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Characterization of diethyl ether adsorption on activated carbon using a novel adsorption refrigerator

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ABSTRACT

In order to remove the limitations originating from inefficient heat and mass transfer in adsorption refrigeration/heat pump, an innovative arrangement design was proposed. It was equipped with meshed multi-tubular involving activated carbon in a sealed cylindrical adsorber. Related aspects of adsorption refrigeration key parameters were addressed. Working pair, activated carbon–diethyl ether, is used in the above system in order to determine the *optimum* adsorption refrigeration parameters.

In order to estimate the adsorption characteristics and the adsorption capacity of the adsorbent, the adsorption isotherms of that adsorbent, with a specific adsorbate, are carried out. The measured adsorption data were adequately described by the Langmuir equation. The adsorption capacity of the diethyl ether on activated carbon at 26, 35, and 50 °C were 0.0159, 0.0220, and 0.0188 mmol/g, respectively.

Two kinetic adsorption models namely pseudo-first and second order kinetic models were investigated. The thermodynamic parameters, ΔH°, entropy, ΔS°, and Gibbs free energy, ΔG°, of the adsorption process were also obtained from the gas adsorption experiments at various temperatures. These values were −45.84 kJ/mol, −88.87 J/(mol K), and −19.27 kJ/mol, respectively.

The pseudo-first order model was not applicable in this adsorption system, suggesting that the adsorption process and the rate-limiting step was the pseudo-second order reaction. Therefore, the dominant mechanism might be a chemisorption process between the diethyl ether molecules and the activated carbon surface. The k_2, however, decreased as the initial diethyl ether pressure increased.

1. Introduction

Most of the refrigeration and heat pump technologies are dominated by vapour compressor system [1]. However, the vapour compressor system is highly concerned with the environmental regulations, as most of the vapour compressor technologies are using refrigerant gases which are known as ozone depleting and global warming gases. Therefore, there is great demand to originate or to develop an alternative to vapour compressor refrigeration devices. Thermally driven, adsorption technology is one of the possible alternatives. In recent years, solid sorption systems driven by low temperature waste heat or solar energy have received increasing attention [1]. In comparison with the existing absorption systems and vapour compression refrigeration systems, the advantages of adsorption systems are less vibration, simple control, low initial investment and expenditure, and less noise [2].

Adsorption is a surface phenomenon occurring at the interface of two phases, in which cohesive forces including Van der Waals forces and hydrogen bonding, act between the molecules of all substances irrespective of their state of aggregation [3]. Surface forces or unbalanced forces at the phase boundary cause changes in the concentration of molecules at the solid/fluid interface. Solid and the fluid adsorbed on the solid surface are referred to as adsorbent and adsorbate, respectively. Adsorption may be due to a physical process generally referred to as physical adsorption, or physisorption, caused by Van der Waals forces, or a chemical process referred to as chemical adsorption or chemisorption, involving valence forces.

However, regardless of the type of adsorption involved, all involve evolution of heat of adsorption. The heat of adsorption is usually small in physisorption processes and large in chemisorption. Adsorbent substances can be restored to original conditions by a desorption process usually involving the application of heat, except in some cases chemisorption processes may be irreversible. Depending upon adsorbent and adsorbate phases, adsorption systems may be classified as solid/gas, solid/liquid, liquid/gas and liquid/liquid [4].

Adsorption characteristics of adsorbents are determined by the adsorption isotherms, for the amount a substance adsorbed [4]. Adsorption is always accompanied by evolution of heat, the quantity of which depends upon the magnitude of the Van der Waals

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forces involved, phase change, electrostatic energies and chemical bonds. Heats of adsorption are either derived from adsorption isotherms, generally referred to as the isosteric heat of adsorption or determined experimentally using the calorimetric method, referred to as differential heat of adsorption [4–6].

Adsorption refrigeration/heat pump systems works as following: the refrigerant is vapourized by the heat from cooling space and the generator (absorbent tank) is cooled by ambient air. The vapour from the cooling space is leaded to the generator tank and absorbed by adsorbent. The rest of the refrigerant is cooled. In the regeneration process, the adsorbent is heated at a high temperature until the refrigerant vapour in the adsorbent is desorbed out, goes back and condenses in the refrigerant tank (condenser).

This process relies on adsorption capacity of a particular solid for particular gas between two temperatures. Targeted gases are adsorbed by a solid material at low temperature, approaching a state of gas phase/adsorbed phase equilibrium. The latent heat of adsorption is rejected to a cryogenic bath or to the environment. In the case of a vacuum pump, the pressure of the vacuum chamber is reduced; in the case of the compressor, fresh gases from the environment further feed the compressor. Next, when the temperature of the adsorbent is raised, the adsorption capacity of the solid is reduced and the gas is releases either to the environment or to a closed volume that becomes pressurized (desorption (generation) process). The heat necessary for the generation process can be supplied by a low-grade heat source, such as solar energy. There are several factors for design of an adsorber (adsorption compressor), including adsorbent material selection, heat and mass transfer, and material properties.

