

CHAPTER 4



RESULT AND DISCUSSION

The chapter concentrates on the result and discussion obtained from study. Not only, there is a study on the effect of various factors on the performance of the adsorption, but the properties of adsorbents are also described. The results and discussions of all adsorbents were divided into two groups. The first was chitin and chitosan prepared in the laboratory. The second was chitosan purchased from Sea Fresh Co., Ltd. The result of adsorption cutting fluid of all adsorbents is presented as follows:

4.1. Preliminary experimental

4.1.1. Effect of motor stirrer speed

In this section, relationship between speed of motor stirrer and adsorption capacity was considered, as shown in Figure 4.1 and 4.2. Adsorption capacity of cutting fluids on either chitosan beads or blended chitosan/PVA increases when speed of stirrer used in mixing process increases from 600 rpm to 21000 rpm (Reynolds number vary in range 1.2×10^6 to 42.1×10^6 , the calculated show in Appendix I). Still increasing in the speed, the capacity does not change. The size of oil droplets in the emulsion is reduced from 0.02 to 0.005 mm when the speed increases from 1200 rpm to 21000 rpm.

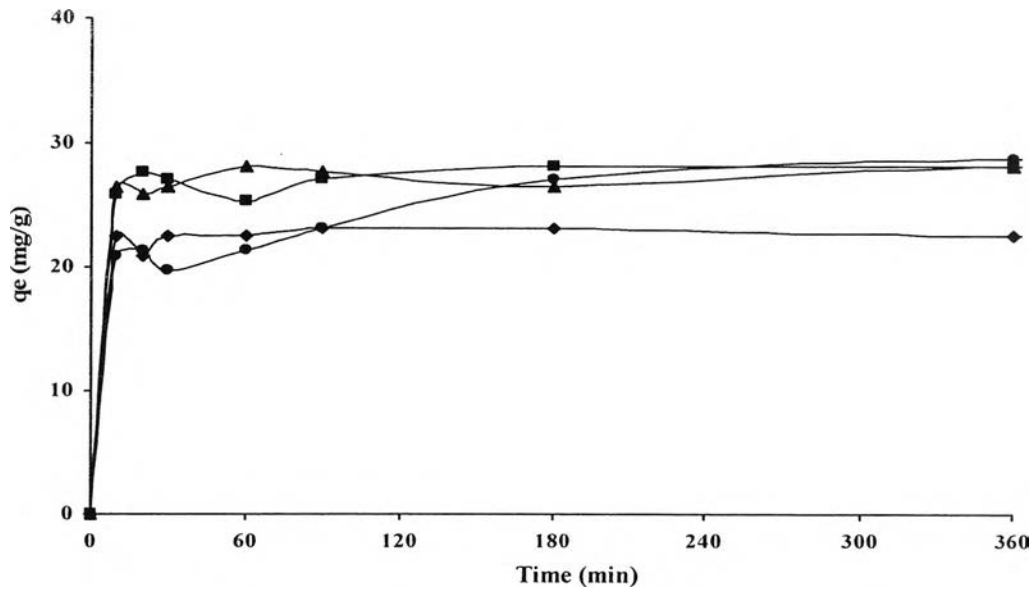


Figure 4.1 Adsorption capacity of cutting fluids on 2 g chitosan prepared in this work as a function of stirrer speed when the initial concentration of cutting fluids is at 0.1 % w/v and pH 3 ◆ 600 rpm, ■ 1200 rpm, ▲ 2000 rpm and ● 21000 rpm

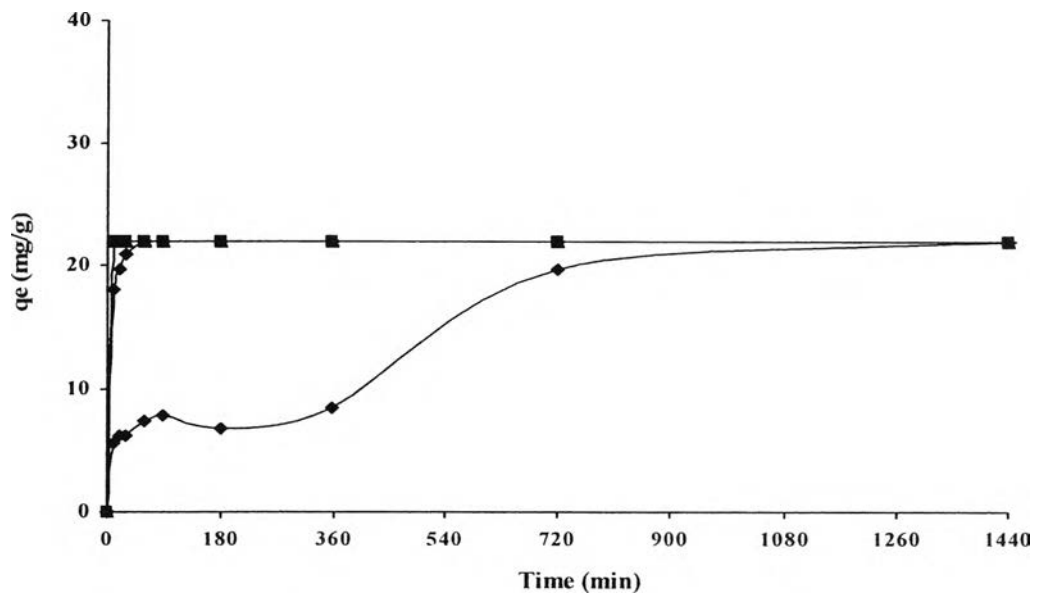


Figure 4.2 Adsorption capacity of cutting fluids on 2 g blended chitosan/PVA as a function of stirrer speed when initial cutting fluids concentration at 0.1 % w/v and pH 3 of ◆ 600 rpm, ■ 1200 rpm, ▲ 2000 rpm and ● 21000 rpm

The smaller the size of oil droplets, the higher the speed is required, as shown in Figure 4.3. Therefore, the droplet disperses very well in the emulsion and then leads to transformation to the adsorbents. From the above, cutting fluids will be prepared using speed of stirrer at 1200 rpm for 10 min.

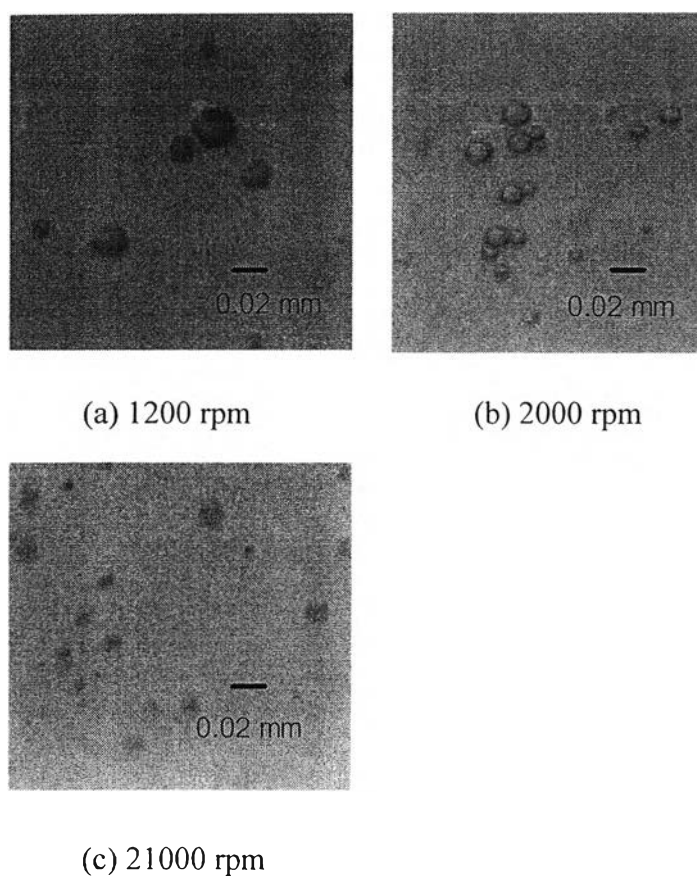


Figure 4.3 Optical micrograph of cutting fluid emulsion dispersion in water:

(a) 1200 rpm; (b) 2000 rpm and (c) 21000 rpm

4.1.2. Source of chitosan

Appearance of chitin extracted from a black tiger shrimp was faded orange flakes. The flakes were insoluble in a diluted acid, base and deionized water. From the experiments, it was found that 237.35 g of chitin was extracted from 864.10 g of dried black tiger shrimp shell.

Appearance of chitosan was faded yellow flakes, glossy and insoluble in deionized water and diluted base. Chitosan is dissolved by acid. It was found that 168.25 g of chitosan was extracted from 202.46 g of chitin flakes. This chitosan flakes was formed into beads. Adsorption on chitosan prepared in this work and on chitosan purchased from Sea Fresh Co., Ltd., was compared. It was found that adsorption capacity of cutting fluids on both chitosans is not much different, as shown in Figure 4.4.

Considering adsorption capacity of cutting fluids on chitosan prepared in the laboratory and chitosan purchased from Sea Fresh Co., Ltd., under the condition of 1.00 % w/v cutting fluids concentration and pH 3. The chitosan from both sources had the same degree of deacetylation (% DD > 90%). They also had the same functional group in structure shown in Figure 4.5. But chitosan purchased from Sea Fresh Co., Ltd., would be used in batch and continuous experimental modes since this chitosan discharged less waste in laboratory.

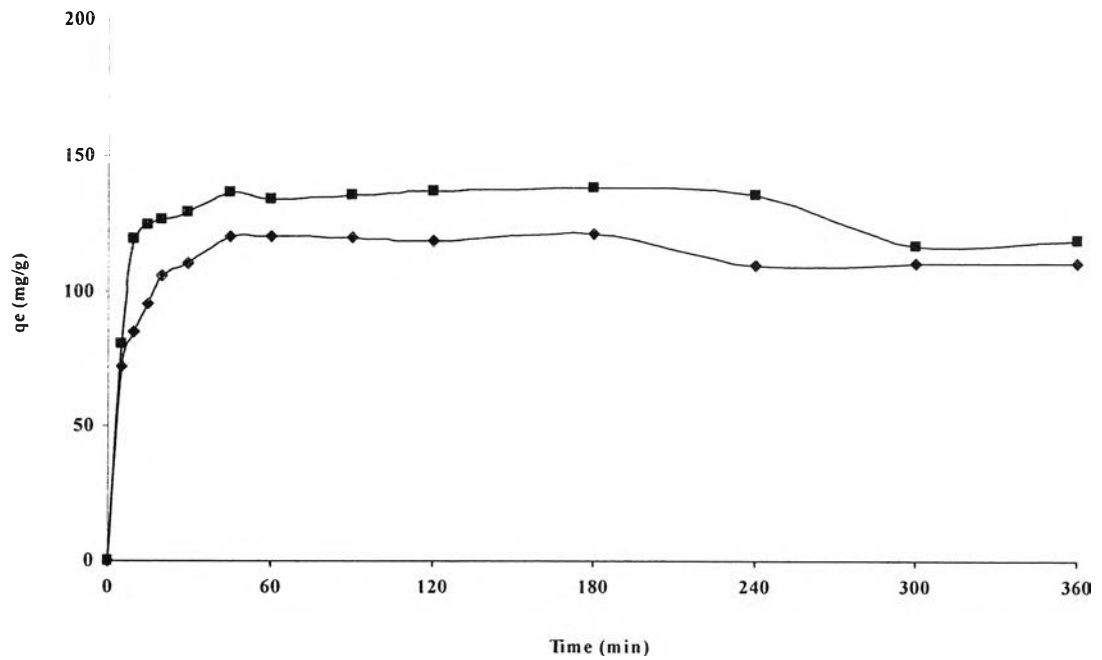


Figure 4.4 Comparing adsorption capacity on 2 g initial cutting fluids at 1.00 % w/v and pH 3 of \blacklozenge chitosan from black tiger shrimp \blacksquare chitosan from Sea Fresh Co. Ltd.

