Development of equilibrium and dynamic models for an adsorption refrigeration system

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ORIGINAL RESEARCH ARTICLE

ABSTRACT

Adsorption refrigeration systems are thermally driven systems. Solar radiation, waste energy from heat engine can be used to power these systems. Theoretical study and simulation work of adsorption-based cooling systems require the knowledge about the adsorption pair characteristics and capacities at different conditions of working pressures and temperatures. After reviewing different parameters on which adsorption refrigeration performances are dependent, simple equilibrium and dynamic models are developed. These models can be used for generating simulation results of different combinations of adsorbate and adsorbent. Furthermore, some coefficients and parameters which are required for solving the governing equations and have been determined experimentally by different researchers for each combination of the adsorption pair are also included in the paper. The present model adopts the Dubinin-Astakhov adsorption equation, which has been used by different researchers in their study.

KEYWORDS

activated carbon–methanol; adsorption; dynamic model; equilibrium model; refrigeration

1. INTRODUCTION

The physical adsorption cooling system is similar to the basic vapour compression refrigeration setup, except that the power compressor in the former is replaced with a thermal compressor. This system consists of an adsorber/ desorber bed, a condenser and an evaporator along with heating and cooling arrangements. The adsorber bed is composed of solid adsorbent that has an ability to physically adsorb and desorb the refrigerant vapour. This system operates intermittently through four different and consecutive processes. These include: heating and pressurization process, constant pressure desorption process, cooling and depressurization process and constant pressure adsorption process.

A basic adsorption cycle operates on the basis of the adsorption of a refrigerant vapour (adsorbate) into an adsorbent (solid matrix) at low pressure and the subsequent desorption at a high pressure by heating the adsorber bed. In the simplest case, an adsorption refrigerator can be considered to be an adsorber/ desorber bed connected with an evaporator and condenser through valves. Different processes of basic adsorption cycle are explained below.

Process 1-2 (Heating and Pressurisation): The adsorber (adsorbent), filled with adsorbed refrigerant, is heated by an external heat source ($Q_H$) from an initial ambient temperature ($T_1$) to a temperature ($T_2$). The valves are kept closed so that the adsorbed mass of refrigerant remains constant ($x_1$). The pressure of the adsorber bed increases from the point of evaporating pressure ($P_1 = P_E$) up to the condensing pressure ($P_2 = P_C$) while the adsorber temperature rises. This step is equivalent to the ‘compression’ in the vapour-compression cycle (Figure 1a).

Process 2-3 (Desorption and Condensation): When pressure of the adsorber bed reaches the condenser pressure ($P_C$), the valve connecting the adsorber bed and the condenser is opened and the...
sur and das, journal of environment and biotechnology research, vol. 6, no. 1, pages 64-81, 2017

<table>
<thead>
<tr>
<th>Nomenclature</th>
<th>Description</th>
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<tbody>
<tr>
<td>C</td>
<td>Constant of Clausius – Clapeyron equation</td>
</tr>
<tr>
<td>k, n</td>
<td>Adsorptive parameters of adsorbent- adsorbate pair</td>
</tr>
<tr>
<td>Δh_{ads}</td>
<td>Heat of adsorption, (kJ/kg)</td>
</tr>
<tr>
<td>Δh_{des}</td>
<td>Heat of desorption, (kJ/kg)</td>
</tr>
<tr>
<td>l_{ref}</td>
<td>Latent heat of refrigerant (kJ/kg)</td>
</tr>
<tr>
<td>h_{ref}</td>
<td>Enthalpy of refrigerant (kJ/kg)</td>
</tr>
<tr>
<td>m_{ad}</td>
<td>Mass of adsorbent (kg)</td>
</tr>
<tr>
<td>m_{cu}</td>
<td>Mass of copper (kg)</td>
</tr>
<tr>
<td>T</td>
<td>Average temperature of the adsorber bed (K)</td>
</tr>
<tr>
<td>T_{ad}</td>
<td>Temperature at the end of adsorption (K)</td>
</tr>
<tr>
<td>T_{as}</td>
<td>Temperature at the beginning of adsorption (K)</td>
</tr>
<tr>
<td>T_{3}</td>
<td>Temperature at the end of desorption (K)</td>
</tr>
<tr>
<td>T_{4}</td>
<td>Temperature at the beginning of adsorption (K)</td>
</tr>
<tr>
<td>T_{5}</td>
<td>Temperature of refrigerant leaving the condenser (K)</td>
</tr>
<tr>
<td>T_{6}</td>
<td>Temperature of refrigerant leaving the evaporator (K)</td>
</tr>
<tr>
<td>T_{inlet}</td>
<td>Inlet temperature of hot water (K)</td>
</tr>
<tr>
<td>T_{outlet}</td>
<td>Outlet temperature of hot water (K)</td>
</tr>
<tr>
<td>T_{cold}</td>
<td>Inlet temperature of cold water (K)</td>
</tr>
<tr>
<td>X</td>
<td>Mass ratio of adsorbed mass to that of the adsorbent (kg/kg)</td>
</tr>
<tr>
<td>U_{o}</td>
<td>The overall heat transfer coefficient (kW/m²-K)</td>
</tr>
<tr>
<td>m_{cwo}</td>
<td>Mass flow rate of cold water(kg/s)</td>
</tr>
<tr>
<td>m_{chw}</td>
<td>Mass flow rate of hot water (kg/s)</td>
</tr>
<tr>
<td>m_{st}</td>
<td>Mass of stainless steel (kg)</td>
</tr>
<tr>
<td>Q_{sli}</td>
<td>Rate of sensible heat of adsorbent (kJ/s)</td>
</tr>
<tr>
<td>Q_{cond}</td>
<td>Rate of heat rejection at condenser (kJ/s)</td>
</tr>
<tr>
<td>Q_{ads}</td>
<td>Rate of adsorption heat of refrigerant (kJ/s)</td>
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<tr>
<td>Q_{evp}</td>
<td>Heat exchange in evaporator (kJ)</td>
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<tr>
<td>R</td>
<td>Gas constant for refrigerant (kJ/kg-K)</td>
</tr>
<tr>
<td>c_{p,liq}</td>
<td>Specific heat of liquid refrigerant at a constant pressure,(function of temperature)</td>
</tr>
<tr>
<td>c_{v,ref}</td>
<td>Specific heat of gas refrigerant at a constant volume,(function of temperature)</td>
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<td>c_{p,ref}</td>
<td>Specific heat of gas refrigerant at a constant pressure,(function of temperature)</td>
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<tr>
<td>c_{at}</td>
<td>Specific heat of steel (kJ/kg- K)</td>
</tr>
<tr>
<td>c_{cu}</td>
<td>Specific heat of copper (kJ/kg- K)</td>
</tr>
<tr>
<td>c_{c,(T)}</td>
<td>Specific heat (function of temperature) of activated carbon (kJ/kg- K)</td>
</tr>
<tr>
<td>c_{w,h}</td>
<td>Specific heat of hot water(kJ/kg- K)</td>
</tr>
<tr>
<td>T_{C}</td>
<td>Saturation temperature of the condenser (K)</td>
</tr>
<tr>
<td>T_{E}</td>
<td>Saturation temperature of the evaporator (K)</td>
</tr>
</tbody>
</table>

adsorber continues to be heated. Due to heating, the refrigerant vapour is desorbed from the adsorbent and moves towards the condenser. Thus, the pressure of the bed remains constant. As the process progresses, a greater amount of refrigerant is desorbed and temperature of the bed keeps on increasing. During the process, the mass of refrigerant adsorbed by the adsorbent decreases from x_{2} to x_{3} and the temperature of the bed increases from T_{2} to T_{3}, while pressure of the bed remains constant.

The desorbed vapour, after reaching the condenser, rejects heat to the cooling fluid (process 2 – 5) and it is condensed to liquid. This process is equivalent to ‘condensation’ in the vapour-compression cycle (Figure 1b).

Process 2-C (Isobaric de-superheating and condensation of adsorbent/refrigerant): During the desorption process 2 – 3, the refrigerant vapour is desorbed at bed temperature and leaves the condenser. This refrigerant is first de-superheated (sensibly cooled) from the bed temperature to the saturation temperature (T_{c}) corresponding to the condenser pressure (P_{c}) and then condensed to liquid after rejecting latent heat of vaporization to the cooling fluid.

Process C-5 (Isobaric sub-cooling of adsorbent/refrigerant): After being condensed to saturated liquid, the refrigerant may be further cooled sensibly to reduce its temperature. The refrigerant leaves the condenser at temperature T_{5}, which is less than the saturation temperature (T_{c}). This is the process of sub-cooling of the refrigerant (Figure 2).

Process 5-E (Throttling of adsorbent/refrigerant): After the condenser, the refrigerant flows through an expansion valve or throttling valve where the pressure of the refrigerant reduces significantly. As a result, the condenser pressure (P_{c}) converts to the evaporator pressure (P_{e}). During throttling, a part of the liquid refrigerant is evaporated, which causes further cooling of the refrigerant. Temperature of the refrigerant decreases from T_{5} to T_{6} and the corresponding pressure falls from P_{c} to P_{e} (Figure 1c).

