CHAPTER 3

MATERIALS AND METHODOLOGY

This chapter describes the properties of the materials that are used in all the present experiments. It also describes the procedures employed in each experiment and all the apparatus used in this work. In addition, the analytical methods, in particular the determination of the swelling of adsorbents, the humidity of adsorbents and heat of combustion measurements are considered in this part. Furthermore, the measurements of surface area, pore diameter, contact angle, Zeta potential, Fourier transform infra-red spectroscopy (FT-IR), Heat of combustion, CHN and Scanning electron microscope (SEM) are described.

3.1. Materials

Materials used through out this present study are summarized in Table 3.1.

Table 3.1 General properties of materials used in this study.

Name	Chemical formula	Molecular weight (g/mol)	Purity (Percent)	Company (country product)
1. Acetic acid	CH_3COOH	60.05	99.8	BDH (England)
2. Acetone	CH_3COCH_3	58.08	≥ 99.5	BDH (England)
3. Benzoic anhydride	$C_{14}H_{10}O_3$	226.23	≥ 95.0	Fluka (USA)
4. Calcium chloride dihydrate	$CaCl_2.2H_2O$	147.02	98-103	Ajax Finechem (Australia)
5. Calcium sulfate didydrate	$CaSO_4.2H_2O$	172.10	> 99	Fluka (Switzerland)
6. Chitosan flake	$(C_6H_{11}NO_4)_n$	700,000	DD > 95	Sea Fresh (Thailand)
7. Ethanol	CH_3CH_2OH	46.07	99.99	Carlo Erba (France)
8. Ethylene glycol diglycidyl ether (EGDE)	$C_8H_{14}O_4$ $OHC(CH_2)_3$	174.20	≈ 50	Fluka (USA)
9. Glutaraldehyde (GLA)	CHO	100.12	25	Ajax Finechem (Australia)

Table 3.1 General properties of materials used in this study. (Continued)

Name	Chemical formula	Molecular weight (g/mol)	Purity (Percent)	Company (country product)
10. Hexadecyltrimethyl ammonium bromide (C-Tab)	$C_{19}H_{42}BrN$	364.46	≥ 96	Fluka (Switzerland)
11. Iron (III) nitrate nonahydrate	$Fe(NO_3)_3.9H_2O$	404.00	> 99.0	Fluka (Switzerland)
12. Iron (II) sulfate heptahydrate	$FeSO_4.7H_2O$	278.02	99.0	Ajax Finechem (Australia)
13. Lithium chloride	LiCl	42.40	99	APS (Australia)
14. Methanol	CH_3OH	32.04	99.99	Fresher Scientific UK (UK)
15. N, N dimethylacetamide	C_4H_9NO	87.12	98.0	Fluka (Switzerland)
16. Polyvinyl alcohol	$(C_2H_4O)_n$	72000	86.5-89.0	BDH (England)
17. Polyoxyethylene Sorbitanmonooleate (Tween 80)	$C_{12}H_{10}ClNO_3$	251.70	Commercial	Honghuat (Thailand)
18. Sodium chloride	NaCl	58.44	99.5	Carlo Erba (France)
19. Sodium lauryl sulphate	$CH_3(CH_2)_{11}OSO_3Na$	288.38	> 97	Ajax Finechem (Australia)
20. Sodium sulfate anhydrous	Na_2SO_4	142.04	> 99.50	Fresher Scientific UK (UK)
21. Sodium tripolyphohphate	$Na_5P_3O_{10}$	367.86	85	Signa-Aldrich (Germany)
22. Cutting fluids	-	-	Commercial	Rifle Brand (Thailand)

3.2. Preparation adsorbents

In order to study the efficiency of the adsorbents on adsorbing the cutting fluids, two types of adsorbents were employed, i.e. chitin and chitosan beads prepared in the laboratory and chitosan purchased from Sea Fresh Co., Ltd. Furthermore, each group was divided into subgroup depend on the concentration of chitosan solution, the modified chemical chitosan and the modified surfactant chitosan in which each adsorbent was prepared in the form of beads. For a clear presentation, the full list of adsorbents prepared and used in the present study is summarized in Table 3.2 and in the following sections.

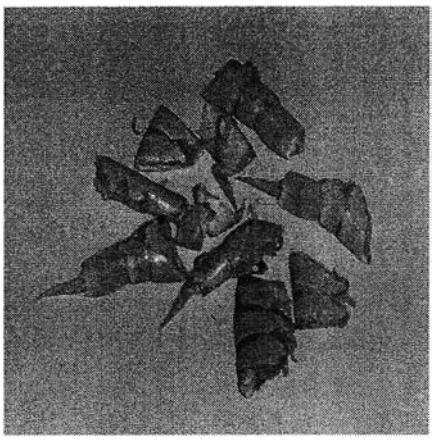
Table 3.2 Adsorbents of cutting fluids

a) Chitosan bead prepared from laboratory
i. Chitosan bead
ii. Modified chitosan bead
- Crosslinking chitosan with glutaraldehyde
- Blended chitosan/PVA 1:1
b) Chitosan bead prepared from Sea Fresh Co. Ltd.
i. Chitosan bead
- 1.20 % w/v of chitosan solution
- 1.70 % w/v of chitosan solution
- 2.00 % w/v of chitosan solution
- 2.20 % w/v of chitosan solution
ii. Modified chemical chitosan bead
- Crosslinking chitosan with glutaraldehyde
- Blended chitosan/PVA 1:1
- Blended chitosan/PVA 1:2
- Crosslinking blended chitosan/PVA 1:1 with glutaraldehyde
- Crosslinking blended chitosan/PVA 1:2 with glutaraldehyde
- Benzoyl chitosan
- Quateraminated chitosan
iii. Modified surfactant chitosan bead
- Chitosan-sodium lauryl sulfate
- Chitosan-hexadecyltrimethyl ammonium bromide
- Chitosan- polyoxyethylene sorbitanmonooleate
- Blended chitosan/PVA-sodium lauryl sulfate
- Blended chitosan/PVA-hexadecyltrimethyl ammonium bromide
- Blended chitosan/PVA-polyoxyethylene sorbitanmonooleate

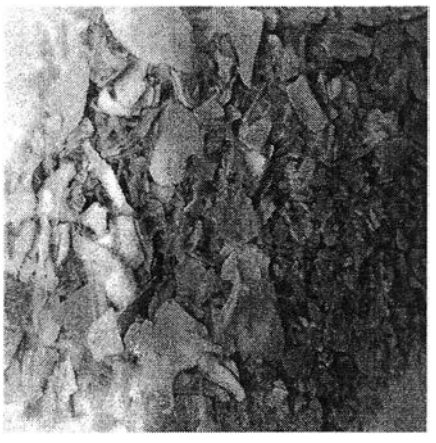
3.2.1. Preparation of chitin and chitosan from laboratory

