RESULTS AND DISCUSSION

1. The preliminary orthophosphate adsorption study

At the beginning of this work, orthophosphate adsorption on the different natural adsorbents, diatomite, perlite, kaolin, natural zeolite, and ball clay, was studied. These natural adsorbents are inexpensive and can be found available everywhere in Thailand.

Diatomite is a type of soil, it is occurred from the sediment of carcass and vegetable and can be found in the north of Thailand such as Lumpang province. In nature, it is white, light, porous, and dissolvable in water. After calcination at 750ºC, it turns to be hard and undissolvable in water. To study the adsorption, the orthophosphate concentration of 5 and 30 mg-P/L with the shaking time of 3 and 4 hours, respectively, the results were shown in Appendix B. The orthophosphate adsorption was about 9 % and 2% per 1 g diatomite.

Perlite is a rock, found at an extinct volcano in Lopburi province of Thailand. It is dark grey, heavy, high density, and undissolvable in water. With the same experimental conditions, the adsorption data was shown in Appendix B. The result showed the negative orthophosphate adsorption indicating that there could be orthophosphate released from perlite during experiment.

Kaolin has similar physical properties to diatomite but more crumbly, fragile, and heavy. In this work, kaolin was obtained from Chiangmai province. The uncalcined kaolin and the calcined one at 750ºC were used to study its orthophosphate adsorption. With the same experimental conditions, the adsorption results were shown in Appendix B. The adsorption capability of both adsorbents was in the range of 7-17% per 1 g kaolin.

Ball clay is the sediment found in the north of Thailand. It is hard, light, dark color like charcoal but more dense. With the same experimental conditions, the adsorption data was shown in Appendix B. The maximum adsorption of both the uncalcined ball clay and the calcined one at 750ºC was in the range of 18-37% per 1 g ball clay.

The amount of orthophosphate adsorption on all adsorbent was summarized as shown in Table 7. Without calcination, ball clay had higher adsorption capability than kaolin and natural zeolite; after calcination at 750ºC, natural zeolite had the highest orthophosphate adsorption of 27.16 mg-P/L per gram adsorbent, which was equivalent to 90%, at initial orthophosphate concentration of 30 mg-P/L. From these results, natural zeolite came to ones' interest leading to the further study. Due to the low orthophosphate adsorption capability of diatomite, perlite, kaolin, and ball clay, the studies on their orthophosphate adsorption were discontinued.

Table 7 The orthophosphate adsorption on the adsorbents

Calcination temperature (°C)	Initial orthophosphate concentration (mg-P/L)	The amount of orthophosphate adsorption ((mg-P/L)/ 1g adsorbent) (% adsorption)				
		Natural zeolite	Diatomite	Perlite	Ball clay	Kaolin
Uncalcined	5	0.43 (8.60%)	-	-	1.72 (34.4%)	0.86 (17.20%)
	30	0.50 (1.67%)	-	-	5.18 (17.27%)	2.17 (7.23%)
750 °C	5	4.38 (87.6%)	0.32 (6.40%)	-0.04	1.55 (31.00%)	0.70 (14.00%)
	30	27.16 (90.50%)	1.05 (3.50%)	-2.98	6.34 (21.13%)	3.30 (11.00%)

2. Characterization

2.1 Surface area, pore volume, and pore size

The surface area, pore volume, and pore size of mordenite after calcination at various temperatures were shown in Table 8. In BET measurement, the sample was outgased at 300ºC for 3 hours. In addition, the surface area and the micropore volume were calculated for each sample, using Barrett- Joyner- Halenda (BJH) method.

Table 8 indicated that natural zeolite was highly microporous due to high surface area and discrete pore size. When increasing the temperature of calcination, the surface area of natural zeolite was decreased. The calcination of natural zeolite was clearly affected the change in surface area and porosity, which was shown by nitrogen adsorption isotherms in Appendix C. The isotherms showed the slightly rising of adsorption volumes when P/Po got close to 0.90 and then rapidly increasing from P/Po of 0.90 to 1.00 except at temperature of calcination 450ºC, which the adsorption volume was hardly changed. Additionally, the effect of calcination temperature indicated that when increasing temperature of calcination, the adsorption volumes were also increased. The surface area at multipoint of uncalcined natural zeolite was 126.20 m^2/g and after calcined at 150, 300, 450, 600, 750, and 900ºC were 126.80, 65.09, 34.58, 18.18, 18.25, and 2.68 m^2/g, respectively. When the temperature of calcination increased, the surface area tended to decrease and rapidly dropped at the temperature of calcination at 900ºC. The pore volume of uncalcined natural zeolite was 0.17 ml/g and decreased after calcination especially at the temperature of 450ºC, the pore volume was as low as 0.02 ml/g. The pore size of uncalcined natural zeolite was 19.40 Aº and tended to decrease after calcination at increasing temperature but rapidly increased at the calcination temperature of 900ºC. The results showed that the high calcination temperature made internal structure collapsed by removing water and organic compounds from the adsorbents and caused the surface area, pore size and pore volume to decrease. At the calcination temperature of 900ºC, the pore size was rapidly increased which could be resulted from the change of surface structure.

Table 8 Surface characterization of natural zeolite

Data	sample						
	uncalcined	calcination					
		150ºC	300ºC	450ºC	600ºC	750ºC	900ºC
surface area at multipoint (m^2/g)	126.20	126.80	65.09	34.58	18.18	18.25	2.68
surface area at single point (m^2/g)	126.26	124.80	64.97	34.54	18.11	18.16	2.66
pore volume (ml/g)	0.17	0.10	0.13	0.02	0.08	0.10	0.07
pore size (Aº)	19.40	21.19	14.31	14.37	14.25	14.34	30.64

2.2 Morphology of natural zeolite

The morphology of natural zeolite particles was shown in Figure10 and 11.

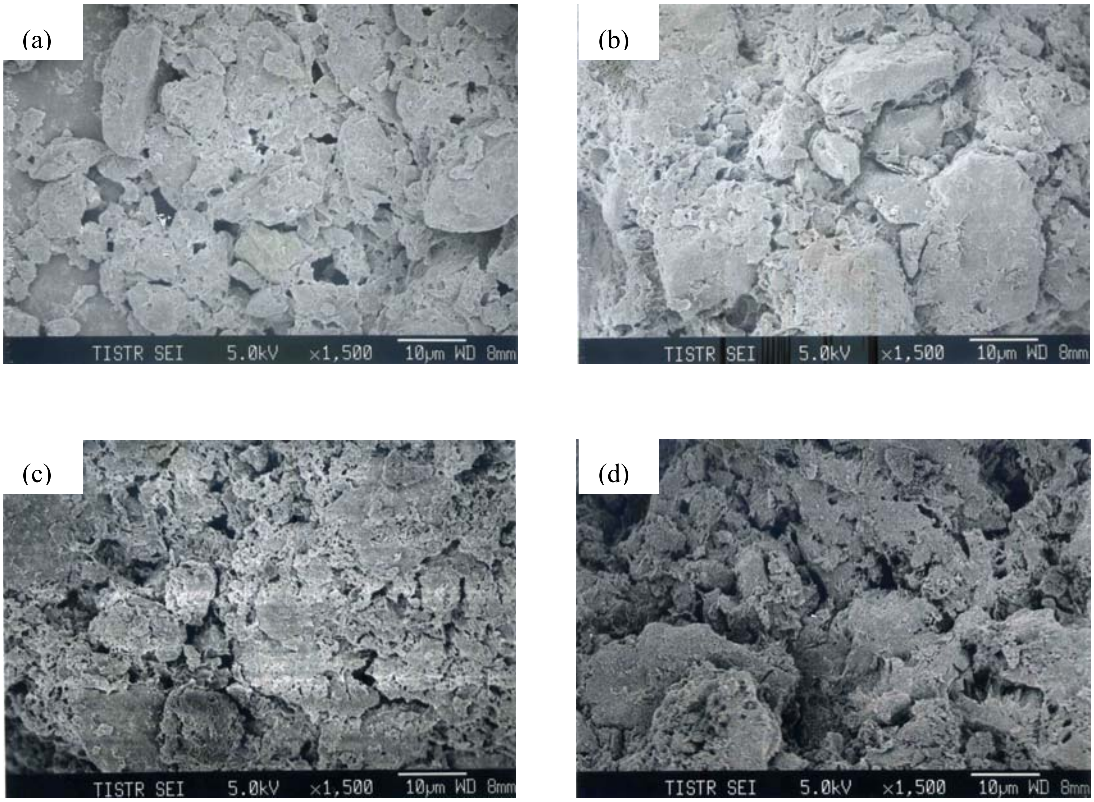

Figure 10 SEM image of natural zeolite (x 1,500): (a) uncalcined, (b) calcination at 450ºC, (c) calcination at 600ºC, (d) calcination at 750ºC

From both figures, SEM images could not clearly reveal the difference in morphology between the calcined natural zeolites at various temperatures and the one without calcination. However, the different sample grain size seen in the images could be dependent on the grinding step in sample preparation.