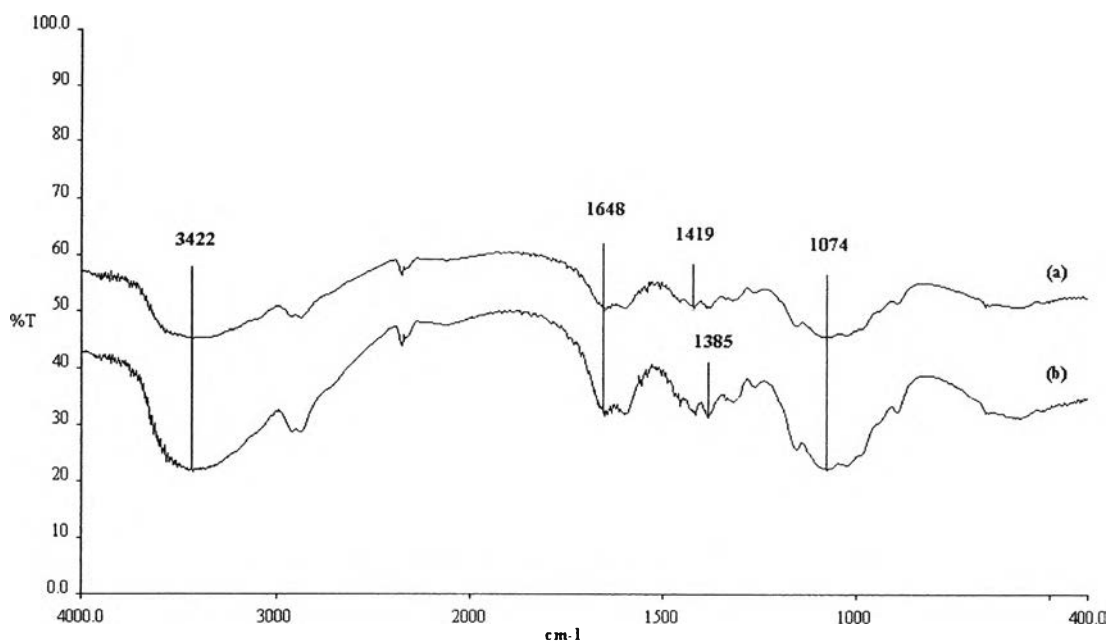


Figure 4.5 FT-IR spectra of chitosans (a) from black tiger shrimp (b) from Sea Fresh Co., Ltd.,

4.1.3. Concentration of chitosan solution

Effect of concentration of chitosan solution on adsorption capacity was shown in Figure 4.6. Increasing chitosan concentration from 1.2 % w/v to 2.0 % w/v, the capacity increases from 90 to 135 mg/g when using 2 g chitosan beads and 1.0 % w/v initial concentration of cutting fluids at pH 3. Further increasing the chitosan solution concentration to 2.2 % w/v to the beads, it was found that the capacity drops significantly. This is due to viscosity of the solution. The viscosity increases with the solution concentration the great the viscosity of the solution, the dense beads are obtains. The viscosity of chitosan solution change in the range 486.1 to 380.3×10^3 cP for chitosan solution 1.2% to 2.2 % w/v, respectively. Therefore, the chitosan solution concentration at 2.0 % w/v was chosen to prepare the beads for further studies.

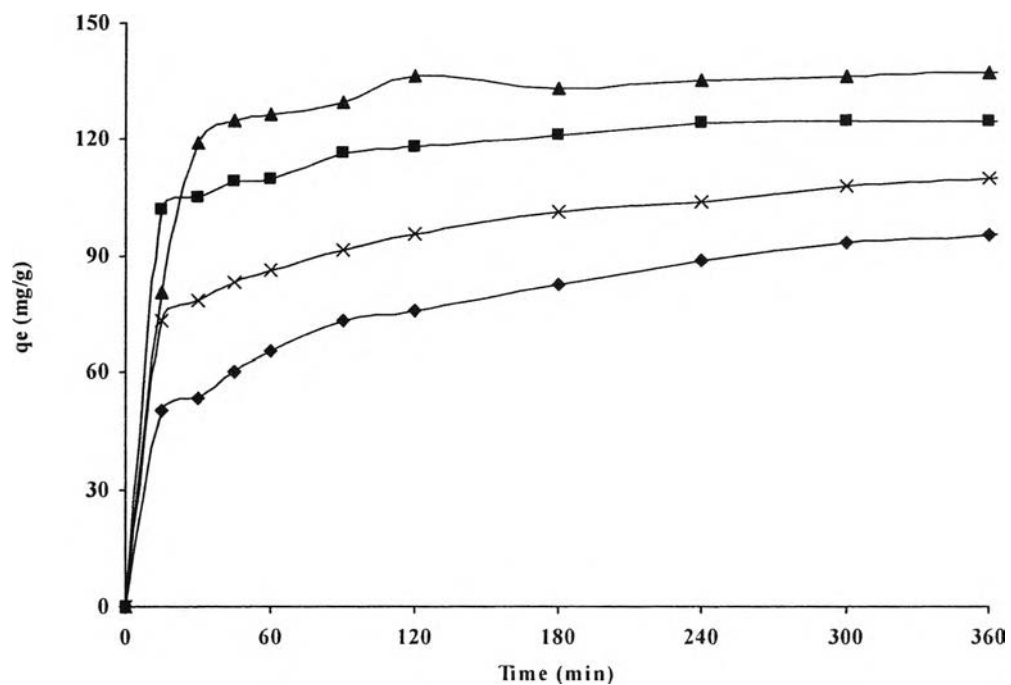


Figure 4.6 Adsorption capacity of cutting fluids by variation chitosan solution

concentration at cutting fluids concentrations of 1.00 % w/v and pH 3 of concentration of chitosan solution ◆ 1.20 % w/v, ■ 1.70 % w/v, ▲ 2.00 % w/v and × 2.20 % w/v

4.1.4. Ratio of chitosan to polyvinyl alcohol

Cutting fluids adsorption capacity as a function of chitosan polyvinyl alcohol ratio was studied, as shown in Figure 4.7. Capacity was decreased when the fraction ratio of chitosan to polyvinyl alcohol increased from 1:1 to 1:2. Hydroxyl groups in the structure of polyvinyl alcohol form hydrogen bonding with hydroxyl groups in the chitosan. Therefore less hydrophilic property was obtained as addition of polyvinyl alcohol. Excess polyvinyl bonds with amino groups in chitosan [32] consequently lead to less capacity. In addition, contact angle of blended chitosan/PVA 1:1 (19.78°) is less than that of chitosan (25°) and blended chitosan/PVA 1:2 (25°) where the amplitude of contact angle is presented in parenthesis. From above, blended chitosan/PVA 1:1 was chosen to study in the next section.

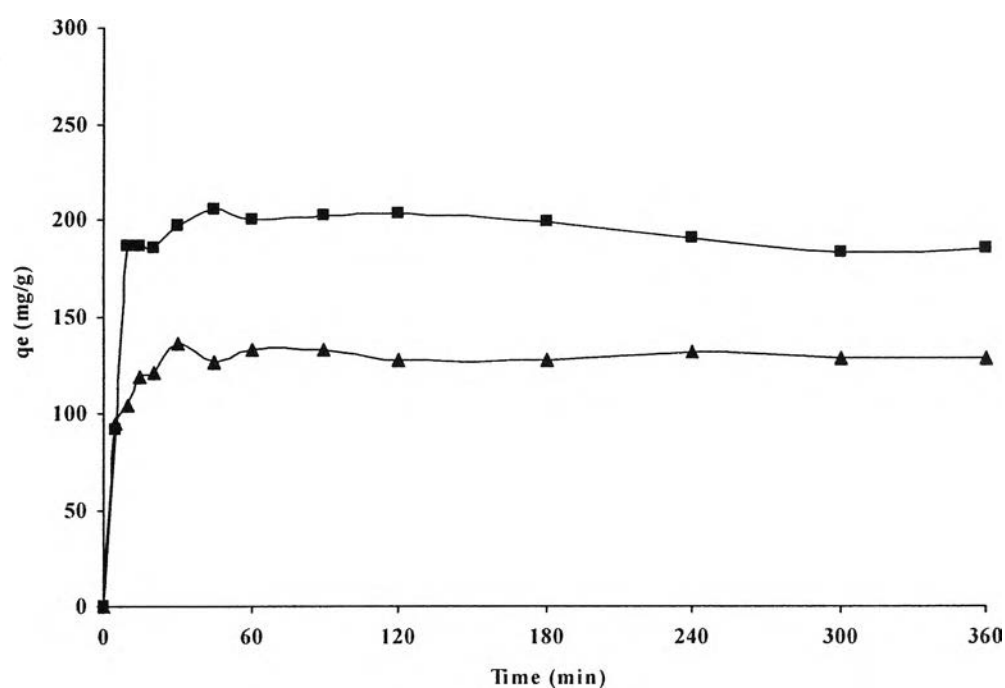


Figure 4.7 Adsorption capacity of cutting fluids on ■ blended chitosan/PVA 1:1, ▲ blended chitosan/PVA 1:2 when the initial cutting fluids is 1.0 % w/v at pH 3

4.1.5. Crosslink with glutaraldehyde

Owing to the limitation of application of chitosan and blended chitosan/PVA in acidic condition, crosslinking is then introduced to eliminate this limit. The chitosan which crosslinked with glutaraldehyde is very stable even in either acidic or basic solution [33, 34]. Therefore, crosslinking with glutaraldehyde is introduced to blended chitosan/PVA 1:1. Figure 4.8 shows the effect of crosslinking with glutaraldehyde on adsorption capacity. The adsorption capacity decreases with increasing percentage of glutaraldehyde. This is due to bonding between glutaraldehyde and amino groups in chitosan. Therefore, there is not enough adsorbed site on the adsorbent. Comparison effect of crosslinking on adsorption capacity when using different adsorbents is shown in Figure 4.9. Crosslinking with glutaraldehyde does not encourage an adsorption because of leaking of adsorbed sites. Therefore, crosslinking chitosan with glutaraldehyde and crosslink blended chitosan/PVA 1:1 are not chosen to investigate in the further studies.

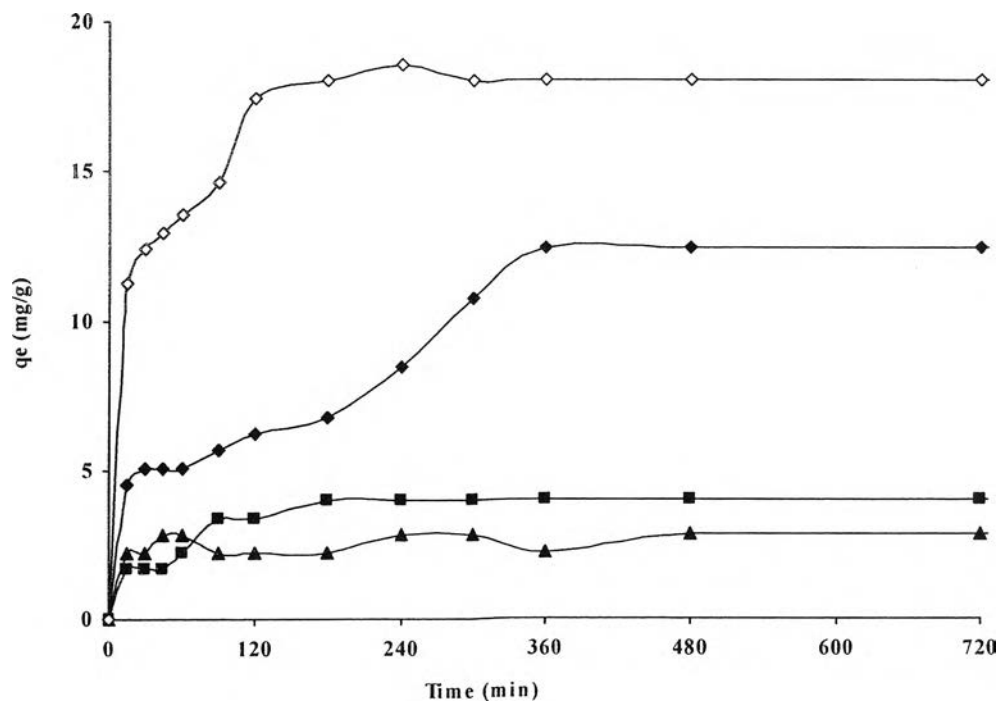


Figure 4.8 Adsorption capacity of 0.1 % w/v cutting fluids and pH 3 on chitosan which crosslink with GLA \diamond 0.1 %, \blacksquare 1.5 %, \blacktriangle 2.5 % and \diamond chitosan