The chitin was prepared from the fresh shell of black tiger shrimp. The fresh shrimp was washed by water to eliminate scraps of meat from the shell. After that the shell was dried in the sun and incubated by oven at a temperature 60 to 70 ^{0}C for 6 h (see Figure 3.1a). Then the shells of black tiger shrimp was reduced in size by blender (see Figure 3.1b). 20 g of dry shells black tiger shrimp were then demineralized by soaking in 300 cm^3 of 1.25 M hydrochloric acid for 2 h. The mixture was stirred by magnetic stirrer (Schott model SLR, Germany) at a speed of 300 rpm at room temperature. The shells of black tiger shrimp were then washed by water several times until pH of the solution became the same as that of the fresh water. Then the shells were deproteined by boiling in 300 cm^3 of 1 M sodium hydroxide for 2 h. The mixture was stirred by magnetic stirrer at a speed of 300 rpm at 80 to 90 ^{0}C. The shells were then washed by water several times until pH of the solution became the same as that of the fresh water. The product was flake chitin (see Figure 3.1c)

After obtaining the flake chitin, the chitosan was prepared by the following procedures. 20 g of flake chitin were deacetylated by 400 cm^3 of 50 % w/v of sodium hydroxide for 2 h. The mixture was stirred by magnetic stirrer at a speed of 300 rpm at 110 to 120 ^{0}C. The chitosan was then washed by water several times until pH of the solution became the same as that of the fresh water. The product was flake chitosan (see Figure 3.1d)



(a) dried shell of black tiger shrimp



(b) blended shell of black tiger shrimp

(c) flake chitin

(d) flake chitosan

Figure 3.1 Chitin and chitosan from shells of black tiger shrimp

3.2.1.1. Preparation of chitosan beads

2.0 g of chitosan flake was dissolved into 100 cm^3 of 2 % v/v aqueous acetic acid solution. The mixture was mixed by motor stirrer (IKA Labortechnik model RW at 20.n, Malaysia) 300 rpm for 24 h at room temperature to obtain a clear yellow solution. White hydrogel beads were formed when dropping the solution into 300 cm^3 of a 1 M NaOH solution through a needle (Ø 1.2 mm.) by a peristaltic pump. The hydrogel beads were allowed to soak in the NaOH solution for 12 h and then washed by deionized water (Elga model OS007BPM1, UK) several times until pH of the solution became the same as that of the fresh deionized water. The chitosan beads

were stored in deionized water for further use. Figure 3.2 shows chitosan beads prepared from shells of black tiger shrimp.

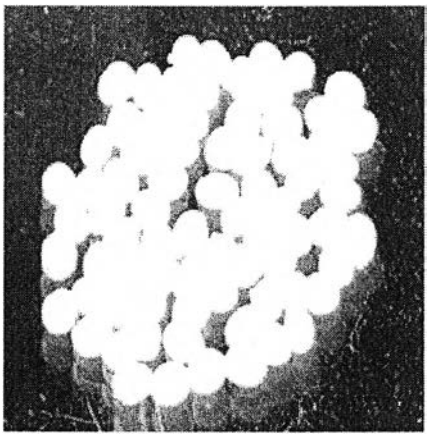


Figure 3.2 Chitosan beads from shells of black tiger shrimp

3.2.1.3. Modified chemical chitosan beads

Two modified chemical chitosan were used in the first group of adsorbent as follows:

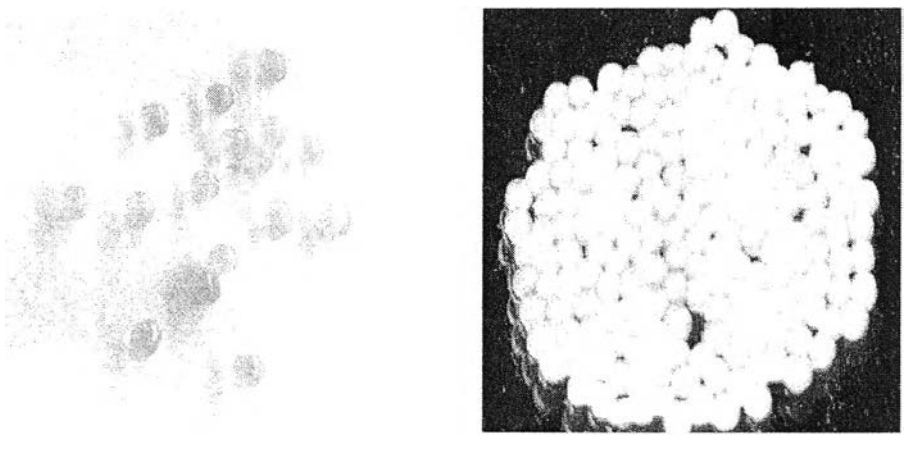
a) Crosslinking chitosan with glutaraldehyde beads

To crosslink amino groups of chitosan, 1 g of chitosan beads were soaked in 15 cm^3 0.05 % v/v of glutaraldehyde solution. The mixture was stirred by a magnetic stirrer at 100 rpm for 12 h at room temperature. The beads was washed using deionized water for 3 times to eliminate the excess glutaraldehy. The crosslinking chitosan with glutaraldehyde beads were stored in deionized water for further use (see Figure 3.3 a).

b) Blended chitosan/polyvinyl alcohol beads ratio 1:1

4.0 g of powder polyvinyl alcohol was dissolved in 100 cm^3 of deionized water at 500 rpm, 70 ^{0} C with a contact time of 4 h. The solution was released at room temperature and then 200 cm^3 of chitosan solution was blended with 100 cm^3 of polyvinyl alcohol solution. These mixtures were stirred by magnetic stirrer at 500 rpm, 70 ^{0} C and contact time of 6 h. The blended solution was released at room

temperature. The solution was then dropped into 300 cm^3 of a 1 M NaOH solution to form hydrogel beads through a needle (Ø 1.2 mm.) by a peristaltic pump. The hydrogel beads were allowed to sink in the NaOH solution 12 h for hardening. The hydrogel beads were then washed by deionized water several times until the solution pH became the same as that of the fresh deionized water. The blended chitosan/polyvinyl alcohol beads ratio 1:1 were stored in deionized water for further use (see Figure 3.3b).



(a) (b)

Figure 3.3 Adsorbent beads

(a) crosslinking chitosan with glutaraldehyde beads and

(b) blended chitosan/polyvinyl alcohol beads ratio 1:1

3.2.2. Preparation adsorbents from chitosan of Sea Fresh CO., LTD.

3.2.2.1. Preparation chitosan beads

1.2 g of chitosan flake was dissolved into 100 cm^3 of 2 % v/v aqueous acetic acid solution. The mixture was mixed by motor stirrer (IKA Labortechnik model RW 20.n, Malaysia) at room temperature and 300 rpm for 24 h. The solution was clear yellow colour and had viscosity. The solution was then dropped into 300 cm^3 of a 1 M NaOH solution to form hydrogel beads through a needle (Ø 1.2 mm.) by a peristaltic pump. The hydrogel beads were allowed to sink in the NaOH solution for 12 h for

hardening. The hydrogel beads had a white colour. The hydrogel beads were then washed by deionized water several times until pH of the solution became the same as that of the fresh deionized water. The chitosan beads were stored in deionized water for further use (see Figure 3.4a).

In addition, effect of the amount of chitosan in chitosan beads was also investigated in this study. The 1.7 g, 2.0 g and 2.2 g of chitosan flake were prepared following the above method. Figure 3.4 b, c and d show chitosan beads prepared from chitosan solution 1.7 g, 2.0 g and 2.2 g, respectively.