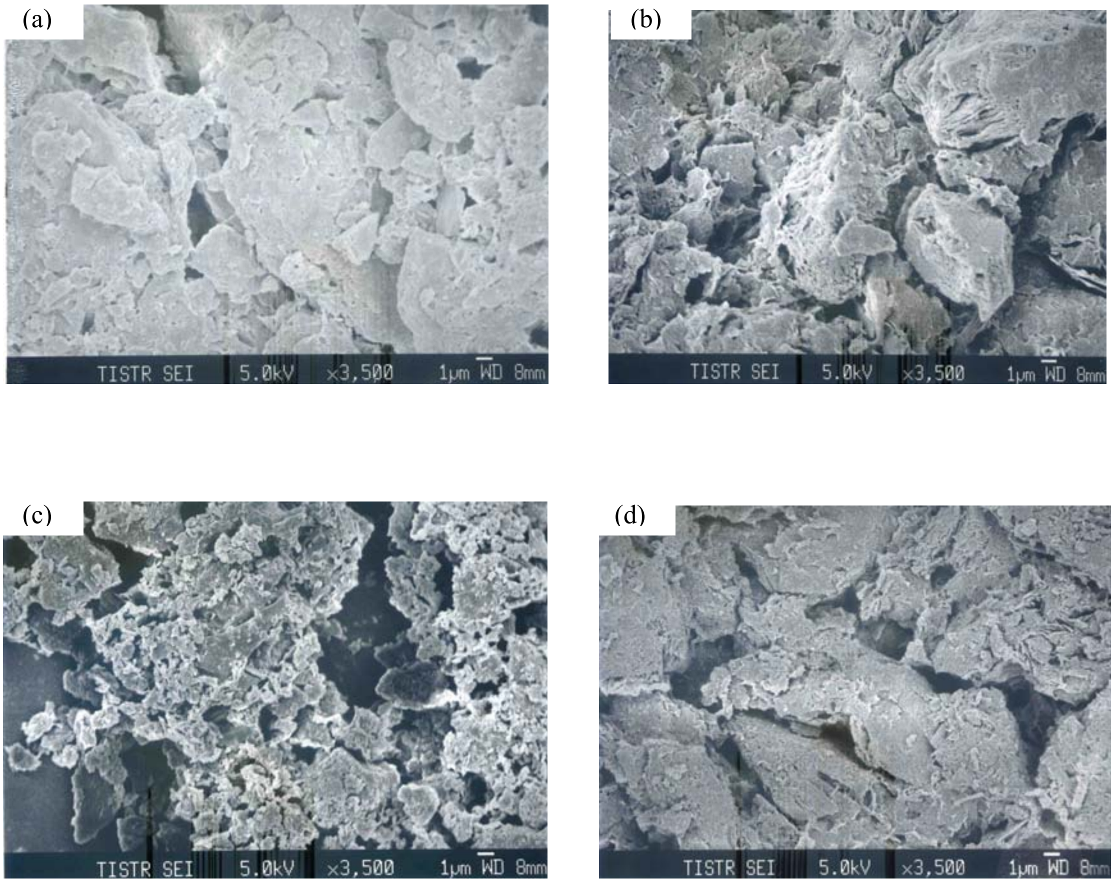

Figure 11 SEM image of mordenite (x 3,500): (a) uncalcined, (b) calcination at 450ºC, (c) calcination at 600ºC, (d) calcination at 750ºC

2.3 The chemical composition on surface of natural zeolite

The chemical compositions on the surface of natural zeolite obtained by EDS were shown in Table 9. The uncalcined natural zeolite and the ones with calcination did not show much difference in surface composition. There were 60-80%wt SiO_2 and approximately 10%wt Al_2O_3 and the rest was approximately 10%wt of metal oxides. The chemical compositions of mordenite via EDS measurements were agreed with the study of Covarrubias *et al*. (2005) with 70.66%wt SiO_2, 12.69%wt Al_2O_3, and approximately 17%wt of metal oxides. The different amount of chemical compositions on the surface of natural zeolite could affect the orthophosphate adsorption at the surface. There was a study of Yu (1997) stating that the Al-O sites of Al_2O_3 group at the surface could adsorb orthophosphate with the strong coordination adsorption.

Table 9 Chemical compositions on surface of natural zeolite

samples	components (%wt)						
	SiO_2	Al_2O_3	CaO	K_2O	FeO	Na_2O	MgO
uncalcined	65.07	10.89	18.76	1.99	1.26	1.07	0.96
uncalcined after adsorbed	81.15	10.91	3.57	1.43	1.02	1.42	0.50
calcination at 150°C	77.57	12.02	3.64	2.17	2.16	1.21	0.83
calcination at 300°C	79.64	11.27	3.45	1.79	1.88	1.09	0.66
calcination at 450°C	78.75	11.28	4.77	1.67	1.68	1.07	0.77
calcination at 450°C after adsorbed	59.31	9.03	27.26	1.29	1.32	0.88	0.91
calcination at 600°C	78.52	11.69	3.75	1.92	1.72	1.32	0.76
calcination at 750°C	71.65	13.70	6.50	3.04	2.82	1.02	0.94
calcination at 750°C after adsorbed	77.28	10.87	6.00	2.22	1.56	0.91	1.15
calcination at 900°C	78.19	11.29	5.04	1.58	1.31	1.48	0.84

2.4 The structure of natural zeolite

XRD provided information and was a recognized method for identifying crystalline mordenite. A crystal was a three-dimentional pattern of electron density. The internal electrons in crystal lattice determined the directions and intensities of scattered X-ray beams. Peaks of atoms in the crystal defined the symmetry of electron density distribution and size of unit cell in three-dimensional portion of crystal. The XRD information showed that the natural zeolite used in this work was mordenite by having the major intensity at 2θ = 11, 15, 20, 23, 26, 28, 29, and 32°. Therefore, natural zeolite used in this work would be called as mordenite from now on. The unit cell of mordenite was orthorhombic having axial: a=18.16 A°, b=20.45 A°, c=7.54 A° and angular relationship: $\alpha=\beta=\gamma = 90°$. Molecular formula of mordenite was $(Ca, Na_2, K_2) Al_2Si_{10}O_{24}.7H_2O$. When increasing the temperature of calcination to 300°C, the major peaks was increased in height, and then decreased with the increasing temperature. The decrease in XRD intensity showed the decrease in mordenite structure; until at the calcination temperature of 900°C, structure of mordenite turned into aluminum silicate (Al_2SiO_5) of Kyanite and silicon oxide (SiO_2) by having the major intensity of 2θ = 22, 27, 29, and 51°. The orthophosphate adsorption capability was possibly related to the crystal structure.

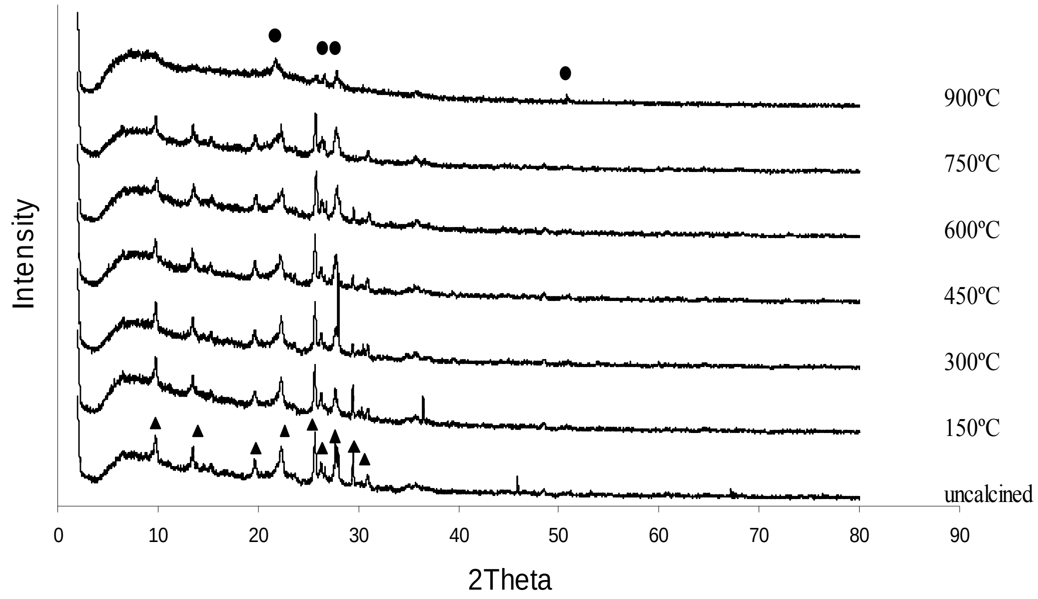

Figure 12 XRD patterns of the mordenite calcination at various temperatures

▲ mordenite , ● aluminum silicate of Kyanite and silicon oxide

2.5 Molecular structure by FTIR

In order to investigate the molecular structure of mordenite in term of functional groups, FTIR was used to study the mordenite before and after adsorption. FTIR spectra of mordenite at various calcination temperatures were given in Appendix F.

The wave numbers obtained from this work confirmed that there were Si-O, Al-O, SiO-H, and Si(OH)Al bonds presented in the structure of mordenite and after orthophosphate adsorption, there were PO_4^{3-}, $H\ PO_4^{2-}$, and $H_2\ PO_4^-$ presented in mordenite. The observed wave numbers were agreed to the experimental values from other studies as presented in Table 10. The information from FTIR results confirmed the presence of PO_4^{3-}, $H\ PO_4^{2-}$, and $H_2\ PO_4^-$ ions in the adsorbed mordenite, however, it could not show the adsorption sites where orthophosphate ions were attracted to Si, Al, or any other sites on the surface.

Table 10 Interpretation of mordenite at various conditions from FTIR spectra

Functional group	Wave number (cm^{-1}) (observed)	Wave number (cm^{-1}) (references)
νSi-O	1085-1052	1081-1059 [a]
νAl-O	790	785-775 [a]
SiO-H	3453-3439	~3480 [a]
Si(OH)Al	3638-3623	~3650-3648 [a]
PO_4^{3-}	1056	1006 [c]; 1048, 966, 569 [b]
$H\ PO_4^{2-}$	1056,875	1077, 989, 850 [b]; 1666, 677, 512 [c]
$H_2\ PO_4^-$	1056, 875	1160, 1074, 940, 870 [b]; 1621, 601 [c]

[a] Mohamed, M.M., *et al.* (2005)

[b] Arai, Y. and Sparks, D.L. (2001)

[c] Wu, P.X. and Liao, Z.W. (2005)

3. Adsorption of orthophosphate in prepared wastewater

In the measurement of orthophosphate adsorption, Spectronic G5 was used and the calibration of orthophosphate standard was performed. The calibration curve of orthophosphate concentration was shown in Appendix G.

3.1 Orthophosphate adsorption

3.1.1 The effect of temperature on calcination

Prior to the orthophosphate adsorption, the appropriate condition for the orthophosphate adsorption of calcination temperatures, orthophosphate concentrations, and shaking periods were studied. The measurement of orthophosphate in solutions was preceded by ascorbic method.