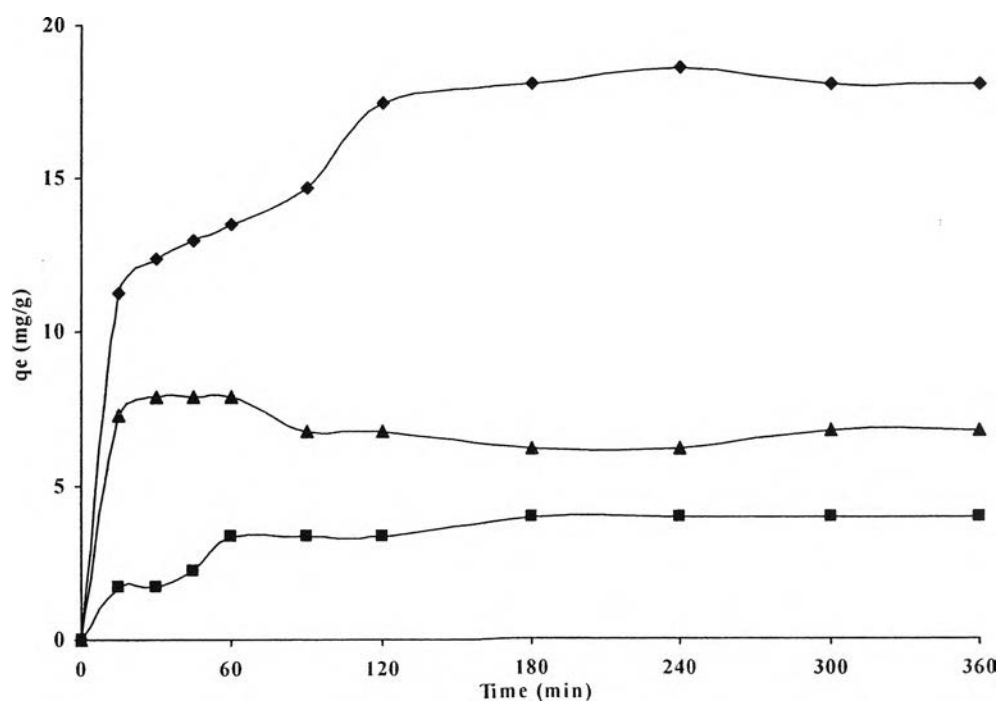


Figure 4.9 Adsorption capacity of 0.1 % cutting fluids at pH 3 on \diamond chitosan, \blacksquare crosslinking chitosan with GLA and \blacktriangle blended crosslink chitosan/PVA with 1.5 % w/v GLA

From preliminary adsorption of cutting fluids, it suggests that chitosan and blended chitosan/PVA 1:1 are a new adsorbent for adsorbing cutting fluids from wastewater of machinery process. Thus, modification of chitosan is needed to increase adsorption capacity.

4.2. Batch mode

In this section, effects of parameters on adsorption capacity are investigated. The chosen parameters are initial cutting fluids concentration, pH condition, salt and type of adsorbent. Type of adsorbents used in this section were chitosan (CH), blended chitosan/PVA 1:1 (CH/PVA), benzoyl chitosan (BCH), quateraminated chitosan (QCH), chitosan-sodium lauryl sulfate (CH-SDS), chitosan-hexadecyltrimethyl ammonium bromide (CH-C-Tab), chitosan- polyoxyethylene sorbitanmonooleate (CH-Tween 80), blended chitosan/PVA-sodium lauryl sulfate (BCH-SDS), blended chitosan/PVA-hexadecyltrimethyl ammonium bromide (BCH-C-Tab) and blended chitosan/PVA-polyoxyethylene sorbitanmonooleate (BCH-Tween 80).

4.2.1. Initial cutting fluids concentration

Effect of initial cutting fluids concentration on adsorption capacity is shown in Figure 4.10. When initial concentration increases from 0.1 % w/v to 1.00 % w/v, the capacity of all adsorbents increases. When increasing initial cutting fluids concentrations from 0.1 to 1.0 % w/v, the cutting fluids gradient between bulk phase and surface of adsorbents enhances cutting fluids diffusion to the adsorbed site. Furthermore adsorption capacity of Chitosan, blended chitosan/PVA 1:1, benzoyl chitosan and quateraminated chitosan were less significant when compared with the adsorption capacities of other adsorbents. This is due to all adsorbent sites are occupied and there is not enough sites to adsorb more cutting fluids. Comparison

adsorption capacity on adsorbents, it was found that CH-SDS and BCH-SDS showed higher adsorption capacity. Sodium lauryl sulphate interacted with amino groups of chitosan to render more hydrophobic. The CH-SDS and BCH-SDS interact with cutting fluids through hydrophobic interaction. This indicated that the substituted methylene groups in CH-SDS and BCH-SDS (see FT-IR section) on amino groups of chitosan has higher binding affinity for the adsorption of cutting fluids.

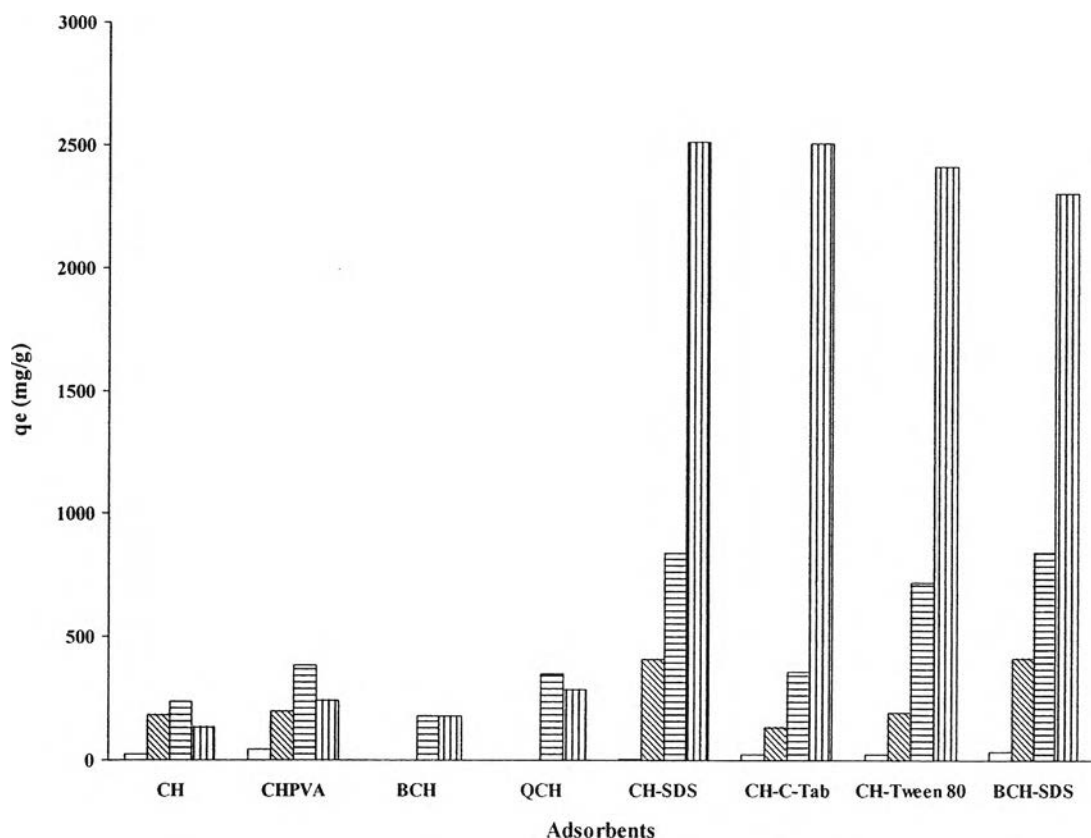


Figure 4.10 Adsorption capacity of adsorbents at pH 3 with initial concentration of cutting fluids as \square 0.1 %, $\backslash\backslash\backslash$ 0.5 %, \equiv 1.0 % and $\parallel\parallel$ 3.0 % w/v

Application of adsorption to cutting fluids effluent from turning processes were done. The characteristic of the effluent is shown in Table 4.1. The adsorption capacity is presented in Table 4.2. The heat of combustion of adsorbents before adsorption cutting fluids is lower than after adsorption cutting fluids and cutting fluids effluent.

The heat of combustion of CH, CH/PVA, BCH, QCH, CH-SDS, CH-C-Tab, CH-Tween 80 and BCH-SDS increase as 17.1, 9.2, 23.0, 25.8, 21.3 8.4 10.0 and 21.1, respectively for cutting fluids while cutting fluids effluent increase as 16.4, 8.7, 24.0, 25.6, 30.0, 8.1, 10.0 and 20.8 kJ/g, respectively. The capacity obtained from synthetic cutting fluids is closed to that obtained from the effluents. This implies that, this work can be applied to the wastewater treatment.

Table 4.1 Characteristics of cutting fluids effluent from turning processes

Parameters	Concentration (mg/l)
COD	12 000
Oil and grease	2342
Total solid	4941
pH 5.96	

Table 4.2 Adsorption capacity on adsorbents at pH 3

Adsorbents	Adsorption						
	Before	After					
		Synthetic cutting fluid			Cutting fluids effluent		
	ΔH (kJ/g)	q_e (mg/g)	ΔH (kJ/g)	% COD removal	q_e (mg/g)	ΔH (kJ/g)	% COD removal
CH	35.5	130.6	52.6	18.8	668.9	51.9	97.7
CHPVA	43.5	242.1	52.7	24.8	664.7	52.2	86.1
BCH	29.1	175.7	52.1	40.0	735.4	53.1	64.3
QCH	26.8	282.7	52.6	16.5	735.4	52.4	87.4
CH-SDS	27.3	2515.8	48.6	99.3	590.1	57.3	97.8
CH-C-Tab	29.4	2507.9	37.8	99.3	264.6	37.5	96.4
CH-Tween 80	27.6	2417.8	37.6	78.7	290.5	37.6	62.0
BCH-SDS	29.1	2310.1	49.2	98.8	692.6	50.9	98.0

Figure 4.11 shows the FT-IR spectra of cutting fluids and cutting fluids effluent. It was found that the main component of cutting fluids was mineral oil. The alkane appeared at 2925 and 2855 cm^{-1} , methylene and methyl appeared at 1465 and 1375 cm^{-1} . The long chain of the methylene group, more than four carbon atoms, appeared

at 720 cm^{-1} . The emulsifiers may be a naphthenic or sulfonic acid groups which included aromatic at 1555 cm^{-1} , S=O and S-O at 1175 and 1055 cm^{-1} , respectively. The H-bonding of water in cutting fluids appeared as broad peak at $3600\text{--}3200\text{ cm}^{-1}$ [35-38]. The FT-IR spectra of cutting fluids effluent did not appear to be a long chain and additive of emulsifiers. It presented alkene at 1647 cm^{-1} . While H-bonding of water in cutting fluids effluent appeared as broad peak larger than cutting fluids. The absence of long chain and emulsifiers may occur from friction and heat which destroys the chemical structure of cutting fluids effluent, while bacteria growing in water have destroyed the long chain of mineral oil.

