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Thermally Treated Alum Sludge as Novel Adsorbent of Carbon Dioxide (CO_2)

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Abstract: Dewatered alum sludge from drinking water treatment plants was exploited as carbon dioxide (CO_2) adsorbent in a fixed-bed column system. In this study, the effects of 6 parameters including particle size of adsorbent, heat treatment of adsorbent, adsorbents dosage, adsorption temperature, flow rate of adsorbate and CO_2 concentration on the fixed-bed adsorption of CO_2 were investigated using Response Surface Methodology (RSM). The experimental data was successfully fitted with the regression model to identify the significant parameters and predict the optimum value parameters for maximizing CO_2 adsorption capacity. Analysis of Variance (ANOVA) revealed that CO_2 concentration was the most significant factor influenced the CO_2 adsorption capacity. The experimental data of CO_2 adsorption capacity were in a good agreement with the predicted data from the regression model. The highest fixed-bed CO_2 adsorption capacity of 10.028 $mmol.g^{-1}$ (441.24 $mg.g^{-1}$) was achieved using 1 g of 450-500 μm of 800°C thermally treated alum sludge at CO_2 concentration of 8000 $mg.L^{-1}$ with a flow rate of 90 $mL.min^{-1}$ at 25°C. The results suggested that thermally treated alum sludge is a promising solid adsorbent for CO_2 capture.

Key words: Optimization, fixed-bed, adsorption, carbon dioxide, thermally treated sludge

INTRODUCTION

Carbon dioxide (CO_2) has been identified as the main contributor to the total global greenhouse gases emission followed by methane (NH_4), nitrogen oxide (NO_x) and other gases which are accounted 77, 14, 8 and 1%, respectively (Sarkar *et al*., 2015). The emissions of CO_2 from industrial, transportation, fossil fuel power plants and de-carbonization are the major sources for the increaseof CO_2 level in the atmosphere (Yu *et al*., 2012). According to Zhao *et al*. (2017) the level of CO_2 in the atmosphere currently has been increased to 6 billion tons per year (Zhao *et al*., 2017). For this reason, there is a global research effort to reduce the level of CO_2 from the sources of emissions and thus, stabilize its level in the atmosphere (Shafeeyan *et al*., 2012).

One of the most important technologies that are being developed by the most countries to mitigate the climate change is based on carbon Capture and Carbon Storage (CCS) which involves the separation of CO_2 from flue gas streams prior to discharge into the atmosphere. Numerous CO_2 separation techniques such as chemical absorption (Zhang *et al*., 2015), adsorption using solid adsorbent, chemical looping combustion (Juan *et al*., 2012), membrane separation (Luis *et al*., 2012), hydrate-based separation (Babu *et al*., 2015) and cryogenic distillation (Tuinier *et al*., 2010) are increasingly reported to reduce the emission of CO_2. Among these techniques, chemical absorption using alkanoamines solutions is commonly adopted in the industry due to its higher CO_2 separation efficiency (>90 %) at low concentration of flue gas (Leung *et al*., 2014). However, this technique has some drawbacks including energy-intensive regeneration process, equipment corrosion, high volume of solvents required and production of harmful volatile degradation compounds (Fredriksen and Jens, 2013).

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Alternatively, adsorption with solid adsorbent offers a great potential such as provides an efficient energy CO_2 separation and reversible process. The solid adsorbents can be recycled and more economical than the conventional chemical absorption process. In recent years, various porous solid adsorbents such as activated carbon (Cen *et al*., 2016), 13X zeolite (Dantas *et al*., 2011), calcium oxide (Besson *et al*., 2012), metal-organic frameworks (Serre *et al*., 2007), hydrotalcite (Leon *et al*., 2010) and organic-inorganic hybrids (Shanmugam *et al*., 2012) have been reported for CO_2 capture. However, all these solid adsorbents are limited with its high-cost production. In order to reduce the production cost of solid adsorbents for CO_2 capture, the use of waste materials from agricultural and industrial operations as potential solid adsorbents are suggested because of its highly abundant waste and low-cost materials (Olivares-Marin and Maroto-Valer, 2012). Alum sludge, a by-product of water treatment plants is seemed to be a good candidate as low-cost material for CO_2 adsorption due to the fact that it can be obtained in large quantities (80,000 tons/year) and its surface contains suspension of silica, hydrated aluminium oxide and iron oxide which preferentially adsorbed by CO_2 (Owaid *et al*., 2013; Yang *et al*., 2014). Recently, our research team found that the thermally treated alum sludge was mesoporous material and its pore diameter was enhanced after thermal treatment (Soleha *et al*., 2016). This unique characteristic may indicate that thermally treated alum sludge could be a promising solid adsorbent for CO_2 capture. To the best our knowledge, this is no single report on the utilization of thermally treated alum sludge as CO_2 solid adsorbents. Furthermore, the performance of treated alum sludge towards CO_2 adsorption is still unknown which could be interesting to be investigated.