Research has shown that solid adsorption technology has a promising potential for competing with conventional absorption and vapour compression technologies. The commercial solid/vapour adsorption systems are still non-existent [7]. There are two types of adsorbates used with the activated carbon, ammonia and methanol. Many investigations focus on the activated carbon–ammonia system during the current decades [7]. Wang et al. (2005) demonstrated a heat pipe type adsorption ice-maker designed for fishing boats with specific cooling power and coefficient of performance about 731 W/kg and 0.41, respectively, at the evaporating temperature −15 °C [8]. A multifunction heat pipe adsorption refrigerator, using compound adsorbent-ammonia working pair, was studied by Wang et al. (2004) [9]. The chemical adsorbent $CaCl_2$ has the problems of expansion and agglomeration [10]. Kumita et al. (2002) studied the adsorption equilibria of ethanol and methanol vapours on activated carbon fibre (ACF) and granular one (GAC) at 30 and 50 °C. The cooling effect in an ideal cycle of adsorption refrigerators was estimated under the typical operating temperature conditions from the predicted isotherms. The results obtained showed that the ACF with large surface area has high adsorptive capacity for both ethanol and methanol vapours. El-Sharkawy et al. (2006) also improved the performance of thermally powered adsorption/cooling systems by selecting a new adsorbent/refrigerant pair. Adsorption equilibrium data of ethanol onto Unitika activated carbon fibre (ACF) of types (A-20) and (A-15) were measured. It was found that ACF (A-20)/ethanol pair has considerably higher adsorption capacity than ACF (A-15)/ethanol pair. Zisheng et al. (2006) [11] overcome these problems by appropriate technology. The compound adsorbent was mixed with $CaCl_2$ and activated carbon by a mass ratio of 4:1, can improve the adsorption performance greatly. In this paper, new adsorbent–adsorbate combination, the activated carbon and the diethyl ether, will be investigated.

Activated carbons have been used as adsorbents in various industrial fields, such as solvent recovery, gas separation, catalysts, wastewater treatment and deodorization [3]. The activated carbons are characterized by a strong adsorption capacity that is attributed to their large internal surface area, high porosity, and high degree of surface reactivity [3]. Activated carbon contains heteroatoms on its surface and the main heteroatom is oxygen. Different functional groups can be derived from these chemical heteroatoms. The most common are: carboxyl, lactonic, carbonyl and phenolic. Moreover, activated carbons can show acidic and basic pH values in aqueous solution. The basic properties are ascribed to the presence of basic surface oxides. Carbons with low oxygen content show basic properties and anion exchange behaviour. The acidic surface properties are due to the presence of acidic surface groups. Carbons with high oxygen content, on the other hand, show acidic surface properties and cation exchange behaviour [12].

Diethyl ether with the chemical formula $(C_2H_5)_2O$ is a polar molecule that can interact with the carbon surface via dispersive interactions of its hydrocarbon moiety, two ethyl groups. It can also be hydrogen bonded to oxygen containing surface functional groups such as carboxylic and phenolic compounds. In addition, ether is capable of donating a pair of electrons from the oxygen lone pairs and thus interacts with the electron pair receptors on the surface as a Lewis base [13]. The heat of diethyl ether adsorption on carbon black was reported to be about 36 kJ/mol [14].

The performance of this system is largely determined by heat transfer process. Good heat transfer can significantly improve the efficiency of the heat pump and enhancement of bed thermal conductivity. Mass transfer resistance is due to gas flow through the bed consisting of a porous medium and to gas diffusion inside adsorbent particles [15].

The heat and mass transfer limitations result in extended durations of the adsorption heat pump cycles [16]. An innovative arrangement design equipped with a multi-tubular involving adsorbent in meshed tubes in a sealed cylindrical adsorber is proposed to eliminate the limitations originating from inefficient heat transfer in adsorption heat pumps. Such an arrangement, which allows a good contact between the metal and the adsorbent and within the adsorbent layer itself, would provide the opportunity of shortening the cycles to a great extent. One working pair, activated carbon–diethyl ether, is proposed in the system to determine the *optimum* adsorption refrigeration parameters.

It is of importance to precisely analyse the performance of an adsorption refrigeration cycle, based on an accurate determination of the adsorbent–adsorbate (refrigerant) behaviour and on an exact understanding of the influence of operating conditions and the working pair characteristics on the performance [17]. This includes evaluation of the adsorption capacity, rate of adsorption and the effect of various adsorption refrigeration parameters.

Therefore, the aim of this paper is to design of an innovative adsorber by taking into account the heat and mass transfer effect, study the equilibrium adsorption isotherms, adsorption kinetic rate and investigate the effect of a number of key parameters on the adsorption process and develop a complete, precise and clear understanding of the adsorption refrigeration using the activated carbon. Thermodynamic parameters are also calculated for the system.

2. Experimental

2.1. Materials

Activated carbon, NORIT PK 1-3 was obtained from NORIT, Holland in a granular bead form. It was produced by steam activation. Some of the physical and chemical properties for NORIT PK 1-3 are presented in Table 1.

The carbon was sieved by using a Sieve Shaker, HAVER & BOECKER EML, the range collected was 850–1000 μm. The carbon particles were sealed in plastic bags for further use in the adsorption experiments without any further treatment.

Table 1
Some chemical properties for NORIT PK 1-3.

Typical analysis[a]		
Apparent bulk density	g/l	260
BET	m^2/g	1190
Iodine adsorption	mg/g	800
Ash content	%	7
Moisture (as packed)	%	2
Particle size		
>3.4 mm	%	1
>2.4 mm	%	25
>1.7 mm	%	55
>1.0 mm	%	92
Density backwashed and drained	g/l	230
D60/D10		1.9
Total pore volume	cm^3/g	1.2
Supernatant, pH		9.49

[a] Norit data sheet.