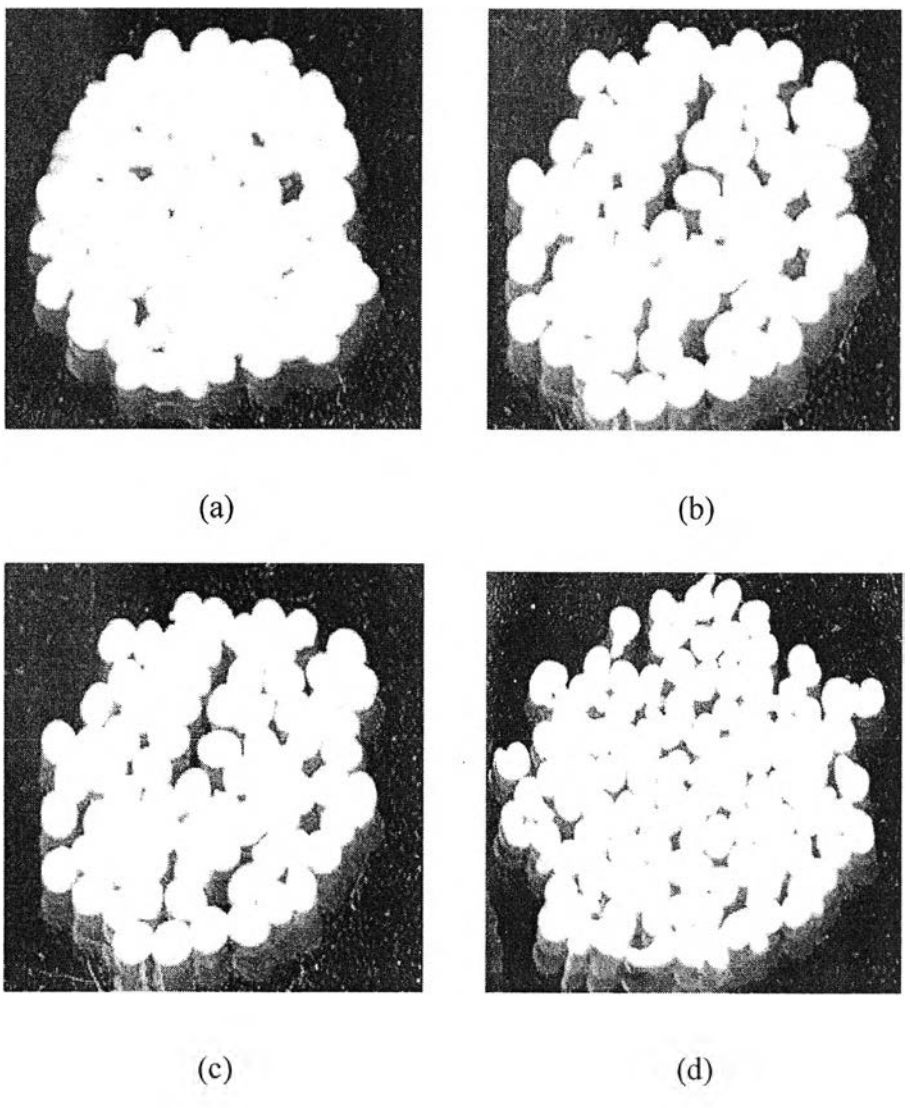


Figure 3.4 Morphological of chitosan beads prepared from chitosan solution (a) 1.2 g, (b) 1.7 g, (c) 2.0 g and (d) 2.2 g

3.2.2.2. Modified chemical chitosan beads

Seven modified chemical chitosan beads were prepared and investigated in this study. The details of each preparation were summarized below;

a). Crosslinking chitosan with glutaraldehyde beads

0.1 % v/v of glutaraldehyde solution was prepared from 25 % v/v concentrated glutaraldehyde solution. The ratio of chitosan to glutaraldehyde solution was 1 g of chitosan beads to 15 cm^3 of glutaraldehyde solution. This method was done at room temperature with a magnetic stirrer at 100 rpm and contact time of 12 h. After that deionized water was used to wash the excess glutaraldehy. Finally, the crosslinking chitosan with glutaraldehyde beads were stored in deionized water for further use.

In order to investigate the effects of glutaraldehyde concentration, the crosslinking of chitosan with the variation of glutaraldehyde concentration between 0.5 and 2.5 % v/v were also studied.

b). Blended chitosan/polyvinyl alcohol beads ratio 1:1

4.0 g of powder polyvinyl alcohol were dissolved in 100 cm^3 of deionized at 500 rpm, 70 ^{0} C with a contact time of 4 h. The solution was released at room temperature and then 200 cm^3 of chitosan solution was blended with 100 cm^3 of polyvinyl alcohol solution. These mixtures were stirred by magnetic stirrer at 500 rpm, 70 ^{0} C and contact time of 6 h. The blended solution was released at room temperature. It appeared clear yellow solution and had little viscosity. The solution was then dropped into 300 cm^3 of a 1 M NaOH solution to form hydrogel beads through a needle (Ø 1.2 mm.) by a peristaltic pump. The hydrogel beads were allowed to sink in the NaOH solution 12 h for hardening. The hydrogel beads were then washed by deionized water several times until pH of the solution became the same as that of the fresh deionized water. The blended chitosan/polyvinyl alcohol beads ratio

1:1 were stored in deionized water for further use. Figure 3.5 shows blended chitosan/polyvinyl alcohol beads ratio 1:1.

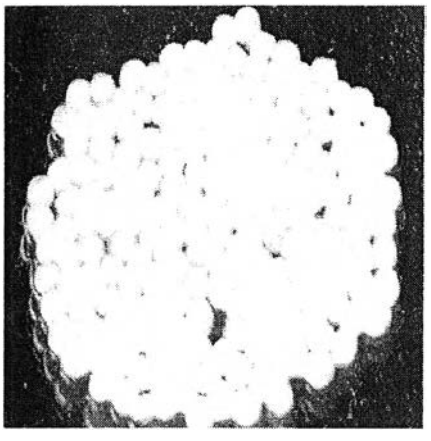


Figure 3.5 Blended chitosan/polyvinyl alcohol beads ratio 1:1

c). Blended chitosan/polyvinyl alcohol beads ratio 1:2

To study the effect of the amount of polyvinyl alcohol, 8 g of powder polyvinyl alcohol were dissolved in 100 cm^3 of deionized at 500 rpm, 70 ^{0} C with a contact time of 4 h. The solution was released at room temperature. Then 200 cm^3 of chitosan solution was blended with 100 cm^3 of polyvinyl alcohol solution. These mixtures were stirred by magnetic stirrer at 500 rpm, 70 ^{0} C with a contact time of 6 h. The blended solution was released at room temperature. After that, the solution was dropped into 300 cm^3 of 1 M NaOH solution to form hydrogel beads through a needle (Ø 1.2 mm.) by a peristaltic pump. The hydrogel beads were allowed to sink in the NaOH solution 12 h for hardening. The hydrogel beads were then washed by deionized water several times until pH of the solution became the same as that of the fresh deionized water. Finally, the blended chitosan/polyvinyl alcohol beads ratio 1:2 were stored in deionized water for further use. Figure 3.6 shows blended chitosan/polyvinyl alcohol beads ratio 1:2.

