

Experimental Study of Adsorption Rate of R507A on Activated Carbon

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This article deals with the experimental study of adsorption rate of R507A on highly porous activated carbon of type Maxsorb III by constant volume variable pressure (CVVP) method over a temperature ranging from 20 to 60°C. These data are useful for the operation of adsorption chillers and these data are unavailable in the literature. Data obtained from the kinetic studies were treated according to the various kinetic models with the Fickian diffusion model being the most suitable overall. Guided by the experimental measurements, the surface diffusion is also estimated and is found that it follows the classical Arrhenius law within the experimental range.

Key words: *Adsorption rate, Maxsorb III, R507A, CVVP*

1. Introduction

Highly porous activated carbons have many intrinsic characteristics that are superior as compared with the palletized or granular activated carbon fiber, for example, the large surface area, fast inter-particle adsorption kinetics. It could be used in applications such as gas separation, gas storage and catalytic reactions¹⁻³. The uptake behaviour of highly porous activated carbon/R507A pair seems to be a promising pair for low temperature cooling applications.

The refrigerant R507A is an azeotropic blend consisting of 50% R125 (pentafluoroethane) and 50% R143a (1,1,1-trifluoroethane) by weight. The refrigerants R125 and R143a are hydrofluorocarbons and they do not contribute to the stratospheric ozone layer. It has relatively smaller GWP compared with the CFCs and the ODP is zero. It is also non-flammable and the level of acidity is significantly small (below 1.0 ppm).

In order to develop adsorption based systems, it is inevitable to determine adsorption isotherms, kinetics of the assorted adsorbent-refrigerant pair. It is essential to estimate the kinetics of adsorbent-refrigerant pair accurately for design purposes and improving understanding of chillers. Design

codes of the chiller must be equipped with the correct isotherms, isosteric heat of adsorption and the coefficients of uptake model. With these key data available, only then the numerical modeling of the processes of the chiller operation can be estimated accurately with a high level of confidence⁴.

In this article, adsorption kinetics of R507A on Maxsorb III specimen has been experimentally evaluated by constant volume variable pressure (CVVP) method when the temperatures are varying from 20 to 60°C. To analyze the experimental data, the Fickian diffusion model is used and found to be fairly consistent within the acceptable experimental uncertainties.

2. Experimental

2.1 Materials

The highly porous activated carbon (Maxsorb III specimen) labeled as MSC-30 has been supplied by the Kansai Coke and Chemical Co. Ltd., Japan. It has a Brunauer-Emmet-Teller (BET) surface area of 3,140 m²/g and micropore volume of 1.7 cc/g. The mean particle diameter of Maxsorb-III specimen is 72 μm, ash content is less than 0.1%, moisture of no more than 0.8% and pH value is 4.1.

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2.2 Experimental setup

Figures 1 and 2 show the photograph and schematic diagram of the experimental test rig, respectively. The experimental setup comprises (i) a charging tank made of stainless steel (SS 304) with a volume of 2570 cc whose volume was inclusive of related piping and valves, (ii) an adsorption tank made of stainless steel (SS 304) with a volume of 2427 cc, whose volume was again inclusive of related piping and valves, (iii) two constant temperature baths of model HAAKE-F8-C35 and Polyscience on which the both the charging and adsorption tanks are immersed to control the temperatures of both charging and adsorption tanks, (iv) a KYOWA PGA-10KA pressure transducer with an uncertainty of 0.1% of full scale and a pressure range of 0-1 MPa, (v) Class-A type Pt 100 Ω resistance temperature detector (diameter = 1/16 inch) with an uncertainty of ± 0.1 K for temperature measurement, (vi) four thermistors (Model: Omega 4407) with a resistance of 5000 Ω at 25°C with an uncertainty of $\pm 0.2^\circ\text{C}$ and maximum operating temperature of 150°C connected with the activated carbon for direct temperature measurement, (vii) a vacuum pump a BOC Edwards direct drive vane vacuum pump to a vacuum level of 0.05 mbar, and (viii) Agilent data logger to record the data. Three filters (diameter = 5 μm) that are capable of stopping migration of activated carbon particles during evacuation and desorption were fitted at three different exits of the adsorption tank.

2.3 Experimental procedure

Prior to experiment, the entire test rig is evacuated for 24 hours using a BOC Edwards direct drive vane vacuum pump to a vacuum level of 0.05 mbar. During the evacuation, the test system is regenerated in situ 120-130 °C for 12 h to desorb any residue gas in the system. At the end of regeneration process, the test system is purged with helium gas with a purity of 99.9995% and evacuated further to achieve low vacuum conditions. The evacuation and helium purging is continued several times to ensure that there is no residual gas left in the system. Based on the measurements, there is no measurable interaction between the inert gas and the adsorbent, as the effect if the partial pressure of helium in the tanks is found to be small.