Process E-6 (Isobaric evaporation of adsorbent/refrigerant): After entering the evaporator, the refrigerant starts to evaporate by extracting heat from the surrounding, thus producing the cooling effect. The refrigerant leaves the evaporator either at a saturated condition (T_{e} or at a superheated condition (T_{w}) with the degree of superheating at (T_{w} – T_{e}). The evaporated refrigerant is then adsorbed at the bed temperature (which varies from T_{4} to T_{1}). Thus, the refrigerant absorbs some heat from the bed as it is heated from T_{E} or T_{E} to reach the bed temperature before it is adsorbed in the bed (Figure 1c).
Process 3-4 (Cooling and Depressurization): After desorption, the adsorber has a little amount of adsorbed mass ($x_3$). The bed along with the adsorbed refrigerant is then cooled by heat transfer fluid at the second heat sink (TCS) at a constant mass ($x_3$). The pressure of the adsorber drops from the condensing pressure ($P_C$) to the evaporating pressure ($P_E$) due to the decrease in the adsorber temperature from $T_3$ to $T_4$. (Figure 1d).

Process 4-1 (Adsorption and Evaporation): The adsorber keeps releasing heat while being connected to the evaporator. Adsorption process starts after evaporation. In the evaporator, the adsorbate/refrigerant is in its saturation state and it boils while extracting heat from the surrounding. Thus, the cooling effect takes place. The valve between the evaporator and the adsorber is opened after the adsorber reaches $P_E$. The evaporated adsorbate molecules are fixed to the solid matrix of the adsorbent surface and adsorption mass increases from $x_4$ to $x_1$. During adsorption, heat is released from the adsorber bed and the adsorption surface restores its initial state at the end of this process (Figure 1e).

Figure 2. P-T-X diagram for a basic adsorption system.

2. DEVELOPMENT OF NUMERICAL MODELS

The physical adsorption process has been mathematically explained by different scientists (Henry, Langmuir, Gibbs, Freundlich, Braunauer, Emmet, Teller, Toth, Unilon) (Brunauer et al. 1938; Dubinin et al., 1947; Ponec, 1974; Dubinin and Stoeckli, 1980; Oscik and Cooper, 1982; Evans et al., 1986; Mahle et al., 1994; Do, 1998; Tokarev et al., 2002; Niida et al., 2002; Liu and Leong, 2006; Hamamotoa et al., 2006; Wang and Chua, 2007; Gramado, 2009; Louajaria et al., 2011; Zhao et al., 2012; Zhou et al., 2012; Thu et al., 2013;
Ouchi et al., (2014) by employing different methods, based on (i) the adsorption speed, (ii) single molecular layer adsorption, (iii) Polanyi adsorption potential theory and Dubinin micropore/minipore filling theory, as well as (iv) capillary condensation (considering effect of energy distribution in micropores). Among these theories, the 'Micropore Volume Filling Theory', proposed by Dubinin–Radushkevich (Brunauer, 1945) and co-workers, for adsorption from the gas phase and the 'Potential Theory', proposed by Eucken–Polanyi (Chihara and Suzuki, 1983), are the most accepted ones to describe the adsorption phenomenon. This theory was later extended by Stoeckli (Sakoda and Suzuki, 1984) in a manner which is analogous to the global integral equation used in adsorption of energetically heterogeneous solids. This theory, describing a continuous distribution of pore sizes ε (or generally pore characteristics), was later modified by Dubinin–Radushkevich and Dubinin–Astakov (D–A) (Cho and Kim, 1992).

According to Polanyi the adsorption potential energy (ε) is independent of temperature [van der Walls forces are also independent of temperature] i.e.,

\[
\left( \frac{\partial \varepsilon}{\partial T} \right)_{V_s} = 0 \tag{1.a}
\]

\( V_s \) is adsorption volume of the adsorption phase.

Therefore, potential energy ε is a function of \( V_s \) and suitable for all temperature ranges for known gases.

\[
\varepsilon = f(V_s) \tag{1.b}
\]

From Equation (1.a), adsorption potential (ε) is a function of P and T for a certain adsorbate whose R value is constant i.e,

\[
\varepsilon(P_1, T) = RT \ln \frac{P_2(T)}{P_1(T_s)} \tag{1.c}
\]

According to theory of Dubinin and Radushkevich (Wang et al., 2014) the adsorption potential energy (ε) (is made up of the micropores of activated carbon with the efficient radius in the range of 18 - 20 \( \times 10^{-10} \) m) expressed as a Gaussian distribution function, the volume \( V \) occupied by the adsorbate is related to total pore volume \( V_o \) and to ε by the following equation

\[
V = V_o \exp \left[ -\left( \frac{B}{\beta^2} \right) \varepsilon^2 \right] \tag{1.d}
\]

where \( \beta \) is the affinity coefficient, taken as the ratio of the adsorbent molar volume at a temperature T to that of a reference gas (normally benzene) at the same temperature. It is a quantity that depend upon the adsorbate only. By convention as reference benzene has been chosen with \( \beta (C_6H_6) = 1 \) (Wood, 2001). B in eqn. (1.d) is a function of the adsorbed microstructure. Decrease of B value increases the micro-porosity of adsorbent.

The D–R equation is given as,

\[
V(T, P_1) = V_o(P_1) \exp \left[ -\left( \frac{B}{\beta^2} \right) \frac{RT_1 \ln \left( \frac{P_2}{P_1} \right)}{P_1} \right] \tag{1.e}
\]

In addition the correlation between temperature and pressure for saturated adsorbate can be represented by the Clausius – Clapeyron equation

\[
\ln P = A - \frac{C}{T} \tag{1.f}
\]

where A and C depend on adsorbate. Substituting Eqn. (1.e) in Eqn. (1.f), the D-R equation can be written in terms of temperature

\[
V(T, T_s) = V_o(T_s) \exp \left[ -\left( \frac{B}{\beta^2} \right) \frac{RT \ln \left( \frac{P_2}{P_1} \right)}{P_1} \right] \tag{1.g}
\]

Accordingly, introduction of the density \( \rho(T) \) of adsorbate at the adsorbent temperature in D-R equation, adsorbed mass \( M(T, T_s) \) becomes

\[
M(T, T_s) = M_o(T_s) \exp \left[ -\left( \frac{B}{\beta^2} \right) \frac{RT \ln \left( \frac{P_2}{P_1} \right)}{P_1} \right] \tag{1.h}
\]

where, \( M_o(T_s) = V_o(T_s) \times \rho(T_s) \)

This equation gives an estimate of the quantity of the adsorbate that can be adsorbed by the adsorbent porous matrix at any given temperature. The D–R equation describes fairly well many carbonaceous solids with low degree of burned-out. For carbonaceous solids resulting from a high degree of burn-out during activation, the degree of heterogeneity increases because of a wider pore size distribution, and for such cases the D–R equation does not describe well the equilibrium data.

To take into account of this surface heterogeneity, Dubinin and Astakhov proposed another equation (D–A) of the following form:

\[
M(T, T_s) = M_o(T_s) \exp \left[ -\left( \frac{B}{\beta^2} \right) \frac{RT \ln \left( \frac{P_2}{P_1} \right)}{P_1} \right] \tag{1.i}
\]
To allow a better fit to some of the adsorbent characteristics in Eqn. (1.i), a variable index \( n \) is introduced instead of 2. Introducing the mass ratio \( x \) of adsorbed mass to the mass of adsorbent in Eqn. (1.i)

\[
x = \frac{M(T)}{M_{ad}} \text{ kg/kg} \tag{1.j}
\]

where, \( M \) is the mass of adsorbate in kg and \( M_{ad} \) is the mass of adsorbent in kg, \( M_s \) is the mass of adsorbate at saturated temperature in kg. So Eqn. (1.i) can be written in terms of mass ratio becomes,

\[
x(T, T_s) = x_o(T_s)\exp\left[-k\left(\frac{T}{T_s}-1\right)^n\right] \tag{1}
\]

where,

\[
k = \left(\frac{B}{\beta^2}\right)(RC)^n \tag{2}
\]

where, \( k, n \) are experimental constants, which are calculated by different researchers as shown in Table 1.

Literature (Critoph, 1991; San and Lin, 2008; Wang and Zhai, 2010; Wang et al., 2011; Choudhury et al., 2013) shows that the performance of an adsorption system depends on adsorbent-adsorbate pair characteristics and system operating conditions such as generator temperature, atmospheric temperature, evaporator and condenser temperature, mass of adsorbate going through the cycle, the isosteric heat of adsorption and desorption and their dependency on temperature and pressure. The important working pairs studied in the literature as absorbent/adsorbate for adsorption cooling were investigated and compared by different researchers (Qasem and El-Shaarawi, 2015; Khattab, 2004; Wang et al., 2006; Alghoul et al., 2007; Wang et al., 2009; Louajari, 2011; Hassan et al., 2011; Heninger et al., 2012; Schicktanz, 2012; Gordeeva and Aristov, 2014; Schicktanz et al., 2012; Hassan and Mohamad 2013; Hasan et al., 2015).