To enhance the performance of thermally treated sludge towards CO_2 adsorption, it is necessary to find an optimum conditions for the preparation and operating conditions. Various parameters such as particle size of adsorbent, heating temperature, adsorbent dosage, flow rate of CO_2 gas and concentration of adsorbate can be controlled to improve CO_2 adsorption capacity. For this purpose, the experimental design based Response Surface Methodology (RSM), a multivariate statistical technique could provide statistical models to evaluate the interaction effect between the independent variables on the response and determine the optimum process (Rashid *et al*., 2016). In contrast to conventional method which only evaluates one variable at a time (OFAT), RSM is able to simultaneously optimize two or more independent variables at one time that could reduce the total number of experiments (Tang *et al*., 2011). As a result, the cost and time of experiment are minimized. A few experiments related to the optimization of CO_2 adsorption based RSM have been published, indicating the possibilities of this approach (Garcia *et al*., 2011; Serna-Guerrero *et al*., 2010; Mulgundmath and Tezel, 2010). The main aim of this study was to employ RSM based composite central design to investigate the effect of parameters (particle size of adsorbent, heating temperature, adsorbents dosage, flow rate of CO_2 gas and concentration of adsorbate) and optimize these parameters for the CO_2 adsorption.

MATERIALS AND METHODS

Preparation of adsorbents: The dewatered alum sludge was collected from the drinking water treatment plant located in Putrajaya, Malaysia. The collected alum sludge was thermally treated at different temperatures of 100, 450 and 800°C for 7 h using a muffle furnace before cooling down to room temperature. The thermally treated alum sludge samples were further ground and sieved to the selected range particles size of 100-150, 250-300 and 450-500 μm before being used as CO_2 adsorbent in the fixed-bed column system.

Characterization of adsorbents: A Perkin Elmer Fourier Transform Infrared (FTIR) spectrometer was used to analyse the functional groups of the adsorbent with the highest adsorption efficiency. The crystallinity of the adsorbent sample was determined by X-Ray Diffractometer (XRD) (Bruker AXS, model D8 Advance) (Germany) with Cu (K_α) source at 40 kV and 40 mA. The XRD pattern was recorded from 2θ 5-70°.

Experimental design: The effects of 6 independent variables on the fixed-bed adsorption of CO_2 such as particle size of adsorbent (100, 300 and 500 μm), temperature of thermal treatment (100, 450 and 800°C), adsorbents dosage (1, 5.5 and 10 g), adsorption temperature (25, 52.5 and 80°C), flow rate of CO_2 (0.03, 0.06 and 0.09 $L.min^{-1}$) and CO_2 concentration (400, 4200 and 8000 $mg.L^{-1}$) were investigated using half factorial Faced Centred Central Composite Design (FCCCD) by Minitab Software Version 16. Each variable was evaluated at three levels; Low (-1), medium (0) and high level (+1) as shown in Table 1.

A total of 49 experiments were designed fr these 6 variables which consisted of 32 points, 12 axial points and 5 center points were randomly carried out. Meanwhile the response of the designed experiments was based on the CO_2 adsorption capacity ($mmol.g^{-1}$).

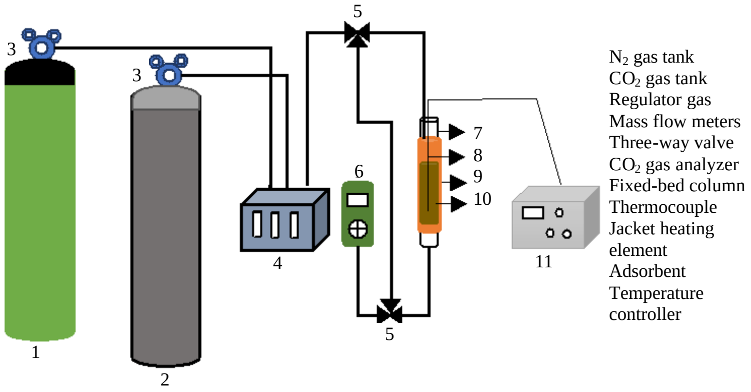

Fig. 1: Schematic diagram of experimental set-up for fixed-bed CO_2 adsorption

Table 1: The parameters and their levels (actual and coded)

Parameters	Unit	Low level (-1)	Center level (0)	High level(+1)
Adsorbent particle size (A)	µm	100	300	500
Temperature of treatment (B)	°C	100	450	800
Adsorbent dosage (C)	g	1	5.5	10
Temperature of adsorption (D)	°C	25	52.5	80
Flow rate of CO_2 (E)	$L.min^{-1}$	0.03	0.06	0.09
CO_2 concentration (F)	$mg.L^{-1}$	400	4200	8000

