

Synthesis and Characterization of Cassava Starch Graft Poly(acrylic acid) and Poly[(acrylic acid)-*co*-Acrylamide] and Polymer Flocculants for Wastewater Treatment

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ABSTRACT: Starch-*g*-poly(acrylic acid) and poly[(acrylic acid)-*co*-acrylamide] synthesized via chemically crosslinking polymerization were then each mixed with inorganic coagulants of aluminum sulfate hydrate [Al₂(SO₄)₃·18H₂O], calcium hydroxide [Ca(OH)₂], and ferric sulfate [Fe₂(SO₄)₃] in a proper ratio to form complex polymeric flocculants (CPF). All CPFs exhibited low water absorbency than those of the uncomplexed superabsorbent copolymers. The color reduction by the CPFs was tested with both synthetic wastewater and selected wastewater samples from textile industries. The synthetic wastewater was prepared from a direct dye in a concentration of 50 mg dm⁻³ at pH 7. The CPFs of poly[(acrylic acid)-*co*-acrylamide] with calcium hydroxide at a ratio of 1:2 is the most effective CPF for the wastewater color

reduction. The CPF concentration of 500 mg dm⁻³ could reduce the color of the synthetic wastewater containing the direct dye solution by 95.4% and that of the industrial wastewater by 76%. Starch-*g*-poly(acrylic acid)/Ca(OH)₂ CPF can reduce the synthetic direct dye and the industrial wastewater by 74% and 18%, respectively. Chemical oxygen demand, residual metal ion concentrations, pHs, turbidity of the wastewater were also investigated and the potential use of the complex polymer flocculants for textile wastewater treatment was indicated. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2915–2928, 2006

Key words: swelling; radical polymerization; polysaccharides; metal-polymer complexes; hydrogels

INTRODUCTION

Superabsorbent polymers are highly hydrophilic, three-dimensional polymeric networks that have attracted much attention as functional polymers that possess properties of water absorption.¹ Superabsorbent polymer can be prepared by various methods such as irradiation^{2–5} and chemical crosslinking.^{6–9} In recent years, considerable researches have been experimented on the characterization and swelling behavior of superabsorbent polymers prepared by copolymerization and crosslinking of one or more monofunctional monomers or one multifunctional monomer or by crosslinking of a homopolymer or copolymer in solution.^{7,10}

Textile industry involves a number of wet processes that may use many dyes and solvents. Among those processes, wastewater is a major source of pollutants.

It is typically alkaline and has high biological oxygen demand (BOD) values (700–2000 mg dm⁻³) and high chemical oxygen demand (COD) values at approximately 2–5 times the BOD level.¹¹ Wastewater also contains solids, oil, and toxic organics, including phenols from dyeing and finishing and halogenated organics from processes such as bleaching. Dye wastewaters are frequently highly colored and may contain heavy metals such as mercury, arsenics, copper, and chromium. Implementation of cleaner production processes can yield both economic and environmental benefit. Many attempts have been made to develop new methods for wastewater treatment in textile industry through coagulation techniques such as precipitation using inorganic coagulants of calcium hydroxide or aluminum sulfate^{2,12–14}; precipitation using cationic polymer and ferric chloride. Some research groups have used various absorbents for the removal of acidic and basic dyes from aqueous solutions.^{15–17}

In general, the sorption mechanisms present three main steps for the pollutant sorption onto solid sorbents. For the use of polymeric sorbents, the presence of functional groups in copolymer can provide the specific characteristics such as complexation, high surface area for absorption; the sorption mechanism of

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polysaccharide-based materials is different from those of other conventional absorbents.¹⁸ These mechanisms are complicated because of the presence of different interactions.

In this present research, we synthesized the polymeric superabsorbent polymers of poly[(acrylic acid)-*co*-acrylamide] and cassava starch-*g*-poly(acrylic acid) by chemical crosslinking polymerization by adapting the procedure by Kiatkamjornwong et al.⁹ to the current system. The swelling properties and absorption characteristics of poly[(acrylic acid)-*co*-acrylamide] and cassava starch-*g*-poly(acrylic acid) superabsorbent polymer were investigated. Water absorbency of the synthesized polymers is presented and discussed. These copolymers with inorganic compounds such as aluminum sulfate, calcium hydroxide, and ferric sulfate were each mixed to form complex polymeric flocculants (CPFs). These CPFs have been characterized and applied in wastewater treatment. The effective dye-adsorption of the copolymer complexes were studied with synthetic direct dyes, sirius blue K-CFN. Color reduction of the reactive dye, acid dye, and mixtures of dyes from the textile finishing industry was investigated for COD, pH, and turbidity and their effectiveness was discussed.

EXPERIMENTAL

Materials

Acrylamide (AM, Siam Resin and Chemicals, Thailand) and the anionic comonomer, acrylic acid (AA, Siam Resin and Chemicals, Thailand) were used as monomers. *N,N'*-methylenebisacrylamide (*N*-MBA, Nicalai Tesque, Kyoto, Japan) was used as a crosslinker. Ammonium persulfate initiator (APS, Merck, Hohenbrunn, Germany) and the coinitiator *N,N,N',N'*-tetramethylethylenediamine (TEMED, Sigma-Aldrich, St. Louis, MO) were used as a redox couple. To prepare a graft polymer of cassava starch-*g*-AA, cassava starch (Thai Wah, Thailand) was used as a grafting substrate.

For adsorption studies, a commercial dye named sirius blue K-CFN (Dystar, Thailand), inorganic coagulants of aluminum sulfate [$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$], calcium hydroxide [$\text{Ca}(\text{OH})_2$, Merck, Darmstadt, Germany], and ferric sulfate [$\text{Fe}_2(\text{SO}_4)_3$, Carlo Erba, MI] were used as received.

Synthesis

Preparation of poly[(AA)-coacrylamide] superabsorbent polymers

A mixture of 100 cm³ aqueous solution of monomers with an AM-to-AA ratio of 1 : 9 by mole and APS/TEMED was placed in a 250-cm³ reaction flask. This round-bottomed flask was equipped with a mechani-

cal stirrer agitated with a rate of 250 rpm, at 45°C in nitrogen atmosphere for 30 min. The resulting polymer was dewatered and precipitated with methanol, cut into small pieces of submillimeter particles, dried at 50°C for 24 h in a vacuum oven to a constant weight and then milled.⁹

Preparation of cassava starch-*g*-poly(AA)

Gelatinization of cassava starch. Cassava starch of 24.0 g was mixed with 160 cm³ of distilled water in a 1000-cm³, 4-necked round bottom flask. The mixture was mechanically stirred at 360 rpm under heating within the temperature range of (80 ± 2)°C in nitrogen gas atmosphere for 30 min to form a soft paste.

Graft copolymer of AA onto cassava starch. The gelatinized starch was then cooled to 32°C. Then 0.4 g of APS, 0.16 g of TEMED, 0.16 g of *N*-MBA, and a mixture of water (160 cm³) dissolving 16.0 g of AA were added into the reaction bottle. The reaction mixture was stirred under the nitrogen atmosphere for 10 min. The reaction product was precipitated with acetone and dried at 65°C in an oven for 24 h.