Researchers revised several refrigerants that work with carbon adsorbent while a lot of adsorption refrigeration materials are carefully reviewed (Ponec, 1947; Oscik and Cooper 1982; Critoph and Vogel, 1986; Meunier, 1988; Wang, 2001; Hamamoto et al., 2006; Kubota et al., 2008; Xia et al., 2008; Hassan, 2012; Afshar, 2012; Hassan and Mohamad, 2013; Lu et al., 2013; Wang et al., 2013; Ji et al., 2014; Hong et al., 2015). Many researchers conducted with adsorption refrigeration through either theoretical analysis or prototypes experimental works or the both (Wang, 2011; Chekirou, 2014; Mitra, 2014; Qasem and El-Shaarawi, 2015; Fada, 2015).

This literature review indicates that there is limited information regarding the physics of the transfer processes associated with adsorbent beds. Despite the above effort detailed information on the modeling of heat and mass transfer in the adsorption refrigeration module is limited. In order to further investigate the characteristic of the module, a modified adsorption cooling model is designed in current study and detailed study of heat and mass transfer performances are presented. This research aims to explore the thermodynamic processes of intermittent

### Table 1. Different values of \( x_o, k \) and \( n \) for D-A equation.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorbate</th>
<th>( x_o ) (kg/kg)</th>
<th>( k )</th>
<th>( n )</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon 35</td>
<td>CH(_3)OH</td>
<td>0.45</td>
<td>13.38</td>
<td>1.5</td>
<td>Do, 1998</td>
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<td>Activated carbon 34</td>
<td>CH(_3)OH</td>
<td>0.284</td>
<td>10.21</td>
<td>1.39</td>
<td>Bansal, 2005</td>
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<td>Activated carbon 35</td>
<td>NH(_3)</td>
<td>0.29</td>
<td>3.57</td>
<td>1.38</td>
<td>Ruthven, 1984</td>
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<td>Activated carbon 208</td>
<td>NH(_3)</td>
<td>0.290</td>
<td>3.1853</td>
<td>1.095</td>
<td>Leite, 2000</td>
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<tr>
<td>Activated carbon 208</td>
<td>R-32</td>
<td>0.476</td>
<td>2.4634</td>
<td>1.388</td>
<td>Leite, 2000</td>
</tr>
<tr>
<td>Activated carbon 208</td>
<td>n-Butane</td>
<td>0.259</td>
<td>1.2895</td>
<td>1.143</td>
<td>Leite, 2000</td>
</tr>
<tr>
<td>Monolithic carbon</td>
<td>NH(_3)</td>
<td>0.270</td>
<td>4.3772</td>
<td>1.196</td>
<td>Olivier et al., 1994</td>
</tr>
<tr>
<td>Monolithic carbon</td>
<td>R-32</td>
<td>0.461</td>
<td>2.6729</td>
<td>1.333</td>
<td>Olivier et al., 1994</td>
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<td>0.237</td>
<td>1.3693</td>
<td>1.392</td>
<td>Olivier et al., 1994</td>
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<tr>
<td>PVOC Base carbon</td>
<td>NH(_3)</td>
<td>0.232</td>
<td>4.6342</td>
<td>1.806</td>
<td>Thu, 2013</td>
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<td>LM127 carbon</td>
<td>NH(_3)</td>
<td>0.3629</td>
<td>3.6571</td>
<td>0.94</td>
<td>Saha et al, 2001</td>
</tr>
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<td>LM128 carbon</td>
<td>NH(_3)</td>
<td>0.333</td>
<td>3.6972</td>
<td>0.99</td>
<td>Scholl et al, 1993</td>
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<td>Silicagel</td>
<td>H(_2)O</td>
<td>0.346</td>
<td>5.6</td>
<td>1.6</td>
<td>Akiyoshi et al., 1984</td>
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<tr>
<td>Zeolite</td>
<td>H(_2)O</td>
<td>0.261</td>
<td>5.36</td>
<td>1.73</td>
<td>Solmus et al., 2010</td>
</tr>
</tbody>
</table>
adsorption cooling systems through investigating the main parameters those affect the cycle performance. Here, we analyse and discuss the heat and mass transfer processes, identify the parameters which influence the system performance and generate a mathematical model. On the basis of this model, computer simulation results of cycles are presented and discussed. It is hoped that such a study will lead to optimize the design of the module, for the commercially availability and to encourage its wide spread application.

2.1. Formulation of heat of adsorption / desorption

An absorption refrigeration is a simple thermodynamics system which exchanges heat with its surroundings, if, $Q_G$ = heat supplied at the time of desorption, $Q_E$ = heat absorbed by the refrigerant at evaporator, $Q_C$ = heat rejected in the condenser, and, $Q_{AD}$ = heat released at the time of adsorption.

Accordingly, from the 1st law of thermodynamics, energy balance equation at steady state can be formulated as:

$$Q_G + Q_E - Q_C - Q_{AD} = 0$$

As the adsorption process is exothermic, heat is released by the system and the adsorption heat is considered negative.

In the adsorption process, three types of heat are used: i) Integral heat of adsorption ii) Differential heat of adsorption, and iii) Isosteric heat of adsorption.

i) Integral heat of adsorption: Under a constant pressure and variable uptake (x) condition, the total heat released from the initial state to the final state is considered as integral heat adsorption.

ii) Differential heat of adsorption: It refers to the change in integral heat of adsorption with a change in uptake (x) or variable loading.

iii) Isosteric heat of adsorption: One of the basic quantities in adsorption studies is the isosteric heat, which is the ratio of the infinitesimal change in the adsorbate enthalpy to the infinitesimal change in the amount adsorbed. The phenomenon of heat release is important in the kinetic studies because when heat is released due to adsorption, the released energy is partly absorbed by the solid adsorbent and partly dissipated into the surrounding. The part absorbed by the solid increases the particle temperature. This rise in temperature slows down the adsorption kinetics because the mass uptake is controlled by the rate of cooling of the particle during the later course of adsorption.

In practice, the difference between differential heat of adsorption and isosteric heat of adsorption is so small that both of them can be considered to be identical. This kind of heat can be calculated by Clapeyron equation where differential/ isosteric heat is defined in terms of enthalpy ($\Delta h_{is}$) and formulated as:

$$\Delta h_{is} = -R \left[ \frac{d \ln P}{dT} \right]_x$$

where, at pressure P and temperature T, constant loading of adsorbate is $x$ kg/kg of adsorbent (solid). Integrating the above equation from $P_1$ to $P_2$ and $T_{Sat}$ to T, we get,

$$\int_{P_1}^{P_2} \partial \ln P = - \frac{\Delta h_{is}(x)}{R} \left[ \int_{T_{Sat}}^{T} \frac{1}{T} \right]$$

$$\ln \left( \frac{P_2}{P_1} \right) = - \frac{\Delta h_{is}(x)}{R} \left[ \frac{1}{T} - \frac{1}{T_{Sat}} \right]$$

Equation (4) can also be written in the following way

$$\Delta h_{is} = RT^2 \left[ \frac{\partial \ln P_1}{\partial T} \right]$$

$$\frac{T}{T_{Sat}} = 1 + \frac{1}{K} \ln \left( \frac{x}{x_0}^{\frac{1}{n}} \right)$$

Clapeyron equation (Eqn. 1.f) can be written as:

$$\ln P_1 = A - \frac{C}{T_S}$$

where,

$$T_S = \frac{C}{A - \ln P}$$

After substituting Eqn. (9) in Eqn. (8)

$$T = \left( \frac{C}{A - \ln P_1} \right) \left[ 1 + \frac{1}{K} \ln \left( \frac{x}{x_0}^{\frac{1}{n}} \right) \right]$$

$$\ln P_1 = A - \frac{C}{T} \left[ 1 + \frac{1}{K} \ln \left( \frac{x}{x_0}^{\frac{1}{n}} \right) \right]$$

Differentiating the above equation with respect to T
\[
\frac{d}{dT} \left( \ln P_1 \right) = \frac{C}{T^2} \left[ 1 + \frac{1}{k} \ln \left( \frac{x}{x_0} \right)^{\frac{1}{n}} \right] \quad (12)
\]

at \( x = \) constant loading (isosteric process)

Substituting Eqns. (11) and (7) in Eqn. (12), we get,

\[
\frac{d}{dT} \left( \ln P_1 \right) = \frac{C}{T^2} \left( \frac{T}{T_s} \right) = \frac{C}{T} \cdot \frac{1}{T_s} = \frac{\Delta h_{is}}{RT^2} \quad (13)
\]

Therefore, isosteric heat of adsorption/desorption is expressed as:

\[
\Delta h_{is} = R \cdot C \cdot \frac{T}{T_s} \quad (14)
\]

2.2. Thermodynamic modeling of a basic adsorption cycle

A basic adsorption/desorption refrigeration system has been considered in order to analyse the heat and mass transfer processes and to identify those parameters which influence the system performance. The referred system has four basic components. Desorber/adsorber (the heart of the system), evaporator, condenser, receiver and throttling valve. Desorber/adsorber is attached to both the evaporator and condenser with two valves (Figure 1). To develop a mathematical model of different processes for an adsorption refrigeration system, the following assumptions are made:

2.2.1 Assumptions for mathematical model

- The adsorption bed is composed of activated carbon pellets (adsorbent) of uniform size.
- The bed porosity is also uniform throughout.
- There is no phase change in the adsorbent surface and pores.
- The gaseous adsorbate (refrigerant) behaves as an ideal gas.
- The pressure is constant in the condenser and in the evaporator.
- Mass transfer within the adsorber/desorber bed occurs only in the vapour phase of the adsorbate.
- There is no temperature gradient between the adsorbate gas and the adsorbent bed.
- Specific heats of the adsorbed materials (steel, copper, etc.) are constant throughout the process.
- There is no loss of refrigerant when flowing through the system.
- No desorption takes place till reaching the point of condensing pressure during the period of isosteric heating.

