CHAPTER III

EXPERIMENTAL

3.1 Chemicals

3.1.1 Acrylamide, AM from Siam Chemical & Industry Co., Ltd.

C_3H_5NO, colorless solid

$MW = 71.08\ g\ mol^{-1}$

3.1.2 Acrylic acid, AA from Fluka (Buchs, Switzerland)

$C_3H_4O_2$, liquid

$MW = 72.06\ g\ mol^{-1}$

3.1.3 *N, N'*-Methylenebisacrylamide, N-MBA analytical grade from Fluka (Buchs, Switzerland)

$C_7H_{10}N_2O_2$, solid

$MW = 154.17\ g\ mol^{-1}$

3.1.4 Amonium Persulphate, APS analytical grade from Merck (Hohenburnn, Germany)

$(NH_4)_2S_2O_8$, solid

$MW = 228.20\ g\ mol^{-1}$

3.1.5 *N, N, N', N'*- Tetramethylethylenediamine, TEMED analytical grade from Fluka (Buchs, Switzerland)

$C_6H_{16}N_2$, liquid

$MW = 116.21\ g\ mol^{-1}$

3.1.6 Aluminium sulphate, analytical grade from Ajax (Seven Hills, Australia)

$Al_2(SO_4)_{3.}18H_2O$, solid

MW = 666.45 g mol^{-1}

3.1.7 Sodium carbonate, analytical grade from Ajax (Seven Hills, Australia)

Na_2CO_3, solid

MW = 105.99 g mol^{-1}

3.1.8 Acetone, BDH (Bangkok, Thailand)

$C_3H_6O_2$, liquid

MW = 58.08 g mol^{-1}

3.1.9 Potassium bromide, analytical grade from Ajax (Seven Hills, Australia)

KBr, solid

MW = 119.01 g mol^{-1}

3.1.10 Hydrochloric acid, analytical grade from Fluka (Buchs, Switzerland)

HCl, liquid

MW = 36.46 g mol^{-1}

3.1.11 Nitric acid, analytical grade from Fluka (Buchs, Switzerland)

HNO_3, liquid

MW = 63.01 g mol^{-1}

3.1.12 Hydrofluoric acid, analytical grade

HF, liquid

MW = 20.01 g mol^{-1}

3.1.13 Hydrobromic acid, analytical grade from Fluka (Buchs, Switzerland)

HBr, liquid

MW = 80.91 g mol^{-1}

3.1.14 Sodium thiosulphate, analytical grade from Ajax (Seven Hills, Australia)

$Na_2S_2O_3.5H_2O$, solid

MW = 248.18 g mol^{-1}

3.1.15 Dimethyl phathalate 99.5%, analytical grade from Sigma-Aldrich, (Stockholm, Sweden)

$C_{10}H_{10}O_4$, liquid

MW = 194.19 g mol^{-1}

3.1.16 Sodium sulphate, analytical grade from Ajax (Seven Hills, Australia)

Na_2SO_4, solid

MW = 142.04 g mol^{-1}

3.1.17 Ethyl acetate, analytical grade from Ajax (Seven Hills, Australia)

$C_4H_8O_2$, liquid

MW = 88.11 g mol^{-1}

3.1.18 Congo red, Direct red 28 C.I. 21200 from Fluka (Buchs, Switzerland),

$C_{32}H_{22}N_6Na_2O_6S_2$, solid

MW = 696.66 g mol^{-1}

3.1.19 Direct blue 71 C.I. 34140 from Sigma-Aldrich (St. Louis, USA),

$C_{40}H_{23}N_7Na_4O_{13}S_4$, solid

MW = 1029.88 g mol^{-1}

3.2 Glassware

3.2.1 500-ml four-necked round-bottomed flask

3.2.2 Condenser

3.2.3 Thermometer

3.2.4 Volumetric flask

3.2.5 Other general laboratory glassware

3.3 Apparatus

3.3.1 Flow meter : Cole Parmer, Illinois, USA

3.3.2 Stirring type : Semicircular Teflon Paddle

3.3.3 Mechanical stirrer : IKA Euro-ST B, Germany

3.3.4 Water Bath : Mammert W 350, Swabach Germany

3.3.5 Oven : D 7200, Tuttlingen, Germany

3.3.6 Magnetic stirrer : Mag-mixer model MD200

3.3.7 Scanning Electron Microscope (SEM) : Jeol model JSM-6400, Japan

3.3.8 Nuclear Magnetic Resonance Spectrometer (NMR) : Unity Inova-500, Switzerland

3.3.9 Inductive Couple Plasma Atomic Emission Spectrometer (ICP-AES) : Perkin Elmer model PLASMA-1000, UK

3.3.10 Fourier Transform Infrared Spectrophotometer (FT-IR) : Nicolet Impact 410, Madison, USA

3.3.11 UV-Visible Spectrophotometer : UV-2550, Shimadzu, Japan

3.3.12 Analytical Balance : Mettler AE 260, Greifensee Switzerland