Preparation of complex polymeric flocculants

A solution containing 20 g of poly[(AA)-*co*-AM] or starch-*g*-poly(AA) was stirred in distilled water. Then, 10.0 g each of the inorganic coagulants of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, $\text{Ca}(\text{OH})_2$, or $\text{Fe}_2(\text{SO}_4)_3$ was dissolved in distilled water (250 cm³). The polymer suspension was poured in a 2000-cm³ four-necked round-bottomed flask equipped with a reflux condenser and a mechanical stirrer stirring at 150 rpm for 30 min. The inorganic solution was added and stirred for 6 h at 60°C in nitrogen gas atmosphere. The complex flocculant formed was filtered, washed with distilled water twice and dewatered with methanol. It was cut into small pieces of submillimeter particles and vacuum dried at 65°C for 24 h and cooled in a desiccator to get a constant weight and then milled.

Preparation of synthetic and industrial wastewater

Synthetic wastewater containing 50 mg dm⁻³ dye solution was prepared by direct dye sirius blue K-CFN (Dystar) in distilled water. The industrial wastewater was obtained from two textile finishing factories, A and B. Water samples were taken from both the dyeing process unit and composite effluent. The wastewater properties for pH, turbidity, initial COD, and their properties are summarized in Table I.

Characterization

Identification of the functional groups

The Fourier Transform Infrared Spectrophotometry (FTIR, Model 1760×, Perkin-Elmer Infrared Spec-

TABLE I
Properties of Wastewater from the Textile Factories

Sample/dilution	Dye color	pH	Turbidity (NTU)	Initial COD (mg dm ⁻³)	Other properties
Factory A					
A1/0	Direct/black	8.2	9.99	NA	
A1/10	Direct/black	7.8	5.89	91.8	Anionic, water sol., low fasten, ionic bond dye
A2/0	Reactive/blue	11.0	9.99	NA	
A2/500	Reactive/blue	9.4	0.18	77.8	
A2/1000	Reactive/blue	9.3	0.17	21.4	Anionic, water sol., high fasten, covalent bond dye
A3/0	Mixed/purple	12.2	9.99	NA	
A3/2	Mixed/purple	10.8	8.39	477.4	Composite wastewater
Factory B					
B1/0	Acid/black	4.4	9.99	NA	
B1/100	Acid/black	4.2	0.32	213.3	Anionic, water sol., low fasten, ionic bond dye
B2/0	Mixed/grey	7.2	9.99	NA	
B2/2	Mixed/grey	7.0	9.99	502.1	Composite wastewater

trometer) was used to identify the functional groups of the copolymers and the dye. The copolymer was ground with the dried KBr powder (spectrophotometric grade). The copolymer–KBr powder was dried, pressed, and subjected to FTIR spectrophotometric analysis.

Since no information of the dye is available and it could be mixed with additives, we have to investigate its functional groups for discussion purpose. The dye (0.125 g) was dissolved in distilled water and made up to 250 cm³. Sodium chloride solution (25% w/w) was added drop by drop into the dye solution. The original blue color was changed to purple along with precipitation of light, fluffy powder. The tube containing the powder was centrifuged at 6000 rpm for 20 min to collect the dye at the bottom of the tube. The supernatant was decanted and the dried powder was obtained after drying in an oven. The dye powder before and after the salting out was subjected to IR spectroscopy.

Morphology and element analysis of the copolymers and their cpfs

Morphology of the copolymers and CPFs was viewed by scanning electron microscopy (SEM), before wastewater treatment. Detailed morphology of surface structures and mapping densities of the incorporated metal ions were studied by SEM/(Energy dispersive X-ray Spectroscopy, EDXS, JSM-T 220A JEOL) without cross section. The thickness of gold coated on the copolymer was 25 nm.

Water absorption capacity of superabsorbent polymers

The swelling measurements of the copolymer were carried out in water at room temperature. Distilled

water of 200 g was added to 0.1 g of the dry copolymer (W_0) in a 400-cm³ glass beaker with a glass cover. The polymer was allowed to swell for 24 h. The fully swollen gel was then separated from unabsorbed water by filtering through a 100-mesh sieve aluminum screen covered with a lid for about 2 h at room temperature to drain off the interparticle and surface water, and the swollen copolymer gel was weighed (W_1). The water absorbed by the copolymers is also quantitatively represented by the equilibrium water content. In this research the water absorbency was calculated as the maximum swelling of the copolymers shown in eq. (1)

$$\text{Water absorbency (Q), } g g^{-1} = (W_1 - W_0)/W_0 \quad (1)$$

Construction of a calibration solution

A stock solution of 1000 mg dm⁻³ was prepared by dissolving 0.1000 g of the direct dye (sirius blue K-CFN) in 100 cm³ water. Six calibration points were constructed by drawing 1, 2, 3, 4, 5, and 6 cm³ of the dye solution in six volumetric flasks of 100 cm³ and the full volume was made up with distilled water to give 10, 20, 30, 40, 50, and 60 mg dm⁻³. Color measurement was carried out by the UV–vis spectrophotometry on Spectronic-20 Spectrometer (Model Genesys, Thermo Electron, USA) at the maximum absorption at 590 nm.

Application for wastewater treatment

Color reduction

Poly[(AA)-*co*-AM] or starch-*g*-poly(AA) superabsorbent polymers in the concentrations of 250 or 500 mg dm⁻³, containing inorganic coagulants in polymer-to-

TABLE II
The Composition and Percentage Concentration of the Elements of the Polymer and Complex Polymers

Element	Type of polymer							
	Starch-g-poly(acrylic acid)				Poly[(acrylic acid)-co-acrylamide]			
	Neat Polymer	Al complex	Ca complex	Fe complex	Neat Polymer	Al complex	Ca complex	Fe complex
C	36.26	41.54	17.10	36.06	40.36	40.63	8.11	39.93
O	49.25	51.94	45.44	46.93	45.43	46.63	41.47	56.74
Na	0.34	0.38	–	0.83	13.95	1.19	–	0.81
Al	–	4.81	–	–	0.19	5.51	–	1.27
S	–	1.16	–	0.95	0.08	1.39	–	0.66
Mg	–	–	0.30	–	–	–	0.58	–
Ca	–	–	44.20	–	–	–	49.57	–
Fe	–	–	–	14.27	–	–	–	0.59
K	14.14	0.16	0.25	–	–	–	–	–

coagulant ratios of 1:0.5 (2:1), 1:1, and 1:2 were each added into the dye wastewater solution. The mixtures were stirred using the Jar test at 120 rpm for 3 min and then the stirring rate was reduced to 30 rpm for 30 min and it was left for 30 min to complete the reaction. After the adsorption, the dye solution was separated by decantation from the swelling superabsorbent polymers. The dye solution was analyzed by the UV-vis spectrophotometry, the absorbance of these solutions was taken at 585 nm against distilled water used as a reference.