- The isosteric (\( x = \) constant) heating and cooling processes are considered as constant volume process.
- The refrigerant vapour enters the condenser as soon as it is desorbed from the desorber, i.e., there is no heat loss within the desorber or in the passage between the adsorber and the condenser.
- The heat capacity of the adsorbate in the adsorbed state is equal to that of the vapour phase.

2.2.2 Desorption process

Process 1-2 (Isosteric Heating): The desorber bed is initially under the evaporator pressure (PE) and at temperature (\( T_1 \)) it is filled with adsorbed adsorbate. Then it is heated at a constant adsorbate mass ratio (\( x = x_1 \)) from an initial temperature of \( T_1 \) (which may be considered the same as the ambient temperature) and from the pressure of \( P_E \) to a temperature \( T_2 \), at which point the pressure increases to \( P_C \) (condenser pressure) (Figure 2). In this process, the adsorbate and the desorber bed are sensibly heated with an increase of pressure. Since the process 1 – 2 is an isosteric process, \( T_2 \) can be calculated by equating the adsorbate mass ratios at points 1 and 2 as follows:

\[
x_1(T_1, T_E) = x_2(T_2, T_C) \quad (15)
\]

Adsorbed mass ratio \( x_1 \) and \( x_3 \) can be calculated from Eqn. (1)

\[
x_1(T_1, T_E) = x_0(T_E) \exp \left[ -k \left( \frac{T_1}{T_E} - 1 \right)^n \right] \quad (16)
\]

where \( T_E \) is the saturation temperature (evaporator temperature) at evaporator pressure (\( P_E \))

\[
x_2(T_2, T_C) = x_0(T_C) \exp \left[ -k \left( \frac{T_2}{T_C} - 1 \right)^n \right] \quad (17)
\]

where \( T_C \) is the saturation temperature (condenser temperature) at condenser pressure (\( P_C \)).

By substituting (16) and (17) in equation (15), we get,

\[
T_2 = T_C \left[ 1 + \frac{n}{k} \ln \frac{x_0(T_E)}{x_0(T_C)} \right] \left( \frac{T_1}{T_E} - 1 \right)^n \quad (18)
\]

For the process 1-2, the refrigerant absorbs heat from the adsorbent bed at a constant volume process (since there is no desorption) and its temperature increases from \( T_1 \) to \( T_2 \). If the mass of the adsorber is
Then, the mass of the adsorbed refrigerant during the process 1 – 2 is $x_1 \times m_{ad}$. The sensible heat gain of different components during this process can be calculated as:

**Sensible heat gain of refrigerant:**

\[ (Q)_{1-2,REF} = \int_{T_1}^{T_2} m_{ad} \cdot x_1 \cdot c_{v,ref}(T) \, dT \quad (19) \]

$c_{v,ref}(T)$ is the specific heat of refrigerant at a constant volume, which is a function of temperature.

**Sensible heat gain of adsorbent:**

\[ (Q)_{1-2,AD} = \int_{T_1}^{T_2} c_{ad}(T) m_{ad} \, dT \quad (20) \]

**Sensible heat gain of the bed:**

\[ (Q)_{1-2,BED} = \int_{T_1}^{T_2} (c_{st} m_{st} + c_{cu} m_{cu}) \, dT \quad (21) \]

$c_{st}$ and $c_{cu}$ refer to the specific heat in steel and copper, respectively, $m_{st}$ and $m_{cu}$ refer to the mass of stainless steel and copper, respectively, used in construction of the adsorbed bed.

Therefore, the total heat added during this process is a summation of the above three components and is given by:

\[ (Q)_{1-2} = (Q)_{1-2,REF} + (Q)_{1-2,AD} + (Q)_{1-2,BED} = \int_{T_1}^{T_2} m_{ad} \cdot x_1 \cdot c_{v,ref}(T) + c_{ad}(T) m_{ad} \, dT \quad (22) \]

**Process 2-3 (Isobaric heating and desorption):**

After attaining the condensation pressure ($P_C$), desorption of refrigerant is started. The desorber bed is heated from $T_2$ to the maximum bed temperature of $T_3$ through constant pressure ($P_C$) (Figure 2). If the maximum adsorbate mass ratio is $x_1$ and the minimum adsorbate mass ratio at temperature $T_3$ is $x_3$, then the change of adsorbent mass ratio in this process is $(x_1 - x_3)$ kg/kg.

The adsorbed mass $x_3$ can be calculated from Eqn. (1)

\[ x_3(T_3, T_C) = x_0(T_C) \exp\left[-k\left(\frac{T_3}{T_C} - 1\right)^n\right] \quad (23) \]

where $T_C$ is the saturation temperature at condenser pressure ($P_C$).

During the process 2 – 3, the total sensible heat gain can be calculated as it is done for the process 1 – 2:

\[ (Q)_{2-3,REF} = \int_{T_2}^{T_3} m_{ad} \cdot x(T) \cdot c_{p,ref}(T) \, dT \]

\[ (Q)_{2-3,AD} = \int_{T_2}^{T_3} c_{ad}(T) m_{ad} \, dT \]

\[ (Q)_{2-3,BED} = \int_{T_2}^{T_3} (c_{st} m_{st} + c_{cu} m_{cu}) \, dT \]

\[ (Q)_{2-3,BED} = \int_{T_2}^{T_3} m_{ad} \cdot x(T) \cdot c_{p,ref}(T) + c_{ad}(T) m_{ad} \, dT \quad (24) \]

Since the process 2 – 3 takes place at a constant pressure, for estimating the sensible heat gain of the refrigerant, the specific heat at a constant pressure of the refrigerant (adsorbate) has to be applied. Since desorption of refrigerant takes place during this process, the heat of desorption is to be transmitted. The total heat of desorption for the process 2 – 3 is estimated as:

\[ (Q)_{2-3,DES} = \int_{T_2}^{T_3} h_{id} \cdot m_{ad} \frac{dx(T, T_C)}{dT} \, dT \quad (25) \]

where $m_{ad}$ is the mass of adsorbent in kg, $\Delta h_{id}$ is the heat of desorption per kg of desorbed refrigerant and $(dx(T, T_C))/dT$ is the temperature rate of desorption at temperature $T$.

The heat of desorption is calculated from Eqn. (14)

\[ \Delta h_{id} = R \cdot C \cdot \frac{T}{T_C} \quad (26) \]

where, $T$ is the temperature of the bed during the process 2 – 3, and $T_C$ is the saturation temperature corresponding to the bed pressure, which is equal to the condenser pressure.

During desorption, the mass of refrigerant still remains adsorbed at bed temperature of $T$ and it is expressed by:

\[ x(T, T_C) = x_0(T_C) \exp\left[-k\left(\frac{T}{T_C} - 1\right)^n\right] \quad (27) \]

This can also be calculated as

\[ x(T, T_C) = x_2(T_2, T_C) - \int_{T_2}^{T} \frac{dx(T, T_C)}{dT} \, dT \quad (28) \]

Therefore, at the bed temperature $T$, during the process 2 – 3, the desorbed mass of the refrigerant is expressed by:

\[ m_{ref} = (x_2 - x(T)) m_{ad} \, kg \quad (29) \]

Hence, the total heat transfer during the process 2 – 3 is the sum of the sensible heat transfer as well as the total heat of adsorption and is expressed as:
Here, it is assumed that there is no heat loss for the desorbed refrigerant in the adsorber bed. After being desorbed at temperature $T$, the refrigerant passes to the condenser where it is first de-superheated from temperature $T$ to the saturation temperature corresponding to the condenser pressure and then it is condensed to liquid.

