SUPPORTING INFORMATION

Novel nanostructured carbons derived from epoxy resin and their adsorption characteristics for CO₂ capture

Deepak Tiwari, Chitrakshi Goel, Haripada Bhunia*, Pramod K. Bajpai

Deepak.tiwari@thapar.edu, chitrakshigoel@yahoo.co.in, hbhunia@thapar.edu, pramod.iitk77@gmail.com

Department of Chemical Engineering, Thapar University, Patiala-147004, Punjab, India

*Correspondence to: Haripada Bhunia

Email address: hbhunia@thapar.edu

Phone: +91-9316682355; fax: +91-175-2393005

1. Adsorption kinetics

CO_2 adsorption/desorption on the synthesized adsorbent are necessary to evaluate the performance of adsorbents and to understand overall mass transfer of the process. It is one of the important characteristic in defining adsorption efficiency.[1] Goodness of the model is evaluated by correlation coefficients (R^2). It has been performed by following three models:

The pseudo-first-order kinetic model is given by following differential equation:[2]

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{1}$$

q_e and q_t are the adsorption capacities (in mmol g^{-1}) at various times t and at equilibrium, respectively and k_1 is the pseudo-first order adsorption rate constant (min^{-1}).

Integrating eq. (1) with boundary conditions: $q_t|_{t=0} = 0$ and $q_t|_{t=t} = q_t$, yields

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \tag{2}$$

The pseudo-second-order adsorption kinetic equation can be expressed as an equation:[3]

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{3}$$

where k_2 is the pseudo–second-order adsorption rate constant (g mmol^{-1} min^{-1}).

Integrating eq. (3) with initial conditions, yields

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

(4)

The fractional - order rate equation is given by following differential equation:[4]

$$\frac{dq_t}{dt} = k_n(q_e - q_t)^n t^{m-1} \tag{5}$$

where k_n, m and n are the fractional-order kinetic constant, driving force and diffusion resistance respectively.[5]

Integrating eq-(5) yields

$$q_t = q_e - \frac{1}{\left[\left((n-1)k_n/m\right)t^m + \left(1/q_e^{n-1}\right)\right]^{1/n-1}}$$

(6)

The correctness of models were assessed by error (%)

$$Error\ (\%) = \sqrt{\frac{\sum[q_{t(exp)} - q_{t(pred)}/q_{t(exp)}]^2}{N-1}} \times 100$$

(7)

where, $q_{t(exp)}$ and $q_{t(pred)}$ are experimental and predicted CO_2 loading, respectively.

2. Adsorption isotherms

Equilibrium adsorption data on the synthesized adsorbent were studied by Langmuir,[6] Freundlich,[7] and Temkin[8] models.

Langmuir adsorption isotherm is the simplest and most useful method with assumptions of adsorption has finite capacity for the adsorbate, no interaction between the molecules, etc. It can be written` as:

$$q_e = \frac{q_m K_L P}{1 + K_L P}$$

(8)

q_m is the maximum adsorption capacity (mmol g^{-1}), q_e is the adsorbed capacity at equilibrium (mmol g^{-1}), P (atm) is the partial pressure of CO_2 and K_L (atm^{-1}) is Langmuir adsorption constant.

Freundlich adsorption isotherm is valid for multilayer adsorption on heterogeneous surfaces. It can be given as:

$$q_e = K_F P^{1/n}$$

(9)

where K_F is Freundlich constant and *n* is empirical constant. Values of *n* in the range of 1 – 10 indicates favorable adsorption.

Temkin isotherm assumes that the heat of adsorption decreases linearly rather than logarithmic with coverage.[8] The isotherm equation is:

$$q_e = B\ln(K_T P) \tag{10}$$

where $K_T \, (atm^{-1})$ is the Temkin constant. $B = RT/b$ with *b* (J mol⁻¹) and *R* (8.314 J mol⁻¹ K⁻¹) and *T* (K) is the temperature.

3. Thermodynamic study

The Gibbs free energy shows spontaneity of the adsorption process where higher negative value reflects a more energetically favorable adsorption. The Gibbs free energy change can be obtained from the equation:

$$\Delta G^0 = -RT \ln(K_{eq}) \tag{11}$$

where ΔG^0 and K_{eq} are free energy change and equilibrium constant.[5]

The enthalpy change ΔH° (J mol⁻¹) and the entropy change ΔS° (J mol⁻¹K⁻¹) can be calculated from the slope of van't Hoff equation.[5]

$$\ln(K_{eq}) = -\frac{\Delta H^0}{R}\frac{1}{T} + \frac{\Delta S}{R}$$

(12)

The thermal energy (Q_{th}) needed to regenerate the adsorbent can be obtained from equation (13)

$$Q_{th} = Q_{st} + \text{Sensible heat} \tag{13}$$

where sensible heat is that which brings adsorbent from adsorption to desorption temperature. [5]

$$\text{Sensible heat} = \frac{C_P \Delta T}{adsorption\ capacity}$$

(14)

in which C_P heat capacity and ΔT is temperature difference between adsorption and desorption temperatures.

The isosteric heat of adsorption (Q_{st}) which represent the strength of adsorbate-adsorbent interaction was calculated from the Clausius-Clapeyron equation.[8]

$$Q_{st} = -R \left[\frac{\partial lnP}{\partial \left(\frac{1}{T}\right)} \right]_{q_e}$$

(14)

4. Calculation for energy duty for desorption of CO_2

As, C_P value for EZ-700 = 1.2 J g^{-1} K^{-1}.