3.3.13 Turbidimeter : model 2100P, Hach, Colorado, USA.

3.4 Procedure

3.4.1 Synthesis of aluminium hydroxide ($Al(OH)_3$) suspension

$Al(OH)_3$ 42.5 ml was prepared by slowly dropping 22.5 ml of 0.2 M sodium carbonate into 20 ml of 0.1 M aluminium sulphate with a constant rate of 4 ml min^{-1} under stirring by a magnetic stirrer (Mag-mixer model MD200, Japan) at room temperature. The $Al(OH)_3$ suspension was obtained and used as is.

3.4.2 Synthesis of poly[acrylamide-*co*-(acrylic acid)] and aluminium hydroxide-poly(acrylamide-acrylic acid) (AHAMAA)

a) Synthesis of poly[acrylamide-*co*-(acrylic acid)]

Acrylamide and acrylic acid were added into a 500-ml four-necked round-bottomed flask. This reaction flask was equipped with a mechanical stirrer (IKA model Euro-ST B, Germany), a condenser, and an inlet tube for nitrogen gas and it was immersed in a water bath (Mammert W 350, Swabach, Germany) at the temperature of 45 °C. The mixture was stirred by a small-bladed propeller with 250 rpm under the nitrogen atmosphere for 30 min. The crosslinking agent (N-MBA), initiator (APS) and co-initiator (TEMED) were added and stirred for 30 min. The copolymer was dewatered with acetone, cut into small pieces (about 1x1 cm) and dried in an oven (D7200, Tuttlingen, Germany) at 50 °C for 24 h to a constant weight and then milled.

b) Synthesis of aluminium hydroxide- poly(acrylamide-acrylic acid) (AHAMAA)

AHAMAA were synthesized by polymerization of acrylamide and acrylic acid in the $Al(OH)_3$ suspension in a 500-ml four-necked round-bottomed flask which was equipped with the mechanical stirrer (IKA model Euro-ST B, Germany), the condenser, and an inlet tube for nitrogen gas. The mixture of acrylamide, acrylic acid and $Al(OH)_3$ was stirred by a small-bladed propeller with 250 rpm by the mechanical stirrer (IKA model Euro-ST B, Germany) under nitrogen atmosphere for 30 min in the water bath (Mammert W 350, Swabach, Germany) at a temperature of 45 °C. Then, the crosslinking agent (N-MBA), initiator (APS) and co-initiator (TEMED) were added, respectively. The reaction was then continuously stirred for another 30 min. AHAMAA was dewatered with acetone, cut into small pieces (about 1x1 cm) and dried in the oven at 50 °C for 24 h to a constant weight and then milled.

The synthesis parameters of poly[AM-*co*-(AA)] and AHAMAA are represented in Table 3.1.

Table 3.1 The synthesis parameters of poly[AM-*co*-(AA)] and AHAMAA

Reactants	Concentrations	
	poly[AM-*co*-(AA)]	AHAMAA
Acrylamide: acrylic acid ($x10^{-3}$ mol)	100:0, 98:2, 96:4, 94:6, 92:8, 90:10	100:0, 98:2, 96:4, 94:6, 92:8, 90:10
N-MBA ($x10^{-4}$ mol)	1.2, 2.3, 4.6, 9.2	1.2, 2.3, 4.6, 9.2
APS ($x10^{-4}$ mol)	0.8, 1.6, 3.1, 6.2	0.8, 1.6, 3.1, 6.2
TEMED ($x10^{-4}$ mol)	1.5, 3.0, 6.0, 12.0, 24.0, 36.0, 96.0	1.5, 3.0, 6.0, 12.0, 24.0, 36.0, 96.0
Synthesized $Al(OH)_3$ suspension (ml)	-	42.5

3.4.2.1 Effect of the acrylic acid concentration

The experiment procedure as described in Section 3.4.2 and in Table 3.1 was carried out with various acrylic acid concentrations from 0 to $10x10^{-3}$ mol. The concentrations of the crosslinking agent, initiator and co-initiator were fixed at $4.6x10^{-4}$, $3.2x10^{-4}$ and $12x10^{-4}$ mol, respectively.