The orthophosphate adsorptions with the orthophosphate concentrations of 5, 10, 20, and 30 mg-P/L at various temperatures of uncalcined, 150, 300, 450, 600, 750, and 900ºC were studied. The relation between % adsorption and the period of shaking was plotted as shown in Figure 13, the data was shown in Appendix G. The results showed that uncalcined mordenite having % adsorption of 8% per 1g mordenite and slightly increased to 10-20 % per 1g mordenite when calcined at 150 and 300ºC at initial concentration of 5, 10, 20, and 30 mg-P/L. The % adsorption was negative values at 450 and 600ºC due to possibility of orthophosphate leaching from the bulk of mordenite. At the calcination temperatures of 450 and 600ºC, the pore volume of mordenite was as low as 0.02 ml/g and relatively small of 0.08 ml/g, respectively, this could result in the low orthophosphate adsorption compared to the adsorption of mordenite at other calcination temperatures. The adsorption became as high as 91, 93, 92, and 89% per 1g mordenite when calcined at 750ºC at initial concentration of 5, 10, 20, and30 mg-P/L, respectively. The adsorption was dependent on the calcination temperature of mordenite. Due to the increase in the calcination temperature, the crystal structure and chemical composition on surface of mordenite were changed. From Figure 13, it indicated that the appropriate temperature of calcination was 750ºC.

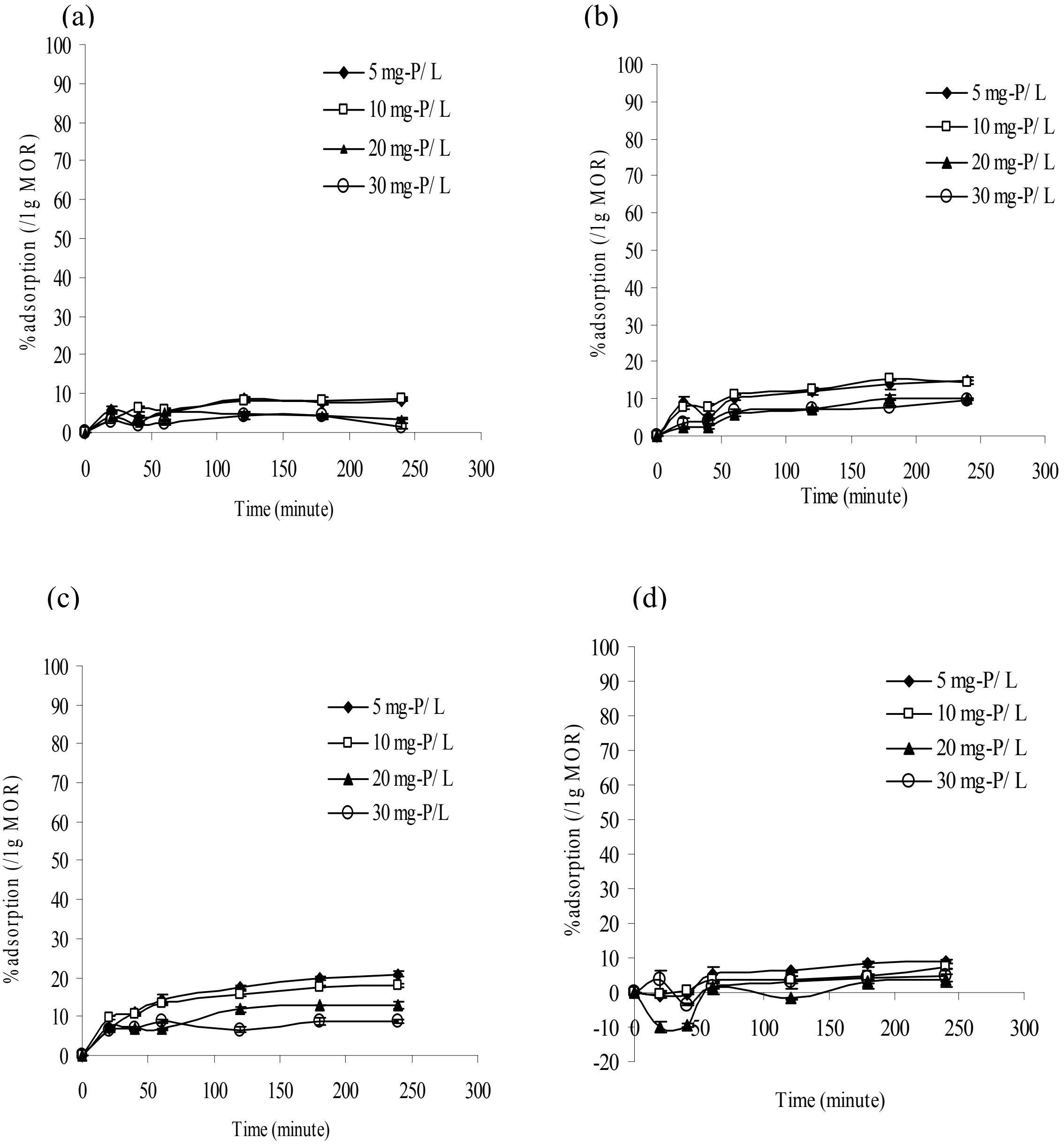
(a) (b) (c) (d)

Figure 13 The effect of adsorbing time and concentration on the removal of orthophosphate from aqueous solutions : (a) uncalcined mordenite, (b) calcined at 150ºC, (c) calcined at 300ºC, (d) calcined at 450ºC, (e) calcined at 600ºC, (f) calcined at 750ºC, (g) calcined at 900ºC

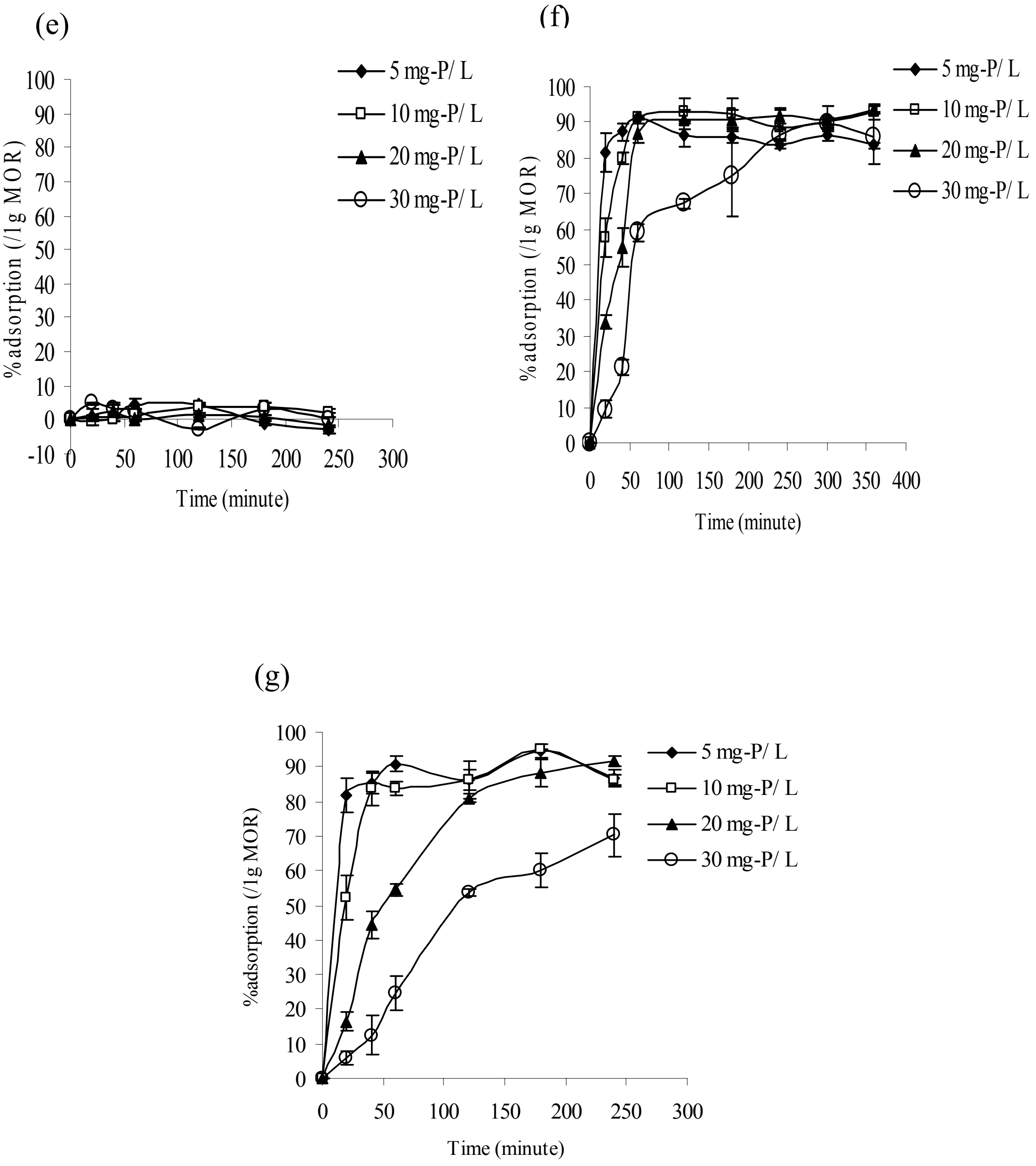

Figure 13 The effect of adsorbing time and concentration on the removal of orthophosphate from aqueous solutions (Cont'd): (a) uncalcined mordenite, (b) calcined at 150ºC, (c) calcined at 300ºC, (d) calcined at 450ºC, (e) calcined at 600ºC, (f) calcined at 750ºC, (g) calcined at 900ºC

3.1.2 The effect of adsorbate concentration

To study the influence of the initial orthophosphate concentration on adsorption, the initial concentration was ranged from 5 to 30 mg-P/L. It was found that an increase of the initial concentration leads to the decrease in % adsorption capability. By decreasing the initial concentration, the percent orthophosphate adsorption was higher. The results between % adsorption and time at different temperatures for concentrations between 5 to 30 mg-P/L were shown in Figure 14. At the initial concentration of 5 mg-P/L, % adsorption of 750 and 900ºC were increasing rapidly to 80 % after 20 minutes and slightly increased to the maximum of 91 % per 1g mordenite after 60 minutes of shaking time, and then it tended to decrease slightly after 1 hour. For other calcination temperatures, % adsorption was approximately 5-15% per 1g mordenite, which was much lower than the ones calcined at 750 and 900ºC. At the initial concentration of 10, 20, and 30 mg-P/L, % adsorption of the calcined mordenite at 750ºC was decreased from 91% to 60% at the shaking time of 60 minutes. Because the orthophosphate molecules were quite large, at the initial concentration of 5 mg-P/L, the orthophosphate molecules in solution were able to adsorb on the surface with less interaction between itself and other orthophosphate molecules. As the initial concentration increased to 30 mg-P/L, there was higher interaction among the adsorbed orthophosphate molecules at the surface. The repulsion between orthophosphate molecules led to the decrease in amount of adsorption on mordenite surface.