Chemical oxygen demand (COD) of the dye solution

After the dye adsorption, the supernatant was filtered out and digested via the wet digestion method at 150°C for 120 min using a thermoreactor (Model ECO 6, Velp Scientifica, Italy). The COD was measured using the dichromate reflux method. The aqueous sample was oxidized with a hot acidified sulfuric solution of potassium dichromate with silver sulfate as a catalyst. The chloride ion was masked with mercury sulfate. The concentration of unconsumed yellowish dichromate ions was then determined photometrically. The method is analogous to EPA 410.4, US Standard Methods 5220 D, and ISO 6060. The measuring concentration range was 50–500 mg dm⁻³ at the wavelength of 449 nm.

Turbidity measurement

The turbidity of samples was measured using a portable turbidimeter (Model 2100P, Hach, Colorado, USA) following the Hach method 8195 for the determination of turbidity by nephelometry.¹⁹ The sample having the turbidities of less than 40 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 40 units, it was diluted with one or more volumes of turbidity-free water until the turbidity falls below 40 units. The turbidity of the original sample was then computed from the turbidity of the diluted sample and the dilution factor.

Residual concentrations of metal ions of CPFs and inorganic coagulants in synthetic dye wastewater treatment

In this experiment, poly(AA-co-AM)/Ca(OH)₂ (at 1 : 1 and 1:2 ratios), and starch-g-poly(AA)/Ca(OH)₂ (at 1 : 2 ratio) were analyzed for their residual ion concentrations after the treatment for the synthetic dye wastewater in comparison with the inorganic coagulants of Al₂(SO₄)₃·18H₂O, Ca(OH)₂, or Fe₂(SO₄)₃. The concentrations for all the CPFs and inorganic coagulants are 500 mg dm⁻³. Atomic Absorption Spectrophotometer (Varian, Spectra - 300) was used to analyze the metal ion concentration.

RESULTS AND DISCUSSION

As shown in Table II, the water absorbency of poly[(AA)-co-AM] is 1216 ± 52 g g⁻¹, and water absorption value of the starch-g-PAA is 209 ± 12 g g⁻¹ times its dried copolymer, which are much higher than those complex polymers with the inorganic coagulants of Al₂(SO₄)₃·18H₂O, Ca(OH)₂, or Fe₂(SO₄)₃. The complex polymeric flocculants of Al₂(SO₄)₃·18H₂O, Ca(OH)₂, or Fe₂(SO₄)₃ reduced water absorbency by 97–99% their original values of the noncomplex superabsorbent polymers.

Characterization of the polymers and their CPFs by spectroscopy

The vibrational absorptions of the functional groups in the FT-IR spectra of the inorganic coagulants, neat

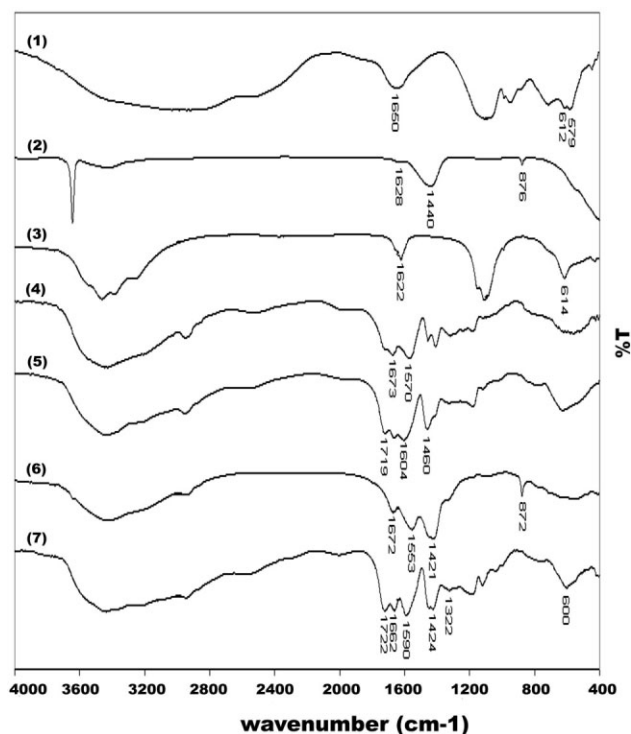


Figure 1 FTIR spectra of coagulants and CPFs, (1) $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, (2) $\text{Ca}(\text{OH})_2$, (3) $\text{Fe}_2(\text{SO}_4)_3$, (4) starch-g-poly(AA), neat polymer, (5) starch-g-poly(AA) and $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, (6) starch-g-poly(AA) and $\text{Ca}(\text{OH})_2$, and (7) starch-g-poly(AA) and $\text{Fe}_2(\text{SO}_4)_3$.

copolymers and the complex polymers were shown in Figures 1 and 2. The stretching vibration of the $\text{C}=\text{O}$ of carboxyl group in the polymer was extremely weak in the complex, but the asymmetric and symmetric vibrations of the $\text{O}-\text{C}-\text{O}$ at 1668 and 1597 cm^{-1} appeared clearly, which implied that the carboxyl group had been ionized to the carboxylate anion. From the spectrum, it could be found that the vibrational peaks of the $\text{C}=\text{O}$, and $\text{C}-\text{N}$ groups in the amide units of the three complex polymers were shifted from 1725 cm^{-1} , $1668\text{--}1565\text{ cm}^{-1}$, and 1445 cm^{-1} , respectively, which indicated that the coordination between the amide group and the metal ion had already been formed.

The significant absorption peaks at $3550\text{--}3200\text{ cm}^{-1}$ (m, b), $3000\text{--}2840\text{ cm}^{-1}$ (w), and $1260\text{--}1000\text{ cm}^{-1}$ demonstrating the $\text{O}-\text{H}$ stretching and $\text{C}-\text{O}$ stretching, respectively, indicate the presence of cassava starch. The starch-g-poly(AA) gives the IR spectrum, which contains the characteristic peaks of cassava starch and AA at $3300\text{--}2500\text{ cm}^{-1}$ (s, b), $1720\text{--}1706\text{ cm}^{-1}$ (m), $1440\text{--}1395\text{ cm}^{-1}$, and $1320\text{--}1210\text{ cm}^{-1}$ for the absorption peaks of the $\text{O}-\text{H}$ stretching, $\text{C}=\text{O}$ stretching, $\text{O}-\text{H}$ bonding, and $\text{C}-\text{O}$ stretching of carboxylic acid, respectively.

In the far IR region, many interesting peaks for the inorganic coagulants and polymer flocculants are

found as follows. The peaks at 579 cm^{-1} ($\text{Al}-\text{O}-$), 612 cm^{-1} ($-\text{O}-\text{Al}$), 918 ($\text{Al}-\text{OH}$), $1120\text{--}1040\text{ cm}^{-1}$ ($\text{S}=\text{O}$ symmetrical stretching), $1200\text{--}1100\text{ cm}^{-1}$ (the $\text{S}=\text{O}$ stretching) and $3600\text{--}2600\text{ cm}^{-1}$ (the $-\text{OH}$ stretching) are the major absorption peaks for aluminum coagulant, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$. The similar peaks were also found in the poly(AA-co-AM)/ $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ at 579 , 608 , and 1620 cm^{-1} . The peaks at 579 , 612 , and 1130 cm^{-1} of the $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ were found in the starch-g-poly(AA)/ $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$.