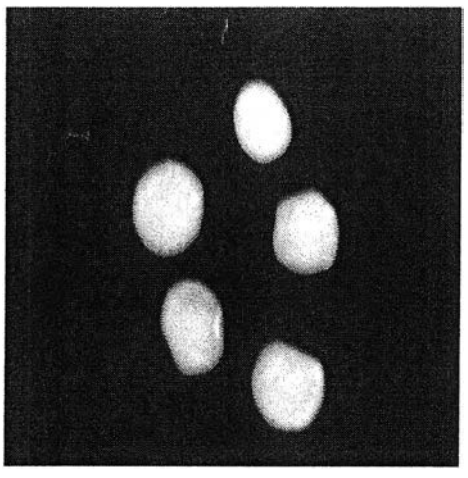


Figure 3.6 Blended chitosan/polyvinyl alcohol beads ratio 1:2

d). Crosslinking blended chitosan/polyvinyl alcohol 1:1 and 1:2 with glutaraldehyde beads

1.5 % v/v of glutaraldehyde solution were prepared from 25 % v/v concentrated glutaraldehyde solution. Then mixed 1 g of blended chitosan/polyvinyl alcohol ratio1:1 beads into 15 cm^3 of glutaraldehyde solution. This method was done at room temperature with a magnetic stirrer 100 rpm for 12 h. After that deionized water was used to wash the excess glutaraldehyde. Finally, the crosslinking blended chitosan/polyvinyl alcohol ratio 1:1 with glutaraldehyde beads were stored in deionized water for further use.

e). Crosslinking blended chitosan/polyvinyl alcohol 1:2 with glutaraldehyde beads

The crosslinking of blended chitosan/polyvinyl alcohol ratio 1:2 with glutaraldehyde concentration of 1.5 % v/v was also prepared using above method (e).

f). Quateramminated chitosan beads

The quateramminated chitosan beads were prepared by dropping 100 cm^3 of chitosan solution into 300 cm^3 of 8.0 % w/v sodium tripoly phosphate solution (TPP) through a needle (Ø 1.2 mm.) by a peristaltic pump and the gelled spheres formed instantaneously. The formed chitosan beads remained in TPP solution for 12 h. The

beads were washed with deionized water several times and then 500 cm^3 of beads were crosslinked with 5.0 % v/v of ethylene glycol diglycidyl ether (EGDE) for 12 h in a water-ethanol mixing solution. The crosslinked chitosan beads were washed with deionized water repeatedly. The quatermary ammonium group of beads prepared from 500 cm^3 of the crosslinked beads were modified with 94 g of 3-chloro-2-hydroxypropyltrimethylammonium chloride in 500 cm^3 dioxane at 70 ^{0} C for 3 h to obtain quateramminated chitosan beads. The quatermary ammonium modified chitosan beads were rinsed with acetone and deionized water to eliminate residue reagents. The quateramminated chitosan beads were stored in deionized water for further use. Figure 3.7 shows quateramminated chitosan beads.

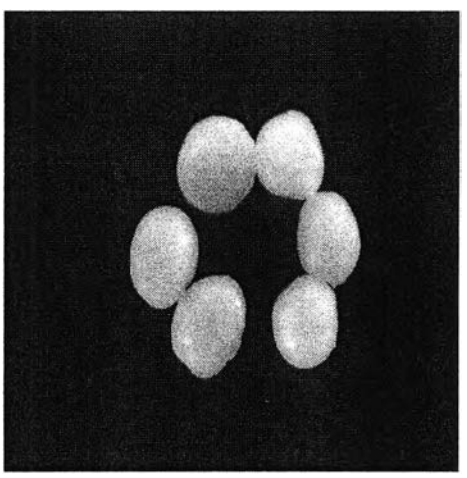


Figure 3.7 Quateramminated chitosan beads

g). Benzoyl chitosan beads

The benzoyl chitosan beads were prepared by dropping 100 cm^3 of chitosan solution into 300 cm^3 of 8.0 % w/v sodium tripoly phosphate solution (TPP) through a needle (Ø 1.2 mm.) by a peristaltic pump and the gelled spheres formed instantaneously. The formed chitosan beads remained in TPP solution for 12 h. The beads were washed with deionized water 2 to 3 times. 500 cm^3 of beads were then crosslinked with 5.0 % v/v of ethylene glycol diglycidyl ether (EGDE) for 12 h in a water-ethanol mixing solution. 500 cm^3 of crosslinked beads were modified with 55 g

of benzoic anhydride in 500 cm^3 of ethanol at room temperature for 12 h to obtain benzoyl chitosan beads. The benzoyl modified chitosan beads were rinsed with acetone and deionized water to eliminate residue reagents. The benzoyl chitosan beads were stored in deionized water for further use. Figure 3.8 shows benzoyl chitosan beads.

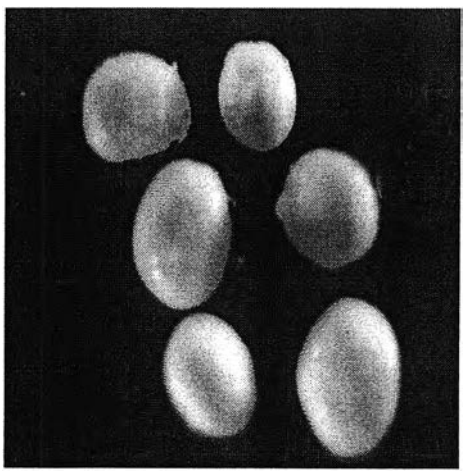


Figure 3.8 Benzoyl chitosan beads

3.2.3. Modified surfactant chitosan

Six modified surfactant chitosan were used in this research as follows:

3.2.3.1. Modified chitosan sodium lauryl sulfate

2.0 g of chitosan flake were dissolved into 100 cm^3 of 2 % v/v aqueous acetic acid solution. The chitosan and solvent were mixed by motor stirrer at room temperature and 300 rpm for 24 h to form a chitosan solution. A 20 critical micelle concentration (cmc) of sodium lauryl sulfate was prepared from about 5.0 g of sodium lauryl sulfate dissolved in 100 cm^3 of deionized water.

The modified chitosan sodium lauryl sulfate fibers were prepared from injection 20.0 cm^3 of sodium lauryl sulfate solution passing syringe and needle (Ø 1.2 mm.) into 100 cm^3 of chitosan solution. The mixture was stirred for 10 min at room temperature and 150 rpm by motor stirrer to form fibers. The fibers were washed by deionized water several times to eliminate sodium lauryl sulfate and acetic acid. The

modified chitosan sodium lauryl sulfate fibers were stored in deionized water for further use. Figure 3.9 shows modified chitosan sodium lauryl sulfate fibers.