2.2.3 Adsorption process

Process 3-4 (Isosteric cooling): At point 3, the desorber bed is at the maximum temperature $T_3$ and contains the minimum amount of adsorbed mass of methanol ($x_{\text{min}} = x_3$) at the condenser pressure ($P_C$). During the isosteric cooling process, cold water is circulated through the desorber bed to reduce the bed temperature from $T_3$ to $T_4$ (Figure 2). In this process, the refrigerant vapour pressure is reduced from $P_C$ to $P_E$ and the bed temperature from $T_3$ to $T_4$.

As the process 3 - 4 refers to isosteric cooling, therefore,

$$x_3(T_3, T_C) = x_4(T_4, T_E)$$

(31)

Adsorbed mass ratio $x_3$ and $x_4$ can be calculated from Eqn. (1)

$$x_3(T_3, T_C) = x_0(T_C)e^{-k\left(\frac{T_3}{T_C} - 1\right)^n}$$

(32)

where $T_C$ is the saturation temperature at condenser pressure ($P_C$)

$$x_4(T_4, T_E) = x_0(T_E)e^{-k\left(\frac{T_4}{T_E} - 1\right)^n}$$

(33)

where $T_E$ is the saturation temperature at evaporator pressure ($P_E$)

Therefore, $T_4$ can be calculated by substituting Eqns. (32) and (33) in Eqn. (30)

$$T_4 = T_E \left[ 1 + n \left( \frac{T_3}{T_C} - 1 \right)^n \frac{1}{k} \ln \frac{x_0(T_C)}{x_0(T_E)} \right]$$

(34)

For the process 3-4, the refrigerant rejects heat from the adsorbent bed in a constant volume process (since there is no adsorption) and its temperature decreases from $T_3$ to $T_4$. If the mass of the adsorber is $m_{\text{ad}}$ and then the mass of the adsorbed refrigerant during the process 3 - 4 is ($x_3 \times m_{\text{ad}}$). The sensible heat loss of different components during this process can be calculated as,

(i) Sensible heat loss of refrigerant:

$$Q_{3-4,\text{REF}} = \int_{T_4}^{T_3} m_{ad} \cdot x_3 \cdot c_{v,ref}(T) \, dT$$

(35)

c$_{v,\text{ref}}$(T) is the specific heat of the refrigerant at constant volume, which is a function of temperature.

(ii) Sensible heat loss of adsorbent:

$$Q_{ad}(3-4_{,\text{AD}}) = \int_{T_4}^{T_3} c_{ad}(T) m_{ad} \, dT$$

(36)

c$_{ad}$ and $c_{\text{ad}}$ are the specific heat of steel and copper, respectively whereas $m_{\text{st}}$ and $m_{\text{cu}}$ are the mass of stainless steel and copper, respectively, used in construction of the adsorbed bed.

Therefore, the total heat lost during this process is the summation of the above three components and is given by:

$$Q_{3-4} = (Q_{3-4,\text{REF}} + (Q_{ad})(3-4_{,\text{AD}}) + (Q_{\text{bed}})3-4_{,\text{BED}} + \int_{T_3}^{T_4} [m_{ad} \cdot x_3 \cdot c_{v,\text{ref}}(T) + c_{ad}(T) m_{ad} + c_{st} \frac{m_{st}}{c_{st}} + c_{cu} \frac{m_{cu}}{c_{cu}}] \, dT$$

(38)

Process 4-1 (Isobaric Cooling and Adsorption): After achieving evaporator pressure ($P_E$), adsorption of the refrigerant is started. Temperature of the adsorber bed is reduced from $T_4$ to $T_1$ at a constant evaporator pressure ($P_E$) (Figure 2). If the minimum adsorbate mass ratio at temperature $T_4$ is $x_4$ and the maximum adsorbate mass ratio at temperature $T_1$ is $x_1$, then the change of the adsorbate mass ratio in this process is ($x_1 - x_4$) kg/kg.

The adsorption mass $x_1$ can be calculated from Eqn. (1)

$$x_1(T_1, T_E) = x_0(T_E) \exp\left[ -k\left(\frac{T_1}{T_E} - 1\right)^n \right]$$

(39)
where $T_E$ is the saturation temperature (evaporator temperature) at evaporator pressure ($P_E$).

During the process 4-1, the total sensible heat loss can be calculated as it is done for the process 3-4

$$\int (Q_{4-1, SEN}) + (Q_{4-1, REF}) = \int T \left[ m_{ad} x(T) \right] c_p \text{d}T$$

(40)

$$c_{ad}(T) = c_p + c_v + c_m$$

Since the process 4 – 1 takes place at a constant pressure ($P_E$ is constant), for estimating sensible heat gain of the refrigerant, specific heat at constant pressure of the refrigerant (adsorbate) is calculated. Since adsorption of the refrigerant takes place during this process, the heat of adsorption has to be rejected for adsorption to take place. The total heat of adsorption for the process 4 - 1 is estimated as:

$$\left(\int T \text{d}T\right)_{T_4}^{T} h_{ia} m_{ad} \frac{dx(T,T_E)}{dT}$$

(41)

where, $m_{ad}$ is the mass of adsorbent in kg, $\Delta h_{ia}$ is the heat of desorption per kg of the adsorbed refrigerant and $(\partial x(T,T_E))/\partial T$ is the temperature rate for adsorption at temperature $T$. $\Delta h_{ia}$ can be calculated from Eqn. (14)

$$\Delta h_{ia} = R \cdot C \frac{T}{T_E}$$

(42)

where, $T$ is the temperature of the bed during the process 4 – 1 and $T_E$ is the saturation temperature corresponding to the bed pressure, which is equal to the evaporator pressure.

During adsorption, the instantaneous mass ratio of the adsorbed refrigerant at bed temperature of $T$ is given by:

$$x(T,T_E) = \frac{x_0(T_E)}{x_0(T_E)} \exp\left[-k\left(\frac{T}{T_E} - 1\right)^n\right]$$

(43)

which can also be calculated as

$$x(T,T_E) = x_4(T_E) + \int_{T_4}^{T} \frac{\partial x(T,T_E)}{\partial T} \text{d}T$$

(44)

Therefore, at any bed temperature of $T$, during the process 4 – 1, the adsorbed mass of refrigerant is expressed as:

$$m_{ref} = (x_4 + x(T)) m_{ad} \text{ kg}$$

(45)

Hence, the total heat transfer during the process 4 – 1 is a sum of the sensible heat transfer and the total heat of adsorption. It is expressed as:

$$\left(\int T \text{d}T\right)_{T_4}^{T} h_{ia} m_{ad} \frac{dx(T,T_E)}{dT} + \int \left[ m_{ad} x(T) \right] c_p \text{d}T$$

(46)

2.2.4. Heat rejection in condenser

The refrigerant enters the condenser at pressure ($P_C$) and at the varying temperature ($T$), it is desorbed from the bed. It is equal to the bed temperature. After reaching the condenser, the refrigerant is de-superheated from temperature $T$ to the saturation temperature ($T_C$) corresponding to the condenser pressure. Then it is condensed to liquid at a constant temperature and pressure. There is a possibility of the liquid refrigerant being sub-cooled up to temperature $T_5$ before it leaves the condenser.

The phenomenon of heat rejection during different processes can be estimated as:

(i) De-superheating of the refrigerant vapour from the state ($T, P_C$) to the state ($T_C, P_C$) (Figure 2):

During the infinitesimal period, when the bed temperature changes from $T$ to $T + \text{d}T$, the mass of the refrigerant desorbed from the bed is given as:

$$m_{ad} x \left(\frac{\partial x(T,T_C)}{\partial T}\right) \text{d}T$$

Therefore, the total heat rejected due to de-superheating when the bed temperature changes from $T_2$ to $T_3$ is estimated as:

$$\int_{T_2}^{T_3} m_{ad} x \left(\frac{\partial x(T,T_C)}{\partial T}\right) \text{d}T$$

(47)

where, $h_{ref}(T,T_C)$ is enthalpy of saturated vapour of the refrigerant at (T, P_C).

(ii) Phase change of the refrigerant from vapour to liquid at ($T_C, P_C$):

The heat released from the refrigerant = Mass of refrigerant x latent heat of condensation

$$\int \left[h_{ref}(T,T_C) - h_{ref}(T,T_C)\right] \text{d}T$$

(48)

where, $h_{ref}(T,C)$ is latent heat of condensation of the refrigerant at the condenser pressure $P_C$ in kJ/kg.

(iii) Sub-cooling of liquid from state ($T_C, P_C$) to the state ($T_5, P_C$) (Figure 2):

During sub-cooling, the liquid refrigerant is sensibly cooled from the state ($T_C, P_C$) to the state ($T_5, P_C$).
Thus, the heat rejected during sub-cooling = Mass of refrigerant × specific heat of liquid refrigerant × change of temperature

\[ = m_{ad}(x_1 - x_2)C_{p,liq}(T_C - T_5) \]  

(49)

where, \( C_{p,liq} \) is the specific heat of the liquid refrigerant at an average temperature of \( T_r \) and \( T_5 \).