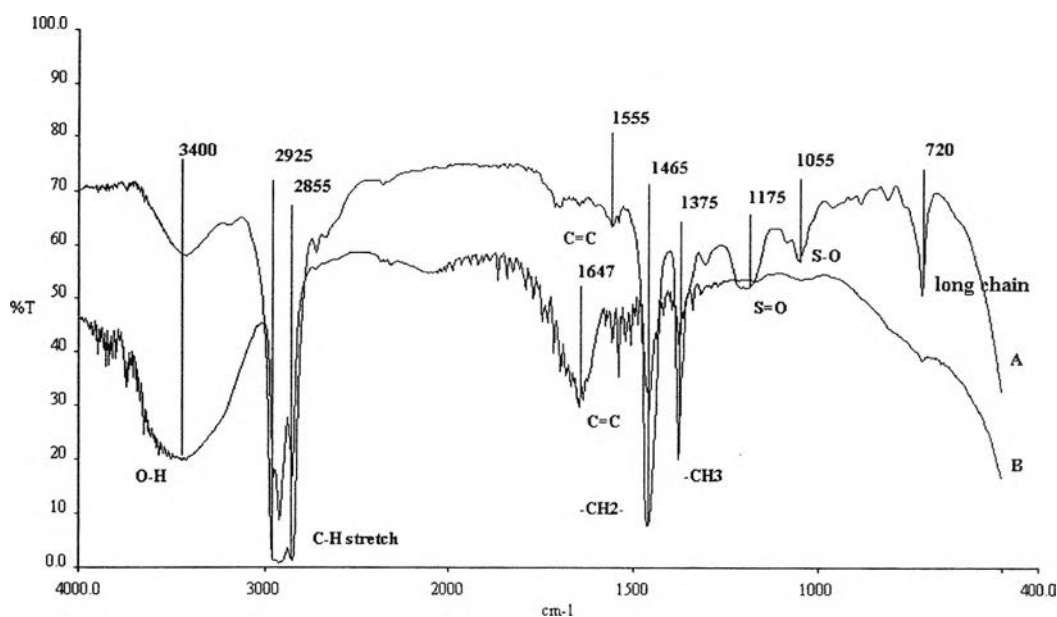


Figure 4.11 FT-IR spectra of (a) cutting fluids and (b) cutting fluids effluent

The spectra of chitosan and blended chitosan/PVA 1:1 before adsorption of the effluent is shown in Figure 4.12 (a) and (b). The chitosan and blended chitosan/PVA 1:1 appeared H-bonding, primary amines and C-O stretched at 3400 , 1557 and 1075 cm^{-1} , respectively. It indicated a different between chitosan and blended chitosan/PVA 1:1 due to different structure. Figure 4.12 (c) and (d) show the spectra of adsorbents after adsorption the effluent. Alkane appeared at 2925 and 2855 cm^{-1} , methylene at

1465 cm^{-1} and methyl at 1375 cm^{-1} . The appearance of alkane, methylene and methyl groups on adsorbents demonstrated that all adsorbents could adsorb the cutting fluids effluent onto the adsorbents.

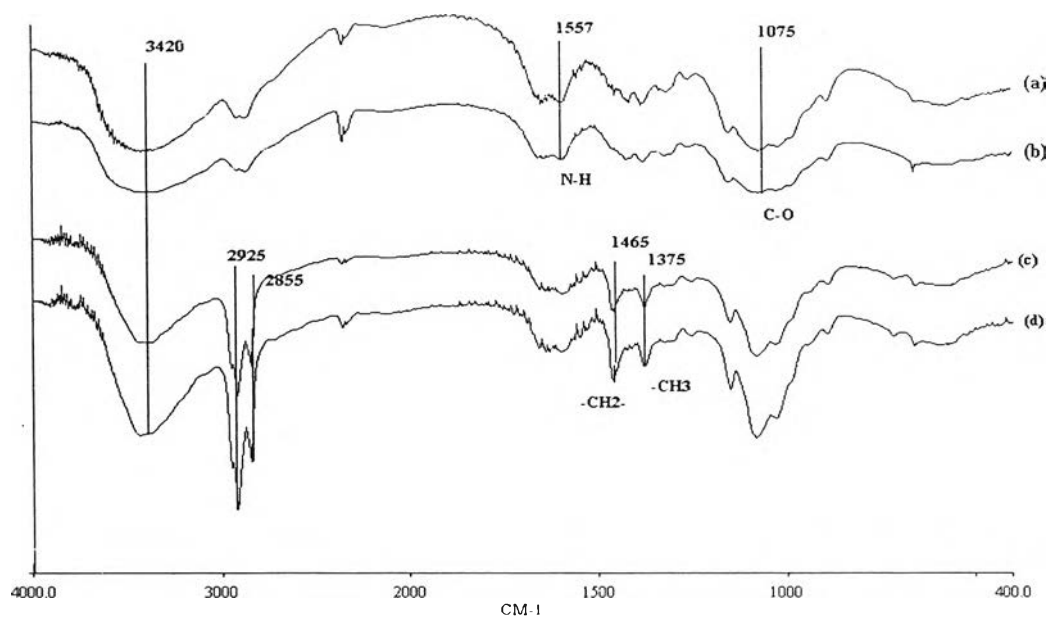


Figure 4.12 FT-IR spectra of adsorbents before and after adsorption cutting fluids effluent before adsorption (a) chitosan and (b) blended chitosan/PVA 1:1 and ; after adsorption cutting fluids effluent (c) chitosan and (d) blended chitosan/PVA 1:1

The spectra of benzoyl chitosan and quateraminated chitosan before adsorption of cutting fluids effluent are shown in Figure 4.13 (a) and (b), respectively. The benzoyl chitosan appeared H-bonding at 3420 cm^{-1} , alkene at 1699 and 1452 cm^{-1} , -N-H stretching at 1540 cm^{-1} , -C-N- stretching at 1275 cm^{-1} and CH aromatic at 708 cm^{-1} . While quateraminated chitosan appeared H-bonding at 3420 cm^{-1} , -N-H stretching at 1640 cm^{-1} , -CH₃ at 1381 cm^{-1} , -C-O stretching at 1075 cm^{-1} and C-Cl at 893 cm^{-1} . Figure 4.13 (c) and (d) shows spectra after adsorption of cutting fluids effluent of all adsorbents. Alkane appeared at 2923 and 2853 cm^{-1} , methylene at 1463 cm^{-1} and methyl at 1377 cm^{-1} . The appearance of alkane, methylene and methyl groups on

adsorbents demonstrated the adsorption of cutting fluids effluent onto benzoyl chitosan and quateraminated chitosan as adsorbents.

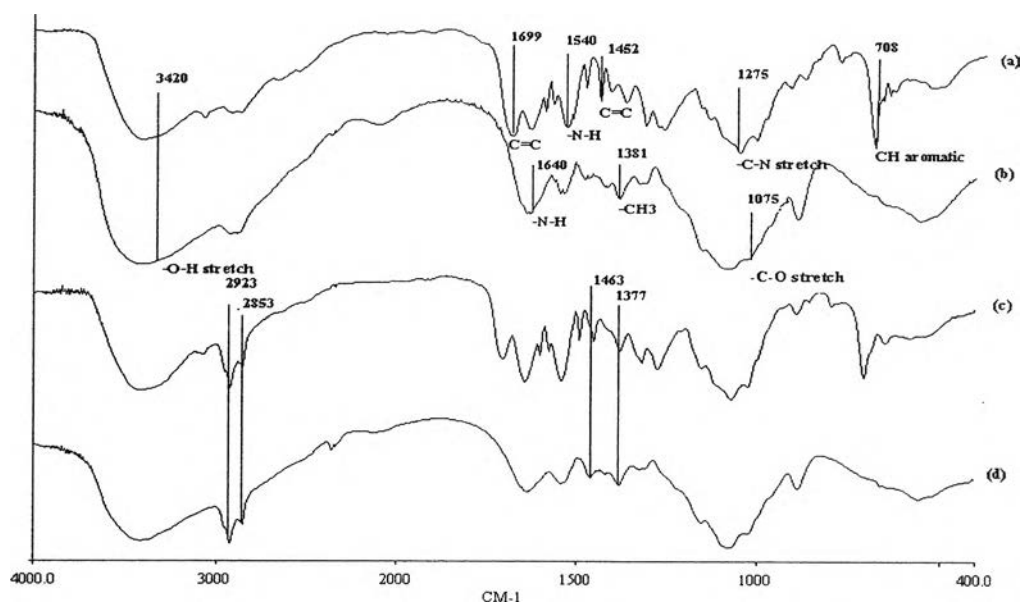


Figure 4.13 FT-IR spectra of adsorbents before and after adsorption cutting fluids effluent before adsorption (a) benzoyl chitosan and (b) quateraminated chitosan; after adsorption cutting fluids effluent (c) benzoyl chitosan and (d) quateraminated chitosan

The spectra of CH-SDS, CH-C-Tab and CH-Tween 80 before and after adsorption are presented in Figure 4.14. Figure 4.14 (a), before adsorption CH-SDS appeared O-H stretching at 3435 cm^{-1} , alkane at 2923 and 2855 cm^{-1} , N-H bending two peaks at 1629 and 1528 cm^{-1} , CH_2 at 1466 cm^{-1} , CH_3 at 1378 cm^{-1} , S=O at 1202 cm^{-1} , R-O-S three peaks at 1087 , 1000 and 816 cm^{-1} , CH_2 long chain more than four atoms at 723 cm^{-1} , S-O at 630 cm^{-1} and =C-H at 583 cm^{-1} . Figure 4.14 (b) and (c), before adsorption CH-C-Tab and CH-Tween 80 appeared O-H stretching at 3435 , N-H bending at 1655 cm^{-1} , and C-O stretching at 1078 cm^{-1} . Figure 4.14 (d), (e) and (f) showed after adsorption cutting fluids effluent of CH-SDS, CH-C-Tab and CH-Tween 80. All adsorbents, alkane appeared at 2923 and 2857 cm^{-1} , methylene at 1463 cm^{-1}

and methyl at 1375 cm^{-1} . The appearance of alkane, methylene and methyl groups on CH-SDS, CH-C-Tab and CH-Tween 80 demonstrated the adsorption of cutting fluids effluent onto adsorbents.

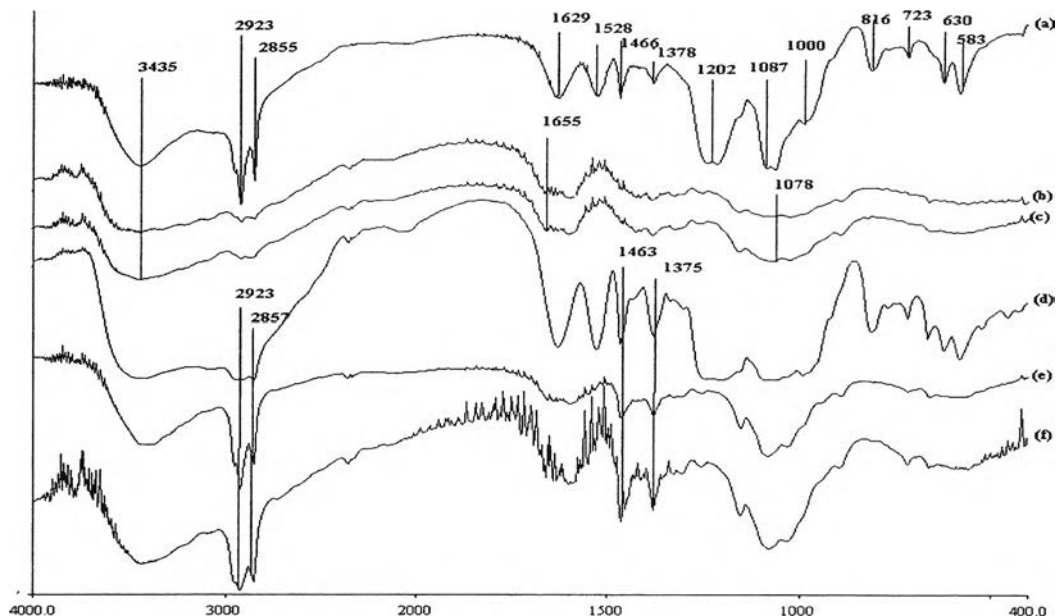


Figure 4.14 FT-IR spectra of adsorbents before and after adsorption of cutting fluids effluent before adsorption (a) CH-SDS, (b) CH-C-Tab and (c) CH-Tween 80; after adsorption cutting fluids effluent (d) CH-SDS, (e) CH-C-Tab and (f) CH-Tween 80

The spectra of BCH-SDS, BCH-C-Tab and BCH-Tween 80 before and after adsorption are presented in Figure 4.15. Figure 4.15 (a), before adsorption BCH-SDS appeared O-H stretching at 3435 cm^{-1} , alkane at 2923 cm^{-1} , N-H bending two peaks at 1629 and 1528 cm^{-1} , CH_2 at 1466 cm^{-1} , CH_3 at 1378 cm^{-1} , S=O at 1202 cm^{-1} , R-O-S three peaks at 1087 , 1000 and 816 cm^{-1} , CH_2 long chain more than four atoms at 723 cm^{-1} , S-O at 630 cm^{-1} and =C-H at 583 cm^{-1} . Figure 4.15 (b) and (c), before adsorption BCH-C-Tab and BCH-Tween 80 appeared O-H stretching at 3435 , N-H bending at 1655 cm^{-1} , and C-O stretching at 1078 cm^{-1} . Figure 4.15 (d), (e) and (f)

showed after adsorption of cutting fluids effluent of BCH-SDS, BCH-C-Tab and BCH-Tween 80. With all adsorbents, alkane appeared at 2923 and 2857 cm^{-1} , methylene at 1463 cm^{-1} and methyl at 1375 cm^{-1} . The appearance of alkane, methylene and methyl groups on BCH-SDS, BCH-C-Tab and BCH-Tween 80 demonstrated the adsorption of cutting fluids effluent onto adsorbents.

