CHAPTER 4

RESULTS AND DISCUSSION

As mentioned in the previous chapter, the experimental studies in this work are divided into three parts. First, the adsorbent material was produced. The weight ratio of bottom ash:FGD gypsum :paddy clay:soil at 22: 7: 45: 26 and firing at 850 ^oC for 420 minutes with a heating rate of 3 ^oC/minute were employed. Second, the physical and chemical properties of adsorbent material were studied. Finally, the adsorption behaviors of methyl orange and iodine on the adsorbent material were evaluated. The equilibrium contact times of methyl orange and iodine on this adsorbent material were also determined. The obtained results are reported and discussed as follows.

Fig 4.1 Adsorbent materials

4.1 Physical and chemical properties of the adsorbent material

4.1.1 Particle size and surface area

The distribution of particle size of ground fired adsorbent powders measured by particle size analyzers was 50.26 µm. The specific surface area of the AM measured by using the Brunauer–Emmet–Teller (BET) method was 4.81 m^2/g. The result was obtained by means of the N_2 adsorption at 77±0.5K using a Quantachrome Autosorb-1 analyzer. Prior to analysis, all samples were degassed under vacuum at 120 ˚C for 3.77 h.

4.1.2 Chemical compositions

The chemical compositions of the adsorbent material were measured using XRF. As shown in Table 4.1, the major chemical components of this material are silica (SiO_2), alumina (Al_2O_3), calcium oxide (CaO) and ferric oxide (Fe_2O_3).

Table 4.1 Chemical compositions of adsorbent materials

Compound	wt.%
SiO_2	49.87
Al_2O_3	15.00
SO_3	4.42
K_2O	3.58
CaO	12.72
TiO_2	1.27
Mn_2O_3	0.24
Fe_2O_3	12.83
ZrO_2	0.06

4.1.3 Slake, water absorption, density and pH

Table 4.2 shows the physical properties of adsorbent material such as slake, water absorption (WA), density and pH. The adsorbent material did not slake when submerged in water for 30 days. It has high water absorption, moderate density and is strongly basic with a pH of 10.

Table 4.2 Physical properties of adsorbent materials (fired at 850 ^{o}C at a rate of 3 ^{o}C/minute)

Weight ratio BA:FGDG:C:SD	Properties				
	Slake	WA (%)	Density (g/cm^{3})	pH	S (m^{2}/g)
22: 7: 45: 26	Not slake	58	1.50	10	4.81

4.2 Adsorption of methyl orange and iodine on the adsorbent materials

The adsorption behavior of adsorbent materials using the batch-type techniques is expressed in the form of equilibrium concentration, C_e, versus adsorbed amount, q_e, of the solute. The adsorbed amount, q_e, was calculated using the equation (1.6). To predict the relationship between the adsorbed amounts and equilibrium concentrations obtained from batch-type tests, the Langmuir and Freundlich isotherm equations were adopted in this study as expressed by equations (1.8) and (1.10).

4.2.1 Effect of contact time

In order to study the time required for equilibrating methyl orange and iodine solutions with the adsorbent material, the contact times were selected at 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130 and 140 minutes, respectively. The sorption experiments were conducted by shaking 0.5000 g sample of adsorbent material in 100 mL of 0.00611 and 0.03055 mmol methyl orange solutions at 120 rpm at 30 ^oC, and 0.500 g sample of adsorbent material in 100 mL of $1.000x10^{-3}$ and $1.000x10^{-5}$ M iodine in 0.10 M KI solution at 120 rpm at 30 ^oC. At the end of the shaking period, the suspension was filtered and measured by UV-Visible spectrophotometer. The adsorbed amounts of methyl orange and iodine were plotted with the contact time.