Thus, the total heat rejected by the refrigerant in the condenser is given by:

\[ Q_{COND} = \int_{T_2}^{T_3} m_{ad} \frac{dx(T, T_C)}{dT} \left[ h_{ref}(T, P_C) - h_{ref}(T, P_C) \right] \]

\[ + m_{ad}(x_1 - x_2)\left[ h_{ref}(T_C) + m_{ad}(x_1 - x_3)c_{p,liq}(T_C - T_5) \right] \]  

(50)

Enthalpy of the refrigerant at which it leaves the condenser can be calculated as:

\[ h_5 (T_C, P_C) = h_{ref}(T_C, P_C) - C_{p,liq}(T_C - T_5) \]  

(51)

where, \( h_{ref}(T, P) \) is enthalpy of the saturated liquid of the refrigerant at \( (T, P) \).

2.2.5 Heat absorbed in evaporator

The refrigerant enters the evaporator at low temperature, pressure and in a binary mixture of liquid and vapour. It extracts heat from the surroundings and transforms to vapour phase while absorbing the latent heat of vapourization. There is a possibility of vapour being superheated to temperature \( T_6 \) in the evaporator before leaving it (Figure 2).

The total heat gain by the refrigerant at the evaporator is (Refrigeration effect), \( (Q)_{EVP}+(Q)_{LAT}+(Q)_{SUP} \)

\[ = m_{ad}(x_1 - x_3)[h_{ref}(T_E, P_E) - h_5] + m_{ad}(x_1 - x_3)c_{p,liq}(T_0 - T_E) \]  

(52)

Here, it is assumed that during throttling of the refrigerant from pressure \( P_c \) to \( P_E \), enthalpy remains constant, i.e., \( h_6 = h_5 \).

2.2.6 Parameters for measuring performance of the cycle

Coefficient of Performance (COP) of the cycle is a ratio of the heat absorbed by the refrigerant in the evaporator as calculated in Eqn. (53) and the net amount of heat supplied to the desorber bed, which can be calculated by summation of Eqns. (22) and (30). Thus, COP is estimated as:

\[ \text{COP} = \frac{(Q)_{EVP}}{(Q)_{1-2}+(Q)_{2-3}} \]  

(53)

Specific cooling capacity (SCC) is the ratio of the cooling capacity to the weight of the adsorbent. Specific cooling power is used to determine the size of the system as it relates to both mass of the adsorbent and the cooling power.

\[ \text{SCC} = \frac{Q_e}{m_{ad}} \]  

(54)

2.3. Dynamic model

A dynamic mathematical model for the adsorption refrigeration system has been developed to calculate and study the rates of heat and mass transfer during different processes of the cycle. Many researchers have analysed the performance of adsorption refrigeration system by dynamic modeling (Khattab, 2004, Myers, 2002, Qasem and El-Shaarawi, 2015, Schicktanz et al., 2012, Syed, 2015, Wang, 1990). Despite these investigations, detailed information on the modeling of heat and mass transfer in the adsorption refrigeration module is limited. In order to further investigate the characteristics of the module, a modified dynamic adsorption cooling model has been developed in the present study. Such a study is expected to help optimize the design of the module for commercial viability and encourage its wide application. The following assumptions were made for developing the model

2.3.1. Assumptions

Assumptions considered mathematical in character have also been studied while developing this model. Two of the primary assumptions are:

(i) An equivalent thermal conductivity is used for the adsorbent. It depends on temperature but it is uniform in both axial and radial directions.

(ii) Heat loss between the adsorber and the atmosphere is considered to be negligible.

2.3.2. Heat transfer between heat transfer fluid and adsorber bed

The rate of heat loss \( (Q_h) \) by the hot water flowing through the adsorber bed at any instant of time can be written as:

\[ \dot{Q}_h = \dot{m}_{hw}c_{pw}(T_{hwi} - T_{hwo}) \]  

(55)

Heat transfer rate \( (Q_h) \) between hot water and desorber bed can also be calculated as:

\[ \dot{Q}_h = U_oA_o(LMTD) \]  

(56)
The Log Mean Temperature Difference (LMTD) during the heat transfer process can be estimated as:

\[
\text{(LMTD)} = \frac{T_{\text{hwi}} - T_{\text{hwo}}}{\ln \left( \frac{T_{\text{hwi}} - T}{T_{\text{hwo}} - T} \right)}
\]  

(57)

\[T_{\text{hwo}}\] can be estimated by combining Eqns. (55), (56) and (57) as follows:

\[
m_{\text{hw}} c_{\text{pw}} (T_{\text{hwi}} - T_{\text{hwo}}) = U_{\text{o}} A_{\text{o}} \frac{T_{\text{hwi}} - T_{\text{hwo}}}{\ln \left( \frac{T_{\text{hwi}} - T}{T_{\text{hwo}} - T} \right)}
\]

(58)

Hence,

\[
T_{\text{hwo}} = T + \left( T_{\text{hwi}} - T \right) e^{-\frac{U_{\text{o}} A_{\text{o}}}{m_{\text{hw}} c_{\text{pw}}}}
\]

(59)

### 2.3.3. Estimation of the overall heat transfer coefficient (U\_o)

As hot or cold fluid flows through the tube and heat is transferred from the adsorbent to the fluid through the tube wall, the total thermal resistance for heat transfer between hot water flowing inside the tube and the adsorbed bed outside the tube can be formulated as:

\[
\frac{1}{U_{\text{o}} A_{\text{o}}} = \frac{1}{h_{\text{i}}} + \frac{\ln \left( \frac{d_{\text{o}}}{d_{\text{i}}} \right)}{2 \pi K_{\text{Cu}} L} + \frac{\ln \left( \frac{d_{\text{o}}}{d_{\text{i}}} \right)}{2 \pi K_{\text{eq}} L} + \frac{R_{\text{fil}}}{A_{\text{i}}} + \frac{R_{\text{i}}}{A_{\text{o}}} + \frac{1}{h_{\text{o}} A_{\text{o}}}
\]

(60)

\[D = d_{\text{o}} + \text{Thickness of activated carbon layer around the tube}\]

### 2.3.4. Estimation of convective heat transfer coefficients (h\_i) and (h\_o)

\[D_{\text{t}} = \frac{4A}{p}; \text{ where,} A = \frac{\pi}{4} d_{\text{i}}^2
\]

(61)

The average velocity (V\_w) of water in the tube is calculated as:

\[
V_{\text{w}} = \frac{m_{\text{hw}}}{\frac{\pi}{4} D_{\text{t}}^2 \rho_{\text{w}}}
\]

(62)

Reynolds number (Re\_w) is calculated to check the type of flow

\[
Re_{\text{w}} = \frac{V_{\text{w}} D_{\text{t}}}{\theta_{\text{w}}}
\]

(63)

If the flow is laminar, Nusselt number inside the copper tube (Nu\_i) is written as (Thirumaleshwar, 2009):

\[
Nu_{\text{i}} = 1.86 \left( \frac{\text{Pr}_{\text{i}}^{\frac{1}{3}}}{\text{Re}_{\text{w}}^{\frac{1}{3}}} \right)^{\frac{1}{3}} \left( \frac{\mu_{\text{w}}}{\mu_{\text{ws}}} \right)^{0.14}
\]

(64)

\[
\text{Pr}_{\text{i}} = \frac{\mu_{\text{w}} c_{\text{pw}}}{K_{\text{w}}}
\]

(65)

Convective heat transfer coefficient between the water and the copper tube is:

\[
h_{\text{i}} = \frac{K_{\text{w}}}{D_{\text{t}}} (Nu_{\text{i}})
\]

(66)

Convective heat transfer coefficient between the copper tube and the adsorbent (considered as packed bed) is written as (Incropera, 2007):

\[
h_{\text{o}} D_{\text{p}} = 0.203 \left( \frac{Re_{\text{m}}}{D_{\text{p}}} \right)^{\frac{1}{3}} (Pr_{\text{m}})^{\frac{1}{3}} + (0.220) (Re_{\text{m}})^{0.8} D_{\text{p}} (Pr_{\text{m}})^{0.4}
\]

(67)

\[
Re_{\text{m}} = \frac{V_{\text{m}} D_{\text{s}}}{\theta_{\text{m}}}
\]

(68)

Average velocity of methanol is:

\[
V_{\text{m}} = \frac{m_{\text{m}}}{\frac{\pi}{4} D_{\text{s}}^2 \rho_{\text{m}}}
\]

(69)

\[
Pr_{\text{m}} = \frac{\mu_{\text{m}} c_{\text{p}}}{}\]

(70)

For square pitch of adsorber shell, the hydraulic diameter (D\_s) is:

\[
D_{\text{s}} = \frac{4 \times \left( \text{Tube Pitch}^2 \times \frac{\pi D^2}{4} \right)}{\pi D}
\]

(71)

### 2.3.5. Governing equations for different processes

In this study, modified Dubinin-Astakhov (D-A) equation (Chekirou et al., 2014) is adopted to express concentration x of the adsorbate as a function of temperature T and pressure P.