3.4.2.2 Effect of the crosslinking agent concentration

In this experiment, the crosslinking agent concentration was varied from $1.2x10^{-4}$ to $9.2x10^{-4}$ mol when the monomer, initiator and co-initiator concentrations were fixed at $4x10^{-3}$, $3.2x10^{-4}$ and $12x10^{-4}$ mol, respectively.

3.4.2.3 Effect of the initiator concentration

The same experimental procedure as described in Section 3.4.2 and in Table 3.1 was carried out with various initiator concentrations from $0.8\text{x}10^{-4}$ to $6.4\text{x}10^{-4}$ mol when the fixed concentrations of acrylic acid, crosslinking agent and co-initiator were at $4\text{x}10^{-3}$, $2.3\text{x}10^{-4}$, and $12\text{x}10^{-4}$ mol, respectively.

3.4.2.4 Effect of the co-initiator concentration

The acrylic acid, crosslinking agent and initiator concentrations were fixed at $4\text{x}10^{-3}$, $2.3\text{x}10^{-4}$, and $1.6\text{x}10^{-4}$ mol, respectively, and the co-initiator concentration was varied from $1.5\text{x}10^{-4}$ to $24\text{x}10^{-4}$ mol.

3.5 Characterization

3.5.1 Identification of functional groups of the copolymer and AHAMAA

The functional groups of $Al(OH)_3$, poly[AM-*co*-(AA)] and AHAMAA were examined by Fourier Transform Infrared Spectroscopy (FTIR, model Nicolet Impact 410, Madison, USA)

3.5.2 Identification of aluminium form of AHAMAA

The forms of aluminium in $Al(OH)_3$ and AHAMAA were examined by ^{27}Al nuclear magnetic resonance (^{27}Al-NMR, model Unity Inova-500, Switzerland).

3.5.3 Morphology of the copolymer and AHAMAA

The surface morphologies of poly[AM-*co*-(AA)] and AHAMAA and element distribution of AHAMAA were investigated using a scanning electron microscope (SEM, model JSM-6400, Japan) without cross-section and SEM was operated at 15 kV accelerating voltage.

3.5.4 Determination of the residual acrylamide/*N, N'*-methylenebis acrylamide monomers

Poly[AM-*co*-(AA)] after the polymerization was stirred in 300 ml distilled water. Based on Method 8032A, sample preparation for determining the residual acrylamide monomer comprises two steps as follows:

Step 1: Bromination

The sample (50 ml) was pipetted and placed in a 100-ml glass-stopperd flask. KBr (7.5 g) was stirred until dissolution in the sample solution. The pH of the solution was adjusted with concentrate HBr until the pH was between 1 and 3. The flask was wrapped with aluminium foil in order to exclude light. Then 2.5 ml of the saturated bromine in water was added and stirred. The flask with the solution was stored in dark at 0 °C for at least 1 h. The excess of bromine was decomposed by adding 1 M $Na_2S_2O_3$ drop by drop until the solution became colorless. Then 15 g of Na_2SO_4 was added and stirred vigorously using a magnetic stirrer.

Step 2: Extraction

The solution was transferred into a 150 ml separatory funnel. The reaction flask was rinsed three times, each with 1 ml aliquot of the distilled water. The rinsing solution was transferred to a separatory funnel. The aqueous solution was extracted twice with 10-ml portion of ethyl acetate for 2 min each extraction. The organic phase was dried with 1 g of Na_2SO_4. The organic phase was transferred into a 25 ml volumetric flask. The aqueous phase (Na_2SO_4 solution) was rinsed with three 1.5 ml portions of ethyl acetate and the rinsings were combined with the organic phase. An exactly 100 μg of dimethyl phthalate was added to the volumetric flask and the solution was made up to 25 ml with ethyl acetate. A 5 μl aliquot of this solution was injected into a gas chromatography (GC-7AG, Shimadzu, Japan)