After evacuation, the charging cell is pressurized with the assorted refrigerant and left to reach an equilibrium state (with the ball valve closed). During charging, it is necessary that the charging pressure should be less than the saturation pressure of the refrigerant at that temperature to ensure no condensation is occurred. At this state the initial pressure and temperature in the charging cell are measured before adsorption. Once equilibrium is achieved, the ball valve between the charging and adsorption tank is opened. The pressure and temperature in the adsorption tank are recorded. With the known initial mass of dry Maxsorb III, the temperature of the test system is varied to calculate uptake of the assorted refrigerant varying with time.



Fig. 1 Photograph of the experimental test rig.

2.4 Data reduction

At initial stage of the experiment, R507A is introduced into the charging cell of a known volume. In the absence of the adsorbent, the initial mass of refrigerant is calculated from the following equation,

$$m_{ref}^i = \rho_{ref}^i (P_{ch_cell}^i, T_{ch_cell}^i) V_{ch_cell} \quad (1)$$

When the adsorption and charging cells are connected, adsorption occurs in the pores of the adsorbent and the void volume in the adsorption cell given by;

$$V_{void} = V_{ads_cell} - \frac{m_{ac}}{\rho_s} - v_{\mu} m_{ac} \quad (2)$$

The adsorbate mass in the adsorption cell can be calculated from,

$$m_{\text{void}} = \rho_{\text{ref}}(P, T_{\text{ads}}) V_{\text{void}} \quad (3)$$

The remaining amount of refrigerant present in the charging cell is calculated from,

$$m_{\text{ref}}^f = \rho_{\text{ref}}^f(P, T_{\text{ch_cell}}) V_{\text{ch_cell}} \quad (4)$$

Therefore, the amount of adsorbed mass can be calculated from,

$$m_{\text{ads}} = m_{\text{ref}}^i - m_{\text{void}} - m_{\text{ref}}^f \quad (5)$$

Finally the specific uptake value or the loading, is determined as,

$$x = \frac{m_{\text{ads}}}{m_{\text{ac}}} \quad (6)$$

3. Mathematical modeling

3.1 Semi-infinite model

I.I. El-Sharkawy et al.⁵⁾ reported that during the initial phase of adsorption surface diffusion coefficient follows the uptake behavior of semi-infinite medium of any particle shape and is expressed by,

$$\frac{C}{C_0} = \frac{2A}{V} \left(\frac{D_s t}{\pi} \right)^{\frac{1}{2}} \quad (7)$$

where A is the area of the adsorbent particle, V represents particle volume and D_s stands for surface diffusion. Maxsorb III samples have been assumed to be spherical.

A plot of the relative uptake and square root of time for each isotherm yields with a slope of

$$\frac{2A}{V} \sqrt{\frac{D_s}{\pi}}$$

Surface diffusion, D_s can be expressed as,

$$D_s = D_{so} \exp\left(-\frac{E_a}{RT}\right) \quad (8)$$

Eq. (8) can be re-arranged as,

$$\ln(D_s) = -\frac{E_a}{R} \frac{1}{T} + \ln(D_{so}) \quad (9)$$

By plotting $\ln(D_s)$ against $1/T$, one can get the numerical values of activation energy, E_a and the pre-exponential coefficient, D_{so} . This plot is popularly known as Arrhenius plot. There exists a linear relationship between $\ln(D_s)$ and $1/T$. The slope yields $-E_a/R$ and the intercept provide the pre-exponential constant, D_{so} from eq. (9).

The Fickian diffusion model is used to evaluate adsorption kinetics of various types of adsorbate pairs. The Fickian model is valid when the diffusivity is independent of sorbate concentration when the system is thermodynamically ideal⁵⁾. The diffusion equation is used to express adsorption rate in spherical shaped adsorbent,

$$\frac{\partial C}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 D_s \frac{\partial C}{\partial r} \right) \quad (10)$$

C is the adsorbate concentration, D_s is the diffusion coefficient; r is the radial coordinate. Considering a constant diffusivity and applying the appropriate initial and boundary conditions, the eq. (10) can be written as⁵⁾,

$$\frac{C}{C_0} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2 \pi^2 D_s t}{R_p^2}\right) \quad (11)$$

where n is an integer from 1 to infinity, R_p is the radius of the particles and C_0 stands for limiting uptake and can be estimated from the following equation.