2.2. Design of adsorption system

An innovative arrangement design equipped with multi-tubular involving activated carbon in meshed tubes in a sealed cylindrical adsorber is proposed. The schematic diagram of the adsorption system and the corresponding draw of the cross-section of the adsorber are illustrated in Fig. 1. This adsorption apparatus (Fig. 1) was utilized to assess the adsorption capacity of the diethyl ether into the activated carbon during the period of adsorption (*t*, min).

Fig. 1 consists of: (i) a multi-tubular adsorber, (ii) a constant temperature water bath, (iii) pressure gauge and (iv) vacuum pump.

Adsorption bed is one of the most important components for an adsorption refrigeration system, and its mass and heat transfer has a strong influence on the system performance. Fig. 1 shows the structure of adsorption bed employed in the adsorption refrigeration system, which is made up of 19 fined tubes to enlarge the heat transfer surface, and every fined tube is filled with the activated carbon. The mass of the activated carbon per bed is 7.8–8.4 g.

2.3. Procedure

Equilibrium adsorption experiments are carried out at three different adsorber temperatures namely at 26, 35 and 50 °C. The adsorber temperature is kept constant by controlling the adsorber water bath temperature (GFL, Gesellschaft fur Lbortechnik mbH, 1083, Germany). Prior to each adsorption process, the activated carbon sample is washed several times by deionized water. Then it

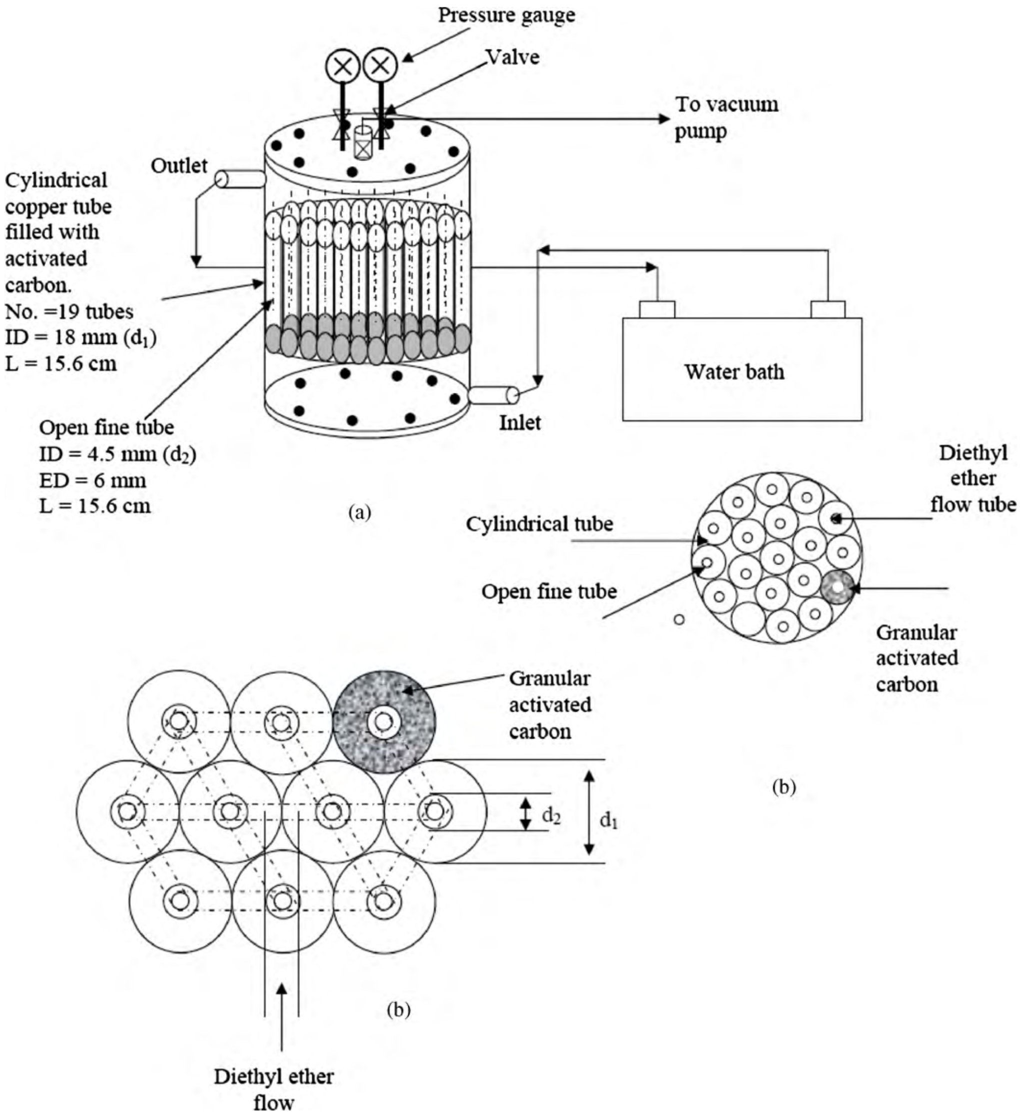

Fig. 1. (a) The adsorption system used in this study and (b) the cross-section of the adsorber.