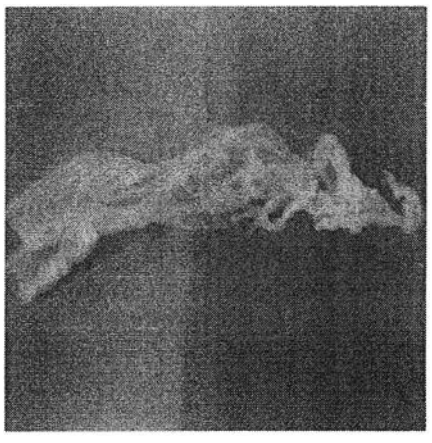


Figure 3.9 Modified chitosan sodium lauryl sulfate fiber

3.2.3.2. Modified blended chitosan/PVA sodium lauryl sulfate

2.0 g of chitosan flake were dissolved in 100 cm^3 of 2 % v/v aqueous acetic acid solution. The mixture was mixed by motor stirrer at room temperature and 300 rpm for 24 h to form a chitosan solution. 4.0 g of polyvinyl alcohol powder (PVA) were dissolved in deionized water. A magnetic stirrer was used at 70 ^0C and 500 rpm for 6 h to form a polyvinyl alcohol solution. The blended chitosan/PVA was prepared by a mixture of 200 cm^3 of chitosan solution and 100 cm^3 of PVA solution. The mixture was blended by magnetic stirrer at 70 ^0C and 500 rpm for 6 h to form blended chitosan/PVA solution. A 20 cmc of sodium lauryl sulfate was prepared from 5.0 g of sodium lauryl sulfate dissolved in 100 cm^3 of deionized water.

The modified blended chitosan/PVA sodium lauryl sulfate fibers were prepared from injection 20.0 cm^3 of sodium lauryl sulfate solution passing syringe and needle (Ø 1.2 mm.) into 100 cm^3 of blended chitosan/PVA solution. The mixing was stirred for 10 min at room temperature and 150 rpm by motor stirrer to form fibers. The fibers were washed by deionized water several times to eliminate sodium lauryl sulfate and acetic acid. The modified blended chitosan/PVA fibers were stored in

deionized water for further use. Figure 3.10 shows modified blended chitosan/PVA sodium lauryl sulfate fibers.

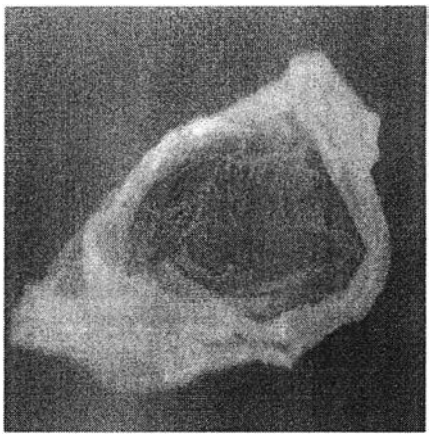


Figure 3.10 Modified blended chitosan/PVA sodium lauryl sulfate fibers

3.2.3.3. Modified chitosan hexadecyl trimethyl ammonium bromide

2.0 g of chitosan flake were dissolved in 100 cm^3 of 2 % v/v aqueous acetic acid solution. The mixture was mixed by motor stirrer at room temperature and 300 rpm for 24 h to form a chitosan solution. A 20 cmc of hexadecyl trimethyl ammonium bromide solution was prepared from 0.704 g of hexadecyl trimethyl ammonium bromide dissolved in 100 cm^3 of deionized water.

The modified chitosan hexadecyl trimethyl ammonium bromide beads were prepared from mixture 20.0 cm^3 of hexadecyl trimethyl ammonium bromide solution into 100 cm^3 of chitosan solution. The mixture was stirred for 6 h at room temperature and 300 rpm by motor stirrer to form chitosan hexadecyl trimethyl ammonium bromide solution. This solution was dropped into a 300 cm^3 of 1 M NaOH solution to form hydrogel beads through a needle (Ø 1.2 mm.) by a peristaltic pump. The hydrogel beads were allowed to sink in the NaOH solution 12 h for hardening. The hydrogel beads were washed by deionized water several times until pH of the solution became the same as that of the fresh deionized water. The modified chitosan hexadecyl trimethyl ammonium bromide beads were stored in deionized water for

further use. Figure 3.11 shows modified chitosan hexadecyl trimethyl ammonium bromide beads.

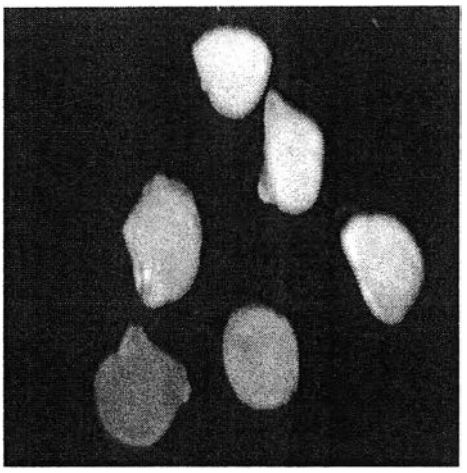


Figure 3.11 Modified chitosan hexadecyl trimethyl ammonium bromide beads

3.2.3.4. Modified blended chitosan/PVA hexadecyl trimethyl ammonium bromide

2.0 g of chitosan flake were dissolved into 100 cm^3 of 2 % v/v aqueous acetic acid solution. The mixture was mixed by motor stirrer at room temperature and 300 rpm for 24 h to form a chitosan solution. 4.0 g of polyvinyl alcohol were dissolved in deionized water. A magnetic stirrer was used at 70 ^{0} C and 500 rpm for 4 h to form polyvinyl alcohol solution. The blended chitosan/PVA was prepared by a mixture of 200 cm^3 of chitosan solution and 100 cm^3 of PVA solution. The mixture was blended by magnetic stirrer at 70 ^{0} C and 500 rpm for 6 h to form blended chitosan/PVA solution. A 20 cmc of hexadecyl trimethyl ammonium bromide was prepared from about 0.704 g of hexadecyl trimethyl ammonium bromide dissolved in 100 cm^3 of deionized water.

The modified blended chitosan/PVA hexadecyl trimethyl ammonium bromide beads were prepared from a mixture of 20.0 cm^3 of hexadecyl trimethyl ammonium bromide solution into 100 cm^3 of blended chitosan/PVA solution. The mixture was stirred for 6 h at room temperature and 300 rpm by motor stirrer to form blended

chitosan/PVA hexadecyl trimethyl ammonium bromide solution. The solution was dropped into 300 cm^3 of 1 M NaOH solution to form hydrogel beads through a needle (Ø 1.2 mm.) by a peristaltic pump. The hydrogel beads were allowed to sink in the NaOH solution for 12 h for hardening. The hydrogel beads were washed by deionized water several times until pH of the solution became the same as that of the fresh deionized water. The modified blended chitosan/PVA hexadecyl trimethyl ammonium bromide beads were stored in deionized water for further use. Figure 3.12 shows modified blended chitosan/PVA hexadecyl trimethyl ammonium bromide beads.

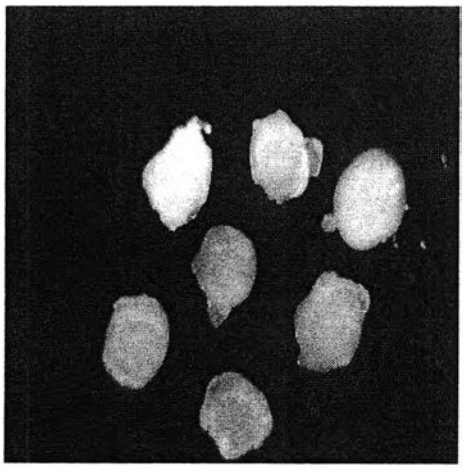


Figure 3.12 Modified blended chitosan/PVA hexadecyl trimethyl ammonium bromide beads

3.2.3.5. Modified chitosan polyoxyethylene sorbetanmonooleate

2.0 g of chitosan flake were dissolved into 100 cm^3 of 2 % v/v aqueous acetic acid solution. The mixture was mixed by motor stirrer at room temperature and 300 rpm for 24 h to form a chitosan solution. A 20 critical micelle concentration (cmc) of polyoxyethylene sorbetanmonooleate solution was prepared from 0.033 g of polyoxyethylene sorbetanmonooleate dissolved in 100 cm^3 of deionized water.