Adsorption of CO_2: A fixed-bed experimental set up for CO_2 sorption is shown in Fig. 1 which mainly consists of feed and purge gases, fixed-bed adsorption system and CO_2 gas detector. The thermally treated alum sludge samples with the desired weight (1, 5.5 and 10 g) were packed into a glass adsorption column (20 mm in diameter and 200 mm in length). The adsorbent samples were further pre-treated at the temperature of 100°C for 30 min before purged with the N_2 gas at 1.5 $L.min^{-1}$ for 15 min. Subsequently, the temperature was adjusted to adsorption temperature studied (25, 52.5 and 80°C) before introducing 400, 4200 and 8000 $mg.L^{-1}$ of CO_2 (in balance of N_2 gas) into the fixed-bed column at flow rate of 0.03, 0.06 and 0.09 $L.min^{-1}$. The fixed-bed temperature was controlled by a temperature controller and measured by a thermocouple while the flow rate of gas was controlled by a mass flow meter which were placed before the inlet of the column. The CO_2 concentrations in the inlet and outlet were monitored online by a gas analyser (KANE100, United Kingdom) every 1 second until the concentration of outlet is equal to the concentration of inlet. The adsorption performance was evaluated as total sorption capacity, q ($mg.g^{-1}$), by Eq. 1:

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

Where:

F = Feed volumetric flow rate ($L.min^{-1}$)
C_o = The CO_2 concentration studied ($mg.L^{-1}$)
C_t = The CO_2 concentration in the outlet ($mg.L^{-1}$)
t = Adsorption time (min)
W = Adsorbent dosage (g)

Data analysis: The experimental data were fitted into the regression model to predict the dependent and independent variables as presented in Eq. 2:

$$Y = \beta_o + \sum \beta_i \chi_i + \sum \beta_{ij} \chi_i \chi_j + \sum \beta_{ii} \chi_{ii}^2 \qquad (2)$$

Where:

Y = The predicted response (CO_2 adsorption capacity)
β_o = The intercept
β_i = Effects of the linear terms, β_{ii} is effects of the quadratic terms
β_{ij} = Effects of the interaction terms
χ_i = Coded value of the corresponding ith factors

All the terms in the regression model was evaluated using F-test for its statistical significant. The final reduced regression model was obtained after the insignificant terms were eliminated. An Analysis of Variance (ANOVA) was employed to evaluate the model fitness between the response and independent variables in order to identify the interaction between variables and predict the optimum value of response. The three-dimensional surface plots response surface was generated to visualize the effect of independent and interactive variables on the CO_2 adsorption capacity. Finally, the response optimizer was used to optimize the responses through graphical analysis.

Adsorption-desorption study: Adsorption-desorption of CO_2 experiments were conducted using a laboratory scale fixed-bed column that used for the adsorption. The adsorption of CO_2 was performed at the optimum adsorption conditions. After the adsorption, the temperature was adjusted to desorption temperature of 100°C before conducting the desorption experiment, where purified N_2 and He gasses were used as desorbents. The 100°C of desorption temperature was chosen rather than higher temperature due to low cost for CO_2 recovery (Chen and Ahn, 2011). Carbon dioxide was desorbed from the CO_{2-} adsorbed sludge using highly purified N_2 gas at a flow rate of 1.0 L.min^{-1} at 100°C until concentration of CO_2 at the outlet equal to 0 mg.L^{-1}. Adsorption was conducted again at the optimum conditions after the desorption to determine the adsorption capacity after the desorption. The adsorption index (AI) (%) was calculated using Eq. 3:

$$AI = \left(\frac{q_i}{q_0}\right) \times 100\% \qquad (3)$$

Where:

q_i = Adsorption capacity of the regenerated adsorbent (mmol.g^{-1})

q_o = Adsorption capacity of the fresh adsorbent (mmol.g^{-1})

The experiments of adsorption-desorption were conducted in duplicates and repeated at different flow rates (1.5, 2.0 and 2.5 L.min^{-1}) of purified N_2. Similar procedure was applied using He gas as the desorbent as well.

Regeneration study: Ten adsorption-desorption cycles were conducted using the optimum adsorption and desorption conditions. The adsorption capacity of the adsorbent was calculated using Eq. 1 to evaluate the adsorption capacity of adsorbent after each adsorption-desorption cycle completed.

RESULTS AND DISCUSSION

Characterization of adsorbents

FTIR analysis: The adsorbent of 800°C thermally treated alum sludge with particle size of 450-500 μm was characterized by FTIR due to its highest adsorption capacity as found in this study. The FTIR spectrum of the 800°C thermally treated alum sludge is shown in Fig. 2. Peaks at 1041, 792 and 414 cm^{-1} in the FTIR spectrum correspond to asymmetric stretching vibration of Si-O-Si, symmetric stretching vibration of Si-O-Si and bending vibration of O-Si-O, respectively which confirmed the presence of silica (SiO_2) in the sludge. The peak at 792 cm^{-1} also may indicates the 4-coordination vibrations of Al(IV)-O and Si-O-Al of kaolin. Soleimani *et al.* (2012) also found vibrations of Al(IV)-O at around 780 cm^{-1} and Si-O-Al at 810 cm^{-1} in calcined kaolin FTIR spectrum.