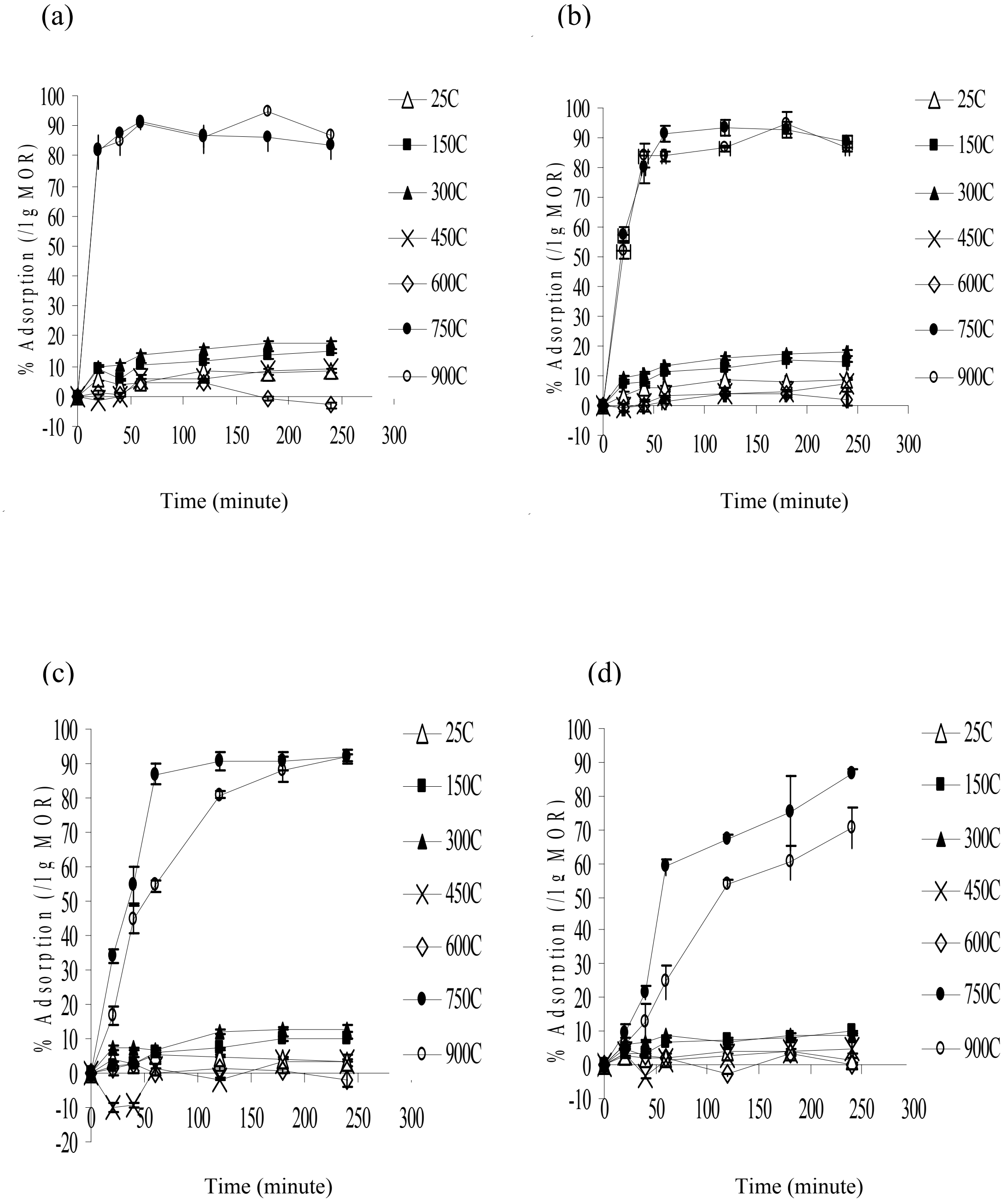

Figure 14 Initial orthophosphate concentration adsorption: (a) 5 mg-P/L, (b) 10 mg-P/L, (c) 20 mg-P/L, (d) 30 mg-P/L

3.1.3 The effect of adsorbing time

%Adsorption can be calculated from the difference between the initial orthophosphate concentration and the remaining orthophosphate concentration after being adsorbed on mordenite. From the previous results, it was shown that the adsorption capability was maximized at 750ºC. To study the appropriate time for adsorption to reach the equilibrium, the amount of adsorption was observed with the increase in adsorbing time until the amount of adsorption became consistent which implied that equilibrium was reached. The results on the adsorption at the calcination temperature of 750ºC could be seen in Figure 14. At initial concentration 5 mg-P/L, the amount of orthophosphate adsorption rapidly reached equilibrium in 1 hour with 91% adsorption and leveled off after 1 hour. At initial concentration of 10 mg-P/L, the amount of orthophosphate adsorption gradually approached the equilibrium in 2 hours with 93%adsorption. At the initial concentration of 20 mg-P/L, the amount of orthophosphate adsorption slightly increased to the equilibrium in 4 hours with 92% adsorption. At the initial concentration of 30 mg-P/L, orthophosphate adsorption rapidly increased to 60%in 1 hour then continued to slowly increase to the maximum adsorption in 5 hours with 89% adsorption, before it tended to decrease. To have the appropriate condition in orthophosphate adsorption, the results led to the adsorbing time of 5 hours and the calcination temperature of 750ºC at the initial orthophosphate concentration of 30 mg-P/L in the further experiments.

3.2 Adsorption isotherm

In this study, Langmuir and Freundlich adsorption isotherms were used to explain behaviors of several material adsorptions. The $C_e(x/m)$ versus

C_e were plotted on x-axis and y-axis, respectively and fitted with Langmuir isotherm from equation 8.

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$$\frac{C_e}{X} = \frac{1}{bX_m} + \frac{C_e}{X_m} \quad \text{or} \quad \frac{C_e}{x/m} = \frac{1}{bX_m} + \frac{1}{X_m} C_e$$

The Langmuir adsorption isotherm at the calcination temperature of 750ºC was shown in Figure 15, the data was plotted between $C_e(x/m)$ and C_e. Other calculation data was shown in Appendix H. The calculation variables from Langmuir adsorption isotherm, such as equation, correlation coefficient of determination (R^2), adsorption maximum, and binding energy were shown in Table 11. By fitting Langmuir adsorption isotherm in Figure 15, R^2 from 60 minutes of shaking time was 0.9965 and R^2 from the average shaking time was 0.9000. The maximum adsorption was increased with the shaking time from 20 minutes to 180 minutes and binding energy was found to decrease with shaking time from 60 minutes to 180 minutes.

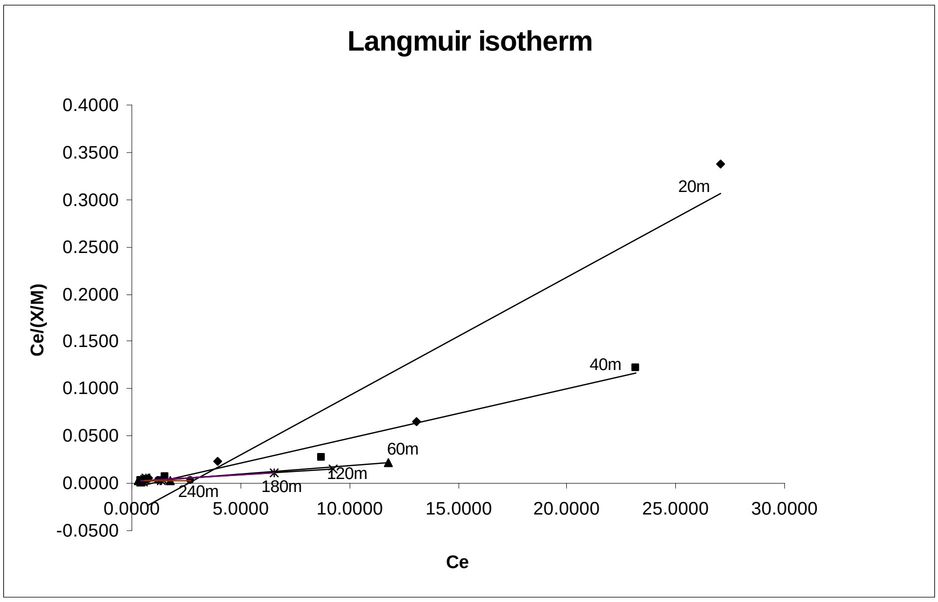


Figure 15 Langmuir adsorption isotherm calcination at 750ºC

Table 11 The calculation variables from Langmuir adsorption isotherm

Shaking time (minutes)	Langmuir isotherm			
	Equation	R^2	Adsorption maximum (X_m) (mg-P/Kg)	Binding energy (b)
20	Y=0.0126x - 0.0327	0.9124	79.36	-0.38
40	Y=0.0053x - 0.0048	0.9717	188.68	-1.10
60	Y=0.0018x + 0.0010	0.9965	555.55	1.80
120	Y=0.0014x + 0.0019	0.9530	714.28	0.74
180	Y=0.0013x + 0.0020	0.8532	769.23	0.65
240	Y=-0.0001x + 0.0034	0.0071	-10000.00	-0.03

To study Freundlich adsorption, log (x/m) versus log C_e was plotted on y-axis and x-axis, respectively, as stated in equation 12.

$$\log\left(\frac{C_o - C_e}{m}\right) = \log K + \frac{1}{n}\log C_e \quad \text{or} \quad \log\left(\frac{x}{m}\right) = \log K + \frac{1}{n}\log C_e$$

Freundlich adsorption isotherm for the calcined mordenite at 750ºC was shown in Figure 16, the data was plotted between log x/m and log C_e. Other calculation data was shown in Appendix H. The calculation variables from Freundlich adsorption isotherm, such as equation, correlation coefficient of determination (R^2), K represented the capacity measurement of the adsorbent, and n represented the value of adsorption efficiency (Faust, 1987), were shown in Table 12. By fitting Freundlich adsorption isotherm in Figure 16, R^2 from 60 minutes of shaking time was 0.6971 and R^2 from the average shaking time was 0.5040. After the data at calculation 750ºC were fitting by Freundlich isotherm, the capacity of the adsorbent was increased with the shaking time from 20 minutes to 240 minutes and the value of adsorption efficiency was found to decrease with the shaking time from 20 minutes to 240 minutes.