The IR absorption peak at 876 cm^{-1} exhibited in $\text{Ca}(\text{OH})_2$ spectrum was also found in poly(AA-co-AM)/ $\text{Ca}(\text{OH})_2$ and the starch-g-poly(AA)/ $\text{Ca}(\text{OH})_2$. The peak at 1725 cm^{-1} disappeared, which indicates the incorporation of $\text{Ca}(\text{OH})_2$ in the polymers.

One combination or overtone peak in $\text{Fe}_2(\text{SO}_4)_3$, starch-g-poly(AA)/ $\text{Fe}_2(\text{SO}_4)_3$, and poly(AA-co-AM)/ $\text{Fe}_2(\text{SO}_4)_3$, at $480\text{--}470\text{ cm}^{-1}$ (in both the inorganic coagulant and the CPFs) and one sharp peak at 1010 cm^{-1} (the $\text{S}=\text{O}$ stretching) was found in both the poly(AA-co-AM)/ $\text{Fe}_2(\text{SO}_4)_3$ and starch-g-poly(AA)/ $\text{Fe}_2(\text{SO}_4)_3$. This also indicates the incorporation of $\text{Fe}_2(\text{SO}_4)_3$ in the polymer.

Additionally, the very broad peak scanned from 3500 to 2600 cm^{-1} found in $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ indicated the presence of OH group for the association of a high amount of water. The similar behavior was found in

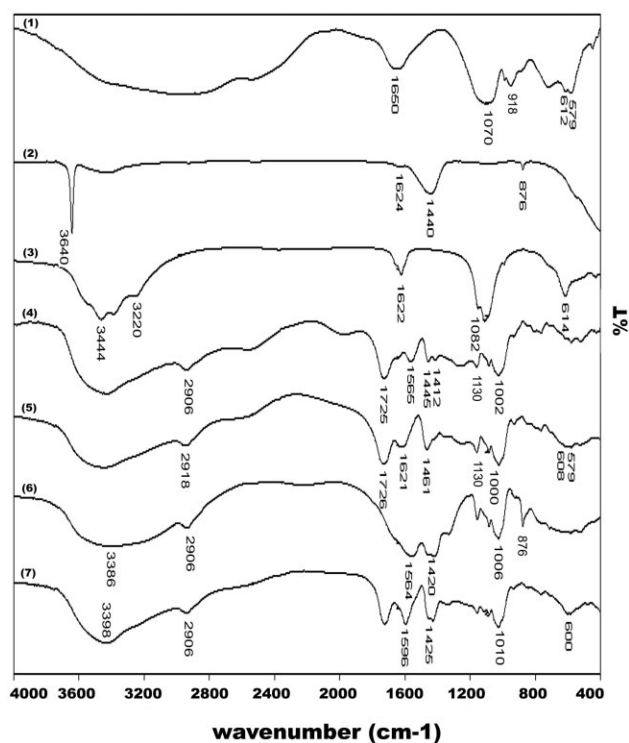


Figure 2 FTIR spectra of coagulants and CPFs, (1) $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, (2) $\text{Ca}(\text{OH})_2$, (3) $\text{Fe}_2(\text{SO}_4)_3$, (4) poly(AA-co-AM), neat polymer, (5) poly(AA-co-AM) and $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, (6) poly(AA-co-AM) and $\text{Ca}(\text{OH})_2$, and (7) poly(AA-co-AM) and $\text{Fe}_2(\text{SO}_4)_3$.

the P(AA-*co*-AM) from which one broad peak spanned from 3700 to 3000 cm^{-1} indicated existence of the hydroxyl group overlapping with the amino group. When the inorganic coagulant was mixed with the copolymer, the broad peak in $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ became much narrower than that of the P(AA-*co*-AM). It can be concluded that the OH in the polymer coordinated with the metal ion of aluminum.

For $\text{Ca}(\text{OH})_2$, a very narrow and sharp peak was found at 3642 cm^{-1} and another narrow peak was found at 876 cm^{-1} , while a broad peak at around 3400 cm^{-1} was found in the polymers. When $\text{Ca}(\text{OH})_2$ was mixed with each polymer, the narrow peak in the coagulant disappeared while the broad peaks became narrower with the presence of the peak at 876 cm^{-1} . This is another evidence to confirm that $\text{Ca}(\text{OH})_2$ has been incorporated with the polymers.

In general, a polymer-metal complex comprises a synthetic polymer and metal ions. The metal ions are bound to the polymer ligand by a coordinate bond. The polymer usually contains anchoring sites such as nitrogen, oxygen, or sulfur resulting from polymerizing monomers possessing the coordinating site or by chemical reaction between a polymer and a low molecular weight compound having coordinating ability.²⁰ In the present work, the coordinating groups could be the carboxylic acid ($-\text{COOH}$) or carboxamide ($-\text{CONH}_2$) groups, which are parts of the repeating units of the polymer ligands interacting with the free metal ion. From the above IR spectra, one could possibly postulate that Al^{3+} , Ca^{2+} , and Fe^{3+} have been introduced into the copolymer matrix, formed as the metal ion complex polymers through more than one coordinations among the higher electronegative ions in the functional groups, i.e., the nitrogen atom of the amide moiety and the oxygen atom of the carboxylate anion. As observed from the IR spectra in Figures 1 and 2, one could postulate that the polymer-metal complex has a greater affinity to the carboxylic acid group than the carboxamide group indicated by the shift of the carboxylate group and the additional peaks of metal-oxygen bond in the far IR region.

Investigation of functional groups of the synthetic direct dye

The IR spectra of the dye before and after salting out are analyzed in which Figure 3(a) is for the dye before the salting out while Figure 3(b) for the one after the salting out. Similar peaks in both cases with slightly shifted wave numbers were observed. Theoretically, direct dye has another name of substantive dyes, which chemical components can be azo compounds, stilbenes, oxazines, or phthalocyanines. They always contain solubilizing groups such as sulfonic acid as a main class where carboxylic and hydroxyl groups are also found in a sodium salt form to ease water solu-

bility, i.e., all of them can ionize in aqueous solution. In other words, they are negatively charged in the whole molecule or the colored parts of the dye are anionic. The IR spectra shown in Figure 3(a,b) give the following wave numbers and the functional groups are assigned as follows: At 3600–2960 cm^{-1} , a rather broad peak could possibly be the $-\text{NH}$ and $-\text{CH}$ stretching. There are two overtone peaks at 2470–2100 cm^{-1} . A relatively broad peak at 1609 cm^{-1} (a sharp peak at 1602 cm^{-1} in Fig. 3b) could be the ring $\text{C}=\text{C}$ stretching. The $\text{C}(\text{=O})_2$ peak at 1488 cm^{-1} (a sharp peak at 1485 cm^{-1} in Fig. 3b) could be assigned for the asymmetrical stretching, and the $\text{S}(\text{=O})_2$ at 1390–1340 cm^{-1} (sharp peaks at 1388–1330 cm^{-1} in Fig. 3b) could be for the symmetrical stretching. A very strong and sharp absorption peak at 1129 cm^{-1} along with a minute peak at 1056 cm^{-1} [several peaks at 1186, 1108, and 1030 cm^{-1} in Fig. 3(b)] should probably be the sulfonate salt. In addition, the broad peak at 1000–800 cm^{-1} [peaks at 902–824 cm^{-1} in Fig. 3(b)] is assigned for the $\text{S}-\text{O}-\text{C}$ stretching. The combination peaks at 900–675 cm^{-1} are possibly for the $=\text{CH}$ bonds in an aromatic compound. To summarize, the direct dye in both spectra should contain the $-\text{NH}$ and $\text{C}=\text{O}$ groups, and the sulfonate group to give the anionic charged molecule, which can interact with the cation in the polymer complex in the color removal process.