The modified chitosan polyoxyethylene sorbetanmonooleate beads were prepared from a mixture 20.0 cm^3 of polyoxyethylene sorbetanmonooleate solution into 100 cm^3 of chitosan solution. The mixture was stirred for 6 h at room temperature

and 300 rpm by motor stirrer to form chitosan polyoxyethylene sorbetanmonooleate solution. The solution was dropped into 300 cm^3 of 1 M NaOH solution to form hydrogel beads through a needle (Ø 1.2 mm.) by a peristaltic pump. The hydrogel beads were allowed to sink in the NaOH solution 12 h for hardening. The hydrogel beads were then washed by deionized water several times until pH of the solution became the same as that of the fresh deionized water. The modified chitosan polyoxyethylene sorbetanmonooleate beads were stored in deionized water for further use. Figure 3.13 shows modified chitosan polyoxyethylene sorbetanmonooleate beads.

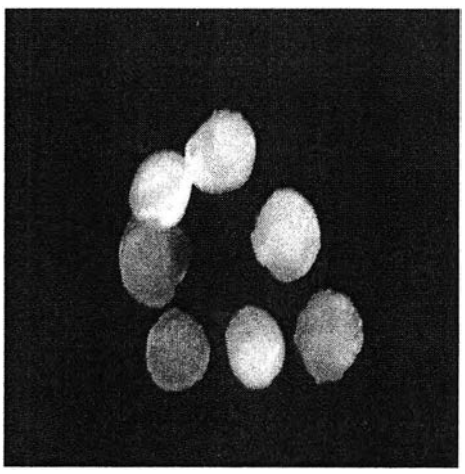


Figure 3.13 Modified chitosan polyoxyethylene sorbetanmonooleate beads

3.2.3.6. Modified blended chitosan/PVA polyoxythylene sorbetanmonooleate

2.0 g of chitosan flake were dissolved into 100 cm^3 of 2 % v/v aqueous acetic acid solution. The mixture was mixed by motor stirrer at room temperature and 300 rpm for 24 h to form a chitosan solution. 4.0 g of polyvinyl alcohol was dissolved deionized water. A magnetic stirrer was used at 70 ^{0} C and 500 rpm for 4 h to form polyvinyl alcohol solution. The blended chitosan/PVA was prepared by a mixture of 200 cm^3 of chitosan solution and 100 cm^3 of PVA solution. The mixtures were blended by magnetic stirrer at 70 ^{0} C and 500 rpm for 6 h to form blended chitosan/PVA solution. A 20 cmc of polyoxyethylene sorbetanmonooleate was

prepared from about 0.033 g of polyoxyethylene sorbetanmonooleate dissolved in 100 cm^3 of deionized water.

The modified blended chitosan/PVA polyoxyethylene sorbetanmonooleate beads were prepared from a mixture of 20.0 cm^3 of polyoxyethylene sorbetanmonooleate solution into 100 cm^3 of blended chitosan/PVA solution. The mixture was stirred for 6 h at room temperature and 300 rpm by motor stirrer to form blended chitosan/PVA polyoxyethylene sorbetanmonooleate solution. The solution was dropped into 300 cm^3 of 1 M NaOH solution to form hydrogel beads through a needle (Ø 1.2 mm.) by a peristaltic pump. The hydrogel beads were allowed to sink in the NaOH solution 12 h for hardening. The hydrogel beads were washed by deionized water several times until pH of the solution became the same as that of the fresh deionized water. The modified blended chitosan/PVA polyoxyethylene sorbetanmonooleate beads were stored in deionized water for further use. Figure 3.14 shows modified blended chitosan/PVA polyoxyethylene sorbetanmonooleate beads.

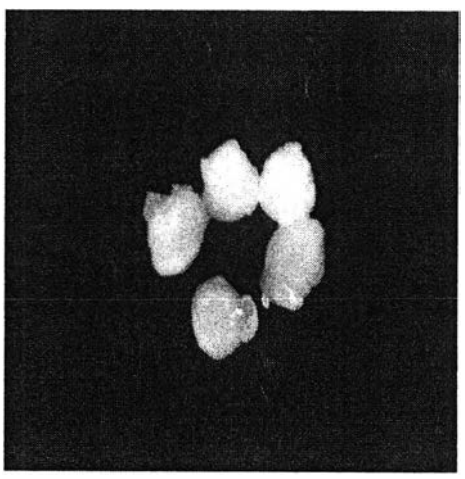


Figure 3.14 Modified blended chitosan/PVA polyoxyethylene sorbetanmonooleate beads

3.3. Research methodology

3.3.1 Cutting fluids adsorption studies

3.3.1.1 Batch adsorption

30 g of commercial cutting fluids were loaded in 1000 cm^3 of deionized water. The emulsions were stirred at 600 to 2000 rpm by motor stirrer for 10 min at room temperature and stirred by blender for 3 min at room temperature at 21000 rpm. The range of initial concentration of cutting fluids was chosen between 0.1 – 3.0 % w/v for these experiments. The pH values of emulsion were adjusted to a range of pH 3 to 11 with 0.1 M HCl and 0.1 M NaOH. A certain amount of adsorbents was taken and placed on filter paper for a few minutes to remove the surface water. The 0.1 to 6.0 g weight of adsorbents were used.

The emulsions and beads were shaken using an orbital shaker (PNP model OS 3) at 120 rpm and room temperature. After equilibrium, the samples were taken to determine the residual cutting fluids in the emulsion. The cutting fluids concentration in the samples were analyzed using a visible spectrophotometer (WTW, model Photo Lab Spektral, Germany) at wavelength 395 nm. The percent removal of cutting fluids was calculated according to:

$$Percent\ removal = \frac{C_0 - C_e}{C_0} \times 100 \qquad (3.1)$$

The adsorption capacity was calculated according to:

$$q_e = \frac{(C_0 - C_e)V}{m} \qquad (3.2)$$

where q_e is the adsorption capacity (mg/g), C_o is the initial cutting fluid concentration (mg/l), C_e is the final or equilibrium synthetic cutting fluid concentration (mg/l), V is the volume of wastewater (l) and m is the weight of adsorbents (g).

To study the ionic strength effect, sodium chloride, sodium sulfate, calcium chloride, calcium sulfate, iron (III) nitrate and iron (II) sulfate concentration were varied from 0.01 to 0.05 M. The effect of salts on adsorption was tested in terms of time to reach maximum adsorption capacity. The temperature range of adsorption was studied from 33 to 48 ^{0} C. The result of temperature can be used to calculate enthalpy (ΔH), entropy (ΔS), Gibbs free energy (ΔG) and activation energy (E_a) of the adsorption.