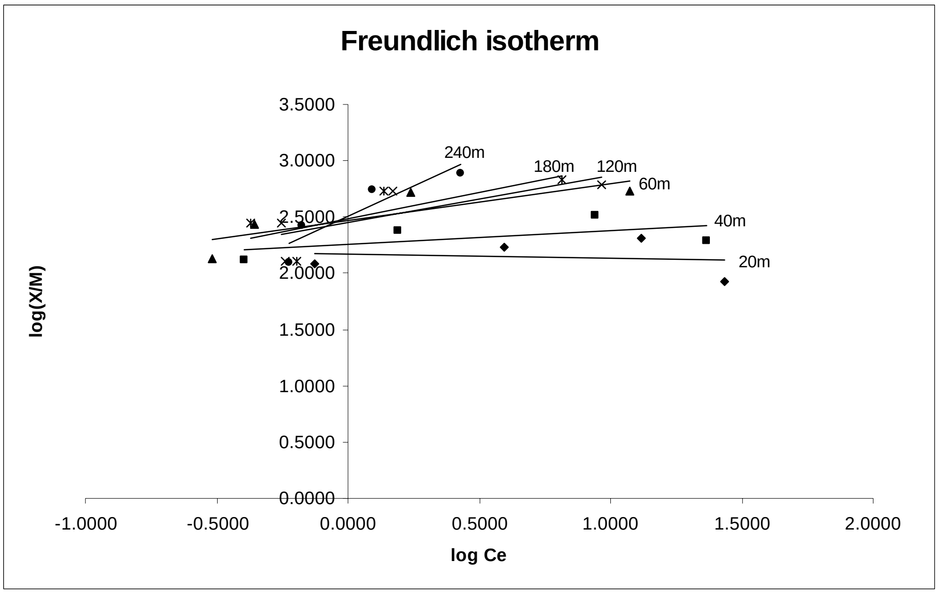


Figure 16 Freundlich adsorption isotherm calcination at 750ºC

Table 12 The calculation variables from Freundlich adsorption isotherm

Shaking time (minutes)	Freundlich isotherm			
	Equation	R^2	K	n
20	Y=-0.0376x + 2.1667	0.0229	146.79	-26.60
40	Y=0.1194x + 2.2599	0.3087	181.93	8.37
60	Y=0.3245x + 2.4671	0.6971	293.16	3.08
120	Y=0.4162x + 2.4504	0.5902	282.10	2.40
180	Y=0.4698x + 2.4833	0.5760	304.30	2.13
240	Y=1.0699x + 2.5047	0.8291	319.67	0.93

The Langmuir adsorption isotherm fitting approach linearity with R^2 of 0.9000 compared to the fitting on the Freundlich adsorption isotherm with R^2

of 0.5040. For these results, the orthophosphate adsorption behavior tended to follow Langmuir adsorption isotherm postulated a monolayer of orthophosphate on mordenite surface with chemisorption.

3.3 Desorption of adsorbed orthophosphate

The study of orthophosphate desorption from surface of mordenite at the selected calcination temperature of 750ºC was shown in Figure 17. The data was presented in Appendix I. In the experiment, the initial orthophosphate concentration was varied from 5-30 mg-P/L, and the desorbing time was varied from 2-6 hours due to the limitation on the shaking bath operation. At the initial orthophosphate concentration of 5 mg-P/L and desorption time of 6 hours, % desorption per 1g of mordenite was 1.48% in the first hour and decreased to 0.29 % per 1g of mordenite after 6 hours. At initial orthophosphate concentration of 10 mg-P/L, % desorption was 1.31% in the first hour and decreased to 1.14 % per 1g of mordenite after 5 hours. At initial orthophosphate concentration of 20 mg-P/L, % desorption was 1.53 % in the first hour and decreased to 0.49 % per 1g of mordenite after 3 hours. At initial orthophosphate concentration of 30 mg-P/L, % desorption was 0.39% in the first hour and 0.29 % per 1g of mordenite after 2 hours. The results showed that adsorbed orthophosphate was difficult to desorb from the surface of mordenite. It could be resulted from the chemisorption by a strong chemical bond between the orthophosphate molecule and the surface followed the assumption of Langmuir adsorption isotherm.

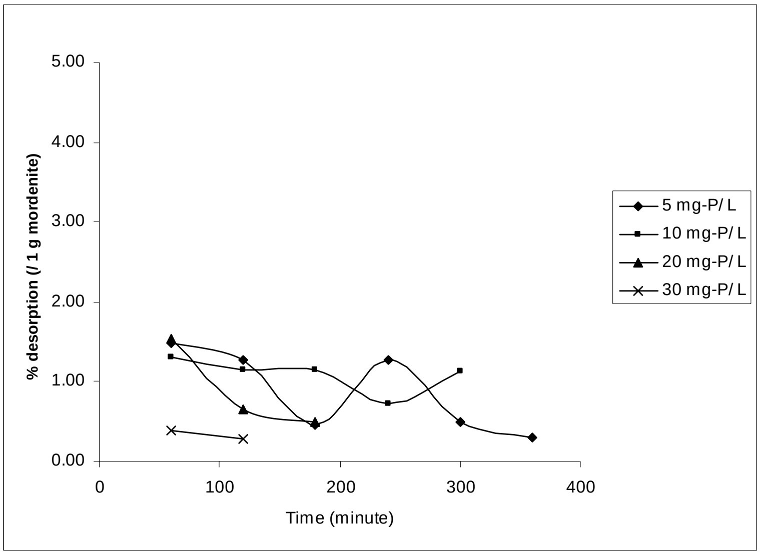


Figure 17 Desorption of orthophosphate after adsorbed on mordenite calcination at 750ºC

4. Analysis amount of metal dissolution

4.1 Metal dissolution in 0.05M EDTA

After suspending mordenite in 0.05M EDTA, the concentration of Fe^{2+} that dissolved from mordenite into 0.05M EDTA was analyzed by AAS. The results indicated that the dissolved Fe^{2+} concentration was 2.09 ppm per 1 g mordenite calcined at 750ºC. By using the EDTA-treated mordenite as an adsorbent in orthophosphate adsorption, the results shown in Appendix J indicated no orthophosphate adsorption on mordenite and it was possible for orthophosphate to leach out from mordenite.

4.2 Metal dissolution in 0.5M HCl

After suspending in 0.5M HCl, the concentration of Fe^{2+} was measured by AAS. The results indicated that the dissolved Fe^{2+} concentration was 2.22 ppm per 1 g mordenite calcined at 750ºC. By using the acid-treated mordenite as an adsorbent in orthophosphate adsorption, the results shown in Appendix J indicated no orthophosphate adsorption on mordenite and it was possible for orthophosphate to leach out from mordenite at the initial orthophosphate concentration of 5 and 30 mg-P/L. However, at the initial concentration of 10 and 20 mg-P/L, orthophosphate was adsorbed on the treated mordenite in the amount of 0.57 and 1.98 mg-P/L per 1 g mordenite. Moreover, to identify the presence of Ca^{2+}, the concentration of Ca^{2+} was also measured by AAS. The results shown in Table 13 indicated that dissolved Ca^{2+} concentration was 159.69 ppm per 1 g uncalcined mordenite. The dissolution Ca^{2+} concentration decreased to 113.54 ppm per 1 g mordenite when calcination temperature increased to 600ºC and increased to 125.29 ppm per 1 g mordenite when calcination temperature was increased to 900ºC.

4.3 Metal dissolution in deionized water

After suspending in deionized water, the concentration of Fe^{2+} and Ca^{2+} were measured by AAS. The results shown in Table 13 indicated that the dissolved Fe^{2+} concentration was approximately 0.12-0.30 ppm per 1g mordenite at all calcination temperatures and without calcination. The dissolved Ca^{2+} concentration was approximately 2.66-4.01 ppm per 1 g mordenite at the calcination temperature of 150-600ºC and one without calcination. The Ca^{2+} concentration increased to 7.84 and 12.97 ppm per 1 g mordenite at the calcination temperature at 750 and 900ºC, respectively.

4.4 Metal dissolution in 0.01M NaOH

After suspending in 0.01M NaOH, the concentration of Fe^{2+} and Ca^{2+} were measured by AAS. The results shown in Table 13 indicated that the dissolved Fe^{2+} concentration was approximately 2.53-3.64 ppm per 1 g mordenite at 150-300ºC and the uncalcined. It decreased to less than 0.20 ppm per 1 g mordenite for calcination temperature at 600-900ºC. The dissolved Ca^{2+} concentration was approximately 0.09-0.16 ppm per 1 g mordenite at uncalcined and all calcination temperature.

From the literature review, there was possibility that Fe^{2+} and Ca^{2+} ions influenced orthophosphate adsorption. In basic solution, Fe^{2+} ions could dissolve from the bulk of mordenite into solution more than Ca^{2+}, which the increase in amount of Fe^{2+} could enhance orthophosphate adsorbed on the surface by coordination adsorption. In acidic solution, Ca^{2+} ions could dissolve from the bulk more than Fe^{2+}, which Ca^{2+} could have orthophosphate adsorbed on the surface by electrostatic adsorption. Therefore, the amount of both metal ions in solution had an effect on orthophosphate adsorption on mordenite surface.