Morphology and densities of the polymers and complex polymers

Surface morphology

The morphology of the CPF is shown in Figures 4 and 5. Considering the surface morphologies of the polymer complexes in Figure 4, one can see a denser and rougher surface in the complex polymer. The neat polymer of AA and AM in Figure 5 has a network surface resulting from the characteristics of AM moiety forming the cyclic imide functional group from crosslinking between two AM chains through imidization.⁴

Densities of the metal in the complex polymers

Figures 6 and 7 show the densities of the metal in the starch-AA copolymers, and poly[(AA)-*co*-AM] with the inorganic coagulants. In Figure 6, the amounts of the Al^{3+} and its distribution in the mapping are similar to that of the carbon, but the Ca^{2+} densities and distribution are higher than that of carbon and the ferric ion are less than the carbon. For Figure 7, most of the aluminum and carbon are overlapped, the calcium ion densities and distributions are larger than those of the carbon; the ferric ion densities and distribution are less than those of the carbon.

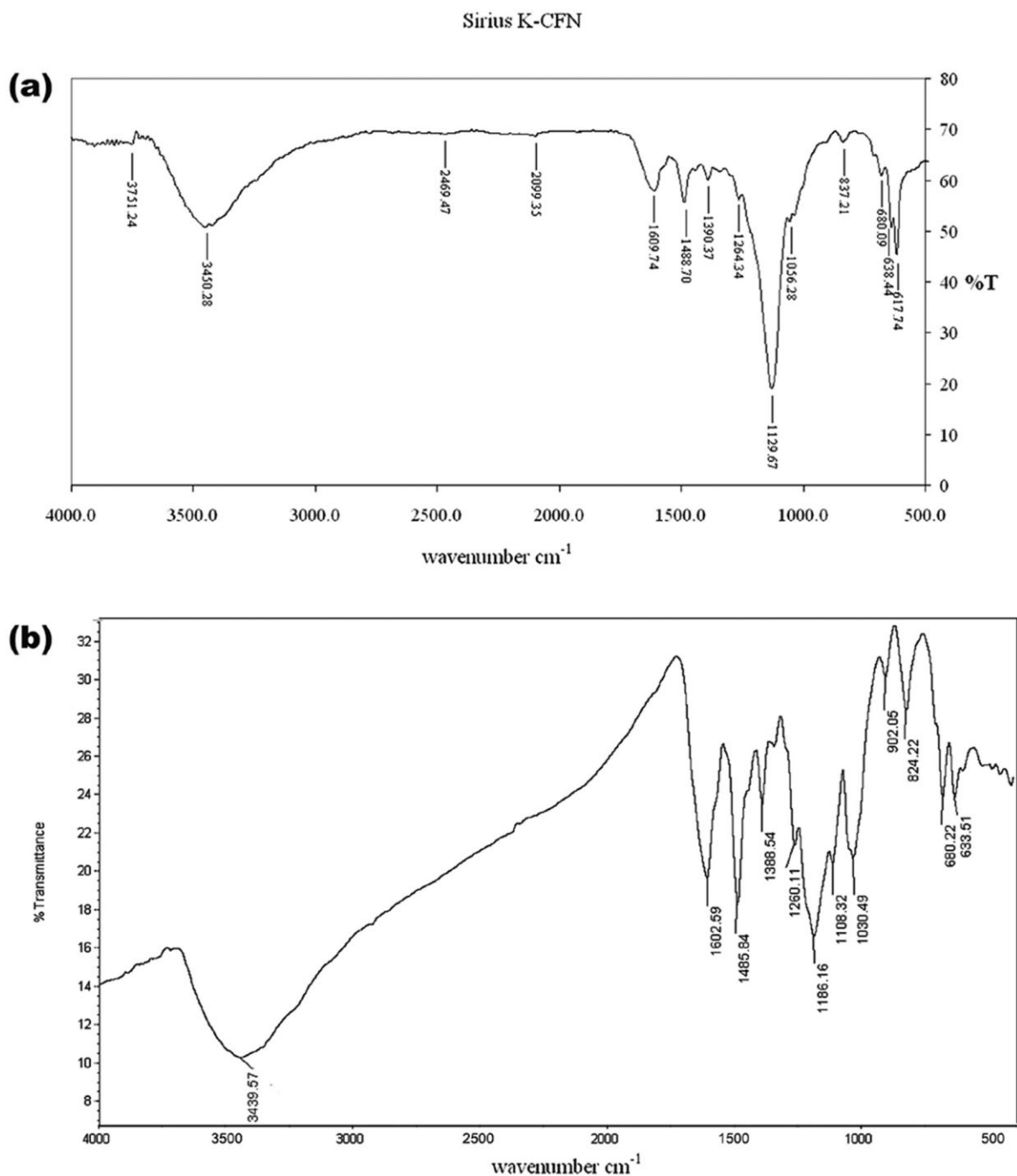


Figure 3 IR spectra of the sirius K-CFN dye before and after salting out.

The composition and percentage concentration of the elements of the polymer and complex polymer are presented in Table II. In Table II, all polymer complexes prepared based on the weight ratio of polymer-to-inorganic coagulant of 1:1 contain different percentage of metal ion concentrations. Poly[(AA)-*co*-AM] complexes with $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, and $\text{Ca}(\text{OH})_2$ accommodated a high percentage concentration of Al and Ca ions but a lower Fe ion when complex forming with $\text{Fe}_2(\text{SO}_4)_3$.

Swelling properties of the poly[(AA)-*co*-AM] copolymers and cassava starch-*g*-poly(AA) and CPFs

As shown in Table III, the water absorbency of poly[(AA)-*co*-AM] is $1216 \pm 52 \text{ g g}^{-1}$, which is much higher than that of the starch-*g*-PAA. As mentioned above, the water absorbency of the starch-*g*-poly(AA) is $209 \pm 12 \text{ g g}^{-1}$ its dried weight, and the water absorbency of the complex polymeric flocculants of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, $\text{Ca}(\text{OH})_2$, or $\text{Fe}_2(\text{SO}_4)_3$ was reduced

