently removed by AC-MNC in aqueous solutions. More than 90% UDMH removal efficiency was obtained within 30 min of contact time, 20 mg of adsorbent at pH 6 and room temperature. Adsorption data were fitted by Freundlich model better than Langmuir model. Furthermore, the kinetic of the adsorption process fitted by pseudo-second-order model. It achieved that adsorption process was endothermic and spontaneous from ΔH° and ΔG° values, respectively. According to better correlation coefficient of Freundlich isotherm model, adsorption of UDMH by this adsorbent is well fitted by Freundlich model. The present study concludes that AC-MNC is a proper adsorbent for this carcinogen and toxic pollutant in the environmental pollution clean-up.

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