Table 13 Metals dissolution in various solutions condition

Calcination temperature (^{o}C)	Metals dissolution in various solutions condition					
	Acidic solution (pH=2)		Neutral solution (pH=6)		Basic solution (pH=12)	
	[Fe^{2+}] (mg/L)	[Ca^{2+}] (mg/L)	[Fe^{2+}] (mg/L)	[Ca^{2+}] (mg/L)	[Fe^{2+}] (mg/L)	[Ca^{2+}] (mg/L)
Uncalcined	0.24	159.69	0.13	3.82	3.64	0.12
150 ºC	0.19	161.11	0.21	3.72	3.58	0.12
300 ºC	0.23	150.88	0.18	4.02	2.53	0.16
450 ºC	0.22	134.13	0.16	3.98	0.67	0.10
600 ºC	0.36	113.54	0.17	2.66	0.11	0.09
750 ºC	0.21	136.75	0.30	7.84	0.19	0.10
900 ºC	0.58	125.29	0.16	12.97	0.18	0.15

5. Zeta potential

As a result of the orthophosphate adsorption experiment, the adsorption tended to increase when increasing the calcination temperature. To extract more information on the orthophosphate capability at different calcination temperature, the orthophosphate adsorption behavior at the surface of mordenite was observed by the zeta potential measurement. The zeta potential before and after the orthophosphate adsorption on the uncalcined and calcined mordenite was investigated. The suspension was measured its initial pH and zeta potential before adjusting the pH. From the initial pH in the neutral or slightly basic range, the suspension was firstly adjusted its pH to 12 by NaOH and gradually decreased its pH of 12 to 2 by HCl. The zeta potential was calculated from equation 21.

$$\zeta = \frac{4\pi\eta}{\varepsilon} \times U \times 300 \times 300 \times 1000 \qquad \text{(eq.21)}$$

Where ζ = zeta potential (mV)

η = viscosity of solution

ε = dielectric constant

$$U = \frac{\upsilon}{V/L}$$

v = speed of particle (cm/sec)

V = voltage (V)

L = the distance of electrode

The zeta potential was measured at each pH leading to the understanding on the adsorption behavior at the mordenite surface. And, to evaluate the proposed reaction at the surface, the equilibrium constant expressed in terms of activity, K^{0}, was considered.

$$\mathrm{H} + \mathrm{L} \rightleftharpoons \mathrm{HL} \qquad \text{(eq.22)}$$

$$K^{0} = \frac{(\mathrm{HL})}{(\mathrm{H})(\mathrm{L})}$$

The experiment was started on the uncalcined mordenite. After measuring the initial pH of 6.87 with the zeta potential of -15.14 as shown in Appendix K, the pH was adjusted to 12 by adding NaOH which caused the surface of mordenite to be deprotonated as shown in eq. 23 and the surface charge became more negatively charged.

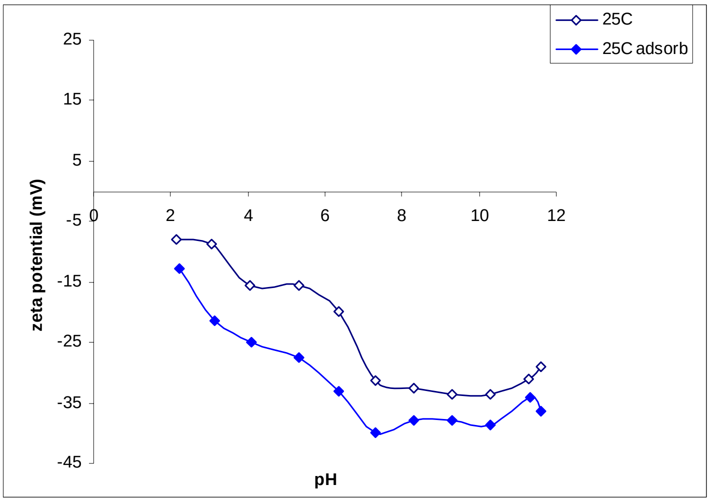
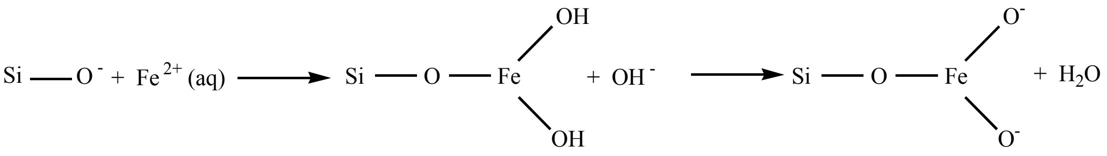


Figure 18 Zeta potential of uncalcined mordenite

$$\mathrm{Si{-}OH} + \mathrm{OH^-} \longrightarrow \mathrm{Si{-}O^-} + \mathrm{H_2O} \qquad \text{(eq.23)}$$

Then, iron ions in the form of Fe^{2+} and Fe^{3+}, which can be released from mordenite in basic solution as shown in the previous result of AAS, would play an important role. Since Fe^{3+} can be easily reduced to Fe^{2+} in the solution as shown in eq. 25, the iron ion referred in this work will be Fe^{2+}. As the pH of the solution became basic, Fe^{2+} attracted to the negative charge of the oxygen atom producing the ion complex at the surface. Due to the high concentration of OH^-, OH^- would deprotonate the complex and leave the complex with the negative charge to lower the zeta potential as shown in eq. 25.

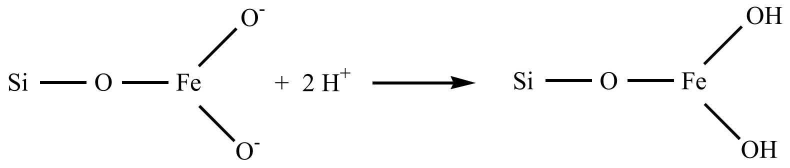
$$\mathrm{Fe^{3+}} + \mathrm{e^-} \rightleftharpoons \mathrm{Fe^{2+}} \qquad \log K^o = 13.04 \qquad \text{(eq.24)}$$



$$\mathrm{Si{-}O^-} + \mathrm{Fe^{2+}(aq)} \longrightarrow \mathrm{Si{-}O{-}Fe}\begin{smallmatrix}\mathrm{OH}\\ \mathrm{OH}\end{smallmatrix} + \mathrm{OH^-} \longrightarrow \mathrm{Si{-}O{-}Fe}\begin{smallmatrix}\mathrm{O^-}\\ \mathrm{O^-}\end{smallmatrix} + \mathrm{H_2O}$$

(eq.25)

To observe the changes at the surface, the solution pH would be changed from basic to acidic. From pH of 12, HCl was added in solution, the surface of mordenite was gradually protonated as showed in eq. 26

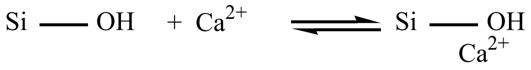


(eq.26)

Along with the decreasing of pH, $Fe(OH)_2$ was dissociated from surface as shown in eq.27.

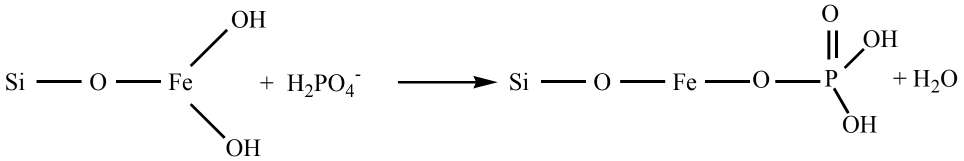
$$Si - O - Fe(OH)_2 + 2H^+ \rightleftharpoons Fe^{2+} + 2H_2O + Si - OH \qquad \text{(eq.27)}$$

From the information on metal dissolution in HCl, the high amount of Ca^{2+} was released from mordenite into the acidic solution. Ca^{2+} would be closely around OH groups of Si atom at surface by electrostatic adsorption as shown in eq.28. From the influence of Si-OH and Si-OH (Ca^{2+}) at surface, the zeta potential became higher positive with decreasing pH.



$$Si - OH + Ca^{2+} \rightleftharpoons Si - \underset{Ca^{2+}}{OH} \qquad \text{(eq.28)}$$

After orthophosphate adsorption, zeta potential at the initial pH of 5.49 was -13.5. When the pH was increased to 12, the behavior was followed eq.26 and orthophosphate ion was adsorbed by the coordinated adsorption of Fe^{2+} on the surface as shown in eq.29. For this reason, the zeta potential after adsorption was higher negatively charged than the one before adsorption.



$$\mathrm{Si{-}O{-}Fe(OH)_2} + \mathrm{H_2PO_4^-} \longrightarrow \mathrm{Si{-}O{-}Fe{-}O{-}P(=O)(OH)_2} + \mathrm{H_2O}$$

(eq.29)

When pH gradually decreased to acidic, the negative charge was lower. An important cause was from the Ca^{2+}ion that covered around the OH group of Si as shown previously in eq.28 leading to the orthophosphate to adsorb on Si-OH(Ca^{2+}) by electrostatic adsorption as shown in eq.30.

$$\underset{\mathrm{Ca^{2+}}}{\mathrm{Si{-}OH}} + \mathrm{H_2PO_4^-} \longrightarrow \underset{\mathrm{Ca^{2+}\ H_2PO_4^-}}{\mathrm{Si{-}OH}} \ .$$

(eq.30)

Because of the reaction in eq.29 and 30, the zeta potential was higher negatively charged than the one before adsorption and the negativity decreased when decreasing pH.

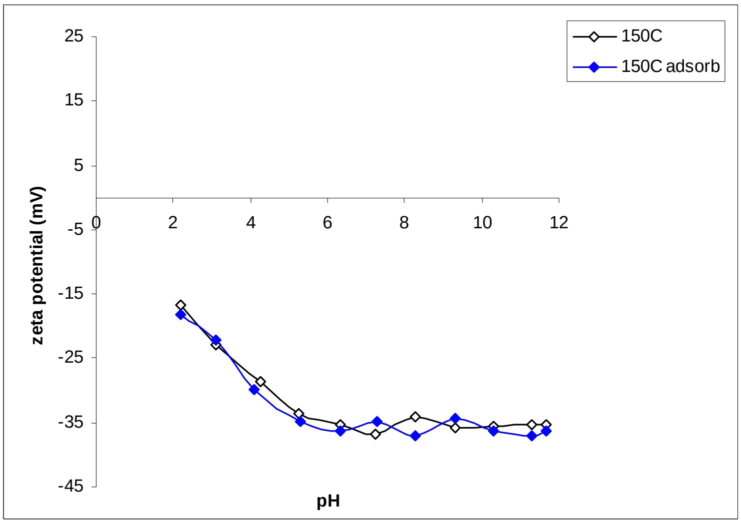


Figure 19 Zeta potential of mordenite calcined at 150ºC

For the calcined mordenite at 150ºC, the zeta potential before orthophosphate adsorption as shown in Figure 19 was quite similar to the zeta potential of the uncalcined mordenite. The behavior was followed eq.23, 24, 25, 26, 27, and 28. After orthophosphate adsorption, the zeta potential was not different which can be implied that orthophosphate was not coordinately bound to the surface. The zeta potential of both before and after orthophosphate adsorption was the same.

