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Isotherms and Thermodynamics of CO_2 Adsorption on Thermally Treated Alum Sludge

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ABSTRACT

The isotherms, and thermodynamics of adsorption of carbon dioxide (CO_2) onto thermally treated alum sludge were successfully investigated in this study. The adsorption of CO_2 was investigated using a fixed-bed column adsorption system. The equilibrium isotherms data were best described by the Freundlich multilayer isotherm model. The feasibility, spontaneity and randomness of the CO_2 adsorption process were confirmed by thermodynamic parameters ($\Delta G°$, $\Delta H°$, $\Delta S°$). This study revealed that 800°C thermally treated alum sludge has a great potential as the adsorbent for CO_2.

INTRODUCTION

Large emission of greenhouse gases into the atmosphere has become a serious problem as it causes climate disasters (Upendar et al. 2012). Carbon dioxide (CO_2) gas is one of the greenhouse gases and a main contributor to the global warming (Monazam et al. 2013). About one-third of the CO_2 gas emission to the atmosphere is from fossil-fuel fired power plants (Monazam et al. 2013). Therefore, development of effective approaches to reduce atmospheric CO_2 level have received great attention and become the global research efforts (Upendar et al. 2012, Monazam et al. 2013).

For decades, CO_2 capture using solvent amine has been employed (Upendar et al. 2012). However, it has several drawbacks such as corrosion, high energy consumption and limitation on concentration of amine used (Upendar et al. 2012, Irani et al. 2016). To overcome these problems, amine-modified solid sorbents were used (Irani et al. 2016) as the adsorption of gases onto solid adsorbents. This is the promising technique (Upendar et al. 2012) due to several advantages such as higher CO_2 adsorption capacity, high selectivity, low equipment cost, easy to handle and low energy requirement for regeneration of adsorbents (Rashidi et al. 2016).

Numerous CO_2 adsorbents were developed from waste materials. Thus, alum sludge which is a waste generated from drinking water treatment plants was used as CO_2 adsorbent in this study. The objectives of this study were to investigate isotherms and thermodynamics of CO_2 adsorption onto 800°C thermally treated alum.

MATERIALS AND METHODS

Preparation of adsorbents: The dewatered alum sludge obtained from a local drinking water treatment plant was thermally treated at 800°C for 7 hours before grinding and sieving to the particles size of 450 to 500 µm. The thermally treated alum sludge was labelled as AS800 and used as the CO_2 adsorbent.

Adsorption of CO_2: For the adsorption experiment, 1 g of AS800 was packed into a glass adsorption column (20 mm in diameter × 200 mm in length) and heated at 100°C for 30 min, before purging with purified N_2 gas at 1.5 $L.min^{-1}$ for 15 min. Subsequently CO_2 gas (in balance of N_2 gas)

with the desired concentration was fed into the column at a flow rate of 0.09L.min^{-1}. The adsorption was conducted at 25°C and the concentrations of CO_2 were measured by a gas analyser (KANE100, United Kingdom) every 1 second until concentration of CO_2 at the outlet of the column similar to the concentration of CO_2 at the inlet of the column.

The adsorption capacity of AS800, q (mg.g^{-1}), was calculated by equation (1).

$$q = \frac{FC_o}{W}\int_0^t \left(1 - \frac{C_t}{C_o}\right)dt \quad ...(1)$$

Where, F is feed volumetric flow rate (L.min^{-1}), C_o is concentration of CO_2 at the inlet of the column (mg.L^{-1}), C_t is concentration of CO_2 at the outlet of the column (mg.L^{-1}), t is adsorption time (min), and W is adsorbent dosage (g).

Adsorption isotherms: The isotherm study of CO_2 was carried out using different CO_2 concentrations of 400, 1000, 2000, 4200, 6000 and 8000 mg.L^{-1}. Subsequently, the experimental data were examined using Langmuir and Freundlich isotherm models, as shown below, respectively.

The Langmuir isotherm model is given by the equation (2):

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b} \quad ...(2)$$

Where, C_e (mg/L) is equilibrium concentration of CO_2, q_e (mg.g^{-1}) is adsorption capacity of CO_2 at equilibrium, q_m (mg.g^{-1}) is maximum monolayer adsorption capacity, and b (L.mg^{-1}) is Langmuir rate constants related to adsorption energy.