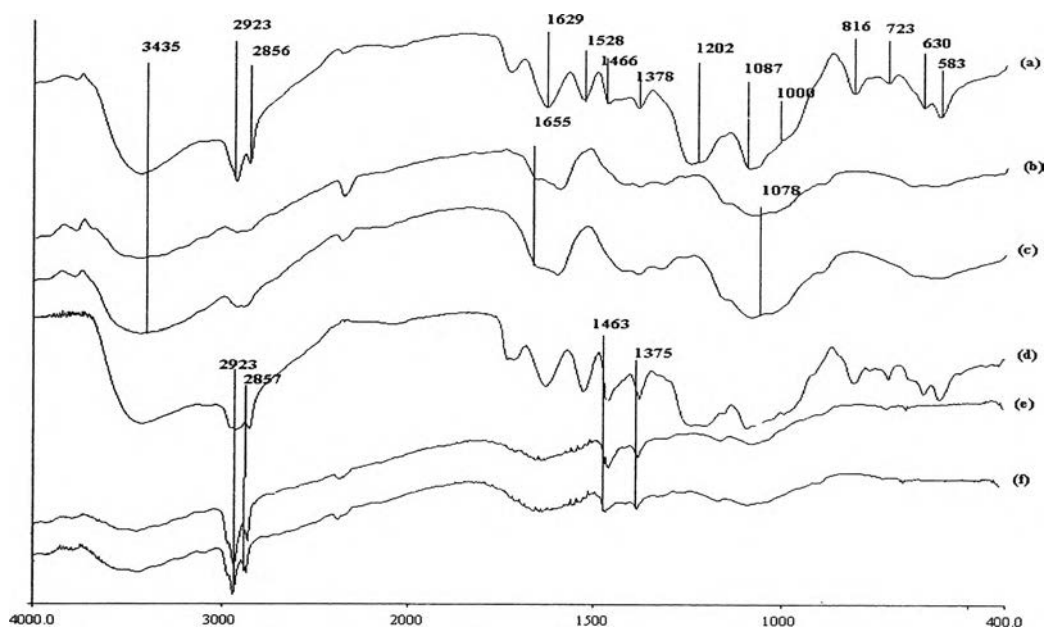


Figure 4.15 FT-IR spectra of adsorbents before and after adsorption of cutting fluids effluent before adsorption (a) BCH-SDS, (b) BCH-C-Tab and (c) BCH-Tween 80; after adsorption cutting fluids effluent (d) BCH-SDS, (e) BCH-C-Tab and (f) BCH-Tween 80

The SEM photographs of chitosan and blended chitosan/PVA 1:1 before adsorption is shown in Figure 4.16 (a) and (b), respectively. The chitosan and blended chitosan/PVA 1:1 showed a bumpy texture and fold of layers which were arranged homogeneously. Figure 4.16 (c) and (d) presented significant changes of structure and appearance on chitosan and blended chitosan/PVA 1:1. The SEM micrographs revealed that most of the chitosan and blended chitosan/PVA 1:1 areas were covered

with a muddy-like substance and this was adsorbed cutting fluids effluent. The surface of chitosan and blended chitosan/PVA 1:1 were spreaded and covered with a muddy-like or rough surface with bubble-like texture due to the cutting fluids effluent molecules which covered the beads. These bubbles were cutting fluids effluent adsorbed onto the chitosan and blended chitosan/PVA 1:1. These confirmed that cutting fluids effluent was adsorbed by adsorbents onto its surface.

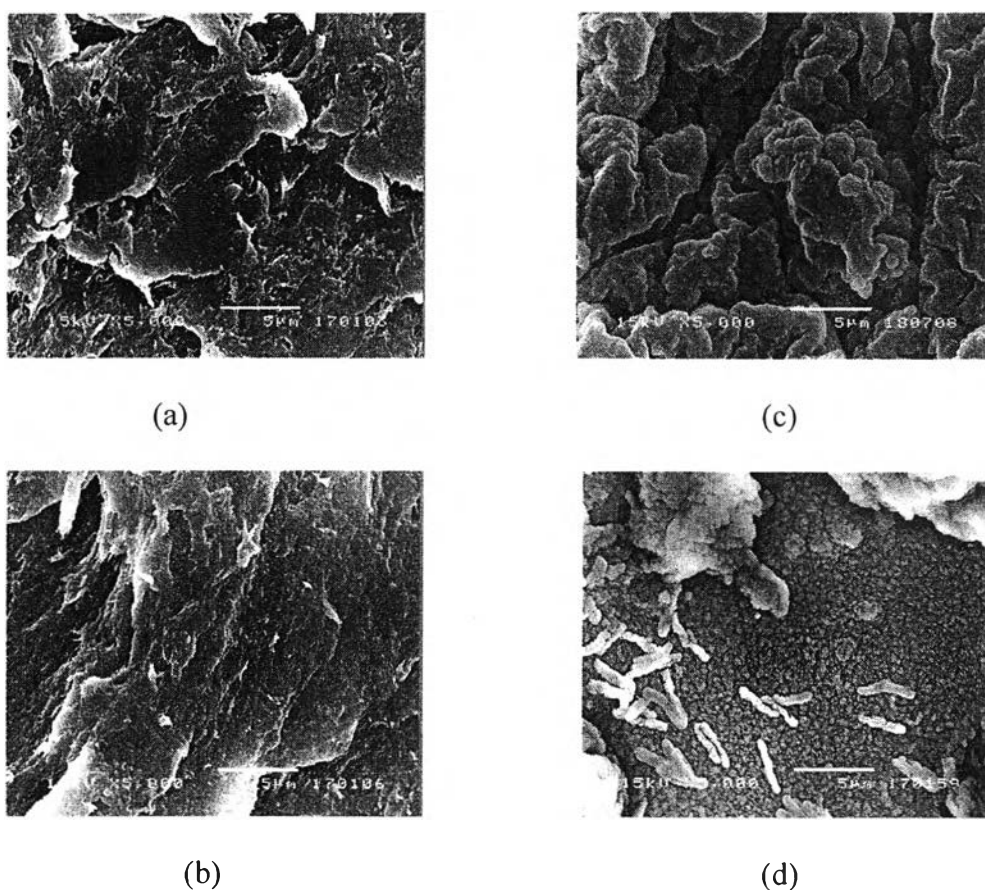


Figure 4.16 Electron microscopic photograph before adsorption cutting fluids effluent of (a) chitosan and (b) blended chitosan/PVA 1:1; after adsorption cutting fluids effluent (c) chitosan and (d) blended chitosan/PVA 1:1 sorbed by adsorbents into its surface. [magnification 5000 times]

The SEM photographs of benzoyl chitosan and quateraminated chitosan before adsorption is shown in Figure 4.17 (a) and (b), respectively. The benzoyl chitosan and

quateraminated chitosan showed a bumpy texture and fold of layers which were arranged homogenously. Figure 4.17 (c) and (d) presented significant change of structure and appearance on benzoyl chitosan and quateraminated chitosan. The SEM micrographs revealed that most of the benzoyl chitosan and quateraminated chitosan areas were covered with muddy-like substance and this was adsorbed cutting fluids effluent. The surface of benzoyl chitosan and quateraminated chitosan were spread and covered with muddy-like or rough surface with bubble-like texture due to the cutting fluids effluent molecules which covered the beads. These bubbles were cutting fluids effluent adsorbed onto the benzoyl chitosan and quateraminated chitosan. It was confirmed that cutting fluids effluent was adsorbed onto the surface of quateraminated chitosan.

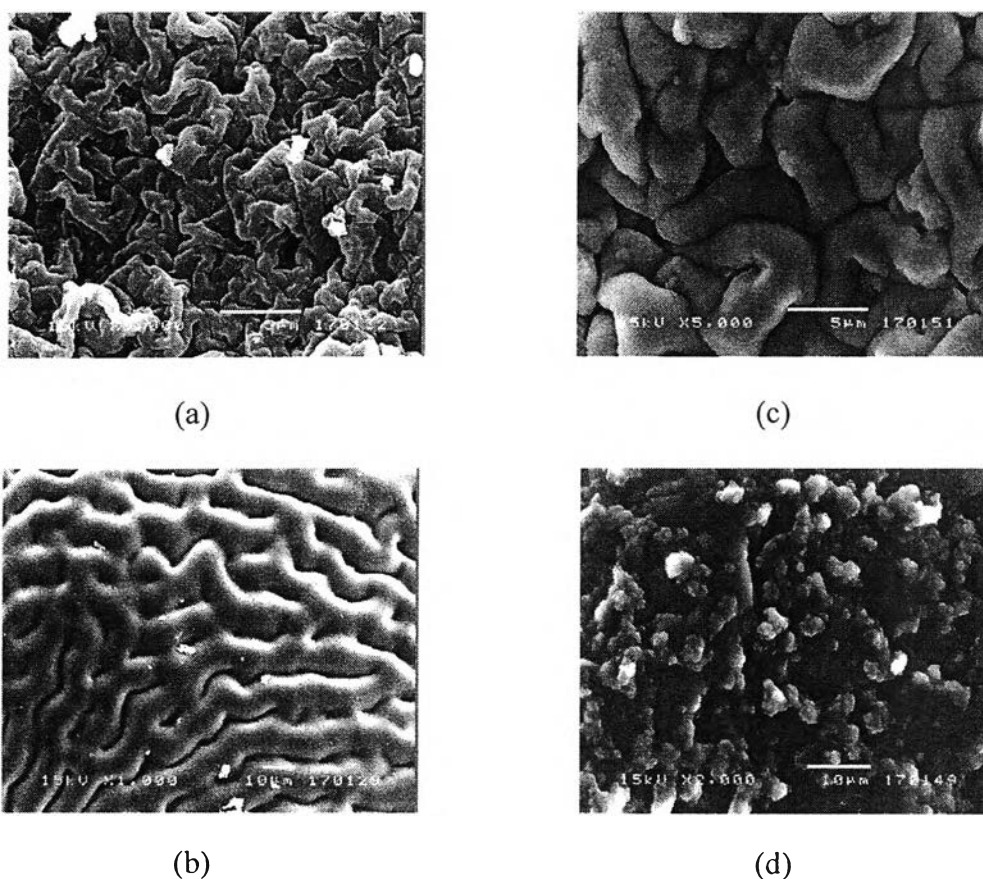


Figure 4.17 Electron microscopic photographs before adsorption cutting fluids effluent of benzoyl chitosan and (b) quaterminated chitosan; after adsorption cutting fluids effluent (c) benzoyl chitosan and (d) quaterminated chitosan. [magnification 5000 times]

The SEM photograph of CH-SDS before and after adsorption is shown in Figure 4.19 (a). Before adsorption, the CH-SDS showed a bumpy texture and fold of layers which were arranged homogenously. Figure 4.19 (b) presented significant change of structure and appearance on CH-SDS. The SEM micrographs revealed that most of CH-SDS area was covered with a muddy-like substance and this was adsorbed cutting fluids effluent. The surface of CH-SDS was spreaded and covered with a muddy-like or rough surface with bubble-like texture due to the cutting fluids effluent molecules which covered the adsorbents. These bubbles were cutting fluids effluent adsorbed

onto the CH-SDS. This confirmed that cutting fluids effluent was adsorbed by adsorbents onto its surface.