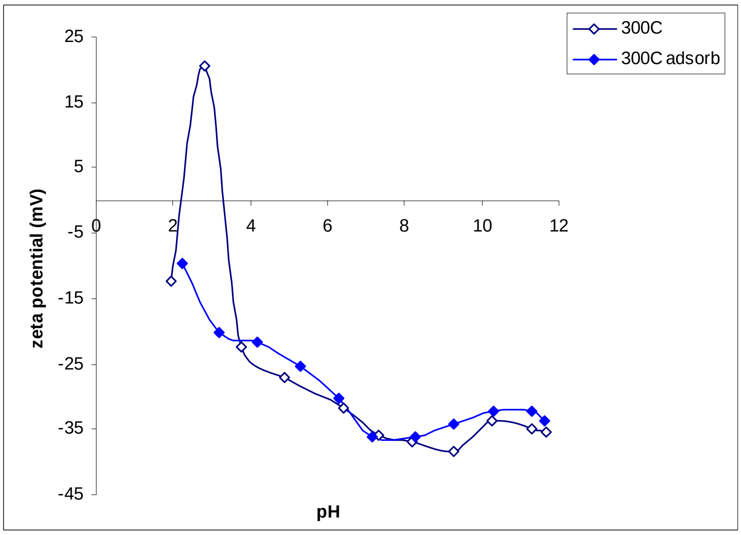


Figure 20 Zeta potential of mordenite calcined at 300ºC

For the calcined mordenite at 300ºC, the zeta potential before orthophosphate adsorption as shown in Figure 20 was quite similar to the zeta potential of the uncalcined mordenite until pH of 4. The behavior at the surface was still followed the eq.23, 24, 25, 26, 27, and 28. After that, the zeta potential was rapidly increased to zero at pH of 3.4 which equaled to the isoelectric point (IEP) of silica. It was point of zero net charge (PZNC). From Table 6, PZNC would be equal to zero when the effective surface charge equals the inner-sphere complex charge and the outer-sphere complex charge. It meant that at this point, the charge of all complexes cancelled out giving the net charge of zero. All Si atoms at the surface were protonated to be Si-OH. Then, when HCl was continued adding to the solution, H^+ would attract OH groups of Si at surface as shown in eq.31.

$$\mathrm{Si} - \mathrm{OH} + \mathrm{H}^{+} \longrightarrow \mathrm{Si} - {}^{+}\mathrm{OH}_2 \qquad \text{(eq.31)}$$

As long as the number of H^+ attracting the OH groups increased, the zeta potential was increased. When the OH groups were fully protonated, the zeta potential reached the maximum. Then, the counter ions of Cl^-, which are fully dispersed in solution, would come close to Si-$^+OH_2$ as shown in eq.32, have electrostatic anion adsorption, and decrease the zeta potential.

$$\mathrm{Si} - {}^{+}\mathrm{OH}_2 + \mathrm{Cl}^{-} \longrightarrow \mathrm{Si} - \overset{\mathrm{Cl}^{-}}{{}^{+}\mathrm{OH}_2} \qquad \text{(eq.32)}$$

At pH 3.4, the zeta potential became zero. This pH equaled PZNC and corresponded to IEP of silica. It was implied that there were a lot of silica at the surface of the calcined mordenite at 300°C.

After orthophosphate adsorption, the zeta potential was quite similar to the zeta potential of the uncalcined mordenite. At pH 4-12, the zeta potential was not more or less different from the one before adsorption. It could be implied that orthophosphate was not coordinately bound to the surface after adsorption.

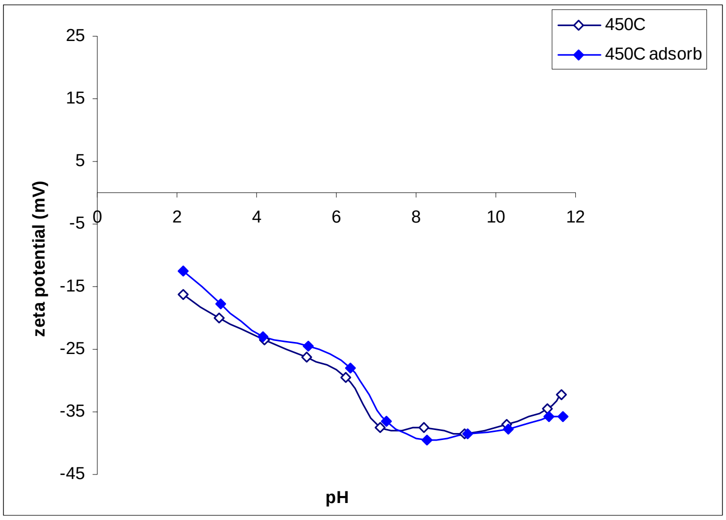


Figure 21 Zeta potential of mordenite calcined at 450ºC

For the calcined mordenite at 450ºC, the zeta potential before orthophosphate adsorption as shown in Figure 21 was quite similar to the zeta potential of the uncalcined mordenite and the calcined one at 150ºC. The behavior was followed eq.23, 24, 25, 26, 27, and 28. After orthophosphate adsorption, the zeta potential was not different which can be implied that orthophosphate was not coordinately bound to the surface. The zeta potential of both before and after orthophosphate adsorption was the same.

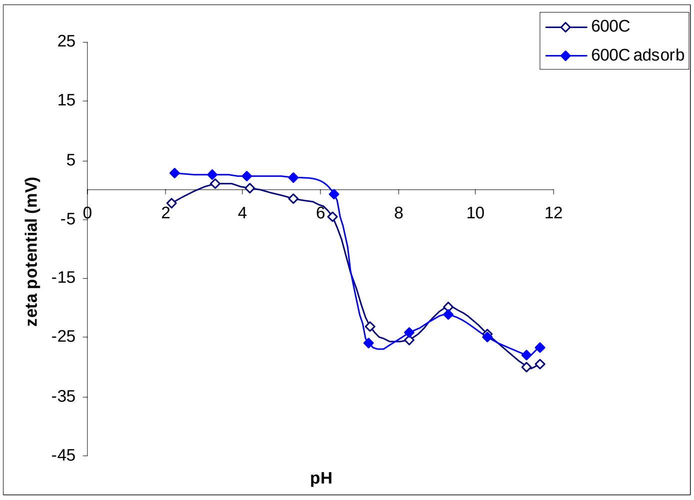


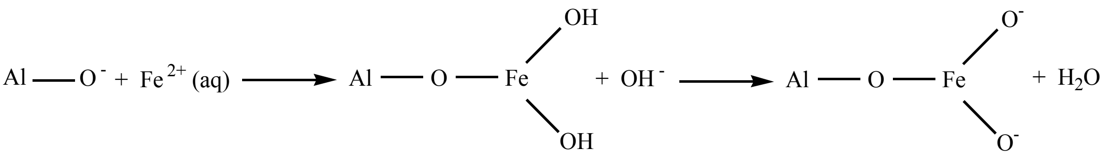
Figure 22 Zeta potential of mordenite calcined at 600ºC

For the calcined mordenite at 600ºC, the zeta potential before orthophosphate adsorption as shown in Figure 22 performed the fluctuation of surface charge when pH of the solution decreased from pH 12 to 8. After pH of 8, the zeta potential was rapidly increased to approach zero charge, which corresponded to PZNC. The zeta potential showed that at this calcination temperature, the surface of the particle tended to change its character. By looking at the zero charge pH of 4.2, it seemed that the increase of the zero charge pH was arised from the migration of Al to the surface. It could be said that PNZC was dependent on the surface composition and it's IEP (IEP_{Si} = 2-3 and IEP_{Al} = 9 (Sposito, 1989)) at the point when PZC was equaled to PNZC. When the zero charge pH was increased from 3.4 to 4.2, at the calcination temperature of 300 and 600ºC, respectively, the surface composition was changed from fully Si to Si with slightly Al. The behavior at the surface was followed eq.23, 25, and 26. In addition, Al would have the same behavior as Si as shown in the following equations.

In the basic solution, Al on the surface of mordenite was deprotonated as shown in eq.33.

$$\mathrm{Al - OH + OH^- \longrightarrow Al - O^- + H_2O} \qquad \text{(eq.33)}$$

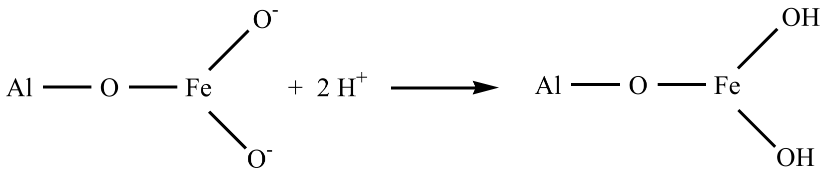
And, along with the deprotonation, the released Fe^{2+} ions could attract to the negative charge of oxygen as shown in eq.34.



$$\mathrm{Al - O^- + Fe^{2+}(aq) \longrightarrow Al - O - Fe(OH)(OH) + OH^- \longrightarrow Al - O - Fe(O^-)(O^-) + H_2O}$$

(eq.34)

When HCl was added to solution in order to decrease the pH solution, the surface of mordenite became protonated as shown in eq.35 and 36.



(eq.35)

$$\mathrm{Al - O^{-} + H^{+} \rightleftharpoons Al - OH}$$

(eq.36)

At the decreased pH, iron oxides could dissociate from surface as shown in eq.37.

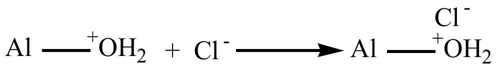
$$\mathrm{Al - O - Fe\,(OH)_2 + 2\,H^{+} \rightleftharpoons Fe^{2+} + 2\,H_2O + Al - OH}$$

(eq.37)

In the acidic solution, ion H^+ would attract OH groups of Al leading the counter ions Cl^- to come close to Al-$^+OH_2$ and decrease the zeta potential as shown in eq.38 and 39. Besides, the released Ca^{2+} from the mordenite surface could attract the OH group of Al by electrostatic adsorption as shown in eq.40.