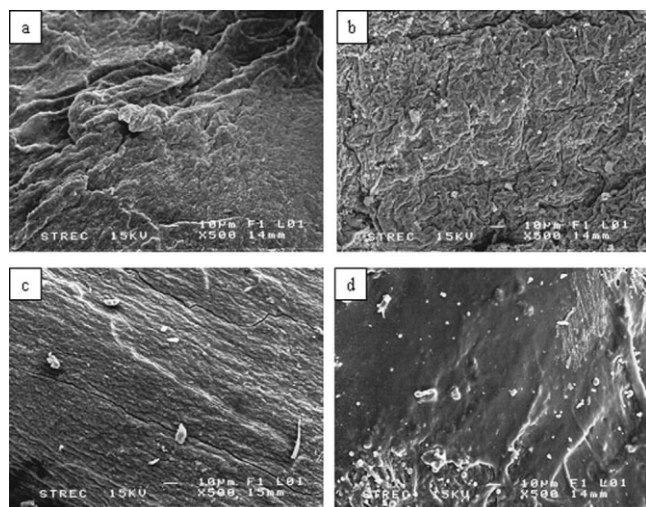


Figure 4 SEM photographs of starch-g-poly(AA) complexed with (a) $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, (b) $\text{Ca}(\text{OH})_2$, (c) $\text{Fe}_2(\text{SO}_4)_3$, the ratio of polymer-to-coagulants of 1 : 1 and (d) starch-g-poly(AA), neat polymer.

by 97-99%. It is noted that the presence of both AM and AA are quite essential to enhance and work synergistically to give high water absorption.^{4,5} With the same weight ratio of polymer to inorganic coagulant in the CPF, we found that the higher the ratio, the larger the water absorbency because of the greater amount of the free hydrophilic groups available for

water absorbency. The higher amount of inorganic coagulant utilizes the free hydrophilic groups which thus reduce the water absorbency. On the other word, the free hydrophilic groups have been complexed with the metal ion.

Wastewater treatment

The use of aluminum sulfate, calcium hydroxide, and ferric sulfate as coagulants for color removal of the synthetic direct dye

The effectiveness of direct dye reduction by the complex polymer flocculants and the inorganic coagulants ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, $\text{Ca}(\text{OH})_2$, $\text{Fe}_2(\text{SO}_4)_3$) is shown in Table III. It shows that the inorganic coagulants gave a much better color reduction in the following order: $\text{Ca}(\text{OH})_2 > \text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O} \cong \text{Fe}_2(\text{SO}_4)_3$. Since the dye has negative charges on its molecule, and the inorganic coagulants can ionize in water as free metal ion which can accommodate and neutralize the negatively charged colloidal dyes. Calcium hydroxide is more effective than the other two inorganic coagulants; its hydroxide is easier to dissolve in water. It can perform the function of dye removal faster and better. On the other hand, the aluminum sulfate and ferric sulfate coagulant need to ionize first to become aluminum hydroxide or ferric hydroxide to behave as a colloid. Therefore the color reduction of the inorganic coagulants can be postulated as the interaction be-

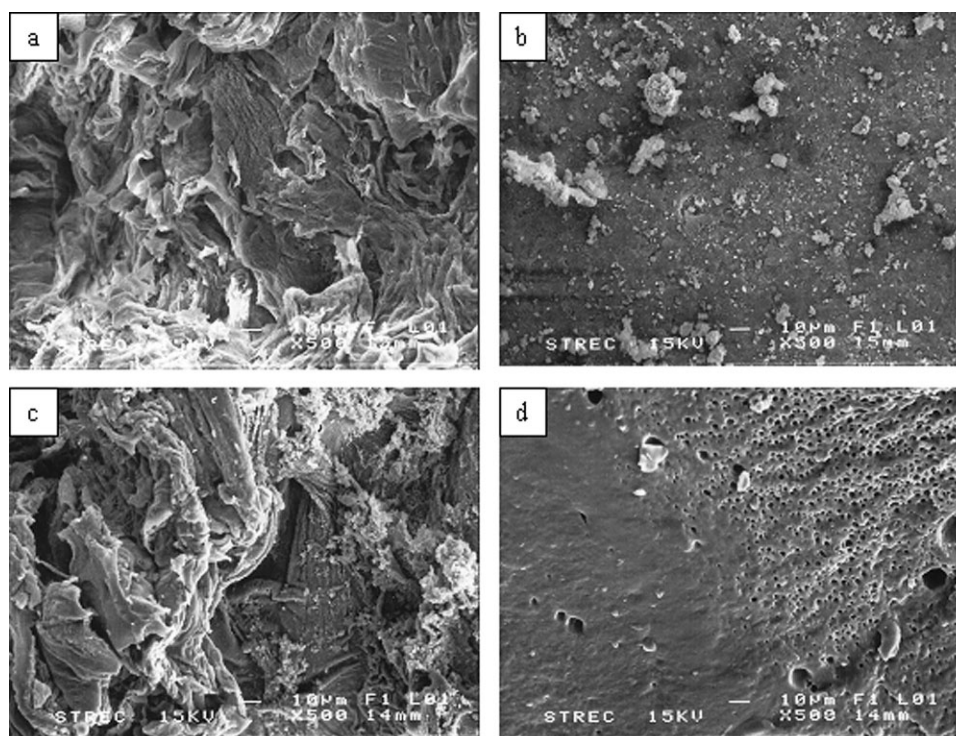


Figure 5 SEM photographs of poly(AA-co-AM) complexed with (a) $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, (b) $\text{Ca}(\text{OH})_2$, (c) $\text{Fe}_2(\text{SO}_4)_3$, the ratio of polymer-to-coagulants of 1 : 1 and (d) poly(AA-co-AM), neat polymer.