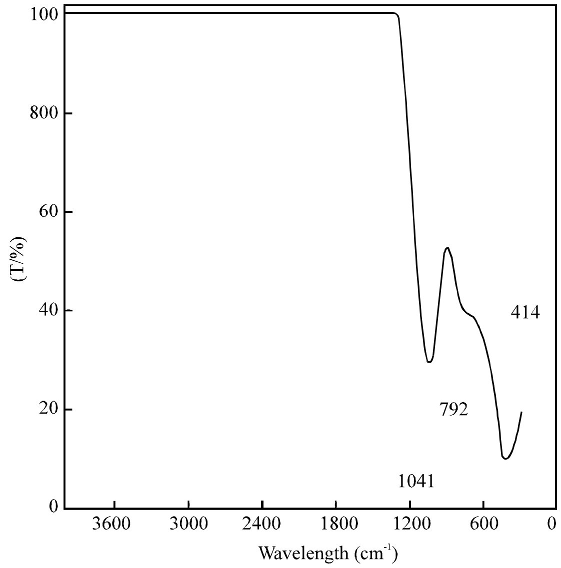

Fig. 2: FTIR spectrum of 800°C thermally treated sludge

Table 2: Height and Full Width at Half Maximum (FWHM) of peaks of the adsorbent

Peak	FWHM (°)	Center (2θ)	Height (Counts)
1	0.119	19.42	274.3
2	0.305	20.67	164.7
3	0.203	26.42	738.8

XRD analysis: The crystal structure of 800°C thermally treated alum sludge has been reported by Soleha *et al.* (2016). In this research, quantitative crystallinity analysis was conducted by evaluating Full Width at Half Maximum (FWHM) values of the peaks. The small values of FWHM (≤0.305) of these peaks (Table 2) which confirmed that the structure of the sludge is crystal. Tahiri *et al.* (2014) also confirmed the crystallinity of SiO_2 with FWHM value <0.125.

Development of reduced quadratic model and statistical analysis: The FCCCD of RSM was employed to determine the optimum conditions and to evaluate the interaction effects of particle size of adsorbent (A), temperature of treatment (B), adsorbent dosage (C), temperature of adsorption (D), flow rate of CO_2 (E) and CO_2 concentration (F) on the CO_2 adsorption capacity (q) (mmol.g^{-1}). A 49 number of experiments design matrix and the responses are presented in Table 3. Five replicates of the experimental runs (6, 8, 9, 31 and 34) were used for the estimation of pure error.

Using a multiple regression analysis, the experimental results from FCCCD were successfully fitted into the reduced quadratic model equation after eliminating the insignificant terms as shown in Eq. 13. This quadratic equation can provide a good visualization of the influence

Table 3: Experimental design matrix and CO_2 adsorption capacity

							q ($mmol.g^{-1}$)	
Run order	A	B	C	D	E	F	Experimental	Predicted
1	+	+	-	+	+	-	0.520	0.520
2	+	+	+	-	+	-	0.054	0.054
3	+	+	-	-	-	-	0.189	0.189
4	-	+	-	+	-	-	0.199	0.199
5	-	-	+	-	+	-	0.066	0.066
6	0	0	0	0	0	0	0.660	0.660
7	+	-	+	-	+	+	1.442	1.442
8	0	0	0	0	0	0	0.677	0.677
9	0	0	0	0	0	0	0.675	0.675
10	+	+	+	-	-	+	0.446	0.446
11	0	0	+	0	0	0	0.375	0.375
12	+	+	-	+	-	+	3.771	3.771
13	+	+	+	+	-	-	0.020	0.020
14	+	0	0	0	0	0	0.568	0.568
15	0	0	0	0	0	-	0.067	0.067
16	-	0	0	0	0	0	0.768	0.768
17	0	+	0	0	0	0	0.686	0.686
18	-	+	-	-	+	-	0.565	0.565
19	-	+	-	-	-	+	3.969	3.907
20	0	-	0	0	0	0	0.684	0.684
21	+	-	-	+	+	+	11.350	8.450
22	+	-	+	-	-	-	0.022	0.022
23	-	+	+	-	-	-	0.026	0.026
24	+	-	-	+	-	-	0.197	0.197
25	-	-	+	+	+	+	1.277	1.277
26	0	0	0	0	-	0	0.379	0.379
27	-	-	+	+	-	-	0.025	0.025
28	0	0	0	0	0	+	1.512	1.512
29	-	+	-	+	+	+	10.480	10.420
30	-	-	-	-	+	+	10.930	9.256
31	0	0	0	0	0	0	0.660	0.660
32	+	-	-	-	+	-	0.570	0.570
33	+	+	+	+	+	+	0.963	0.963
34	0	0	0	0	0	0	0.660	0.660
35	-	+	+	+	+	-	0.072	0.072
36	0	0	0	+	0	0	0.642	0.642
37	-	-	-	+	+	-	0.528	0.528
38	-	+	+	+	-	+	0.468	0.468
39	0	0	0	-	0	0	0.700	0.700
40	-	-	-	+	-	+	3.789	3.671
41	+	+	-	-	+	+	9.881	10.830
42	-	-	+	-	-	+	0.580	0.580
43	-	+	+	-	+	+	1.829	1.829
44	-	-	-	-	-	-	0.219	0.219
45	+	-	-	-	-	+	4.061	3.796
46	+	-	+	+	-	+	0.462	0.462
47	+	-	+	+	+	-	0.056	0.056
48	0	0	0	0	+	0	0.947	0.947
49	0	0	-	0	0	0	3.570	3.475