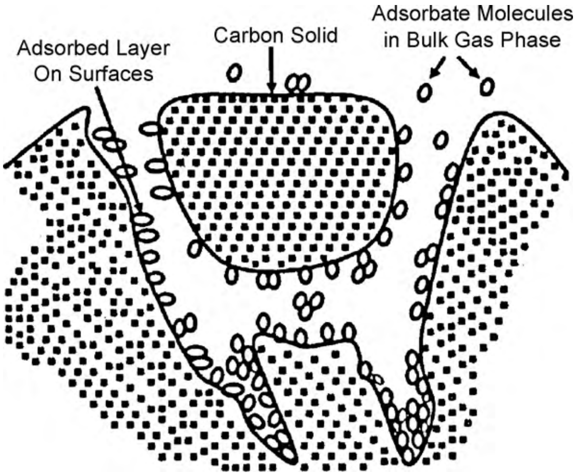

Fig. 2. Adsorption processes in activated carbons: transfer of adsorbate molecules to adsorbent [11].

is placed in an oven for 12 h. The oven temperature is kept constant at 105 °C. After that a 150 g of the activated carbon at fixed particle size (850–1000 μm) is placed into the adsorber to degas it under vacuum condition by a vacuum pump (Mountain 8407—6.0 Single Stage Deep Vacuum Pump) for duration of an hour till reaching to −1.0 atm. During evacuation process the adsorber water bath temperature is kept constant at 26, 35 and 50 °C for an hour. Adsorption process started after 2 h in order to reach the equilibrium condition. Then, a series of experiments was performed using various initial diethyl ether (Fluka, 99.8%), pressures 0.1, 0.15, 0.2, 0.25, 0.3 and 0.35 atm. A specific diethyl ether volume was loaded into the adsorber by stepwise procedure till reaching the required pressure. To measure the amount of diethyl ether adsorbed at equilibrium condition, the pressure gauge reading is taken regularly at different time intervals over 100 min.

3. Results and discussion

The activated carbons are characterized by their strong adsorption capacity, which can be as high as 0.6–0.8 cm^3/g which occur mostly in cavities of molecular dimensions called micropores. Fig. 2 depicts the adsorption process showing transfer of adsorbate molecules through the bulk gas phase to the surface of the solid and diffusion onto the internal surfaces of the pores in the solid adsorbent. Therefore the adsorption capacity of the activated carbon depends on the type of pores and the total surface area available for adsorption [18].

A gas adsorption results in the removal of adsorbates from solution [19]. The concentration of the adsorbate remaining in solution is in a dynamic equilibrium with that on surface. Therefore, there is a distribution of the adsorbate between the liquid and the solid phases. This distribution ratio may be a function of the concentration of the adsorbate, the concentration and nature of competing adsorbates, the nature of the solution, pH, and surface chemistry of solid phase [19]. The characteristics of the adsorbate that are of importance include: solubility, molecular structure, molecular weight and polarity [20]. This distribution is to express the quantity q_e as a function of C_e at fixed temperature, the quantity q_e is the amount of adsorbate adsorbed per unit weight of solid adsorbent and C_e is the equilibrium concentration (Eq. (1)). Thus, the adsorption isotherm is a functional expression for the variation of adsorption with concentration of adsorbate in bulk solution at constant temperature [20]:

$$q_e = \frac{(C_o - C_e)V}{m} \tag{1}$$

C_o is the initial gas concentration (mol/dm^3), C_e is the equilibrium gas concentration (mol/dm^3), V is the gas volume (dm^3) and m is the mass of adsorbent (g).

The concentration in the adsorber may be determined by using the ideal gas law [21]:

$$PV = nRT \Rightarrow C = \frac{P}{RT} \quad \text{where} \quad C = \frac{n}{V} \tag{2}$$

$$\Rightarrow q_e = \frac{(P_o - P_{eq})/RT}{m/V} \tag{3}$$

where P, T and V denote the pressure (atm), temperature (K) and the void volume (dm^3), respectively. R is the universal gas constant (0.08206 dm^3 atm/(K mol)) while C and m represent the concentration of the diethyl ether (mol/dm^3) and mass of the activated carbon used (g), respectively.

The void volume in the adsorber may be expressed as [21]:

$$V = \frac{\pi r^2 L V_o}{100 - V_o} \tag{4}$$

where r denotes the actual radius of the cylindrical tubes ($=d_1 - d_2$) (dm). L is equal to the length of the tubes (dm) (Fig. 1) while V_o represents the percentage of void volume in the adsorber.

The gas adsorption data were further analyzed using the Langmuir model, which is the most frequently applied model [22]. The experimental data were fitted to the Langmuir equation (Eq. (5)) to describe the adsorption of the diethyl ether onto the activated carbon:

$$q_e = \frac{X}{m} = \frac{K_L C_e}{1 + a_L C_e} \tag{5}$$

where q_e is the equilibrium solid phase gas concentration. It is usually expressed as the amount of gas adsorbed per unit mass of adsorbent (mol/g), X the amount of gas adsorbed (mol), m the mass of adsorbent (g), K_L the adsorption constant (dm^3/g), C_e the equilibrium gas phase concentration (mol/dm^3), a_L the Langmuir isotherm constant (dm^3/g); it is related to K_L by $Q_{mon}.a_L = K_L$ and Q_{mon} is the Langmuir monolayer capacity.

The equilibrium adsorbed pressures of the adsorption of the diethyl ether onto the activated carbon as function of time at different temperatures and initial pressures shown are in Fig. 3.