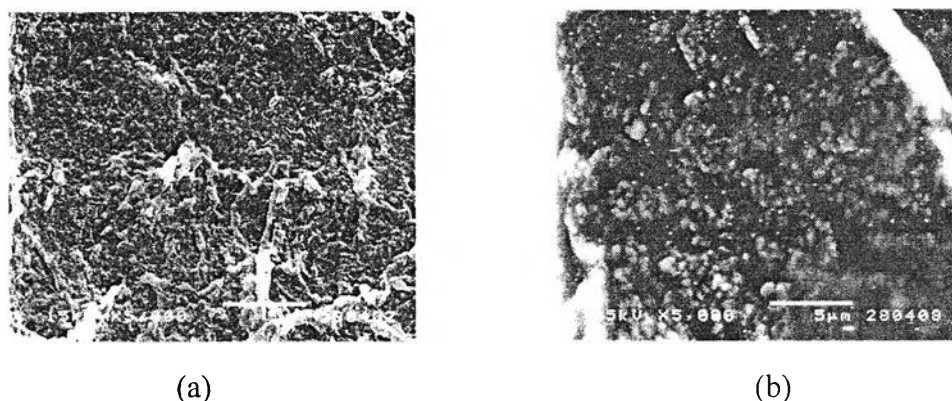


Figure 4.19 Electron microscopic photograph adsorption of cutting fluids effluent on CH-SDS (a) before adsorption and (b) after adsorption [magnification 5000 times]

SEM photographs of BCH-SDS before adsorption is shown in Figure 4.20. The BCH-SDS showed a bumpy texture and fold of layers which were arranged homogeneously. Figure 4.20 (b) presented significant change of structure and appearance on BCH-SDS. The SEM micrographs revealed that most of the BCH-SDS area was covered with muddy-like substance and this was adsorbed cutting fluids effluent. The surface of BCH-SDS was spreaded and covered with a muddy-like or rough surface with bubble-like texture due to the cutting fluids effluent molecules which covered the adsorbents. These bubbles were cutting fluids effluent adsorbed onto the BCH-SDS. These confirmed that cutting fluids effluent was adsorbed by adsorbents onto its surface.

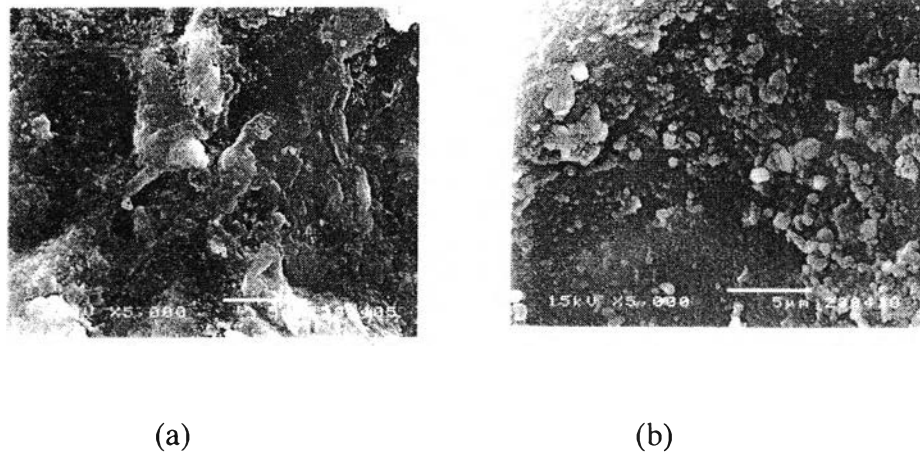


Figure 4.20 Electron microscopic photograph adsorption of cutting fluids effluent on BCH-SDS (a) before adsorption and (b) after adsorption [magnification 5000 times]

The percent CHN of chitosan and blended chitosan/PVA 1:1 before adsorption and after adsorption cutting fluids and cutting fluids effluent is presented in Figure 4.21 (a) – (c). It was found that before adsorption the component of C element from chitosan and blended chitosan/PVA 1:1 was 36.28 and 36.92 % respectively. After adsorption of cutting fluids, the component of C element from chitosan and blended chitosan/PVA 1:1 increased to 46.26 and 40.14 % respectively, while after adsorption cutting fluids effluent the component of C element from chitosan and blended chitosan/PVA 1:1 increased to 38.25 and 37.78 % respectively. The amount of C element after adsorption of cutting fluids and cutting fluids effluent raises compared with the amount before adsorption from all adsorbents. This can be proved that chitosan and blended chitosan/PVA 1:1 as adsorbents can adsorb cutting fluids and cutting fluids effluent.

Figure 4.21 (b) presents the component of H element from chitosan and blended chitosan/PVA 1:1. It was found that before adsorption the component of H element

from chitosan and blended chitosan/PVA 1:1 displayed 8.46 and 8.32 % respectively. After adsorption of cutting fluids, the component of H element from chitosan and blended chitosan/PVA 1:1 showed 9.78 and 7.62 % respectively, while after adsorption cutting fluids effluent the component of H element from chitosan and blended chitosan/PVA 1:1 shows 7.15 and 7.09 % respectively.

Figure 4.21 (c) presents the component of N element in chitosan and blended chitosan/PVA 1:1. It was found that before adsorption the component of N element from chitosan and blended chitosan/PVA 1:1 was 1.87 and 1.78 % respectively. After adsorption of cutting fluids, the component of N element from chitosan and blended chitosan/PVA 1:1 decreased to 1.33 and 0.82 and %, respectively, while after adsorption of cutting fluids effluent the component of N element from chitosan and blended chitosan/PVA 1:1 decreased to 1.61 and 1.55 respectively. It was found that the N element after adsorption of cutting fluids and cutting fluids effluent were decreased from all adsorbents. This advantage to use chitosan and blended chitosan/PVA 1:1 as solid fuel due to reduction of N element reduces oxide of nitrogen (NO_x).

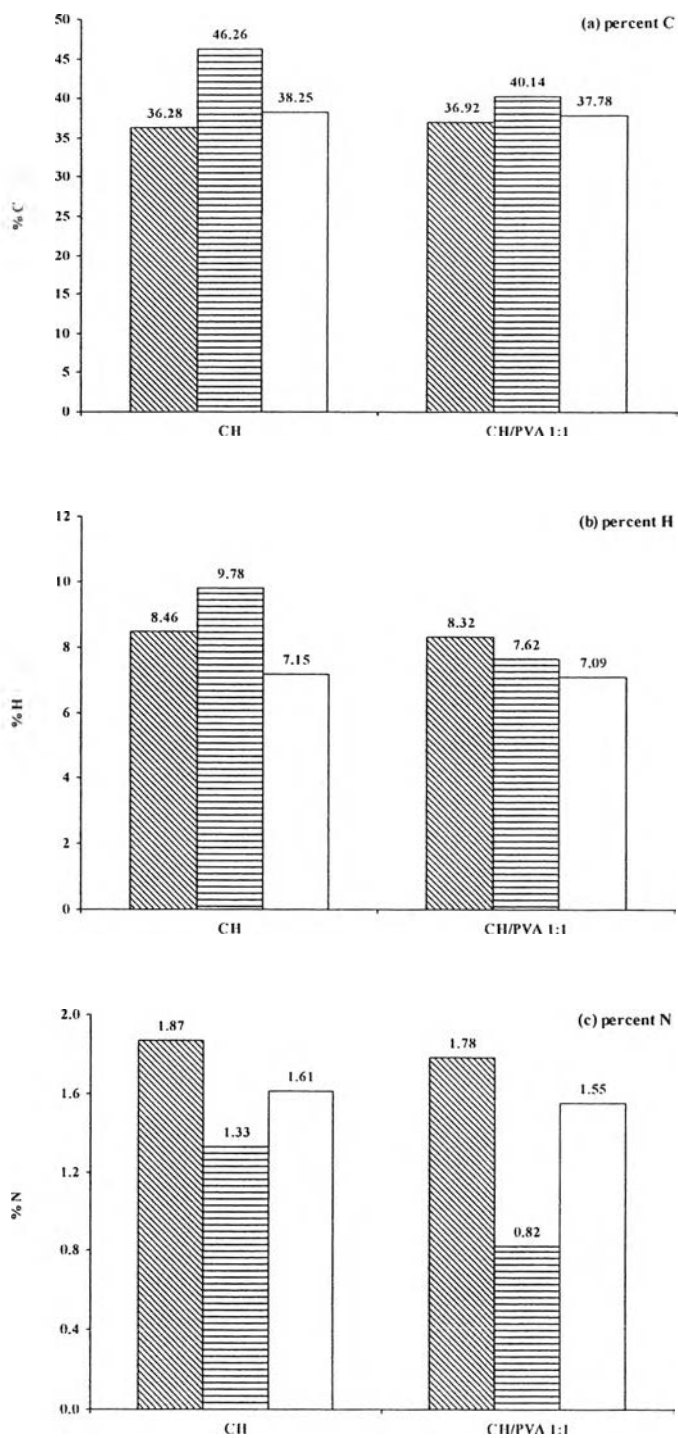


Figure 4.21 Percent CHN of chitosan and blended chitosan/PVA 1:1

(a) percent C, (b) percent H and (c) percent N; ▨ before adsorption cutting fluids, ▨ after adsorption cutting fluids and □ after adsorption cutting fluids effluent

Table 4.3 Percent CHN elements before adsorption, after adsorption cutting fluids and after adsorption cutting fluids effluent of adsorbents

Adsorbents	Before adsorption			After adsorption synthetic cutting fluids			After adsorption cutting fluids effluent		
	C	H	N	C	H	N	C	H	N
CH	36.28	8.46	1.87	46.26	9.78	1.33	38.25	7.15	1.61
CH/PVA	36.92	8.32	1.78	40.14	7.62	0.82	37.78	7.09	1.55
BCH	46.7	6.87	1.05	56.84	9.72	0.73	53.16	7.16	1.03
QCH	35.74	8.26	1.46	51.7	10.11	1.17	51.39	7.79	1.37
CH-SDS	48.52	8.33	2.99	66.46	10.83	1.54	67.7	10.43	1.3
CH-C-Tab	38.35	7.14	7.25	52.6	8.65	4.95	40.52	6.85	5.48
CH-Tween 80	38.32	7.14	7.21	65.45	10.13	2.75	39.45	6.89	5.71
BCH-SDS	48.94	8.35	2.47	62.98	9.64	1.41	52	9.14	2.24
BCH-C-Tab	39.03	7.48	6.85	59.02	9.45	3.82	41.78	7.21	5.21
BCH-Tween 80	38.54	7.1	6.9	58.39	9.26	3.94	40.07	6.97	5.43

The percent CHN of benzoyl chitosan, quateraminated chitosan, CH-SDS, CH-C-Tab, CH-Tween 80, BCH-SDS, BCH-C-Tab and BCH-Tween 80 before adsorption cutting fluids and after adsorption cutting fluids and cutting fluids effluent is summarized in Table 4.3. It was found that before adsorption, the amount of C element, after the adsorption cutting fluids and cutting fluids effluent, raised in all adsorbents. It therefore can be proven that these adsorbents can adsorb cutting fluids and cutting fluids effluent.

Table 4.3 presents the component of H element into adsorbents. The H element has fluctuated after adsorption cutting fluids and cutting fluids effluent which may be neglected for adsorption cutting fluid of adsorbents. The component of N element from adsorbents is higher than after adsorption and present in Table 4.3. It was found that the N element after adsorption of cutting fluids and cutting fluids effluent were

decreased in all adsorbents. This advantage to use adsorbents as solid fuel due to reduction of N element reduces the oxide of nitrogen (NO_x).

To apply as a fuel, heat of combustion of each adsorbent was determined. The heat of combustion indicated that waste coolants can be used as fuel for incineration [39]. Increasing in heat of combustion of each adsorbent after adsorption supports that all adsorbents could adsorb the cutting fluids and the adsorbents could be applied to an incineration as a fuel.

4.4.2. pH condition

Effect of pH condition on adsorption capacity is shown in Figure 4.22 for adsorbent 6.0 g of chitosan, blended chitosan/PVA 1:1, benzoyl chitosan and quateraminated and Figure 4.23 for of 1.0 g of CH-SDS, CH-C-Tab, CH-Tween 80, BCH-SDS, BCH-C-Tab and BCH-Tween 80. More cutting fluids could be adsorbed on adsorbents in acidic condition. CH-SDS shows the highest adsorption capacity around 2516 mg/g, at pH 3. It is noticed that increasing pH of emulsion to the basic, pH 7 to 11, CH-SDS adsorbed less cutting fluids from 747 to 309 mg/g. BCH-SDS still adsorbed more cutting fluids in basic condition. This indicated that pH of fluids play an important role on adsorption. Destabilization of the emulsion was obtained at acidic condition. This was due to the fact that the negative charge of cutting fluids performed stability. More acidic conditions showed a catalyst for the interaction between oil and amino groups of chitosan [40, 41].