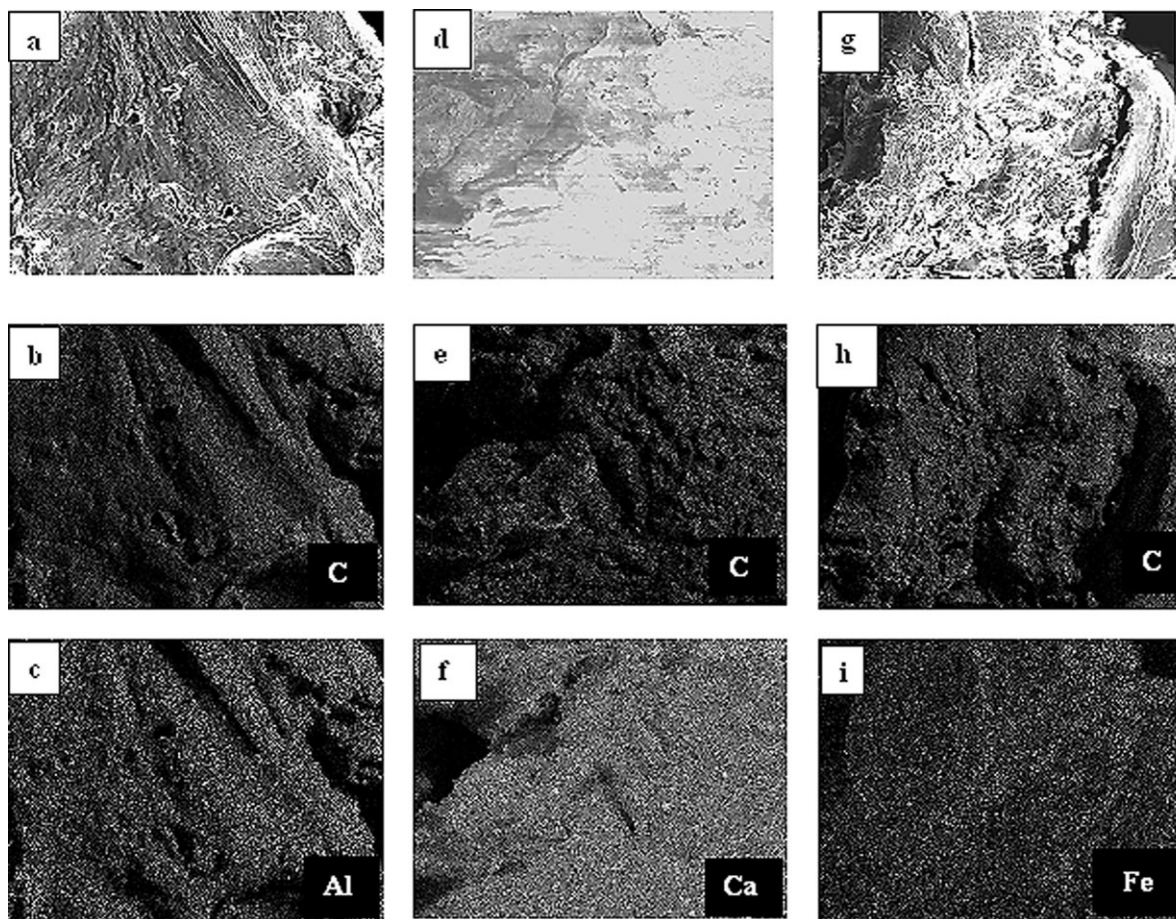


Figure 6 Densities of metal in the complex starch-acrylic acid copolymer by mapping via SEM/EDXS: a, d, and g are the complex polymers of aluminum, calcium, and ferric ions. The micrographs in b, e, and h are the mapping of carbon, and in c, f, and i are the mapping of aluminum, calcium, and ferric ions.

tween the cation of the inorganic coagulant and the active anionic group of the direct dye since this dye contains sulfonic acid group. The binding interaction between the positive metal ion from the CPF and the negatively charged dye promotes the stability of the complex of the metal ion-negatively charged dye. The stronger the interaction, the greater the dye color removal and the corresponding color reduction.

Color reduction of the synthetic direct dye

In the complex polymer flocculants

It is interesting that the high water absorbing polymer alone cannot reduce the dye color because both of them are negatively charged molecules (the anionic absorbent versus the anionic dye molecule). After the superabsorbent polymer had been complexed with the inorganic coagulant to become complex polymer flocculants, the color was dramatically removed when the CPFs are in the contact with it. The CPFs having the lowest water absorbency can remove most of the color

because of the more complexation between the hydrophilic group and the metal ion. It seems that the complex formation is so specific and effective. In Table III, the CPFs of poly(AA-co-AM) containing $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ in the ratio of 1 : 0.5 (2 : 1) and 1 : 1 could not reduce the dye color, the amount of direct dye reduction was negative, while the CPF of poly(AA-co-AM)/ $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ with the ratio of 1 : 2 reduced the amount of direct dye of 14.4%. Similarly, it shows that the CPFs of poly(AA-co-AM)/ $\text{Ca}(\text{OH})_2$ in the ratio of 1 : 0.5 (2 : 1), 1 : 1, and 1 : 2 gave reduced amounts of the direct dye of 25.9, 53.1, 95.4%, respectively. More effective dye reduction was detected when the amount of $\text{Ca}(\text{OH})_2$ was increased. For the CPF of poly(AA-co-AM) and $\text{Fe}_2(\text{SO}_4)_3$, the reduced dye amount could not be detected in all ratios of copolymer-to-inorganic coagulants. The increasing amount of inorganic coagulants was suggested, since the inorganic coagulants of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, $\text{Ca}(\text{OH})_2$, and $\text{Fe}_2(\text{SO}_4)_3$ provided the color reduction value in a range of 98.5% to 100%. The noncomplex superabsorbent polymer is normally classified as the secondary

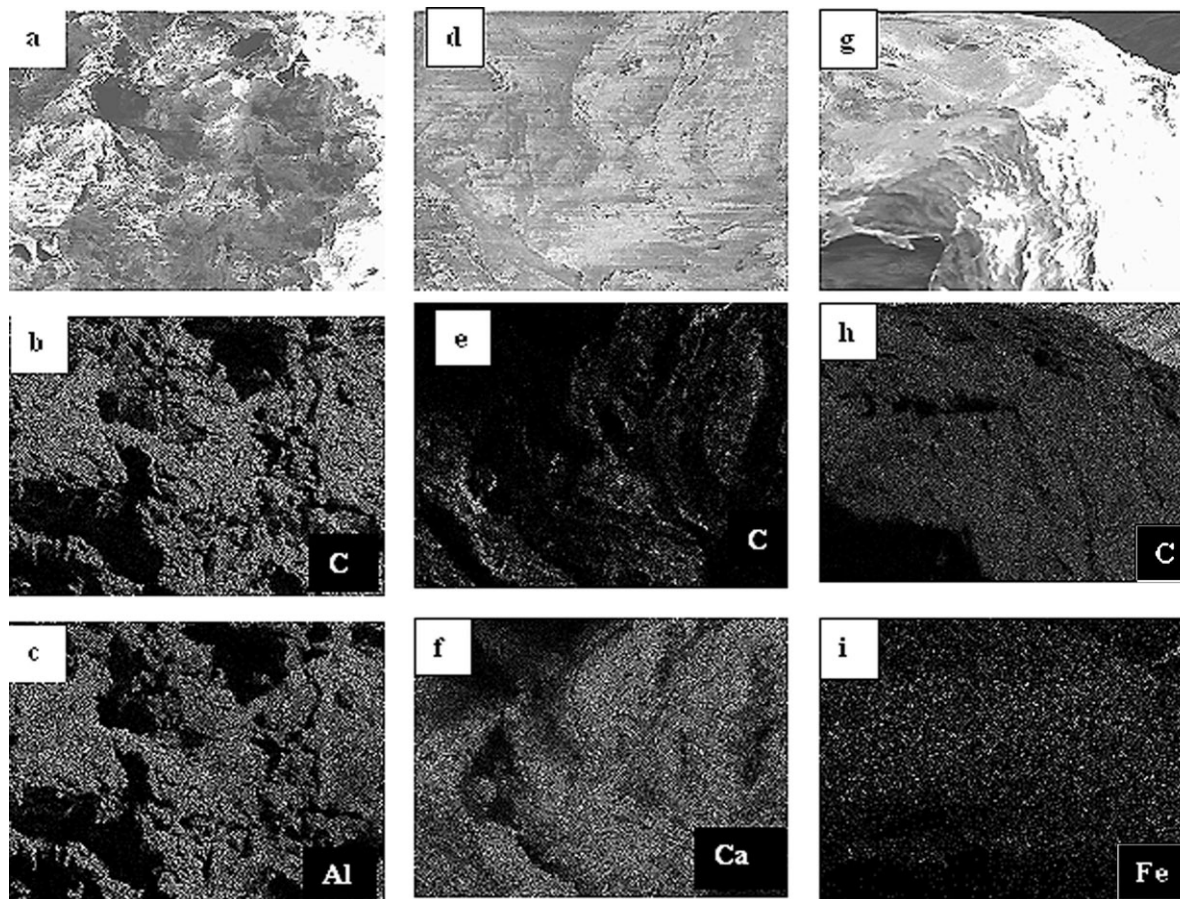


Figure 7 Densities of metal in the complex copolymer of acrylic acid and acrylamide by mapping via SEM/EDXS: a, d, and g are the complex polymers of aluminum, calcium, and ferric ions. The micrographs in b, e, and h are the mapping of carbon, and in c, f, and i are the mapping of aluminum, calcium, and ferric ions.

floculant, whose function of collecting dyes or pollutants has to go through mechanisms of electrostatic sheet or bridging. For the mechanism of electrostatic sheet, the pollutant needs to have the opposite charge to get attraction force to capture the pollutant on the polymer sheet. For the neutralized pollutant, the superabsorbent polymer behaves like a bridge to flocculate the pollutant on its polymeric chains. In the complex polymer flocculant, both mechanisms are expected to take place simultaneously, i.e., it is a type of primary flocculant or coagulant that can effectively remove dyes in wastewater.