Several experiments were carried out to determine the effect of initial diethyl ether pressure on the activated carbon. However, initial pressure (concentration) provides an important driving force to overcome all the mass transfer resistance of the diethyl ether between the aqueous solution and the activated carbon surface. As a result, high initial diethyl ether pressure will enhance the adsorption process [23]. Adsorption kinetic studies were measured as a function of initial diethyl ether pressure and the results are illustrated in Fig. 3.

Fig. 3 indicates that the adsorption of the diethyl ether was very fast in the first few minutes (0–2 min). It is found that the time required to reach the adsorption equilibrium between the activated carbon and the diethyl ether was 45, 30, and 20 min at 26, 35, and 50 °C, respectively. The diethyl ether pressure was decreased in the first contact of the activated carbon with the diethyl ether, where the pressure of the diethyl ether was decreased to 42, 17, 59, 64 and 64% from the initial diethyl ether pressure at equilibrium when the diethyl ether pressures were 0.12, 0.145, 0.245, 0.275, and 0.33 atm, respectively. Steep slope curves of the diethyl ether adsorption onto the activated carbon indicate instantaneous adsorption which may be due to effects of surface functional groups found on the activated carbon surface. Therefore, the adsorption of the diethyl ether is thought to have taken place probably via surface adsorption until the surface functional sites are fully occupied, thereafter, the diethyl ether molecules diffuse into the pores of the activated carbon for further adsorption.

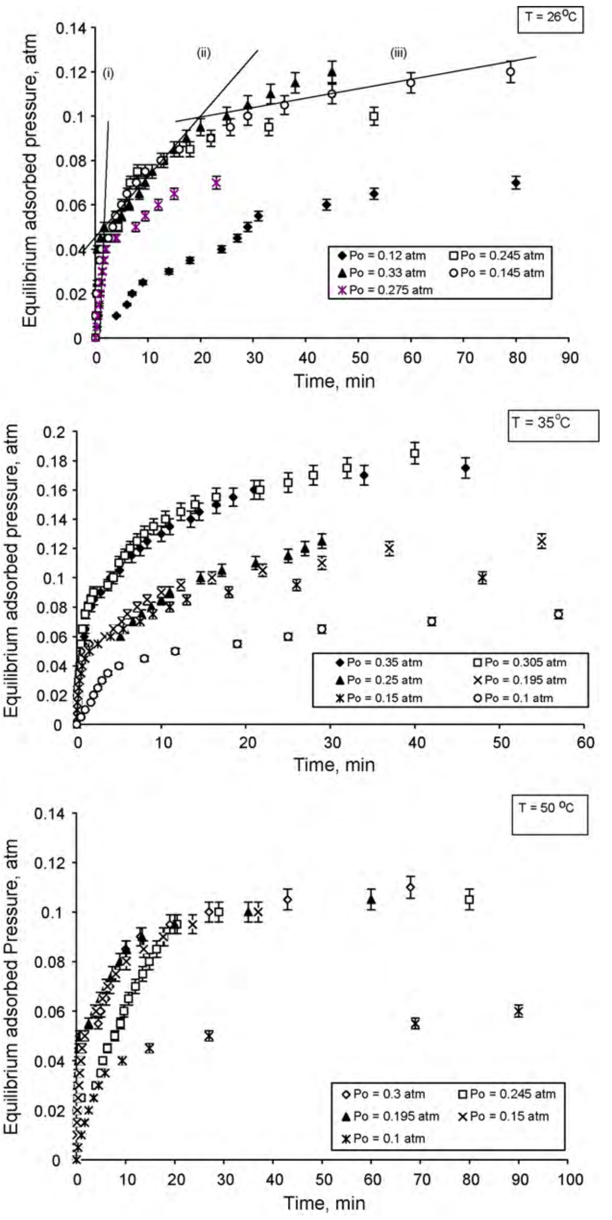

Fig. 3. Adsorption isotherms and adsorption kinetics of the diethyl ether onto the activated carbon at different temperatures and initial pressures. Experimental conditions: mass of the activated carbon = 150 g, volume of the rector = 0.555 dm^3, V_o = 0.71%, and density of the diethyl ether = 0.7134 g/cm^3.

Due to the porosity of the activated carbon, intraparticle diffusion was expected in the adsorption process. It is clear that the curves in Fig. 3 (at 26 °C) represent three distinct phases: (i) instantaneous adsorption of the diethyl ether molecules within 2 min of the contact times and (ii) a gradual attainment of the equilibrium where only about 30% of the adsorption is encountered. This is due to the occupation of the all active sites on the adsorbent surface and (iii) an equilibrium attainment of the diethyl ether molecules onto the activated carbon. In addition, the initial curves are linear and the final portion is also linear. The initial curved portions may be attributed to the boundary layer diffusion effect, while the final linear portions are related to the intraparticle diffusion effects. This effect will be study in the next publications.

Fig. 3 shows the experimental results (*equilibrium adsorbed pressure* versus t) obtained from a series of experiments performed using various initial diethyl ether pressures 0.1, 0.15, 0.2, 0.25, 0.3 and 0.35 atm. A clear feature of adsorption kinetic of the diethyl ether onto the activated carbon is the slow approach to adsorption equilibrium. It is clear from Fig. 3 that the adsorption capacity, q_t, of the diethyl ether increases with time, in particular, in the first 20 min before decreasing indicating multiple-rate processes. The same behaviour was observed by Liu and Huang (2003) [24]. The multiple-rate character may be explained by: (i) heterogeneity of adsorption sites on the adsorbent which may cause differences in adsorption rate and (ii) the adsorption of the adsorbate tends to effect and change the adsorption mechanism and type of bondongs; hence the repulsion forces become stronger as adsorption progresses [24]. It is also noticed that the maximum adsorption capacity increased gradually to reach a constant value beyond which no more is removed from the diethyl ether. Pseudo-first and second order kinetic model were used to investigate the behaviour of the diethyl ether adsorption onto the activated carbon and the results are illustrated in Table 2. It is clear from the experimental results, represented in Fig. 3, that at high initial pressures the lines lie close together. However, for low pressure (0.1 atm) the initial uptake of the diethyl ether is quite rapid, indicating a rapid surface adsorption.