\[
x(T, T_{\text{Sat}}) = x_{\text{o}} (T_{\text{Sat}}) \exp \left[ -k \left( \frac{T}{T_{\text{Sat}}} - 1 \right)^n \right]
\]

(72)

The mass fraction, x, is defined as:

\[
x = \frac{\text{adsorbed mass of adsorbate}}{\text{mass of adsorbent}} \text{ kg/kg}
\]

(73)
Process 1-2 (Isosteric Heating): The adsorbed/desorber bed is initially kept under evaporator pressure \( P_E \) as well as temperature \( T_1 \) and it is adsorbed with adsorbate. Then the bed is heated by external heating source, i.e., hot water, which enters the bed at \( T_{hwi} \) and circulates through the copper tubes. During the process 1 - 2, the adsorbate mass ratio remains constant \( (x = x_1) \) and the bed along with the adsorbed refrigerant get heated in a constant volume process (since there is no desorption) while its temperature rises from \( T_1 \) to \( T_2 \). The pressure of the bed also rises and when the bed pressure reaches the condensation pressure \( (i.e., P_c = P_C) \), the refrigerant is allowed to desorb (Figure 1a). The rates of the sensible heat gain by different components of the bed during this process can be estimated as follows:

(a) Sensible heat gain of the adsorbed refrigerant:

\[
(Q)_{1-2,REF} = m_{ac}x_1 \cdot c_{v,ref} \frac{dT}{dt}
\]  
(74)

\( m_{ac}x_1 \) is the mass of the adsorbed refrigerant, which remains constant during the process 1 - 2; \( x_1 \) is the mass of adsorbed refrigerant per unit mass of the adsorbent; \( c_{v,ref} \) depends on the instantaneous temperature of the bed.

(b) Sensible heat gain of the adsorbent:

\[
(Q)_{ad,1-2} = c_{ac}(T)m_{ad} \frac{dT}{dt}
\]  
(75)

(c) Sensible heat gain of the bed materials can be calculated as the summation of sensible heat gain of the materials, such as, steel and copper, which are used for construction of the adsorber bed.

\[
(Q)_{bed,1-2} = (c_{st}m_{st} + c_{cu}m_{cu}) \frac{dT}{dt}
\]  
(76)

Therefore, the total rate of heat transfer \( ((Q)_{1-2}) \) during this process is the sum of the above three components.

\[
(Q)_{1-2} = (Q)_{1-2,REF} + (Q)_{ad,1-2} + (Q)_{bed,1-2}
\]  
(77)

\[
(Q)_{1-2} = (m_{ac}x_1 + m_{cu}c_{cu} + m_{ad}c_{ad}) \frac{dT}{dt}
\]

where,

\[
m_{ab}c_{ab} = m_{st}c_{st} + m_{cu}c_{cu} + m_{ad}c_{ad}
\]  
(78)

Equating \( (Q)_{1-2} \) with the rate of heat loss by the circulating hot water \( (Q_h) \) and by substituting Eqn. (59), the energy equation becomes,

\[
(m_{ab}c_{ab} + m_{ad}x_1c_{v,ref}) \frac{dT}{dt} = m_{hw}c_{pw}(T_{hwi} - T_{hwo})
\]  
(79)

\[
= m_{hw}c_{pw}(T_{hwi} - T)(1 - e^{-\frac{k}{m_{hw}c_{pw}}})
\]

Solution of this equation gives the instantaneous rates of (i) temperature rise and the heat addition to the bed during the process, and, (ii) total heat addition to the bed and the time required for the bed temperature to reach \( T_2 \).

By equating the adsorbate mass ratios \( (x_1 \text{ and } x_2) \) at points 1 and 2 and by estimating them by using Eqn. (72); \( T_2 \) can be calculated as

\[
T_2 = T_C \left[ 1 + \sqrt{n \left( \frac{T_1}{T_2} - 1 \right)} + \frac{1}{k} \ln \frac{x_0(T_E)}{x_0(T_C)} \right]
\]  
(80)

Isobaric desorption process (2-3): During this process, the bed is heated from \( T_2 \) to the maximum bed temperature of \( T_3 \) while pressure of the bed remains constant \( (i.e., P_c = P_C) \). The instantaneous adsorbed mass fraction,\( x(T) \), reduces as the desorption process progresses from 2 to 3. It is assumed that there is no heat loss for the desorbed refrigerant in the adsorber bed. Thus, after being desorbed at temperature \( T \), the refrigerant passes to the condenser where it is first de-superheated from temperature \( T \) to the saturation temperature \( (T_C) \) corresponding to the condenser pressure \( (P_C) \) and then it is condensed to liquid and may be sub-cooled to temperature \( T_5 \) (so that \( T_5 < T_C \)) (Figure 1b).

During the desorption process, the total amount of heat supplied by hot water to the bed is a sum of: (i) the amount of sensible heat transferred to the adsorbent, adsorber bed materials and refrigerant (mass of which varies with time) to increase their temperature from \( T_2 \) to \( T_3 \); and, (ii) the amount of heat required for desorption of the refrigerant.

Therefore, the energy equation during this process can be written as:

\[
(Q)_{2-3} = (m_{ad}x(T)c_{v,ref} + m_{ab}c_{ab}) \frac{dT}{dt} + h_{d}m_{so} \frac{dx}{dt} = m_{hw}c_{pw}(T_{hwi} - T_{hwo})
\]  
(81)

\[
= m_{hw}c_{pw}(T_{hwi} - T)(1 - e^{-\frac{k}{m_{hw}c_{pw}}})
\]

\[
= m_{hw}c_{pw}(T_{hwi} - T)(1 - e^{-\frac{k}{m_{hw}c_{pw}}})
\]
where \((m_{ad} \times (T) \cdot c_{p,ref} (T) + m_{ab} \cdot c_{ab}) \cdot \frac{dT}{dt}\) is the rate of sensible heat transfer at any point during the process 2 - 3 when bed temperature is \(T\).

The total amount of heat of desorption during the process 2 - 3 can be estimated as:

\[
(Q)_{2-3,\text{DES}} = \int_{T_2}^{T_3} h_{id} \cdot m_{ad} \cdot \frac{dx(T, T_C)}{dT} \cdot dT 
\tag{82}
\]

When \((dx(T, T_C))/dT\) the temperature rate of desorption of refrigerant at temperature \(T\) and \(\Delta h_{id}\) is the heat of desorption per kg of the desorbed refrigerant, which can be estimated as:

\[
\Delta h_{id} = R \cdot C \cdot \frac{T}{T_s} 
\tag{83}
\]

where \(T\) is the instantaneous temperature of the bed during the process 2 - 3 and \(T_s\) is the saturation temperature corresponding to the bed pressure during desorption. Since, bed pressure during the process is the same as the condenser pressure; \(T_s\) can be taken as equal to \(T_C\), and \(C\) is the constant of Clausius - Clapeyron equation.

The adsorbed mass ratio \((x)\) at a given temperature \(T\) during the process 2 - 3 can be calculated from D-A equation as given in Eqn. (72) and the rate of desorption of refrigerant, \((dx/dt)\) is estimated as,

\[
\frac{dx}{dt} = \frac{dx}{dt} = \frac{(x(T, T_C))}{(x(T, T_C))} \cdot \frac{dT}{dT} \cdot \frac{dT}{dT} = \frac{(x(T, T_C))}{(x(T, T_C))} \cdot \frac{dT}{dT} \cdot \frac{dT}{dT} 
\tag{84}
\]

Isosteric cooling Process (3-4): At point 3, the bed temperature reaches the maximum desired value \((T_3)\) and the adsorbed mass fraction of methanol in the bed reaches the minimum \((x_{min} = x_3)\). The bed is then cooled down by circulating cold water through the copper tubes placed inside the desorber bed and by reducing its temperature from \(T_3\) to \(T_4\). It is an isosteric \((x_3 = x_4)\) and isochoric process. In this process, the pressure of the bed is reduced and the process is continued till the pressure of the bed reaches the value equal to the saturation pressure \((PE)\) of the refrigerant corresponding to the evaporator temperature (Figure 1d).

For the process 3 - 4, heat transfer from the adsorbed refrigerant takes place in a constant volume process (since the valves remain closed). Therefore, the total heat lost during this process is summation of heat losses from the refrigerant, adsorbent and bed materials. This total heat loss is also equal to the total heat absorbed by cold water circulating through the tubes:

\[
\dot{Q}_{3-4} = \dot{Q}_{3-4,\text{REF}} + \dot{Q}_{3-4,\text{AD}} + \dot{Q}_{3-4,\text{BED}} 
\tag{85}
\]

Solution to this equation gives the instantaneous rates of (i) temperature fall and heat rejection by the bed during the process, and, (ii) total heat rejection by the bed as well as the time required for bed temperature to reach \(T_4\).