of each parameter and their interactions on the response as well as for the optimization condition of CO_2 adsorption capacity.

$$Y = 0.6857-1.6649\ C+0.962\ E+1.8769\ F+ 1.4605\ C^2-0.7725\ CE-1.5037\ CF+0.9085\ EF \qquad (4)$$

Where:

Y = CO_2 adsorption capacity ($mmol.g^{-1}$)
C = Adsorbents dosage (g)
E = Flow rate of CO_2 ($L.min^{-1}$)
F = Adsorbate concentration ($mg.L^{-1}$)

Table 4: Analysis of variance (ANOVA) for the CO_2 adsorption capacity

Source	Degree of freedom	Sum of squares	Mean square	F-values	p-values (Prob>F)
Model	7	385.544	55.078	107.11	<0.0001
C	1	94.239	94.239	183.27	<0.0001
E	1	31.465	31.465	61.19	<0.0001
F	1	119.775	119.775	232.93	<0.0001
C^2	1	22.202	22.202	43.18	<0.0001
C*E	1	19.096	19.096	37.14	<0.0001
C*F	1	72.354	72.354	140.71	<0.0001
E*F	1	26.412	26.412	51.36	<0.0001
Residual error	41	21.083	0.514	-	-
Pure error	34	1.674	0.049	-	-
Total	48	406.627	-	-	

$R^2 = 0.9482$; R^2 predicted = 0.9201; R^2 adjusted = 0.9393

The positive and negativesigns of coefficients indicates the synergistic and antagonistic effect, respectively. In this case, high CO_2 adsorption can be achieved at the low level of adsorbent dosage and high level of CO_2 flow rate of CO_2 and CO_2 concentration.

The ANOVA results for the reduced quadratic model for the CO_2 adsorption capacity is listed in Table 4. The F-value of model was 107.11 indicated that the model was highly significant with $p<0.0001$ and well fitted to the experimental data. In addition, the goodness of the developed model was evaluated by the coefficients of determination, R^2, R^2 adjusted and R^2 predicted which were calculated as 0.9482, 0.9393 and 0.9201. This implied that 94.82, 93.93 and 92.01% of the total variation in the parameters studied on the CO_2 adsorption could be explained by the developed model. Besides that, the high value of R^2 predicted which is closer to 1 indicates that the stronger developed model could predict the responses (Rashid *et al*., 2011). ANOVA analysis in Table 4 shows that the linear terms (dosage of adsorbent (C), flow rate of CO_2 (E) and CO_2 concentration (F)), interaction terms (CE, CF, EF) and quadratic term (C^2) are highly significant model terms for the CO_2 adsorption with p-<0.0001. Furthermore, the other terms (adsorbent particle size (A), thermal treatment of adsorbent (B), temperature of adsorption (D, AB, AC, AD, AE, AF, BC, BD, BE, BF, CD, DF, ED, A^2, B^2, C^2, D^2, F^2) are insignificant ($p>0.05$) to the CO_2 adsorption which was manually eliminated from the quadratic model equation as shown in Eq. 4 to improve the prediction of the response (Hosseinpour *et al*., 2011). CO_2 concentration had the largest effect on the CO_2 adsorption as indicated by the highest of F-value of 232.93, followed by adsorbent dosage and flow rate of CO_2 with F-values of 183.27 and 61.19, respectively.