At pH more than 3.5, the droplets disperse very well in the emulsion due to the negative surface charge (see zeta potential section in Appendix D). Therefore, the adsorption capacity on adsorbents decreased dramatically in basic condition.

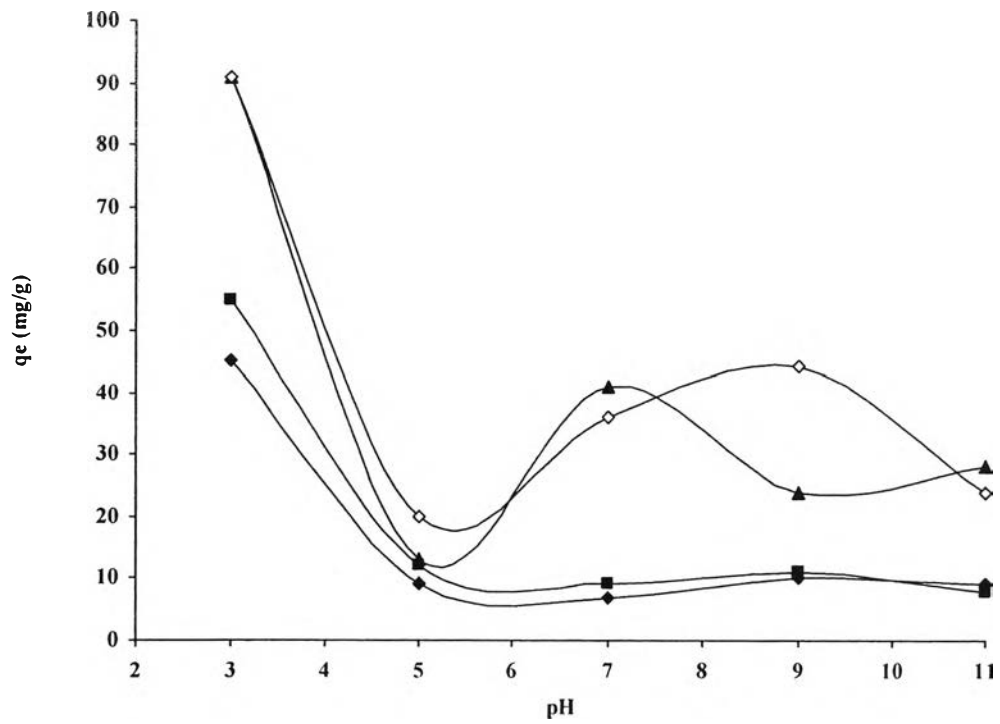


Figure 4.22 Variation pH to adsorption capacity of cutting fluids concentration

1.0 % w/v using adsorbent 6.0 g on ◆ chitosan, ■ blended chitosan/PVA

1:1 ▲ benzoyl chitosan and ◇ quateraminated chitosan

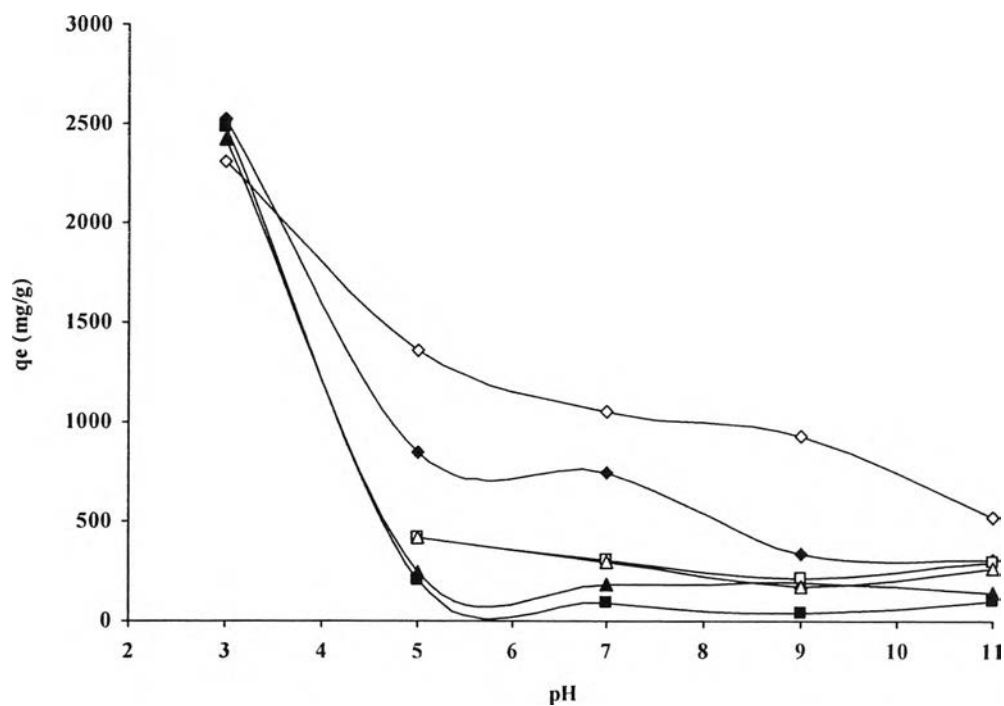


Figure 4.23 Variation pH to adsorption capacity of cutting fluids concentration

3.00 % w/v using adsorbent 1.0 g on ◆ CH-SDS, ■ CH-C-Tab,

▲ CH-Tween 80, ◇ BCH-SDS, □ BCH-C-Tab and △ BCH-Tween 80

4.2.3. Salt effect

Results of salt effect on cutting fluids adsorption on 6.0 g of chitosan and blended chitosan/PVA 1:1 (CH/PVA 1:1) is presented in Figure 4.24 and on benzoyl chitosan and quateraminated chitosan presented in Figure 4.25. The adsorption capacities on chitosan non-adding salts and adding NaCl, CaCl₂, Fe(NO₃)₃, Na₂SO₄, CaSO₄ and FeSO₄ at concentration 0.01 M were 69.8, 134.0, 134.6, 79.8, 32.9, 36.6 and 48.2 mg/g, respectively. The adsorption capacities on blended chitosan/PVA 1:1 were 77.8, 129.7, 133.8, 62.1, 25.0, 40.0 and 44.1 mg/g, respectively. Results of the salt effect on adsorption capacity of benzoyl chitosan and quateraminated chitosan are presented in Figure 4.25. The adsorption capacities on benzoyl chitosan without adding salt and adding NaCl, CaCl₂, Fe(NO₃)₃, Na₂SO₄, CaSO₄ and FeSO₄ at concentration 0.01 M

were 90.5, 132.7, 134.6, 83.2, 51.2 117.3 and 86.9 mg/g, respectively. The adsorption capacities on quateraminated chitosan were 90.8, 132.9, 134.6, 92.3, 65.3, 118.1 and 134.6 mg/g, respectively. Adsorption capacity increased with the addition of salts could be explained by the theory developed by Guoy-Chapman. The cutting fluids emulsion forms an electrical double layer when emulsion contacts with the adsorbents. The addition of salts NaCl and CaCl₂ resulted in reducing the thickness of electrical double layer. This result increases the adsorption of the cutting fluids. Comparing the capacity when adding NaCl and CaCl₂, adsorption capacity increases with the addition of CaCl₂, because the electrical double layer is inversely proportion to the sixth power of the charge on the ion [11] while the adsorption capacity decreased with the addition of sulfate ions i.e. Na₂SO₄, CaSO₄ and FeSO₄. This may be due to the fact that the sulfate ion had an attraction to the amino groups of adsorbents. The addition of Fe(NO₃)₃ into the cutting fluid emulsion did not clearly show any trend of increasing adsorption capacity.

Adsorption capacity increased with the addition of chloride ion due to the emulsion reduces the thickness of the electrical double layer. This results in increasing the adsorption capacity. The addition of Fe(NO₃)₃ into the cutting fluids emulsion did not clearly change any trend of adsorption capacity. The adsorption capacity increased with the addition of sulfate ions i.e. CaSO₄ and FeSO₄ compare to non-adding salt, while the sulfate ion from Na₂SO₄ decreased the adsorption capacity of cutting fluids emulsion.

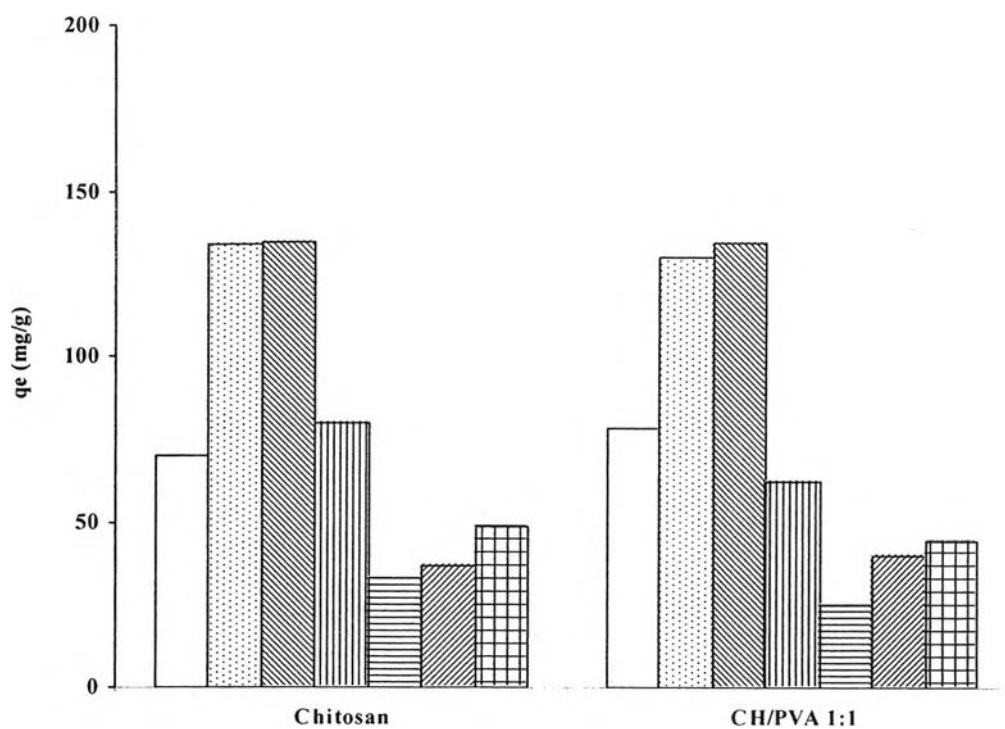


Figure 4.24 Adsorption capacity of cutting fluids on chitosan and blended chitosan/PVA 1:1 (CH/PVA 1:1) when \square non adding salt and adding 0.01 M concentration of salts \boxtimes NaCl, $\backslash\backslash$ CaCl₂, \lll Fe(NO₃)₃, \equiv Na₂SO₄, $///$ CaSO₄ and $\#$ FeSO₄. 6 g of adsorbents were used and the pH condition was at pH 3.