It is important when measuring the amount adsorbed at a specific temperature and pressure to elucidate the adsorption characteristics. The adsorption characteristics in the gaseous phase cannot control the adsorption time as do those in the liquid phase. The smaller pores fill first and then the larger pores. The adsorption isotherm data (Fig. 3) at the elapsed times were applied to the first and second order equations of the typical adsorption rate equation.

Various kinetic models have been reported in the literature to describe the adsorption process [26,27]. Each model has its own limitations and is derived according to certain conditions. In this paper, two kinetic adsorption models will be used to describe the experimental data.

The pseudo-first order equation could be described as [23]:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \Rightarrow \ln(q_e - q_t) = \ln(q_e) - k_1 t \qquad (6)$$

$$\text{By rearranging, } \ln\left(\frac{q_e - q_t}{q_e}\right) = -k_1 t \Rightarrow q_t = q_e(1 - \exp(-k_1 t)) \qquad (7)$$

where q_t is the amount of gas adsorbed on the surface of adsorbent (mg/g) at any time t (min), q_e is the amount of gas adsorbed at equilibrium (mg/g).

To calculate the rate constant of pseudo-first order, k_1, a plot of $\ln(q_e - q_t)$ versus t gives a straight line with slope equals to $(-k_1)$. In many cases the value of q_e is unknown and adsorption tends to become unmeasurably slow. Thus, it is necessary to obtain the real equilibrium adsorption capacity by extrapolating the experimental data to $t = \infty$ or by using a trial and error method [23].

However, the simplest way to describe the kinetics of the diethyl ether adsorption from an aqueous solution could be represented by using a pseudo-second order equation [28]:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t, \qquad h = k_2 q_e^2 \Rightarrow q_t = q_e \frac{q_e k_2 t}{1 + q_e k_2 t} \qquad (8)$$

k_2 is the rate constant of a pseudo-second order equation (g/(mg min)) and h is the initial adsorption rate (mg/(g min)).

The results of pseudo-first and second order equation parameters are presented in Table 2.

It can also be seen that the calculated adsorption capacity, $q_{e,cal}$, from pseudo-second order model agreed well with the experimental values. It is also clear from Table 2 that the pseudo-second order model fitted well with the experimental data at various initial diethyl ether pressures. The pseudo-first order model was not applicable in this adsorption system, suggesting that the adsorption process and the rate-limiting step is the pseudo-second order reaction. Therefore, the dominant mechanism might be a chemisorption process between the diethyl ether molecules and the activated car-

Table 2
First and second order equation of adsorption isotherms of the diethyl ether onto the activated carbon at different temperatures.

Temp. (°C)	P_o (atm)	First order equation				Second order equation			
		$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	k_1 (1/min)	R^2	k_2 (g/(mg min))	h (mg/(g min$^{1/2}$))	$q_{e,cal}$ (mg/g)	R^2
26	0.330	1.4152	1.133	0.069	0.9740	0.1496	0.3155	1.452	0.9695
	0.275	0.8255	0.663	0.153	0.9496	0.3726	0.3077	0.9087	0.9846
	0.245	1.1794	0.794	0.118	0.9622	0.2615	0.3943	1.228	0.9950
	0.145	1.4152	1.017	0.049	0.9731	0.1550	0.3188	1.434	0.9909
	0.120	0.8255	0.886	0.047	0.9745	0.0265	0.0374	1.189	0.9740
35	0.350	1.8946	1.4472	0.1026	0.9735	0.2518	0.9117	1.9029	0.9919
	0.305	2.0028	1.4469	0.0845	0.9447	0.2109	0.8394	1.9952	0.9914
	0.250	1.3532	1.1046	0.0984	0.9739	0.3792	0.6429	1.3021	0.9609
	0.195	1.3532	0.9908	0.0759	0.9492	0.2913	0.5334	1.3532	0.9891
	0.150	1.0826	0.7886	0.1112	0.9595	0.5981	0.7043	1.0852	0.9927
	0.100	0.8120	0.6455	0.0603	0.9636	0.1724	0.1330	0.8786	0.9938
50	0.300	1.1355	0.7915	0.0735	0.9222	0.4182	0.5443	1.1408	0.9930
	0.245	1.0839	1.1194	0.1036	0.9775	0.1301	0.1790	1.1732	0.9667
	0.195	1.0839	0.7317	0.0901	0.9071	0.6003	0.7087	1.0865	0.9950
	0.15	1.0323	0.7740	0.1197	0.9670	0.5989	0.6455	1.0381	0.9923
	0.100	0.6194	0.4093	0.0348	0.8217	0.3111	0.1256	0.6352	0.9978

bon surface. The k_2, however, decreased as the initial diethyl ether pressure increased.