3.3.1.2. Continuous adsorption

10 g of commercial cutting fluids were loaded in 1000 cm^3 of deionized water. The emulsions were stirred by motor stirrer at room temperature for 10 min. The pH values of emulsion were adjusted to pH 3 using 0.1 M HCl. A certain amount of adsorbents was taken and placed on filter paper for a few minutes to remove the surface water. For this investigation, two arrangements, i.e. single column and two columns were set in order to compare the percent removal of cutting fluids. The details of each arrangement were summarized below;

- **The single column**

The single column studies were conducted in a 25 mm diameter, 200 mm long column. 100 g of chitosan beads were placed in the single column at height 180 mm (free board about 20 mm). A 30 mm thick plastic lid was placed on the top of the chitosan beads. Figure 3.15 shows single column for adsorption cutting fluids continuous mode. The cutting fluids was kept in a feed tank where they were continuously mixed using a motor stirrer at 400 rpm to maintain homogeneity of the cutting fluids being fed. From this feed tank, the cutting fluids was pumped and fed into the column at a flow rate of 0.5 cm^3/min in up-flow mode using a peristaltic

pump. The percent removal of cutting fluids was calculated according to Equation 3.1.

The experiment of other adsorbents including blended chitosan/PVA ratio 1:1, quateramminated chitosan, benzoyl chitosan, modified chitosan hexadecyl trimethyl ammonium bromide, modified blended chitosan/PVA hexadecyl trimethyl ammonium bromide, modified chitosan polyoxyethylene sorbetanmonooleate and modified blended chitosan/PVA polyoxyethylene sorbetanmonooleate were also carried out using the above method.

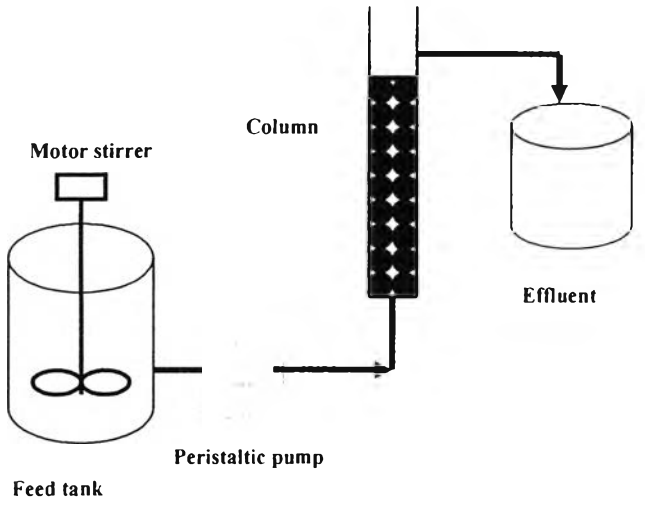


Figure 3.15 Single column

- **Two columns**

Two column studies were conducted in a 25 mm diameter, 200 mm long column. 50 g of chitosan beads were placed in each column at a height 100 mm (free board about 100 mm). A 30 mm thick plastic lid was placed on the top of the chitosan beads. Figure 3.16 shows a two column for adsorption cutting fluids continuous mode. The cutting fluids was kept in a feed tank where it was continuously mixed by using a motor stirrer at 400 rpm to maintain homogeneity of the cutting fluids being fed. From this feed tank, the cutting fluids was pumped and fed into the column at a flow rate of

0.5 cm^3/min in up-flow mode using a peristaltic pump. The percent removal of cutting fluids was calculated according to Equation 3.1.

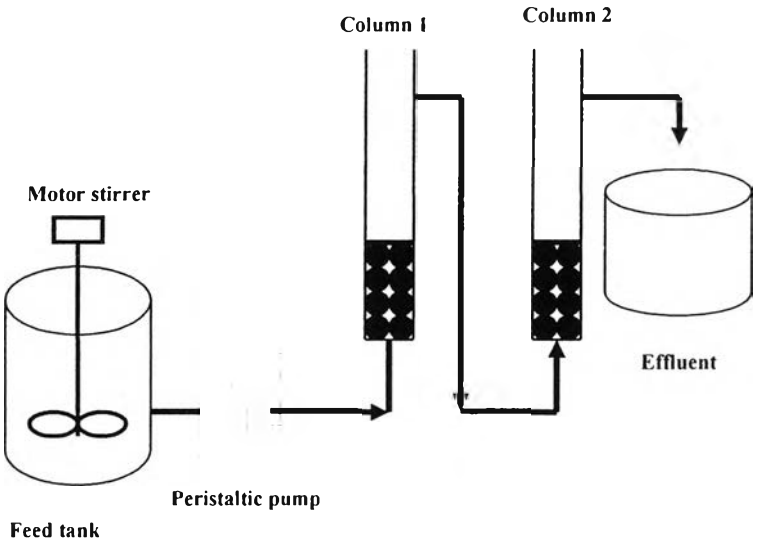


Figure 3.16 Two columns

3.3.2 Measurement of the swelling of adsorbents

The adsorbents were laid on filter paper number 1 to remove water at the surface of adsorbents. One gram of adsorbents was weighed by electronic balance on a watch glass. Deionized water of about 3 to 5 cm^3 were added into a watch glass. After that the adsorbents were laid out for about 12 h and then screened. The adsorbents were weighed by electronic balance. The swelling of adsorbents was calculated as followed.

$$S = \frac{W_1 - W_2}{W_2} \times 100 \qquad (3.3)$$

where S is the percent swelling of adsorbent, W_1 is an initial weight of adsorbent and W_2 is the weight of adsorbent after soaking in deionized water (g).

3.3.3. Measurement of the moisture content of adsorbents

The watch glass was incubated in an oven at 105 ^{0}C for 1 h and then cool down in a desiccator. After that the watch glass was weighed by electronic balance. The

adsorbents were laid on filter paper No. 1 to remove water at the surface of adsorbents. After that, 1 g of adsorbents was measured and put on a watch glass. They were then incubated at 50 ^{0} C for 3 to 5 h and cool down in a desiccator. Finally, the moisture content of adsorbents was calculated by:

$$H = \frac{M_1 - M_2}{M_1} \times 100 \qquad (3.4)$$

where H is the moisture of adsorbent, M_1 is weight of adsorbent before incubated (g) and M_2 is the weight of adsorbent after incubated (g).

3.3.4. Surface area and pore diameter measurement

100 cm^3 of chitosan beads were taken in filter paper number 1 to remove water at the surface of adsorbents and then laid on stainless steel tray. The chitosan beads were frozen by the Ultra Cold Freezer model CTL 407 (CTL company, Spain) at temperature -20 ^{0}C for about 12 h, after that dried at temperature -40 ^{0} C at pressure 1 mm bar by freezer dryer model Lyo Alfa 6 (Telstar company, Spain) for about 6 h. The frozen chitosan beads were stored in a dry bottle cover with a plastic lid and kept in desiccator.

0.1 g of frozen chitosan beads was weighed in a bulb by electronic balance. The BET surface and pore diameter were measured using N_2 adsorption isotherms with Belsorp mini, (Japan) and preheated at 120 ^{0} C for 6 h with Belprep flow, (Japan).