3.5.5 Determination of equilibrium water absorbency of the copolymer and AHAMAA

Water absorbencies of the copolymer and AHAMAA were carried out with distilled water at room temperature in a closed system to minimize water evaporation. Distilled water (200 ml) was added to 0.1 g of the dry poly[AM-*co*-(AA)] or AHAMAA and it was allowed to swell for 24 h. Then, the swollen gel was filtered through a 100-mesh sieve aluminium screen for 2 h. The water absorbency was determined three replications for each poly[AM-*co*-(AA)] or AHAMAA and calculated from the equation [35]:

$$Water\ absorbency(Q) = \frac{(W_e - W_i)}{W_i} \tag{3.1}$$

W_i = the weight of dry poly[AM-*co*-(AA)] or AHAMAA (g)

W_e = the weight of swollen gel (g)

3.5.6 Rheological study

The rheological measurements were conducted using Rheometer (ARES Rheometer, TA Inc., New Castle, USA) at 25 °C with parallel plate geometry (50 mm diameter, 1 mm gap). The strain sweeps were monitored in a range of 0.1-100% for determining the linear viscoelastic range, where storage modulus (G') and loss modulus (G") are independent of the strain amplitude. After the strain sweep test, the frequency sweep measurements were carried out from 0.1 to 100 rad s^{-1} at a constant strain (linear viscoelastic range).

Poly[AM-*co*-(AA)] or AHAMAA was added into distilled water for 24 h swelling at room temperature. Then, the swollen gel was filtered through 100-mesh sieve aluminium screen. This gel was placed on the parallel plate of the rheometer and rheological properties were measured as described above. The effects of strain on the G' and G" at a constant frequency (1 rad s^{-1}) were evaluated. After the strain sweep, the frequency sweep test was carried out between 0.1 and 100 rad s^{-1}.

3.5.7 Determination of the aluminuim concentration in AHAMAA

The AHAMAA 0.04 g was suspensed in a mixture of 10 ml conc. HCl and 10 ml HF and the mixture was heated on a hot plate until dryness. This procedure was repeated for 3 times. A mixture of 6 M HNO_3 and 6 M HCl was then added and heated until dryness. It was then transferred to a 50-ml volumetric flask which volume was made up to the mark with distilled water. The aluminium concentration in the solution was determined by an ICP-AES technique.

3.5.8 Determination of the leaking aluminium concentration

Determination of the free aluminium in the AHAMAA gel was carried out by adding AHAMAA into distilled water and it was kept at room temperature for 15, 30, 45 and 60 days. The swollen gel was filtered through a 100-mesh sieve aluminium screen. The filtrate was determined for the leaking aluminium concentration by the ICP-AES.

3.5.9 Efficiency of the dye removal of poly[AM-*co*-(AA)] and AHAMAA

3.5.9.1 Effect of the reactant concentrations

The effects of the acrylic acid, N-MBA, APS and TEMED concentrations on the Congo red and direct blue 71 removal of poly[AM-*co*-(AA)] and AHAMAA were investigated at room temperature. The 24 ppm of Congo red or

10 ppm of direct blue 71 was used. The dye solution (50 ml) was added to 0.03 g of the dry gel of poly[AM-*co*-(AA)] or AHAMAA and it was allowed to swell for 24 h. The swollen gel was then filtered through a 100-mesh sieve aluminium screen. The filtrate absorption was measured by a UV-visible spectrophotometer (UV-2550, Shimadzu, Japan) at the wavelength of 497 nm and 587 nm for Congo red and direct blue 71, respectively. The percentage dye removal can be calculated from the following equation [36]:

$$\%Dye\ removal = \frac{(C_i - C_e)}{C_i} \times 100 \qquad (3.2)$$

C_i = initial dye concentration

C_e = equilibrium dye concentration

3.5.9.2 Effect of pH of the dye solution

In this experiment, the effect of pH of dye solution was studied at room temperature using 24 ppm of Congo red and 10 ppm of direct blue 71. The monomer, initiator and co-initiator concentration were fixed at $4x10^{-3}$, $2.3x10^{-4}$, $1.6x10^{-4}$ and $12x10^{-4}$ mol, respectively, and this recipe was used to prepare the gel for the dye removal. The pH systems studied are two systems as follows:

(a) The non-buffered system

pH of the dye solutions was adjusted with 0.1 M HCl or 0.1 M NaOH to have the pH in the same range of 3 to 11.