The effect of temperature on the diethyl ether adsorption onto the activated carbon was carried out at 26, 35, 50 °C and the results are illustrated in Fig. 3. It seems that an increase in the temperature leaded to fluctuate in the adsorption capacity, q_t, in which the adsorption capacity was changed from 2.0028 to 0.6194 mg/g when the temperature changed from 26 to 50 °C at different initial pressures. Moreover, the equilibrium time was shorter with increasing temperature. It could be explained that higher temperature increases the reaction rate and decreases the particle density, which forms larger pore size and it is easier for the diethyl ether molecule to diffuse [25].

Examination of Fig. 3 shows that the shape of equilibrium adsorbed pressure versus time plots of the diethyl ether adsorption onto the activated carbon at 26 and 35 °C are quite similar in comparison to that at 50 °C. It could be inferred that the mechanism of the diethyl ether adsorption onto the activated carbon at 50 °C was quite different and the effect of the intraparticle diffusion on the adsorption process was higher. It could be attributed to the adsorption of the diethyl ether molecules at high temperature becoming more important into the pores instead of adsorption on the external surface. The explanation would be considered as the impact of temperature on the diffusion rate of the diethyl ether molecules. The intraparticle diffusion model will be considered in the next studies.

The k_2 of the pseudo-second order model for the diethyl ether adsorption increased from 0.0265 to 0.3111 g/(mg min) with increase in the temperature from 26 to 50 °C at 0.1 atm. It is probably due to the change of mechanism of the diethyl ether adsorption onto the activated carbon upon changing the temperature. The adsorption capacity of the diethyl ether onto the activated carbon decreased from 0.8255 to 0.6194 mg/g when the temperature increased from 26 to 50 °C, indicating that the adsorption process is exothermic in nature. However, at high temperature, the mobility of the diethyl ether molecules will be higher hence the diethyl ether molecules might have the chance to be desorbed from the pores of the activated carbon. As a result the adsorption capacity of the system will be lower.

The experimental points of the pseudo-second order kinetic model reflected high correlation coefficients at all temperatures, indicating a pseudo-second order mechanism. It may be that the rate-limiting step is a chemical adsorption involving valency forces through sharing or exchange of electrons between the diethyl ether molecules and the activated carbon.

The Langmuir type adsorption equilibrium correlations are constructed for the activated carbon/diethyl ether at temperature 26 °C, which is expressed by Eq. (9):

$$q_e = \frac{0.0414C_e}{1+2611C_e} \Rightarrow q_e = \frac{1.69\times 10^{-3}P_e}{1+106.4P_e} \tag{9}$$

3.1. Effect of temperature on the adsorption process

The temperature on the diethyl ether adsorption has two major consequences: (i) increasing the rate of diffusion of the diethyl ether molecules across the external boundary layer and in the internal pores of the activated carbon particle and (ii) changing the equilibrium capacity, q_e, of the adsorbent for a particular adsorbate [29].

Adsorption reactions are normally exothermic; thus the extent of adsorption generally increases with decreasing temperature. The change in the heat content of a system in which adsorption occurs, the total amount of heat evolved in the adsorption of a defined quantity of adsorbate on an adsorbent, is termed the heat of adsorption, ΔH° [20]. While the temperature dependence of equilibrium capacity for adsorption is defined by the parameter ΔH°, the dependence of rate of adsorption is expressed in terms of the activation energy E. Rate of adsorption is related to the activation energy for adsorption by the Arrhenius equation.

The thermodynamic parameters, ΔH°, entropy, ΔS°, and Gibbs free energy, ΔG°, of the adsorption process were obtained from the gas adsorption experiments at various temperatures. When any spontaneous process occurs, there is a decrease in Gibbs free energy ($\Delta G^\circ < 0$). Further, there must also be a decrease in entropy because the molecules lose at least one degree of freedom (of translation) when adsorbed [30]. The heat of adsorption of the activated carbon, ΔH° (kJ/mol), can be calculated by fitting the Langmuir constant, a_L, to the Van Hoff equation. Moreover, the free energy ΔG° (kJ/mol) and entropy ΔS° (J/(mol K)) for the adsorption process can be calculated using the following equations [31]:

$$\Delta G^\circ = -RT\ \ln a_L \tag{10}$$

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ \tag{11}$$

$$\Rightarrow \ln a_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{12}$$

where R is the gas constant (8.3145 J/(mol K)) and T is the temperature in Kelvin. The heat of adsorption of a process can be calculated by plotting of $\ln a_L$ versus $1/T$ for the adsorption process.

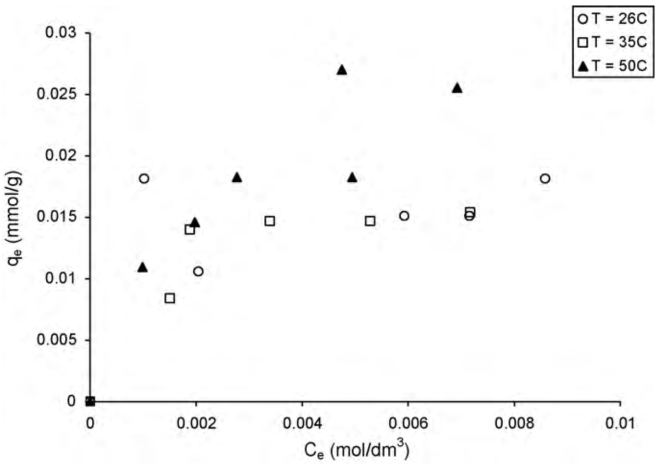

Fig. 4. Adsorption isotherms of the diethyl ether onto the activated carbon at different temperatures. Experimental conditions: mass of the activated carbon = 150 g, volume of the rector = 0.555 dm^3, and density of the diethyl ether = 0.7134 g/cm^3.