$$C_0 = (\text{BET surface area of Maxsorb III})/A_0$$

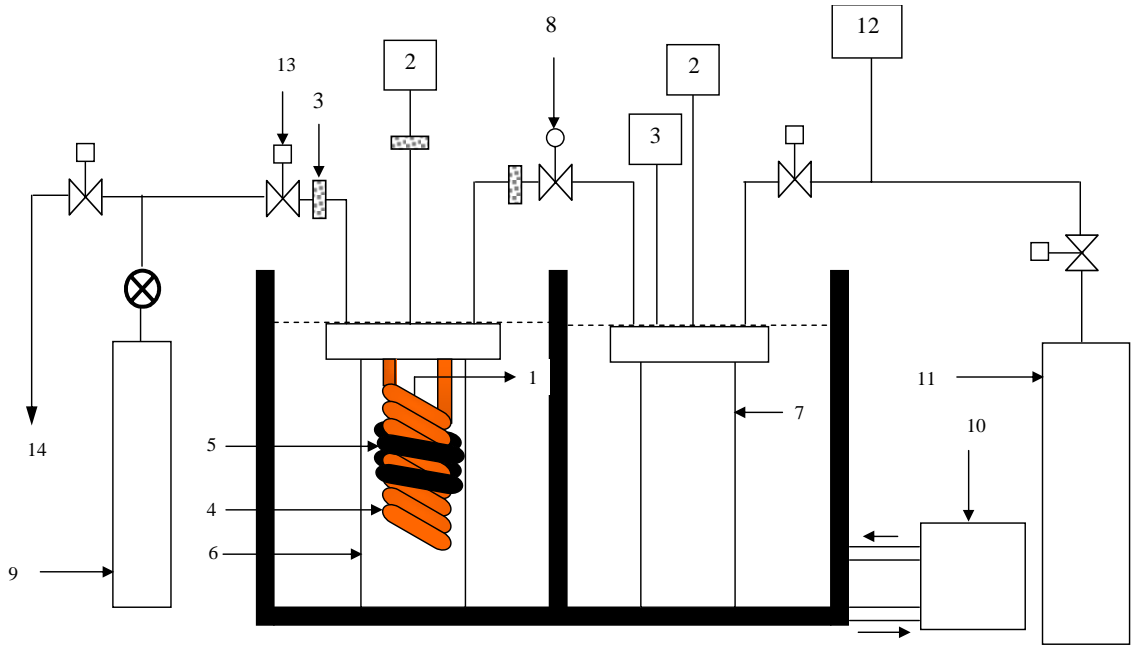
where A_0 is the adsorbate surface area and is calculated by⁶⁾,

$$A_0 = N_A a_0 \quad (12)$$

Where, a_0 is molecular surface area of adsorbate⁶⁾,

$$a_0 = 1.091 \left(\frac{M}{\rho_{lb} N_A} \right)^{\frac{2}{3}} \quad (13)$$

where, M is the molecular weight of adsorbate, ρ_{lb} is the density of liquid phase of adsorbate at boiling point temperature in g/cm^3 .



1: Thermistor; 2: Pressure transducer; 3: Filter; 4: Copper coil; 5: Activated carbon; 6: Adsorption tank; 7: Charging tank; 8: Needle valve; 9: Helium gas cylinder; 10: Water circulator; 11: Refrigerant cylinder; 12: Pressure regulator; 13: Ball valve and 14: To vacuum pump

Fig. 2 Schematic diagram of the experimental test rig.

4. Results and Discussion

Fig. 3 shows the kinetic uptake of R507A on Maxsorb III at four different temperatures. It is observable from Fig. 3 that when the adsorption temperature is 20°C, the Maxsorb III can adsorb R507A as high as 1.2 kg/kg within an adsorption time interval of 1100s. However, when the adsorption temperature is 60°C, only 800 s is required to achieve equilibrium uptake of 0.76 kg/kg.

Fig. 4 depicts plots of relative uptake vs square root of time for Maxsorb III/R507A pair. It is observable from Fig. 4 that solid lines represent the fitting of eq.(11) where the diffusion time constant is calculated assuming semi-infinite model. It is also noticeable from Fig. 4 that an accurate estimation of relative uptake can be evaluated using the Fickian diffusion model which indicates the goodness of fit.