The measurement of other adsorbents included blended chitosan/PVA ratio 1:1, blended chitosan/PVA ratio 1:2, quateramminated chitosan, benzoyl chitosan, modified chitosan hexadecyl trimethyl ammonium bromide, modified blended chitosan/PVA hexadecyl trimethyl ammonium bromide, modified chitosan polyoxyethylene sorbetanmonooleate and modified blended chitosan/PVA polyoxyethylene sorbetanmonooleate were also carried out using the above method.

3.3.5. Contact angle measurement

100 cm^3 of chitosan solution were taken in a beaker. Glass plates were cleaned by acetone and immersed in chitosan solution. The chitosan solution attached on the surface of glass plate and was immersed in 1 M NaOH. Up to this point, the hydrogel was formed. The hydrogel was washed by deionized water several times until pH of the solution became the same as that of the fresh deionized water.

Contact angle was determined using a FTA 200 contact angle instrument. SCA 20 for OCA 15 plus (Germany) and PCA were used to process the data. Contact angle was measured by the sessile drop method using cutting fluid. Each contact angle was reported with the mean value of seven measurements taken at different positions on the glass coated with all adsorbents.

The measurement of other adsorbents included blended chitosan/PVA ratio 1:1, blended chitosan/PVA ratio 1:2, quateramminated chitosan, benzoyl chitosan, modified chitosan hexadecyl trimethyl ammonium bromide, modified blended chitosan/PVA hexadecyl trimethyl ammonium bromide, modified chitosan polyoxyethylene sorbetanmonooleate and modified blended chitosan/PVA polyoxyethylene sorbetanmonooleate were also carried out using the above method.

The modified chitosan sodium lauryl sulfate and modified blended chitosan/PVA sodium lauryl sulfate were prepared in fibers form and fixed on the surface of a glass plate for measuring contact angle.

3.3.6. Zeta potential measurement

0.2 g of dried chitosan beads was grounded into powder and poured into 200 cm^3 of deionized water. The mixture was stirred at 300 rpm for 24 h and then filtrated through filter paper No 1. The supernatant was used for zeta potential measurement.

The measurement of other adsorbents included blended chitosan/PVA ratio 1:1, blended chitosan/PVA ratio 1:2, quateramminated chitosan, benzoyl chitosan, modified chitosan hexadecyl trimethyl ammonium bromide, modified blended chitosan/PVA hexadecyl trimethyl ammonium bromide, modified chitosan polyoxyethylene sorbetanmonooleate and modified blended chitosan/PVA polyoxyethylene sorbetanmonooleate were also carried out using the above method.

For zeta potential measurement of cutting fluids, 0.01 g of cutting fluids was suspended in 200 cm^3 of deionized water. The emulsion was stirred by motor stirrer at room temperature and 1200 rpm for 10 min. The setting time of emulsion was 30 min. The pH of all adsorbents and synthetic cutting fluids were adjusted with 0.1 M HCl or 0.1 M NaOH solutions to the desired level. A Malvern Zetasizer 3000 HSa (Malvern corp., England) was used to determine the zeta potentials.

3.3.7. Fourier Transform Infra-Red spectroscopy (FT-IR)

Functional groups of chitosan adsorbent were analyzed using FT-IR spectra. 3 g of dried chitosan adsorbent were grounded into powder and mixed with 100 mg of KBr in an agate mortar. The mixture was then pressed to form a tablet. Spectra was analyzed using FT-IR (Perkin-Elmer model 2000, (USA)). The spectrum of an empty cell was used as the background. IR spectra in the range 4000 to 400 cm^{-1} were scanned in Spectrum to process the data. An average of 10 scans was made for each chitosan sample at a resolution of 4 cm^{-1}.

The other adsorbents included blended chitosan/PVA ratio 1:1, quateramminated chitosan, benzoyl chitosan, modified chitosan hexadecyl trimethyl ammonium bromide, modified blended chitosan/PVA hexadecyl trimethyl ammonium bromide, modified chitosan polyoxyethylene sorbetanmonooleate and modified blended

chitosan/PVA polyoxyethylene sorbetanmonooleate were also analyzed using the same method, s mentioned above.

3.3.8. Heating value measurement

Bomb calorimeter was used to measure the heating value of adsorbents before and after adsorption cutting fluids of chitosan beads. The Parr model 1341 oxygen bomb calorimeter (Parr Instrument Company (USA)) was used to determine heat of combustion of each adsorbent. The sample was weighed about 1 g in a small cup using electronic balance and then the fuse wire with a length of about 10 cm was fixed onto two electrodes. 1 cm^3 of deionized water was added to the bomb calorimeter. The bomb calorimeter was then closed by a stainless steel lid. Oxygen gas was flowed to bomb calorimeter until the pressure reached 30 atm. Deionized water was added to a vessel of the equipment. The bomb calorimeter was then placed to the vessel and then connected to the electroignition and stirrer. The temperature of the deionized water was recorded until it reached a constant. The stirrer was closed and bomb calorimeter was taken out from the vessel. The pressure in the bomb calorimeter was released slowly. Inner part of the bomb calorimeter was washed by methyl orange. The solution was titrated by sodium carbonate solution. The volume of sodium carbonate solution and length of fuse wire were record. The value of heat of combustion was calculated based on the gross heat of combustion according to

$$H_g = \frac{TW - e_1 - e_2 - e_3}{M} \qquad (3.5)$$

where H_g is the gross heat of combustion (J/g), T is the net corrected temperature rise (K), W is an energy equivalent of calorimeter (J/K), e_1 is a correction in calories for heat of formation of nitric acid (J), e_2 is a correction in calories for heat of formation

of sulfuric acid (J), e_3 is a correction in calories for heat of formation of fuse wire (J) and M is a weight of sample (g).

Heat of combustion of the others adsorbents including blended chitosan/PVA ratio 1:1, quateramminated chitosan, benzoyl chitosan, modified chitosan hexadecyl trimethyl ammonium bromide, modified blended chitosan/PVA hexadecyl trimethyl ammonium bromide, modified chitosan polyoxyethylene sorbetanmonooleate and modified blended chitosan/PVA polyoxyethylene sorbetanmonooleate were also determined, as mentioned above.

3.3.9. CHN measurement

CHN of 0.1 g of dried chitosan before and after adsorption of cutting fluid was analyzed using Leco CHN 2000 (USA).

The other adsorbents including blended chitosan/PVA ratio 1:1, quateramminated chitosan, benzoyl chitosan, modified chitosan hexadecyl trimethyl ammonium bromide, modified blended chitosan/PVA hexadecyl trimethyl ammonium bromide, modified chitosan polyoxyethylene sorbetanmonooleate and modified blended chitosan/PVA polyoxyethylene sorbetanmonooleate were also determined, as mentioned above.

3.3.10. Scanning electron microscope (SEM)

The chitosan beads were dried at ambient atmosphere. Three specimens of chitosan beads were fixed on the stub brass and then coated with a conductive layer (400 Å) of sputtered gold. The surface of chitosan beads before and after adsorption of cutting fluids was analyzed using a scanning electron microscope (SEM, JEOL, Model JSM-5410 LV, Japan) to investigate the surface at 15 kV.

Surface of other adsorbents included blended chitosan/PVA ratio 1:1, quateramminated chitosan, benzoyl chitosan, CH-SDS and BCH-SDS were also determined using SEM, as mentioned above.