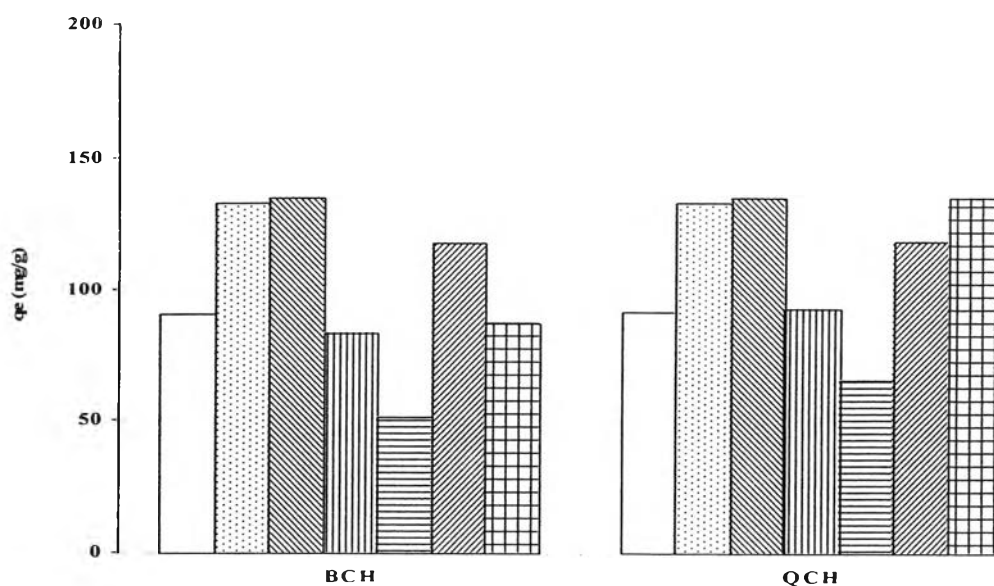


Figure 4.25 Adsorption capacity of cutting fluids on benzoyl chitosan (BCH) and quaterminated chitosan when \square non adding salt and adding 0.01 M concentration of salts \boxtimes NaCl, $\backslash\backslash$ CaCl₂, $\|$ Fe(NO₃)₃, \equiv Na₂SO₄, $///$ CaSO₄ and $\#$ FeSO₄. 6 g of adsorbents were used and the pH condition was at pH 3.

Results of salt additions effect on adsorption capacity of CH-SDS, CH-C-Tab, CH-Tween 80 and BCH-SDS are presented in Figure 4.26. The adsorption capacities on CH-SDS without adding salt and adding NaCl, CaCl₂, Fe(NO₃)₃, Na₂SO₄, CaSO₄ and FeSO₄ at concentration 0.01 M were 141.3, 134.6, 132.5, 94.6, 118.1, 119.9 and 134.4 mg/g, respectively. The adsorption capacities on blended CH-C-Tab were 61.2, 133.1, 134.6, 56.7, 75.8, 85.6 and 132.3 mg/g, respectively. The adsorption capacities on CH-Tween 80 were 95.2, 134.6, 130.8, 64.6, 74.3, 78.3 and 134.6 mg/g, respectively. The adsorption capacities on BCH-SDS were 132.9, 133.6, 95.0, 116.9, 118.1, 134.6 and 141.3 mg/g, respectively.

It was found that the adsorption capacities of CH-SDS and BCH-SDS did not change significantly when adding salts. The adsorption capacities of CH-C-Tab and CH-Tween 80 increased with the addition of chloride salts and FeSO_4 compared to that without addition of these salts. This is due to the fact that emulsion reduces the thickness of the electrical double layer. The addition of $\text{Fe}(\text{NO}_3)_3$, Na_2SO_4 and CaSO_4 salts to the cutting fluids emulsion did not demonstrated the tendency change of adsorption capacity of CH-C-Tab and CH-Tween 80.

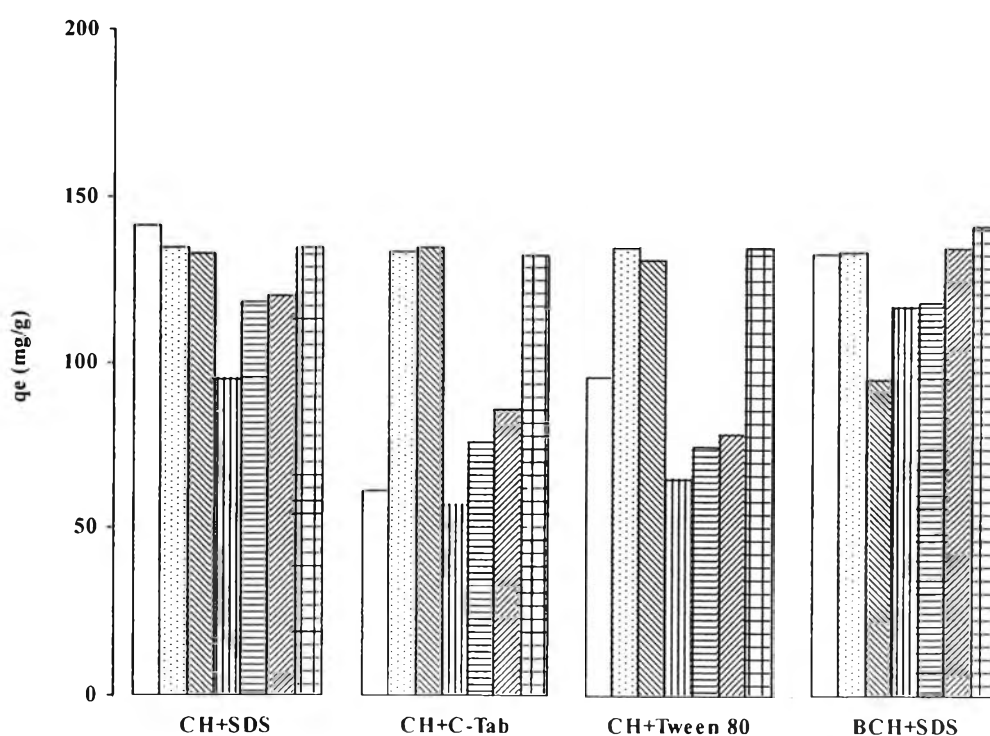


Figure 4.26 Adsorption capacity of cutting fluid on CH-SDS, CH-C-Tab, CH-Tween 80 and BCH-SDS when \square non adding salt and adding 0.01 M concentration of salts NaCl , CaCl_2 , $\text{Fe}(\text{NO}_3)_3$, Na_2SO_4 , CaSO_4 and FeSO_4 . 6 g of adsorbents were used and the pH condition was at pH 3.

It can be concluded that NaCl and CaCl₂ enhanced the adsorption capacity of the cutting fluids emulsion. Adding Na₂SO₄ and CaSO₄ to the emulsion did not encourage capacity of adsorbents. Adding Fe(NO₃)₃ and FeSO₄ did not affect on adsorption capacity.

Results of NaCl concentration on cutting fluids adsorption capacity of 6 g of adsorbents at pH 3 are presented in Figure 4.27. Adding NaCl salt increases the adsorption capacity for chitosan, blended chitosan/PVA 1:1, benzoyl chitosan, quaterminated chitosan, CH-C-Tab and CH-Tween 80. While adding NaCl salt to the emulsion, the capacity of CH-SDS, BCH-SDS did not change much. When adding more NaCl concentrations from 0.01 to 0.05 M, adsorption capacity increases slightly. This is due to reducing of thickness of the electrical double layer. Therefore, adsorption capacity increases with salt concentration. On the other hand, adsorption capacity of CH-C-Tab and BCH-Tween 80 decrease dramatically when adding more NaCl. This showed similar result for pentachlorophenol adsorption on chitosan [42].

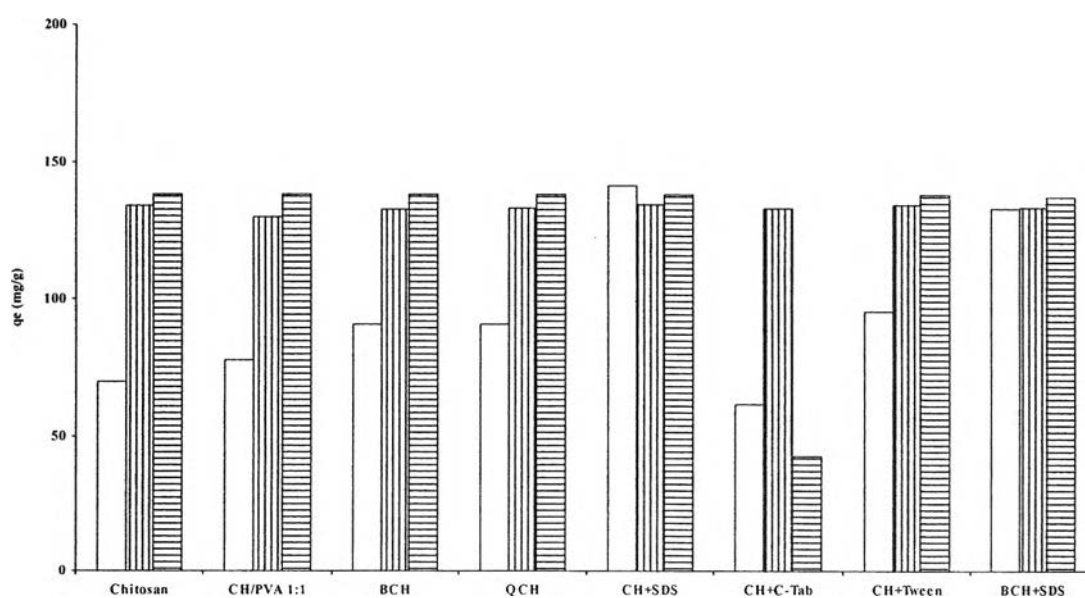


Figure 4.27 Adsorption capacity of cutting fluids when □ non adding salt and adding NaCl concentration ||| 0.01 and ≡ 0.05 M

Results of CaCl_2 concentration on cutting fluids adsorption capacity of 6.0 g of adsorbents at pH 3 are presented in Figure 4.28. A CaCl_2 salt increased the adsorption capacity for chitosan, blended chitosan/PVA 1:1, benzoyl chitosan, quateraminated chitosan, CH-C-Tab and CH-Tween 80. When adding CaCl_2 salt to the emulsion the capacity of CH-SDS did not change significantly. The adsorption capacity of BCH-SDS decreases when adding 0.01 M CaCl_2 . Further increasing CaCl_2 concentration to 0.05 M, adsorption capacity of BCH-SDS little increased. When adding more CaCl_2 concentration from 0.01 to 0.05 M, the adsorption capacity increased slightly. It can be concluded that increasing NaCl or CaCl_2 from 0.01 to 0.05 M does not affect on cutting fluids adsorption capacity.

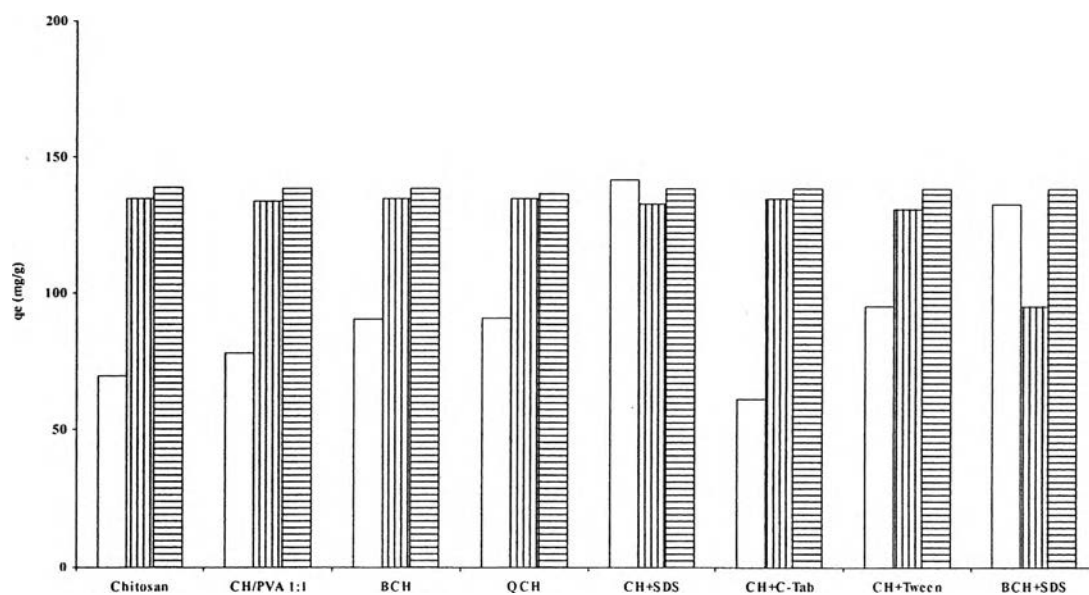


Figure 4.28 Adsorption capacity of cutting fluids when □ non adding salt and adding CaCl_2 concentration ||| 0.01 and ≡ 0.05 M