Table 4.3 Time and q_e to plot the graph effect of contact time of methyl orange.

time(min)	q_e(10ppm)	q_e(2ppm)
10	0.118421	0.028916
20	0.170921	0.028916
30	0.182763	0.031084
40	0.191711	0.031084
50	0.204342	0.046506
60	0.226053	0.05012
70	0.250000	0.05012
80	0.292763	0.048554
90	0.295921	0.048554
100	0.295921	0.048554
110	0.293289	0.048554
120	0.293289	0.048554
130	0.292237	0.048554
140	0.293158	0.048554

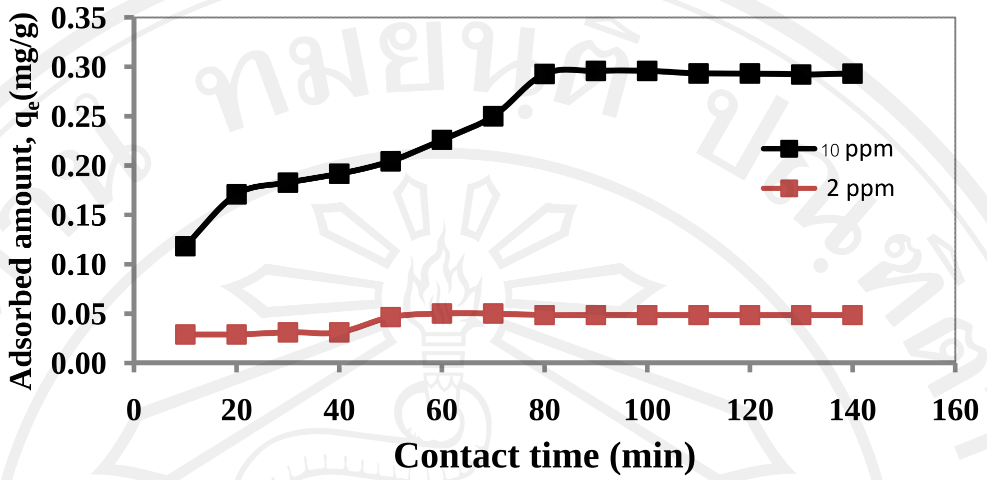

Fig 4.2 Effect of contact time on adsorbed amount of methyl orange onto adsorbent material

Fig 4.2 illustrates the adsorption of methyl orange onto the prepared adsorbent material at various contact times. The amount of methyl orange uptake, q (mg/g), increases with contact time on adsorbent material(AM). Methyl orange uptake increased in the first 80 min, then reached equilibrium when contact time was around 80 min.

Table 4.4 Time and q_e to plot the graph effect of contact time of iodine.

time(min)	$q_e(x10^{-5})$	$q_e(x10^{-3})$
10	0.181818182	0.073684211
20	0.19785124	0.088149123
30	0.199404959	0.09804386
40	0.199404959	0.100438596
50	0.199404959	0.101982456
60	0.199404959	0.101982456
70	0.199404959	0.101982456
80	0.199404959	0.101982456
90	0.199404959	0.101982456
100	0.199404959	0.101982456
110	0.199404959	0.101982456
120	0.199404959	0.101982456
130	0.199404959	0.10254386
140	0.199404959	0.103078947