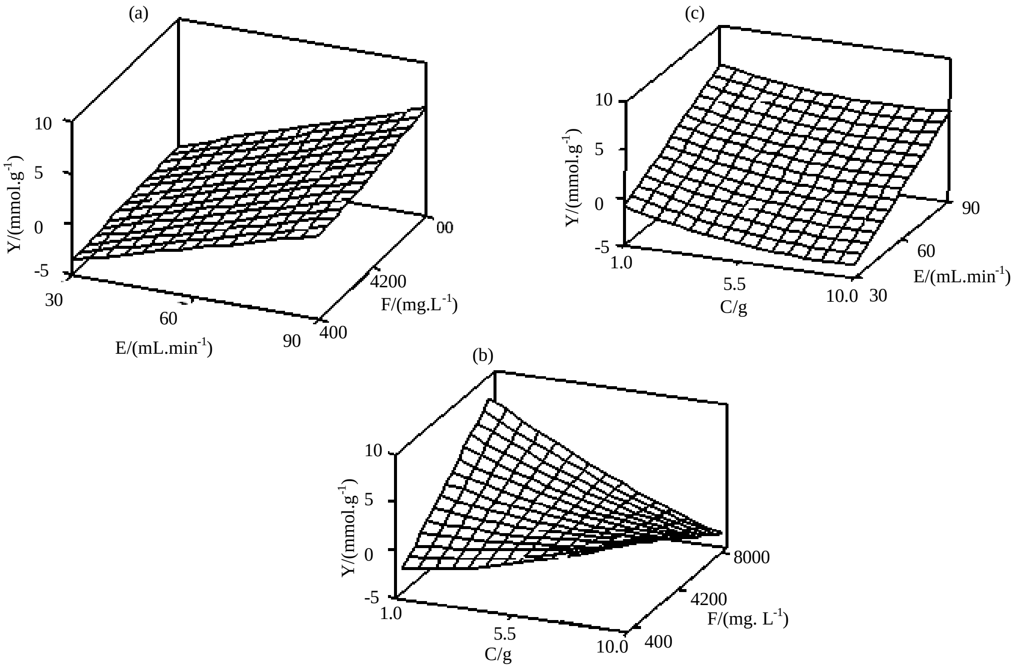

Fig. 3: 3D response surface plots: a) The effect of flow rate of CO_2 (E) and CO_2 concentration (F); b) Adsorbent dosage (C) and CO_2 concentration (F) and c) Adsorbent dosage (C) and flow rate of CO_2 (E) for CO_2 adsorption capacity

Effect of operating variables on the CO_2 adsorption: To evaluate the interaction between significant independent variables such as adsorbents dosage, flow rate of CO_2 and CO_2 concentration and their effects on the CO_2 adsorption, 3-dimensional (3D) response surface plots were constructed (Fig. 3). In these 3D plots, the interaction between two parameters (axis x and y) were evaluated based on the response surface (axis z) while other variables were fixed at centre level (Rashid *et al*., 2012). Based on F-value in ANOVA, the most influence interaction effect between parameters on CO_2 adsorption was adsorbent dosage and CO_2 concentration (CF) followed by the flow rate of CO_2 and CO_2 concentration (EF) and adsorbent dosage and flow rate of CO_2 (CE). Figure 3a demonstrates an increase of CO_2 adsorption is observed when increasing the level of the flow rate of CO_2 (0.03-0.09 L.min^{-1}) and CO_2 concentration (400-8000 mg.L^{-1}) while other parameters were kept constant. This might due to the increase of gas flow rate would increase the contact between CO_2 molecules and adsorbent surface, thus, more CO_2 molecules can be adsorbed. Furthermore, increasing the CO_2 flow rate enhanced the rate of CO_2 molecules diffusion to the adsorbent surface as reported by Saad *et al*. (2016).

Figure 3b depicts 3D surface plots for the interaction effect of adsorbent dosage and CO_2 concentration on CO_2 adsorption capacity. Using fixed adsorbent dosage of 1 g, an increasing of CO_2 concentration from 400-8000 mg.L^{-1} would give substantially increase of CO_2 adsorption capacity. This finding concluded that our thermal treated alum sludge adsorbent contains high mesoporous sites that can easily capture the higher number of CO_2 molecules on its surface. Hook (1997) reported that the increase in CO_2 concentration in a fixed bed system was proportional to the concentration gradient, thus, can overcome the mass transfer resistance, allowing more number of CO_2 molecules can be adsorbed on the adsorbent surface. The effect of CO_2 flow rate and adsorbent dosage on CO_2 adsorption capacity are illustrated by 3D response surface plot in Fig. 3c. It is clearly shown that the parameter of CO_2 flow rate had a larger effect on CO_2 adsorption capacity than the adsorbent dosage. As increasing of adsorbent dosage from 1-10 g, caused the decrease in CO_2 adsorption capacity. Similar results were reported by Tan *et al*. (2014), they found that the highest of CO_2 sorption of 27.01 mg.g^{-1} was achieved using 3 g of $32ACSH_3$ adsorbents andfurther increase of from 4.5-6 g givecaused substantially decrease in the adsorption of CO_2 capacities (17.33 and 14.07 mg.g^{-1}), respectively.