By equating the adsorbate mass ratios \((x_3\) and \(x_4)\) at points 3 and 4 as well as by estimating them by using Eqn. (72), \(T_4\) can be calculated as follows:

\[
T_4 = T_E \left[1 + \sqrt{\frac{T_3}{T_C} - 1}\right] \tag{86}
\]

Process 4-1 (Isobaric Cooling and Adsorption): Adsorption of refrigerant in the bed is started when the bed pressure reaches \(P_E\). During this process, the bed pressure remains constant, the temperature of bed reduces from \(T_4\) to \(T_1\) and the adsorbed mass fraction of the refrigerant in the bed increases from \(x_4\) to \(x_1\) (Figure 1e). Thus, during this process, there is an increase in the adsorbate mass ratio of \((x_4 - x_1)\) kg per kg of adsorbent.

Heat transfer during this process is the sum of: (i) sensible heat transfers from the adsorbent, adsorber bed materials and refrigerant to decrease their temperature from \(T_4\) to \(T_1\), (ii) the heat released during adsorption of refrigerant, and (iii) the heat absorbed by the evaporated refrigerant which leaves the evaporator at temperature \(T_6\) and gets adsorbed in the bed at temperature \(T\) \((T > T_6)\). Thus, the total heat loss during this process can be calculated as:

\[
\dot{Q}_{4-1} = \left[\dot{Q}_{4-1,\text{AD}} + \dot{Q}_{4-1,\text{BED}}\right] 
\tag{87}
\]

The total amount of adsorbed heat during the process 4 - 1 can be estimated as:
where, \( \frac{dx(T,T_e)}{dT} \) is the temperature rate of adsorption of the refrigerant at temperature \( T \) and \( \Delta h_{ia} \) is the heat of adsorption per kg of adsorbed refrigerant, which can be estimated as:

\[
\Delta h_{ia} = -R \cdot C \frac{T}{T_s} \tag{89}
\]

where \( T \) is the instantaneous temperature of the bed during the process \( 4 - 1 \) and \( T_s \) is the saturation temperature corresponding to the bed pressure during adsorption. Since, the bed pressure during the process is the same as the evaporator pressure; \( T_s \) can be considered as equal to \( T_e \).

Heat transfer in condenser: In the condenser, the refrigerant enters at pressure \( P_c \) and at varying temperature \( T \), at which it is desorbed from the bed and becomes equal to the bed temperature. After reaching the condenser, the refrigerant is first de-superheated from temperature \( T \) to the saturation temperature \( T_c \) corresponding to the condenser pressure and then condensed to saturated liquid. After that, it is sub-cooled to a temperature lower than \( T_c \). The heat rejected by the refrigerant is absorbed by the cooling water circulating in the condenser. Since, mass flow rate of the refrigerant entering the condenser is \( m_{ad} \cdot \frac{dx(T,T_c)}{dt} \), heat rejection during different stages can be estimated as the sum of the following components:

(a) Heat rejection due to de-superheating (Figure 2) of the refrigerant vapour from the state \( (T,P_c) \) to the state \( (T_c,P_c) \):

\[
(Q)_{DSUP} = m_{ad} \frac{dx(T,T_c)}{dt} [h_{ref}(T,P_c) - h_{ref}(T_c,P_c)] \tag{90}
\]

(b) Heat rejection due to condensation of refrigerant from saturated vapour to saturated liquid:

\[
(Q)_{LC} = \left( m_{ad} \frac{dx(T,T_c)}{dt} L_{ref} \right) \tag{91}
\]

(c) Heat rejection due to sub-cooling (Figure 2) of the refrigerant from saturated liquid to sub-cooled liquid:

\[
(Q)_{SUB} = \left( m_{ad} \frac{dx(T,T_c)}{dt} c_{p,liq}(T_c - T_s) \right) \tag{92}
\]

where \( c_{p,liq} \) is the specific heat of the liquid refrigerant and \( T_s \) is the exit temperature of the refrigerant from the condenser.

From the equation of heat rejection rate in the condenser with the heat transfer rate to the cooling water, the energy equation becomes

\[
\dot{Q}_{COND} = \dot{Q}_{DSUP} + \dot{Q}_{SUB} + \dot{Q}_{LC}
\]

\[
= m_{ad} \frac{dx(T,T_c)}{dt} \left[ h_{ref}(T,P_c) - h_{ref}(T_c,P_c) + L_{ref}(T_c) + c_{p,liq}(T_c - T_s) \right] \tag{93}
\]

\[
= \dot{m}_{cw} \cdot c_{pw} (T_{cw} - T_{cw}) \tag{94}
\]

This is an approximate equation and can only be used when there is no de-superheating or sub-cooling, i.e., when the refrigerant is at constant temperature of \( T_c \) during the heat transfer process.

The total heat lost in the condenser in one cycle can be estimated as:

\[
\dot{Q}_{COND} = \int_{T_2}^{T_3} m_{ad} \frac{dx(T,T_c)}{dt} \left[ h_{ref}(T,P_c) - h_{ref}(T_c,P_c) \right] dT + m_{ad} (x_2 - x_3) [L_{ref}(T_c) + c_{p,liq}(T_c - T_s)] \tag{95}
\]

Heat Transfer in Evaporator: During the throttling process, the enthalpy of the refrigerant may be assumed to remain constant. Thus, the refrigerant enters the evaporator with an enthalpy of \( h_{ref} \) and it also leaves the condenser at this point. In the evaporator, the refrigerant absorbs heat from the space / substance to be cooled and evaporated to the saturated vapour. There is a possibility for the refrigerant vapour to be superheated (Figure 2) at the evaporator pressure \( P_e \). Thus, the temperature of the refrigerant at the exit of the evaporator is greater than or equal to the saturation temperature \( T_{e} \) corresponding to the evaporator pressure \( P_e \).

Therefore, the heat absorbed by the refrigerant in the evaporator (cooling power) is given by:

\[
\dot{Q}_{EVAP} = (Q)_{LC} + (Q)_{SUB} = m_{ad} \frac{dx(T,T_c)}{dt} \left[ h_{ref}(T_e,P_c) - h_s + c_{p,ref}(T_e - T_s) \right]
\]

\[
= \dot{m}_{cw} \cdot c_{pw}(T_{cw} - T_{cw}) \tag{96}
\]

where, \( h_{ref}(T_e,P_e) \) is the enthalpy of the saturated vapour
of the refrigerant at pressure of $P_E$ or temperature $T_E$.

The exit temperature of the cooling water in the evaporator, $T_{Ewo}$, can be estimated as:

$$T_{Ewo} = T_E + (T_{Ewi} - T_E)e^{-\frac{u_{Ag}}{m_{Ewcpw}}} \quad (97)$$

This is an approximate equation and can only be used when there is no superheating of refrigerant, i.e., where the refrigerant is at constant temperature of $T_E$ during the heat transfer process.

### 3. VALIDATION OF THE MODEL

A detailed thermodynamic and parametric analysis of simple adsorption refrigeration machine using activated carbon AC-35/methanol as adsorbent/adsorbate pair was done by Chekirou et al (W. Chekirou, 2014), where the Dubinin-Astakhov equation is used to describe the isotherm of adsorption. They predicted system performance for different operating conditions. Figure 3 shows comparison between COP achieved by Chekirou (2014) and COP obtained from equilibrium numerical model under variable evaporator temperature. At 4 °C evaporator temperature, the present numerical model result shows 3% higher COP whereas at -10 °C COP 12% lower compare to Chekirou (2014) numerical model. This variation occurs due to the design of the adsorbent bed used by Chekirou (2014) was different. Here calculation was done on single adsorber but they have used nine parallel cylindrical adsorbers.

Qasem and El-Shaarawi (2015) developed an intermittent adsorption refrigeration system numerical model (by EES and MALT lab) using activated carbon (AC-35) and methanol as working pair. They predicted system performance with variation of operating parameters under Dhahran climate conditions. Figure 4 represents comparison between variation of system COP under influence of maximum temperature of the cycle predicted by Qasem and El-Shaarawi (2015) and our numerical model using the same adsorbent bed parameters and operating conditions. Upto 85 °C both curve shows same COP, after that in our model COP lowers 4% compare to Qasem and El-Shaarawi (2015).

The performance results of the present study (for COP) were in close agreement with those of Chekirou (2014) and Qasem and El-Shaarawi (2015). This validates the numerical model.

### 4. CONCLUSIONS

In this work, equilibrium and dynamic models for adsorption refrigeration are developed and discussed. This work has been carried out with the objective of developing a novel analytical and simulation model for predicting the performance of an adsorption refrigeration system. The other important objective of this work is to investigate the effects of different operating parameters on the performance of adsorption refrigeration. The present work gives a review on the equations of state for the adsorption pairs which are commonly used in adsorption cooling systems. Furthermore, a comprehensive reporting
for the experimentally calculated parameters for various combinations of adsorbent and adsorbate is presented. These parameters cover various types of activated carbon, silica gel, and zeolite as adsorbents and methanol, ammonia, water, ethanol, and others as adsorbates.

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