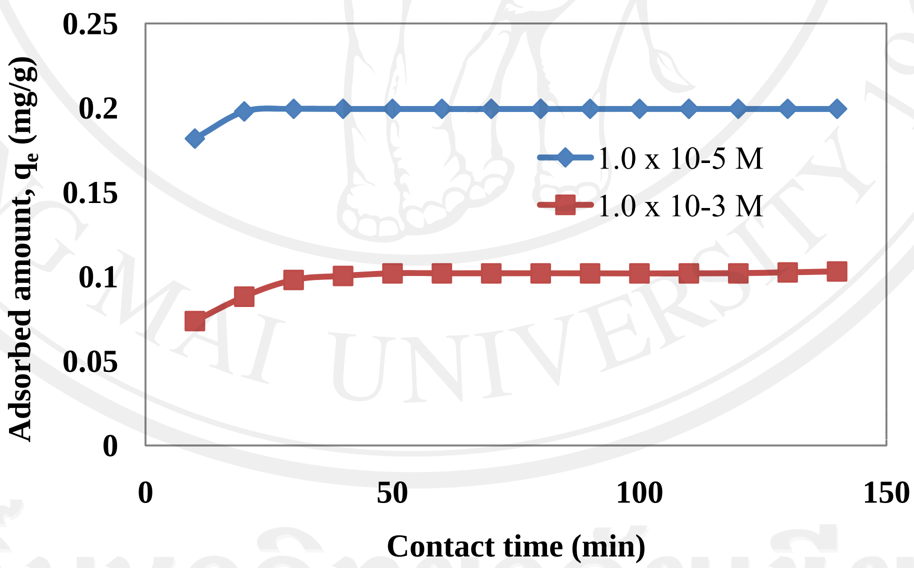

Fig 4.3 Effect of contact time on adsorbed amount of iodine onto adsorbent material

Fig 4.3 illustrates the adsorption of iodine onto adsorbent material at various contact times. The amount of iodine uptake, q (mmol/g), increased with contact time on adsorbent material. Iodine uptake is rapid in the first 30 min, then proceeds at a slower rate, and finally reaches equilibrium when contact time was around 60 min.

4.2.2 Adsorption isotherms of methyl orange and iodine

The adsorption isotherms of methyl orange and iodine adsorbed on the surface of the adsorbent material were carried out at temperature 30 ^{o}C. The Langmuir and Freundlich isotherms were applied to understand the adsorbate–AM interaction. The heterogeneity arises from the presence of different functional groups on the surface and from the various adsorbate–adsorbent interactions. The adsorption data were correlated with both the Langmuir and Freundlich isotherms in the initial concentration ranges from 0.00611 to 0.03055 mmol of MO and from $1.000 x 10^{-3}$ to $8.000 x 10^{-3}$ M of iodine. From the plots (Figs 4.4 to 4.9), the Langmuir values, q_{max} and b, and the Freundlich values, K_F and n, were then calculated and are shown in Tables 4.11 and 4.12.

Table 4.5 C_e and q_e to plot the graph adsorption isotherm of mrthyl orange.

C_e	q_e
1.39759036	0.120482
2.85542169	0.228916
4.34939759	0.33012
5.85542169	0.428916
7.30120482	0.539759
8.8313253	0.633735
10.4096386	0.718072

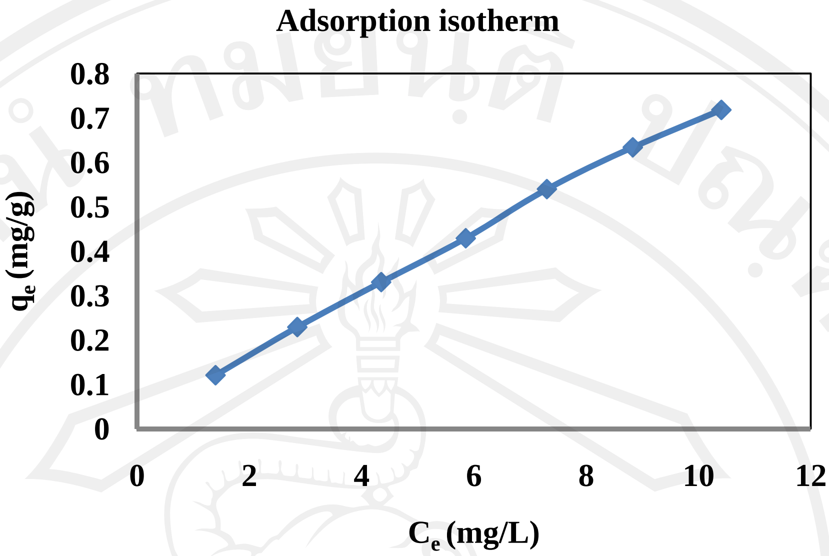

Fig 4.4 Adsorption isotherm for methyl orange on AM at 30 °C

Table 4.6 C_e/q_e and C_e to plot the graph Langmuir isotherm of methyl orange.