Table 5: Predicted and experimental maximum CO_2 adsorption capacity

CO_2 adsorption capacity (mmol.g^{-1})		
Predicted	Experimental	p-value of paired sample t-test
9.835	10.028	0.135

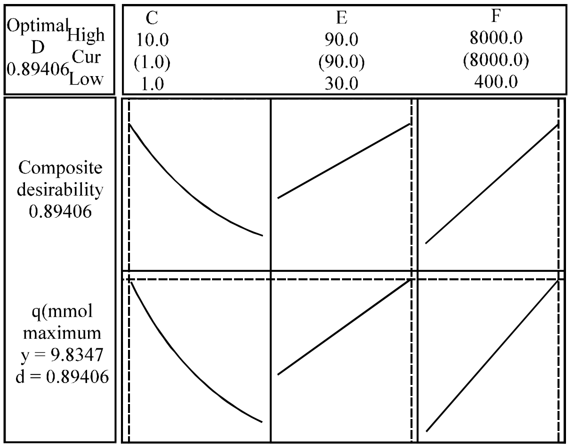

Fig. 4: Response surface optimization plot of CO_2 adsorption

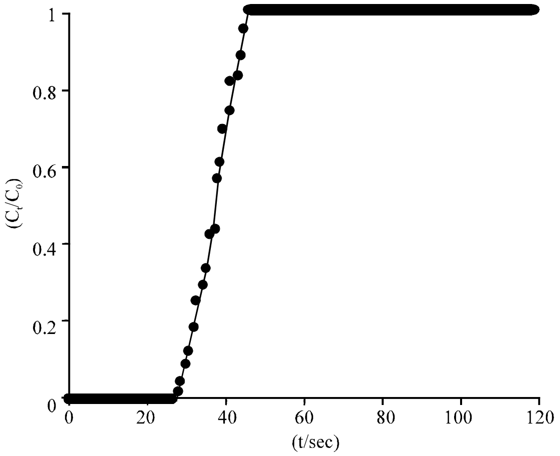

Fig. 5: Breakthrough curve of CO_2 adsorption at the optimum conditions

Response surface optimization: The response surface optimizer option under response surface design type is used to predict the optimum condition for the response. The optimum condition profile for desirable optimum response was chosen after setting up the response to maximize CO_2 adsorption capacity. The maximum CO_2 adsorption capacity of 9.835 mmol.g^{-1} was predicted at the following conditions: 1 g of adsorbent dosage, 0.09 L.min^{-1} of CO_2 flow rate and 8000 mg.L^{-1} of CO_2 concentration with desirability of 0.89406 as illustrated in response surface optimization plot (Fig. 4). To verify the predicted maximum CO_2 adsorption capacity, the experiments were performed at the proposed conditions in 10 replicates. The experimental results showed that the CO_2 adsorption capacity was 10.028±0.373 mmol.g^{-1} which was closed to the predicted value. The paired sample t-test analysis revealed that both adsorption capacities were insignificantly different as indicated by p-values (>0.05) as listed in Table 5. Thus, suggested model was confirmed valid. Figure 5 shows the breakthrough curve of CO_2 adsorption at the optimum conditions which indicated the typical breakthrough curve of an adsorption.

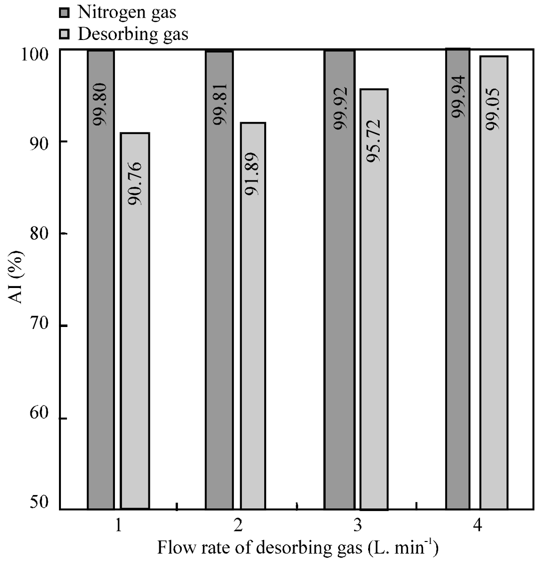

Fig. 6: Carbon dioxide Adsorption Index (AI) of thermally treated alum sludge at various flow rates of desorbents

Adsorption-desorption study: Different adsorbents namely purified N_2 and He gases were used to desorb CO_2 from the adsorbent via. thermal desorption at 100°C and 1 atm at different flow rates (1.5, 2.0 and 2.5 L.min^{-1}). Previous researchers also conducted desorption of CO_2 from the adsorbents around 100°C (Song *et al*., 2013; Chen and Ahn 2011; Auta and Hameed, 2014). In order to evaluate the adsorption capacity after desorption process, the Adsorption Index (AI) (%) was calculated based on the percentage ratio of adsorption capacity of the adsorbent to the fresh one. The CO_2 adsorption indexes using the N_2 and He gases ranged from 99.80-99.94% and 90.76-99.05 (Fig. 6), respectively, showing that the adsorption indexes using the N_2 gas were higher than that of the He gas. Thus, it can be said that the adsorption capacity of the desorbed sludge was closer to that of the fresh sludge using the N_2 gas. In addition, CO_2 desorption