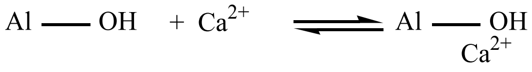
$$\mathrm{Al - OH + H^{+} \longrightarrow Al - {}^{+}OH_2}$$

(eq.38)



$$\mathrm{Al - {}^{+}OH_2 + Cl^{-} \longrightarrow Al - \overset{Cl^{-}}{{}^{+}OH_2}}$$

(eq.39)



$$\mathrm{Al - OH + Ca^{2+} \rightleftharpoons Al - \underset{Ca^{2+}}{OH}}$$

(eq.40)

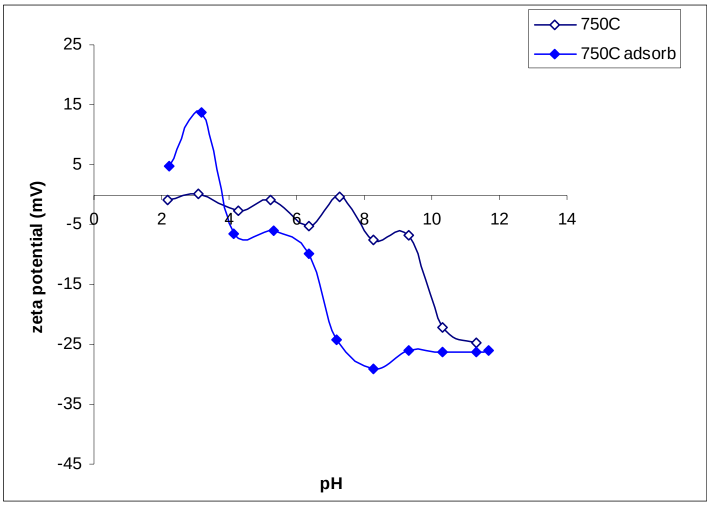
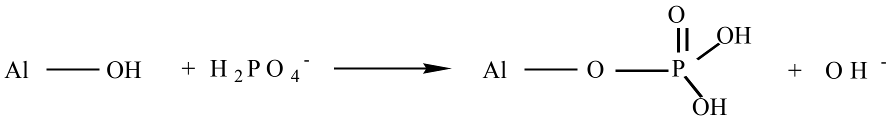


Figure 23 Zeta potential of mordenite calcined at 750ºC

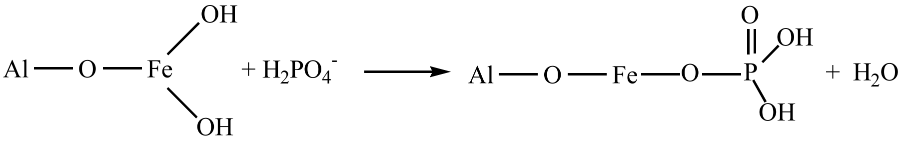
For the calcined mordenite at 750ºC, the zeta potential before orthophosphate adsorption as shown in Figure 23 was approaching zero charge at the pH of 7.2 indicating that the increasing number of Al migrated to the surface of mordenite. After that the zeta potential became fluctuated and approached zero charge again at pH of 5.2 and 3.0 which could be resulted from the competed reaction on the surface between eq.28 and 39.

After orthophosphate adsorption in the basic solution, the zeta potential became more negative than the one before adsorption. It could be resulted from the increase in amount of Al in the surface composition. At the surface, beside the orthophosphate adsorption on Si by following eq. 29, Al also had a high capability to coordinately bind to orthophosphate as shown in eq.41 and 42. This resulted in the high negativity in zeta potential in pH 6-12.



$$Al - OH + H_2PO_4^- \longrightarrow Al - O - P(=O)(OH)_2 + OH^-$$

(eq.41)



(eq.42)

As the pH continued to decrease, the protonation proceeded. At the pH of 3.8, the zeta potential charge became more positive due to the increase in number of Si-$^{+}OH_2$ and Al-$^{+}OH_2$ presented at the surface until it reached the maximum. The positive charge at O would lead the counter ions of Cl^-, which are fully dispersed in system, to come close to Si-$^{+}OH_2$ and Al-$^{+}OH_2$ and decrease the zeta potential as shown in eq.32 and 39.

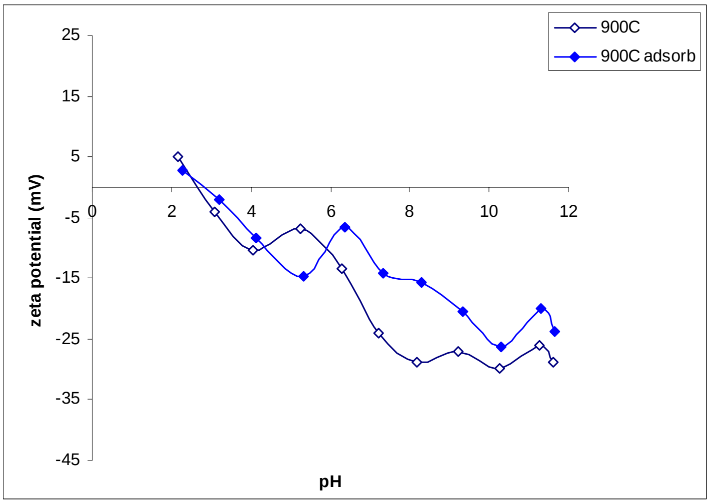
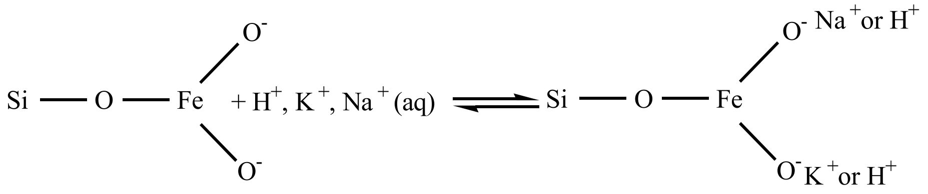


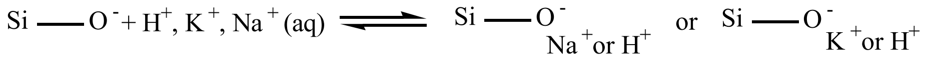
Figure 24 Zeta potential of mordenite calcined at 900°C

From XRD pattern as shown in Figure 12, it was shown that the structure of the calcined mordenite at 900°C was transformed into the aluminum silicate (Al_2SiO_5) of Kyanite and silicon oxide (SiO_2). The zeta potential before orthophosphate adsorption as shown in Figure 24 tended to become less negative as decreasing pH of the solution. The behavior on the surface was followed the reaction of SiO^- and AlO^- as shown in eq.25-28, 31, and 34-38. At the pH of 2.6, the zeta potential became zero which corresponded to the IEP of silica. This indicated that the main surface composition was Si.

After orthophosphate adsorption, the zeta potential was less negative at the pH 6.3-12. It could be implied that as the pH was decreased, there were other cations, such as K^+ and Na^+, attracted to the O^- at the surface. K^+ and Na^+ would compete with H^+ and electrostatically bind to O^- as shown in eq.43-44.



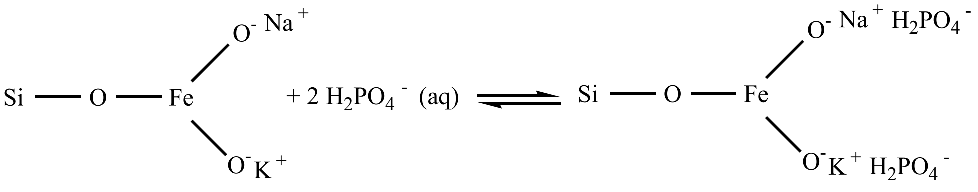
(eq.43)



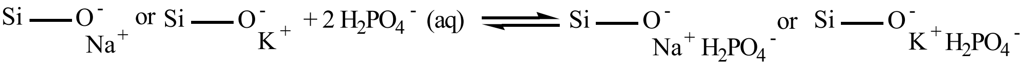
$$\mathrm{Si{-}O^- + H^+, K^+, Na^+\,(aq) \rightleftharpoons Si{-}\underset{Na^+ or\ H^+}{O^-}\quad or\quad Si{-}\underset{K^+ or\ H^+}{O^-}}$$

(eq.44)

Due to Na^+ and K^+ having larger size than H^+, the $H_2PO_4^-$ adsorption would be in a distance from O^- as shown in eq.45-46. $H_2PO_4^-$ would be around Na^+ and K^+ and away in the diffuse layer. Because the zeta potential was measured the surface potential at the surface of shear, the effect of the negative charge on $H_2PO_4^-$ on the zeta potential would be less, whereas the effect charge on Na^+ and K^+ increased. This would result in less negativity in the zeta potential.



(eq.45)



$$\mathrm{Si{-}O^{-}\,Na^{+}\ or\ Si{-}O^{-}\,K^{+} + 2\,H_2PO_4^{-}\,(aq) \rightleftharpoons Si{-}O^{-}\,Na^{+}\,H_2PO_4^{-}\ or\ Si{-}O^{-}\,K^{+}\,H_2PO_4^{-}} \quad \text{(eq.46)}$$

To understand the adsorption capability on mordenite at different calcination temperatures, the information on zeta potential was evaluated and compared to the results from the adsorption experiments. The zeta potential study was not able to explain the orthophosphate adsorption behavior at the calcination temperature of 150ºC. From the adsorption experiment, calcined mordenite at 150ºC could adsorb orthophosphate in the amount of 1-3 mg-P/L but there was not clearly different in zeta potential values of before and after orthophosphate adsorption. At the calcination temperatures of 450ºC and 600ºC, the results from adsorption experiment showed a small orthophosphate adsorption of less than 1 mg-P/L which agreed with the zeta potential values of before and after orthophosphate adsorption. Moreover, the small orthophosphate adsorption at 450ºC could be affected by the considerably small pore volume shown in Table 8. At the calcination temperature of 750ºC and the uncalcined, the information from zeta potential could explain the adsorption behavior which was fully agreeable to the adsorption experiment. The information from zeta potential was proposed in order to explain the adsorption behavior at the calcination temperature of 900ºC which was disagreeable to the adsorption experiment because the surface was adsorbed with cations such as Na^+ and K^+.

However, pH of the orthophosphate adsorption experiment was in the range of pH 6-11. Thus, the information retrieved from zeta potential measurement could explain the orthophosphate adsorption behavior in the range of pH 6-11. The adsorption was in the range of chemisorption.