The Freundlich isotherm model is expressed as:

$$log\ q_e = log\ K_F + \frac{1}{n} log\ C_e \quad ...(3)$$

Where, q_e (mg.g^{-1}) is adsorption capacity of CO_2 at equilibrium, K_F (mg.g^{-1}) is the Freundlich rate constant, n is the adsorption intensity and C_e (mg.L^{-1}) is equilibrium concentration of CO_2.

For Langmuir isotherm plot, C_e/qe *was* plotted against C_e, while $log\ q_e$ was plotted against $log\ C_e$ to obtain Freundlich isotherm model. The coefficient of determinations, R^2, obtained from the plots, were used to determine the best fitted adsorption isotherm model.

Thermodynamics study: The thermodynamics study of CO_2 adsorption was carried out at the optimum adsorption conditions at different adsorption temperatures of 298, 308, 318, 328, 338 and 348 K. Thermodynamics parameter such as Gibbs free energy change (ΔG°), heat of adsorption, (ΔH°), and standard entropy (ΔS°) were determined using Gibbs-Helmholtz and van't Hoff equations, as expressed in equations 4-6, respectively.

The Gibbs-Helmholtz equation:

$$\Delta G^\circ = -RT \ln K_c \quad ...(4)$$

Where, R is the universal gas constant (8.314 J.K^{-1}.mol^{-1}), T is temperature (K), and K_c is equilibrium constant (L.mol^{-1}). The equilibrium constant, K_c (L.mol^{-1}) could be calculated using equation below (Saad et al. 2016):

$$K_c = \frac{q_e}{C_e} \times Mw_{CO_2} \quad ...(5)$$

Where, q_e is equilibrium adsorption capacity (mg/g), C_e is concentration of CO_2 at equilibrium (mg/L) and Mw_{CO2} is molecular weight of CO_2 (g/mol).

The Van't Hoff equation:

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad ...(6)$$

Where, K_c is equilibrium constant (Lmol^{-1}), ΔS° is the standard entropy (J.K^{-1}.mol^{-1}), ΔH° is the heat of adsorption (J.mol^{-1}), R is the universal gas constant (8.314 J.K^{-1}.mol^{-1}) and T is temperature (K). The standard entropy and heat of adsorption were obtained from the plot of ln K_c against 1/T.

RESULTS AND DISCUSSION

Adsorption isotherms: The plots and parameters of the adsorption isotherms of CO_2 at 25°C are presented in Fig. 1 and Table 1, respectively. Obviously, Freundlich isotherm model can describe the isotherm adsorption better than Langmuir isotherm as indicated by higher R^2 value (0.9992). The results also indicated that the adsorption occurs via multilayer adsorption on the heterogeneous sorbent. The Langmuir adsorption model explains a monolayer adsorption on a finite number of equivalent localized sites, whereas Freundlich adsorption model describe multilayer adsorption on a heterogeneous surface (Rashidi et al. 2016).

Thermodynamics study: Table 2 shows the calculated thermodynamic parameters of the CO_2 adsorption process including the change in Gibbs free energy (ΔG°), the change in enthalpy of reaction (ΔH°), and the change in entropy of adsorbate and adsorbent interaction (ΔS°). Fig. 2 shows van't Hoff plot of the CO_2 adsorption on AS800. The negative value of ΔH° at fixed concentration of CO_2 indicated that the nature of CO_2 adsorption process was exothermic (Rashidi et al. 2016). The increase in randomness at the interface between AS800 adsorbent and CO_2 molecules and the affinity of the AS800 towards CO_2 (adsorption) was in-