Adsorption at (30 ˚C, 12.5% CO_2) in N_2 and desorption at 200 ˚C under pure N_2 flow.

Temperature difference, ΔT = (200-30) ˚C = 170 ˚C.

Adsorption capacity of EZ-700 = 0.65 mmol CO_2/g adsorbent

$$= 0.65 * 10^{-3} \text{ mol } CO_2/\text{g adsorbent} = 0.0286 \text{ kg } CO_2/\text{kg adsorbent}.$$

Therefore, sensible heat = $\dfrac{1.2 \times 170}{0.65 \ * \ 10-3}$ J per mole CO_2 = 313.846 kJ per mole CO_2.

Net sensible heat required in this process = (25% of 313.846) kJ per mole CO_2

Sensible heat = 78.46 kJ per mole CO_2.

Isosteric heat of adsorption, Q_{st} = 9.09 kJ per mole CO_2

Thermal energy input = (9.09 + 78.46) kJ per mole CO_2 = 87.55 kJ per mole CO_2

$$= 1.989 \text{ MJ per kg } CO_2$$

Therefore, for desorption of 0.65 mmol g^{-1} of CO_2 (0.0286 kg kg^{-1}), the energy required is 0.057 MJ.

Thus, CO_2 created to produce 0.057 MJ of energy for desorption = 0.005038 kg CO_2.

Table S1 Kinetic parameters of CO_2 uptake on prepared carbons at different temperatures and 10% CO_2 feed concentration.

| Kinetic model	Parameters	Temperature (°C)			
		30	50	75	100
Pseudo-first order	k_1 (min^{-1})	0.19	0.22	0.235	0.268
	q_e (mmol g^{-1})	0.477	0.45	0.321	0.27
	R^2	0.976	0.98	0.988	0.988
	Error %	22.67	5.05	4.93	4.35
Pseudo-second order	k_2 (g mmol^{-1} min^{-1})	1.54	1.21	0.97	1.30
	q_e (mmol g^{-1})	0.51	0.59	0.32	0.30
	R^2	0.992	0.98	0.99	0.993
	Error %	22.40	5.31	2.70	2.19
Fractional order	k_n (mmol^{1-m} g^{m-1} min^{-1})	0.256	0.20	0.18	0.15
	q_e (mmol g^{-1})	0.49	0.41	0.33	0.28
	n	0.72	0.65	0.71	0.77
	m	0.49	0.94	0.68	0.65
	R^2	0.993	0.99	0.996	0.997
	Error %	4.24	3.02	1.77	1.39
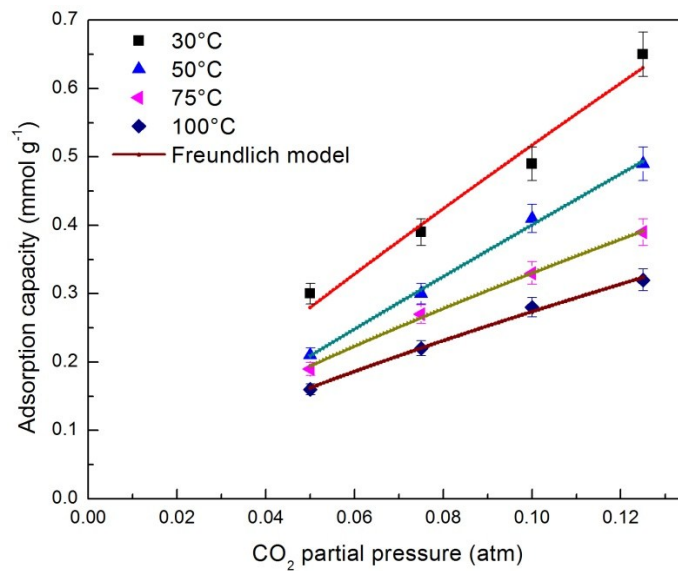
Fig. S2 CO_2 uptake isotherm: Experimental and predicted isotherm model at various temperatures.

References

1.   M. Hema and S. Arivoli, *Int. J.Physical Sci.*, 2007, 2, 10-17.

2.   E. Longhinotti, F. Pozza, L. Furlan, M. d. N. d. M. Sanchez, M. Klug, M. Laranjeira and V. T. Fávere, *J. Brazilian Chem. Soc.*, 1998, 9, 435-440.

3.   M.-S. Chiou and H.-Y. Li, *J. Hazard. Mater.*, 2002, 93, 233-248.

4.   C. Shen, C. A. Grande, P. Li, J. Yu and A. E. Rodrigues, *Chem. Engin. J.*, 2010, 160, 398-407.

5.   C. Goel, H. Bhunia and P. K. Bajpai, *RSC Adv.*, 2015, 5, 93563-93578.

6.   P. S. Kumar, S. Ramalingam, C. Senthamarai, M. Niranjanaa, P. Vijayalakshmi and S. Sivanesan, *Desalination*, 2010, 261, 52-60.

7.   B. Hameed, D. Mahmoud and A. Ahmad, *J. Hazard. Mater.*, 2008, 158, 65-72.

8.   M. Temkin and V. Pyzhev, *Acta physiochim. URSS*, 1940, 12, 217-222.