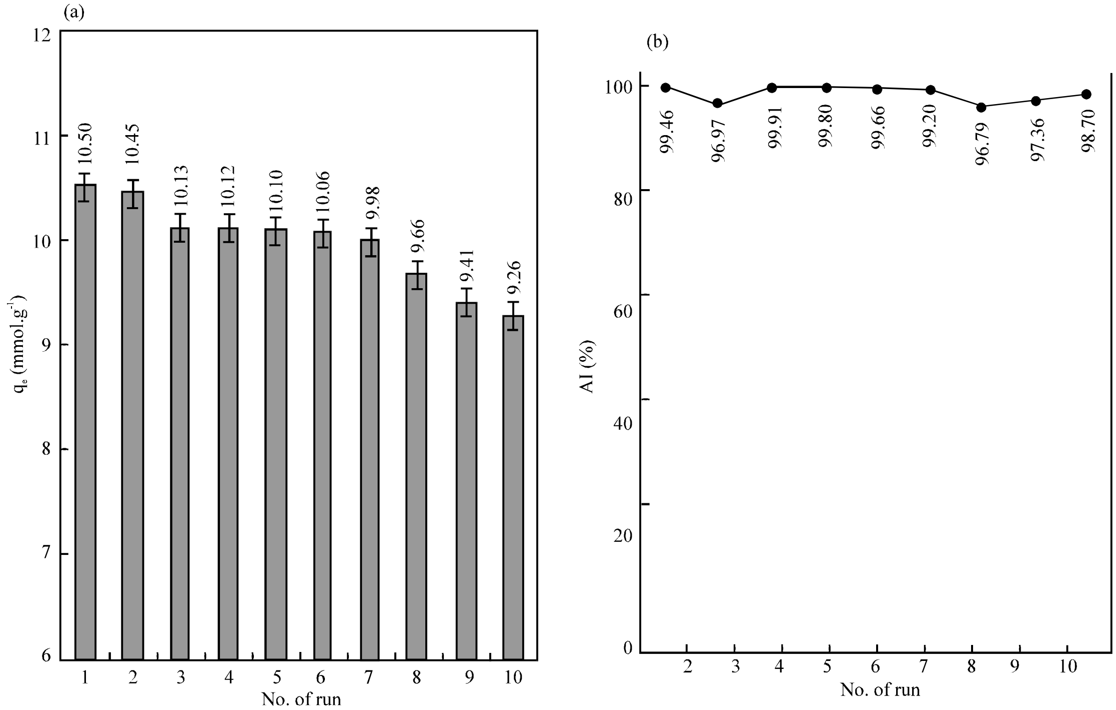

Fig. 7: Ten-cycles of CO_2 adsorption-desorption at the optimum adsorption and desorption conditions

from the surface of the sludge using the N_2 gas would be more economical and thus, N_2 gas was utilised as the desorbent in the regeneration study.

Regeneration of thermally alum sludge: Figure 7 shows the q_e and the CO_2 adsorption indexes of thermally treated alum sludge for 10 cycles of CO_2 adsorption-desorption conducted at 100°C and 1 atm. Obviously, CO_2 can be effectively desorbed from the surface of the sludge and the q_e was almost constant during 10 cycles as indicated by the CO_2 adsorption indexes only showed <1.0% reduction after 10 cycles of adsorption and desorption processes. These results demonstrated that thermally treated sludge can be utilised in long cyclic CO_2 adsorption by using a simple thermal treatment for desorption of the adsorbent. Similar reusability test results were reported in previous study (Hsu *et al.*, 2010).

CONCLUSION

RSM using half factorial faced centred central composite design was employed to optimize fixed-bed adsorption of CO_2 capacity using a novel CO_2 adsorbent i.e., thermal treated alum sludge in order to enhance CO_2 adsorption capacity. Based on the ANOVA analysis in RSM, the CO_2 concentration was found to be most influence parameter affecting the adsorption of CO_2 followed by CO_2 flow rate and adsorbent dosage while the other parameters (particle size of adsorbent, temperature of treatment and adsorption temperature) did not give significant effect. The maximum CO_2 adsorption capacity of 10.028 $mmol.g^{-1}$ was achieved according to the RSM suggestion. The thermally treated alum sludge can be desorbed effectively by a simple thermal treatment at 100°C using 1 $L.min^{-1}$ of N_2 gas as desorbent for 10 cycles of adsorption-desorption.

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