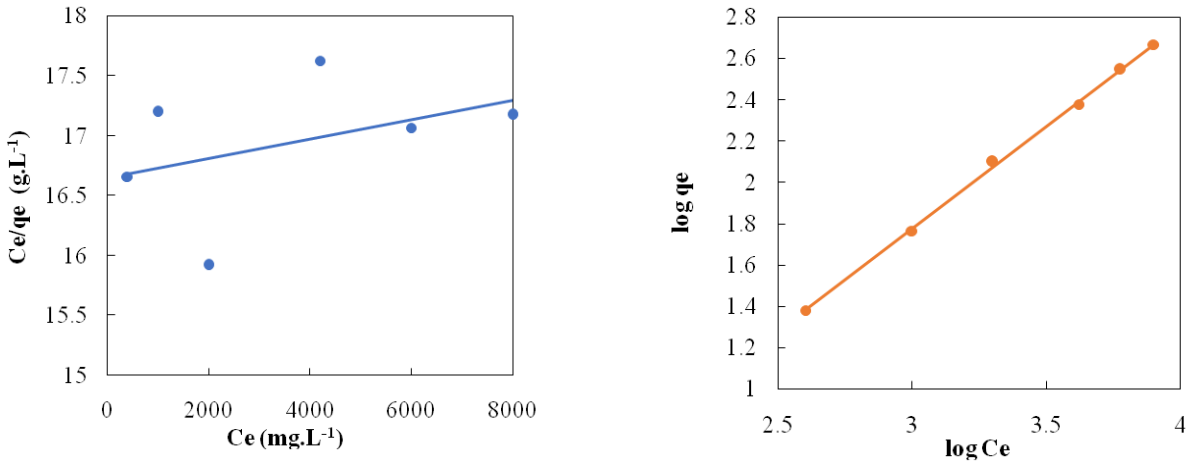

Fig. 1: (a) Langmuir and (b) Freundlich isotherm plots of CO_2 adsorption.

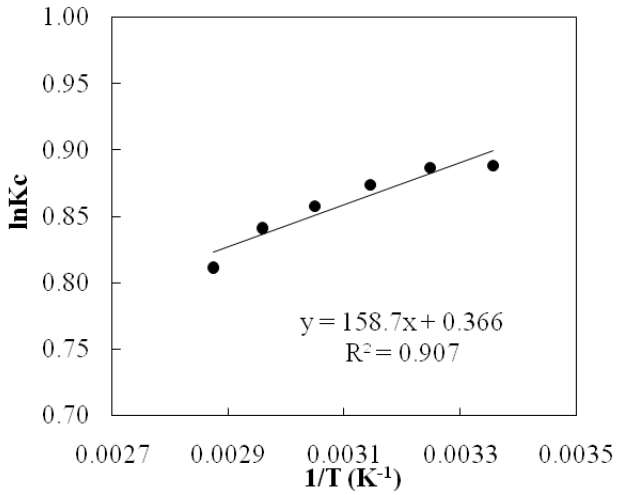

Fig. 2: Van't Hoff plot.

dicated by the positive value of ΔS°. A similar observation was found for adsorption of CO_2 gas at -10 to 40°C by Saad et al. (2016). It can be seen that increasing temperature caused increase in negative ΔG° value, thus the feasibility and spontaneity was favoured in adsorption of CO_2 onto the AS800. A similar trend was found for adsorption of CO_2 gas by RF-700 (Goel et al. 2015).

CONCLUSION

The fixed-bed adsorption of CO_2 using AS800 was investigated in order to evaluate CO_2 adsorption capacity. The adsorption isotherm of CO_2 on AS800 was best explained by Freundlich isotherms model. This indicates that the heterogeneous nature of AS800 surface participated in the CO_2 adsorption. The thermodynamic results revealed that the CO_2 adsorption was favoured exothermically at low temperature onto AS800.

Table 1: Parameters of adsorption isotherms of CO_2 by AS800.

Isotherm model	Parameter	
Langmuir	K_L(L.mg^{-1})	4.80×10^{-6}
	q_m(mg.g^{-1})	12500
	R^2	0.167
Freundlich	K_f(mg.g^{-1})	0.0643
	n	1.0112
	R^2	0.999

Table 2: Thermodynamic parameters of CO_2 adsorption onto AS800.

T (K)	ΔG° (kJ.mol^{-1})	ΔS° (J.K^{-1}.mol^{-1})	ΔH° (kJ.mol^{-1})
298	-2.20	3.048	-1.320
308	-2.27	3.048	-1.320
318	-2.31	3.048	-1.320
328	-2.33	3.048	-1.320
338	-2.36	3.048	-1.320
348	-2.35	3.048	-1.320

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