(b)The buffered system

pH of the dye solutions was adjusted with a buffer solution which was prepared by mixing the proper amounts of 0.2 M boric acid, 0.05 M citric acid and 0.1 M tri-sodium phosphate [37] as follows:

Anhydrous boric acid (12.37 g) and 10.51 g of citric acid monohydrate were dissolved in distilled water and dilute to 1000 ml in a volumetric flask to make a 0.2 M boric acid and 0.05 M citric acid. This is called Solution 1. Solution 2 was prepared by dissolving 38.01 g of tri-sodium phosphate in distilled water and it was diluted to 1000 ml in a volumetric flask to give a 0.1 M tri-sodium phosphate solution. The buffer solutions (Solutions 1 and 2) were mixed at a specific volume in order to control the pH in a range of 3 to 11. The ionic strength can be calculated from the following equation:

$$I = \frac{1}{2}\sum(C_i Z_i^2) \tag{3.3}$$

I = ionic strength (mol-ion dm^{-3})

C_i = ion concentration (mol dm^{-3})

Z_i = charge on individual ion

After the dye solution with various pH in both systems had been prepared, each dye solution (50 ml) was added to 0.03 g of dry poly[AM-*co*-(AA)] or AHAMAA and it was allowed to swell for 24 h. Then, the swollen gel was filtered through a 100-mesh sieve aluminium screen. The filtrate was measured for the absorption by UV-visible spectrophotometer (UV-2550, Shimadzu, Japan).

3.5.10 Adsorption isotherm

The dye solutions of Congo red and direct blue 71 were prepared from a stock solution to the required concentrations. The dye solution (50 ml) was added to 0.03 g of the dry gel of poly[AM-*co*-(AA)] or AHAMAA and it was allowed to swell for

24 h at room temperature. The swollen gel was filtered through a 100-mesh sieve aluminium screen. The absorption of the dye solution after the filtering was determined by the UV-visible spectrophotometer (UV-2550, Shimadzu, Japan). The amount of dye adsorbed was calculated from the following equation [32]:

$$q_e = (C_0 - C_e)\frac{v}{m} \tag{3.4}$$

where q_e is the amount of dye adsorbed per unit weight of poly[AM-*co*-(AA)] or AHAMAA (mg g^{-1}); C_0 is the initial concentration of Congo red or direct blue 71 (mg l^{-1}); C_e is the concentration of Congo red or direct blue 71 at equilibrium (mg l^{-1}); v is the solution volume (l); m is the mass of the poly[AM-*co*-(AA)] or AHAMAA (g) [38].

The linear form of the Langmuir isotherm represents the model of monolayer adsorption. This isotherm is given as in Eq. (2.2):

$$\frac{C_e}{q_e} = \frac{1}{Q_{\max} K_L} + \frac{C_e}{Q_{\max}} \tag{2.2}$$

where C_e is the concentration of dye solution (mg l^{-1}) at equilibrium, q_e is the amount of dye adsorbed per unit weight of poly[AM-*co*-(AA)] or AHAMAA (mg g^{-1}), Q_{max} is the monolayer capacity of the adsorbent (mg g^{-1}) and K_L (or b) is the Langmuir adsorption constant (l mg^{-1}). The plot of C_e/q_e and C_e give Q_{max} and b values from the slope and intercept.

The Freundlich isotherm reveals the multilayer adsorption model. This model is formulated in a linear form as shown in Eq. (2.4):

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \tag{2.4}$$

where C_e is the concentration of dye solution (mg l^{-1}) at equilibrium, K_F is the sorption capacity (mg g^{-1}) and n is an empirical parameter. The plot of ln q_e and ln C_e give n and K_F values from the slope and intercept.

3.5.11 Turbidity measurement

Flocculation tests were carried out in a 100-ml graduate cylinder. The kaolin suspension was placed in the cylinder and then poly[AM-*co*-(AA)] or AHAMAA was added. The cylinder was inverted 10 times [34]. After the mixing, the cylinder was set upright for 3, 6, 9, 15 and 24 h. The turbidity of samples was measured using a portable turbidimeter (Model 2100P, Hach, Colorado, USA). The sample having the turbidities of less than 10 units was allowed to cool to room temperature before analysis. The sample was mixed thoroughly to disperse the solids and was left until air bubbles in these samples were disappeared. The sample was then poured into the turbidimeter tube. The turbidity was read directly from the instrument scale or from the appropriate calibration curve. For sample having turbidity exceeding 10 units, it was diluted with the turbidity-free water until the turbidity was below 10 units. The turbidity of the original sample was then computed from the turbidity of the diluted sample and the dilution factor. The effect of flocculation time of poly[AM-*co*-(AA)] and AHAMAA on the relative turbidity was investigated as follows:

$$relative\ turbidity = \frac{final\ turbidity}{initial\ turbidity} \qquad (3.5)$$