Table 3
Langmuir equation parameters of adsorption of the diethyl ether onto the activated carbon at various temperatures (molecular weight of the diethyl ether = 74 g/mol).

Temperature (°C)	K_L (dm^3/g)	a_L (dm^3/mol)	Q_{mon} (mmol/g)
26	0.0414	2611	0.0159
35	0.0245	1113	0.0220
50	0.0120	636.4	0.0188

The effect of temperature on the adsorption process was investigated. In order to study the effect of temperature on the adsorption process, the equilibrium data at various temperatures were obtained from the Langmuir isotherm model and the results are depicted in Fig. 4. The results of applying Langmuir model to the experimental data are shown in Table 3. The diethyl ether adsorption was increased with the decrease in temperature, suggesting that the number of active surface centres available for adsorption was decreased with temperature and the rate of intraparticle diffusion of the gas molecules might be enhanced.

The adsorption process is contributed by two parts: enthalpy ($\Delta H°$) and entropy ($\Delta S°$) part, which characterize whether the reaction is spontaneous or not. The negative value of free energy of adsorption, $\Delta G°$, indicates that the diethyl ether adsorption onto the adsorbent is spontaneous. The thermodynamic parameters, $\Delta H°$, $\Delta S°$ and $\Delta G°$ of the adsorption process were obtained from the adsorption isotherm experiments at various temperatures and the results are shown in Tables 3 and 4.

A plot of $\ln a_L$ versus $1/T$ was drawn to calculate the thermodynamic parameters for the gas adsorption onto the activated carbon. Mathematical treatment of the experimental data showed that $\Delta H°$ was equal to −45.84 kJ/mol. The exothermic process might be attributed to the relative increase in the escaping tendency of the gas molecules from the solid phase to the bulk phase with the increasing in the temperature [32]. The negative value of $\Delta G°$ represents a spontaneous process and small activation energy of adsorption. A negative entropy change, $\Delta S°$, may be explained in term of restriction of the movement of the diethyl ether molecules to two dimensions on the activated carbon surface, as against three dimensions in the bulk solution (i.e. a decrease in entropy change is indicative of the decrease in the randomness of the system) [33].

Table 4
Thermodynamic parameters.

Parameter	Temperature		
	26 °C	35 °C	50 °C
a_L (dm^3/mol)	2611	1113	636.4
$\Delta S°$ (J/(mol K))	−88.87	−88.87	−88.87
$\Delta H°$ (kJ/mol)	−45.84	−45.84	−45.84
$\Delta G°$ (kJ/mol)	−19.27	−18.47	−17.13

Based on the result published in the literature we would expect the heat of the diethyl ether adsorption to be smaller than 72 kJ/mol and close to the heat of butane adsorption which was reported to be in the range of 50 kJ/mol (the same number of carbon atoms, however, different size of molecule) [34]. It is noteworthy that for the activated carbon used in this study the heat of the diethyl ether adsorption is 45.84 kJ/mol which is very close to the value of the heat measured on carbon black and that is reported in the literature (36 kJ/mol) [14] which was measured at 393–433 K by means of inverse gas chromatography. This indicated that the adsorption occurred in very narrow pores, similar to the sizes of the diethyl ether molecule which is in fact expected.

4. Conclusion

The present study established and described successfully the characterization of the diethyl ether adsorption on the activated carbon using a novel adsorption refrigerator. The innovative arrangement design was equipped with a multi-tubular involving the activated carbon in meshed tubes in a sealed cylindrical adsorber.

The following conclusions have been drawn:

1. Initial pressure (concentration) provided an important driving force to overcome all the mass transfer resistance of the diethyl ether between the aqueous solution and the activated carbon surface. As a result, high initial diethyl ether pressure enhanced the adsorption process.
2. The time required to reach the adsorption equilibrium between the activated carbon and the diethyl ether was 45, 30, and 20 min at 26, 35, and 50 °C, respectively.
3. A clear feature of adsorption kinetic of the diethyl ether onto the activated carbon is the slow approach to adsorption equilibrium.
4. The pseudo-second order model fitted well with the experimental data at various initial diethyl ether pressures. The pseudo-first order model was not applicable in this adsorption system, suggesting that the adsorption process and the rate-limiting step is the pseudo-second order reaction.
5. The mechanism of the diethyl ether adsorption onto the activated carbon at 50 °C was quite different and the effect of the intraparticle diffusion on the adsorption process was higher. It could be attributed to the adsorption of the diethyl ether molecules at high temperature becoming more important into the pores instead of adsorption on the external surface.
6. The exothermic process might be attributed to the relative increase in the escaping tendency of the gas molecules from the solid phase to the bulk phase with the increasing in the temperature.

In conclusion, adsorption refrigeration/heat pump is a potential alternative to traditional refrigerator provided that it can be produced at a reasonable price. In the coming future publications, we propose to carry out the following tasks: (a) produce a set of raw and modified Jordanian adsorbents with different functional groups, (b) screen a number of combinations of adsorption materials and working fluids, (c) estimate the adsorption characteristics and the adsorption capacity of adsorbents and (d) simulate and construct a prototype which is best suited for use in developing sunny countries.

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