C_e/q_e	C_e
11.6000000	1.39759
12.4736842	2.855422
13.1751825	4.349398
13.6516854	5.855422
13.5267857	7.301205
13.9353612	8.831325
14.4966443	10.40964

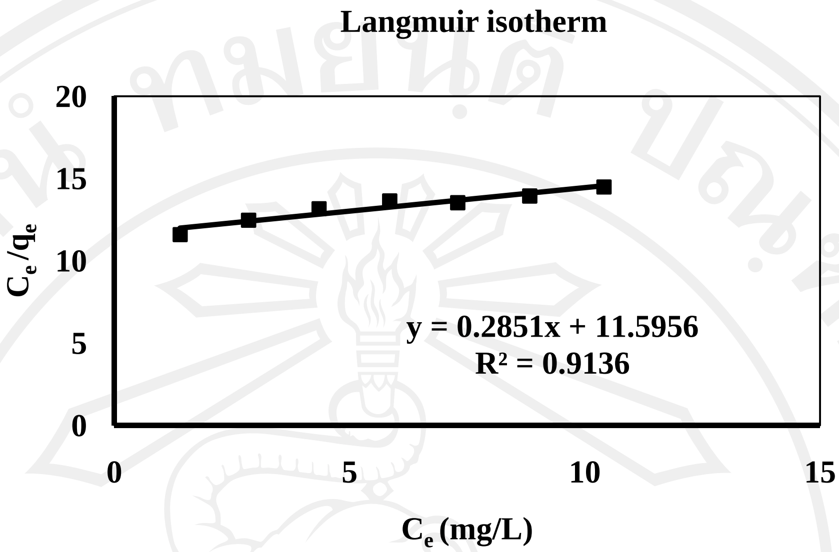

Fig 4.5 Langmuir isotherm of methyl orange on AM at 30 °C

Table 4.7 log C_e and log q_e to plot the graph Freundlich isotherm of methyl orange.

$\log(C_e)$	$\log(q_e)\times10^3$
0.145380	2.080922
0.455670	2.359676
0.638429	2.518672
0.767558	2.632372
0.863395	2.732200
0.946026	2.801908
1.017436	2.856168

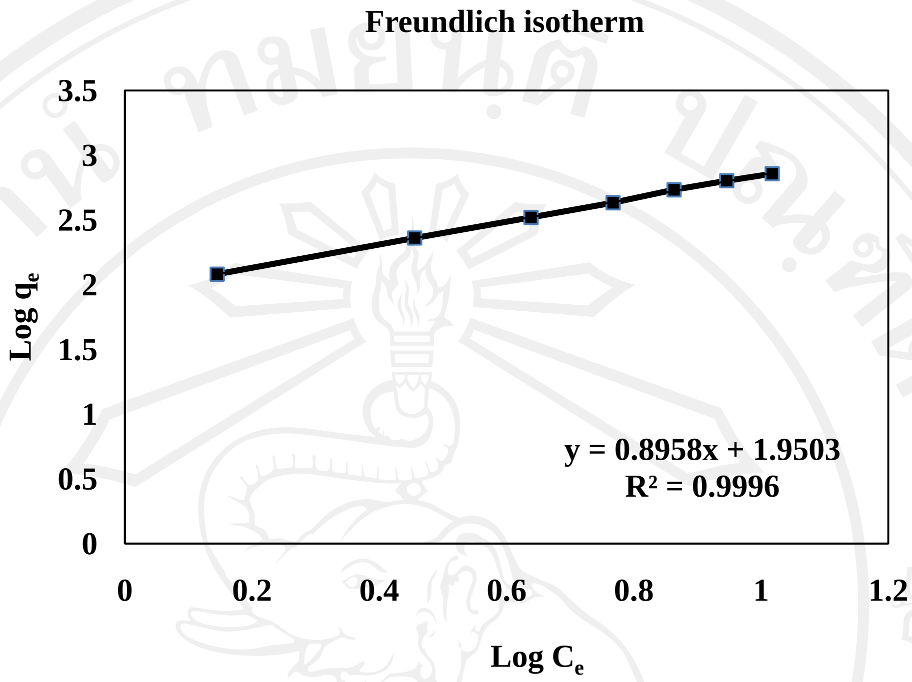

Fig 4.6 Freundlich isotherm of methyl orange on AM at 30 °C

Table 4.8 C_e and q_e to plot the graph adsorption isotherm of iodine.