A linear relationship between $\ln(D_s)$ and $1/T$ is observed in Fig. 5. It is also visible from Fig. 5 that the diffusivity of Maxsorb III increases with the adsorption temperature which ultimately agrees well with the Arrhenius trend.

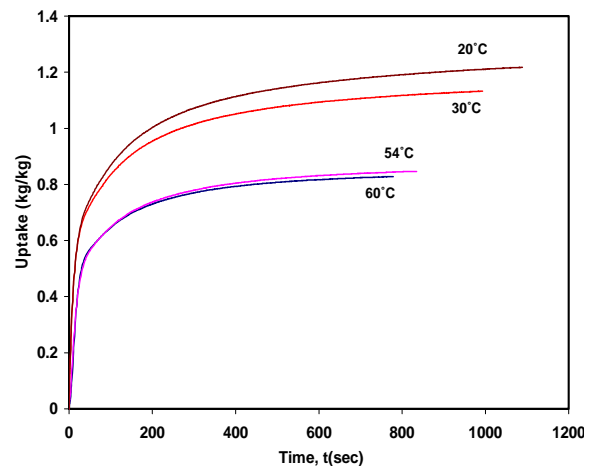


Fig. 3 Kinetic uptake of R507A on activated carbon.

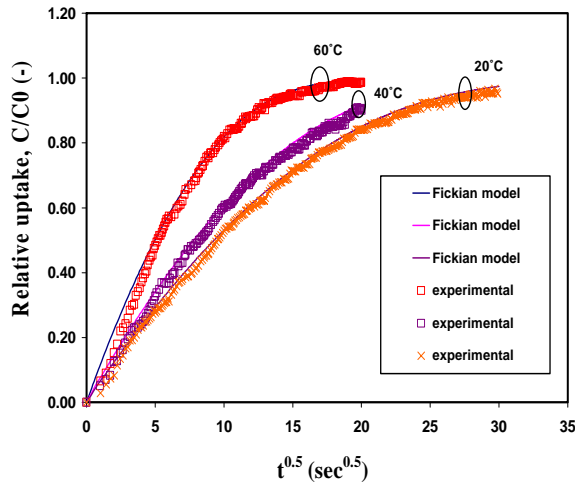


Fig. 4 Relative uptake vs square root of time.

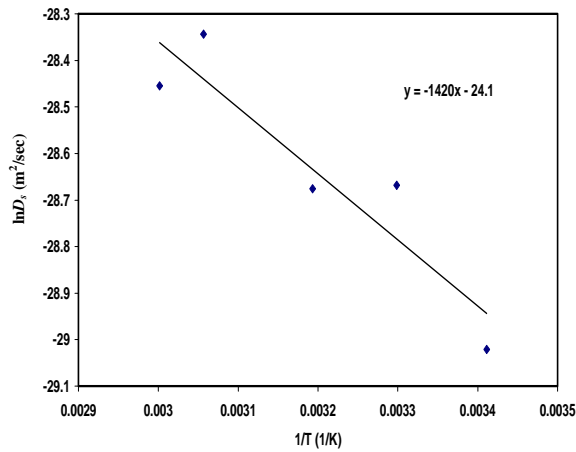


Fig. 5 Plot of $\ln D_s$ vs $1/T$.

4. Conclusions

Adsorption kinetics of Maxsorb III-R507A pair has been evaluated by CVVP method over a wide range of temperatures of 20 to 60°C. The Fickian diffusion model is used to analyze the experimental data and are found to be fairly consistent within the acceptable uncertainties. The present kinetics data of R507A are useful in designing adsorption chiller.

Nomenclature

C	adsorption uptake	kg/kg
C_0	limiting adsorption uptake	kg/kg
A	area of particle	m^2
V	volume of particle	m^3
m_{ref}^i	initial refrigerant mass before adsorption	kg
ρ_{ref}^i	initial density of refrigerant	kg/m^3
V_{ch_cell}	charging cell volume	m^3
V_{void}	void volume	m^3
m_{void}	adsorbate mass in void space	m^3
V_{ads_cell}	adsorption cell volume	m^3
m_{ac}	mass of activated carbon	kg
ρ_s	solid carbon density	kg/m^3
V_μ	micropore volume	m^3
D_s	surface diffusion	m^2/sec
t	time	sec
r	radial coordinate	m
E_a	activation energy	J/mol
D_{s0}	pre-exponential coefficient	-
M	molecular weight	kg/kmol
a_0	surface area of adsorbate of 1 molecule	m^2
A	surface area of adsorbate	m^2
N_A	Avogadro's number	-

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