Ce	qe
0.774194	0.045161
1.552419	0.089516
2.358871	0.128226
3.153226	0.169355
3.979839	0.204032
4.814516	0.237097
5.641129	0.271774
6.459677	0.308065

Adsorption isotherm

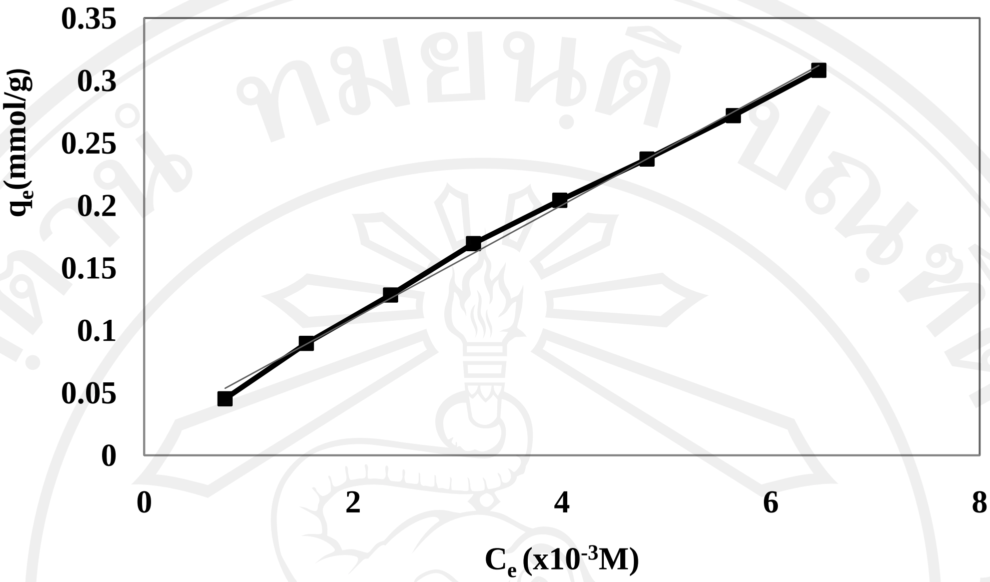

Fig 4.7 Adsorption isotherm for iodine on AM at 30 °C

Table 4.9 C_e/ q_e and C_e to plot the graph Langmuir isotherm of iodine.

Ce/qe	Ce
17.14286	0.774194
17.34234	1.552419
18.39623	2.358871
18.61905	3.153226
19.50593	3.979839
20.30612	4.814516
20.75668	5.641129
20.96859	6.459677

Langmuir isotherm

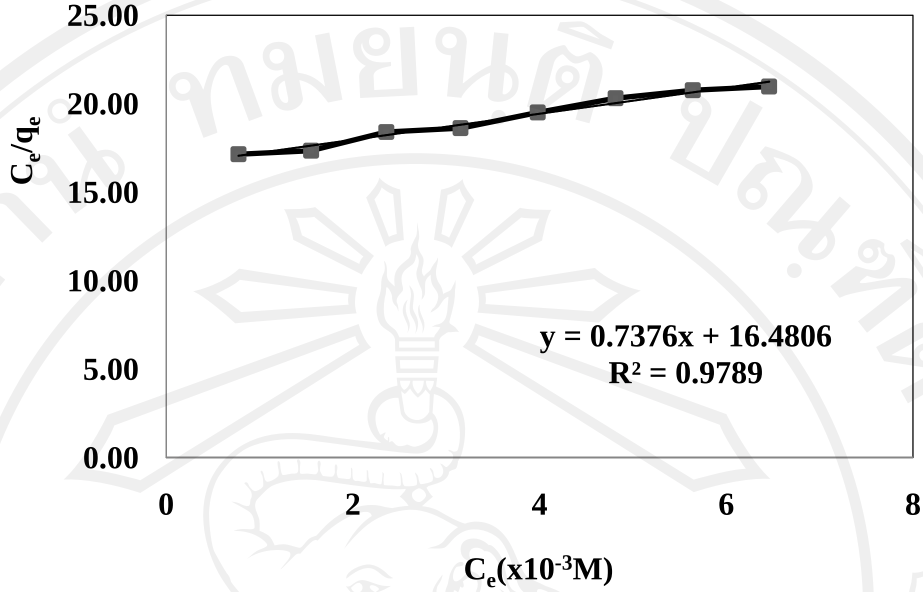

Fig 4.8 Langmuir isotherm of iodine on AM at 30 °C

Table 4.10 log C_e and log q_e to plot the graph Freundlich isotherm of iodine.

$\log(q_e) \times 10^{-3}$	$\log C_e$
1.654766	-0.11115
1.951901	0.191009
2.107975	0.372704
2.228798	0.498755
2.309699	0.599865
2.374926	0.682553
2.434208	0.751366
2.488642	0.810211

Freundlich isotherm

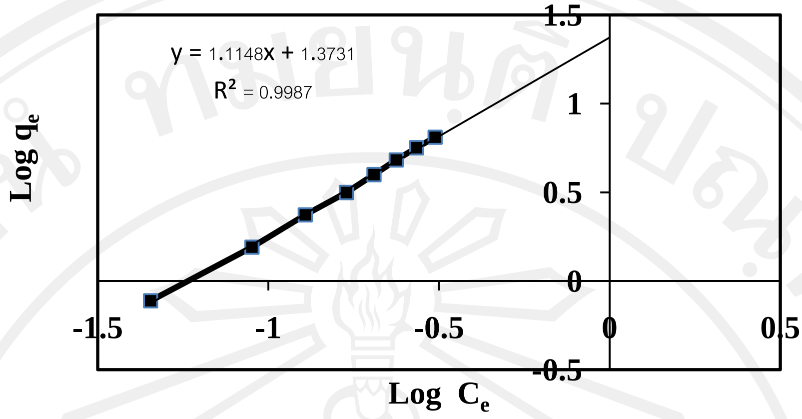

Fig 4.9 Freundlich isotherm of iodine on AM at 30 °C

Table 4.11 Langmuir constants for adsorption of methyl orange and iodine on AM at 30 °C

Parameter	Methyl orange	Iodine
$1/q_{max}$	0.285	0.738
$1/q_{max}b$	11.6	16.5
q_{max}	0.0107 (mmol/g)	1.36 (mmol/g)
b	7.515×10^{-5} (L/mmol)	0.0447 (L/mmol)
R^2	0.9136	0.9789

Table 4.12 Freundlich constants for adsorption of methyl orange and iodine on AM at 30 °C

Parameter	Methyl orange	Iodine
log K_F	1.95	1.37
1/n	0.896	1.11
K_F	89.2	23.6
n	1.12	0.901
R^2	0.9996	0.9987

The graphs in Figs. 4.5, 4.6, 4.8 and 4.9 show the relationship between adsorbed amount of methyl orange and iodine and their equilibrium concentration in solution. These results confirmed that the adsorption behavior on the adsorbent material correspond with both Langmuir and Freundlich isotherms from the linear lines with high R^2 values. All R^2 values in Table 4.11-4.12 are higher than 0.9.

The determined values of the Langmuir adsorption equation parameters, q_{max} and b, are summarized in Table 4.11. According to the Langmuir isotherm equation, the q_e values depend on equilibrium solution concentration. Since the amounts of adsorption increase when the solution concentration increases, therefore, the adsorption behavior of dyes on both absorbent materials tend to be monolayer type confirmed by the Langmuir plots.

The experimental results in Table 4.12 show that practically of the parameters 1/n (or slopes) are closed to one. This indicates that the adsorbed ability is gradually increased with solution concentrations. The determined values of the Freundlich adsorption equation parameters, K_F and n, are summarized in Table 4.12. According to the Freundlich isotherm equation, the q_e values depend on equilibrium solution concentration. The amounts of adsorption increase when the solution concentrations increase.