In CPF of cassava starch-g-poly(AA)/ $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, / $\text{Ca}(\text{OH})_2$, or / $\text{Fe}_2(\text{SO}_4)_3$

In contrast, the basic pH was revealed when the CPF of poly(AA-co-AM)/ $\text{Ca}(\text{OH})_2$ was used. The dye solution was prepared in a concentration range of 50.0 mg dm^{-3} . The CPF of starch-g-poly(AA) and $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, $\text{Ca}(\text{OH})_2$, or $\text{Fe}_2(\text{SO}_4)_3$ of the amount of 500 mg dm^{-3} was used at pH 7. As shown in Table

III, the CPF containing $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ in the ratio of 1:0.5 (2:1) was less effective in reducing the dye content. For the CPF: $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ in the ratios of 1:1 and 1:2, the increased inorganic coagulant amount decreased the dye concentration, i.e., a higher color removal. The CPF of starch-g-poly(AA) with $\text{Ca}(\text{OH})_2$ revealed the highest color reduction in all copolymer-to-inorganic coagulant ratios comparing with other flocculants or coagulants. The most effective polymer flocculant was identified when the CPF of starch-g-poly(AA) of 1:2 was used from which 95.4% of the dye reduction was achieved. Additionally, the amount of the dye reduction in the solution can be increased by increasing the amount of CPF in the treatment.

The pHs of the synthesized wastewater after the treatment in acid with the CPFs of starch-g-poly(AA) and $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, or $\text{Fe}_2(\text{SO}_4)_3$, are obtained as shown in Table I. The inorganic coagulants of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3$ gave low pH values because sulfuric acid was generated and ionized in water. In contrast, the CPF of starch-g-poly(AA) and $\text{Ca}(\text{OH})_2$ were found to give the pH values in a basic

TABLE III
Water Absorbency, % Color Reduction and pH After Treatment of the Complex Polymeric Flocculants
in 500 mg dm⁻³ of Direct Dye Solution of Sirius Blue K-CFN

Type of CPF	Weight ratio of polymer:inorganic coagulant	Water absorbency (Q, g g ⁻¹)	Color reduction (%)	pH (after treatment)
Poly(AA-co-AM)	1 : 0	1216 ± 52	NA	7.0
Poly(AA-co-AM)/Al ₂ (SO ₄) ₃ ·18H ₂ O	2 : 1	8.4 ± 2.2	-0.1	6.3
Poly(AA-co-AM)/Al ₂ (SO ₄) ₃ ·18H ₂ O	1 : 1 (Al = 5.5%)	4.1 ± 0.4	-1.1	5.7
Poly(AA-co-AM)/Al ₂ (SO ₄) ₃ ·18H ₂ O	1 : 2	3.2 ± 0.5	14.4	4.9
Poly(AA-co-AM)/Ca(OH) ₂	2 : 1	3.1 ± 0.4	25.9	10.6
Poly(AA-co-AM)/Ca(OH) ₂	1 : 1 (Ca=49.7%)	2.5 ± 0.9	53.1	11.1
Poly(AA-co-AM)/Ca(OH) ₂	1 : 2	0.4 ± 0.1	95.4	11.7
Poly(AA-co-AM)/Fe ₂ (SO ₄) ₃	2 : 1	5.2 ± 0.5	-0.2	5.6
Poly(AA-co-AM)/Fe ₂ (SO ₄) ₃	1 : 1 (Fe =0.59%)	4.6 ± 1.9	-0.9	5.8
Poly(AA-co-AM)/Fe ₂ (SO ₄) ₃	1 : 2	4.5 ± 0.6	-1.9	5.5
Starch-g-poly(acrylic acid)	1 : 0	209 ± 12	NA	7.0
Starch-g-poly(AA) and Al ₂ (SO ₄) ₃ ·18H ₂ O	2 : 1	6.8 ± 0.5	0.6	6.4
Starch-g-poly(AA) and Al ₂ (SO ₄) ₃ ·18H ₂ O	1 : 1 (Al = 4.8%)	4.1 ± 0.1	14.0	4.1
Starch-g-poly(AA) and Al ₂ (SO ₄) ₃ ·18H ₂ O	1 : 2	2.5 ± 0.4	8.8	4.2
Starch-g-poly(AA) and Ca(OH) ₂	2 : 1	6.2 ± 1.4	25.4	9.9
Starch-g-poly(AA) and Ca(OH) ₂	1 : 1 (Ca=44.2%)	2.0 ± 0.3	68.6	10.7
Starch-g-poly(AA) and Ca(OH) ₂	1 : 2	1.2 ± 0.7	73.8	11.0
Starch-g-poly(AA) and Fe ₂ (SO ₄) ₃	2 : 1	5.3 ± 1.3	6.4	4.3
Starch-g-poly(AA) and Fe ₂ (SO ₄) ₃	1 : 1 (Fe =14.3%)	3.7 ± 0.3	4.2	4.2
Starch-g-poly(AA) and Fe ₂ (SO ₄) ₃	1 : 2	3.4 ± 1.2	11.1	3.6
Al ₂ (SO ₄) ₃ ·18H ₂ O	0 : 1	NA	98.5	4.0
Ca(OH) ₂	0 : 1	NA	99.1	12.2
Fe ₂ (SO ₄) ₃	0 : 1	NA	100	2.75

% color reduction of the direct dye at λ_{\max} at 585 nm, after being treated with 500 mg dm⁻³ of flocculants, initial pH =7. NA = not available.

range because of the basic pH of the inorganic coagulant (Table III).

In comparison, the CPF of poly(AA-co-AM) or starch-g-poly(AA) with inorganic coagulants: Al₂(SO₄)₃·18H₂O, Ca(OH)₂, and Fe₂(SO₄)₃ could be an effective color reducer especially for direct dye in wastewater. The amount of the direct dye adsorbed on the CPF gel of poly(AA-co-AM)/Ca(OH)₂ was higher than that adsorbed on starch-g-poly(AA)/Ca(OH)₂. Polyacrylamide is a nonionic polymer from which the amino nitrogen can interact slightly by its cationic moiety. When synergistically copolymerized with AA, the ionizable groups of the carboxylic acid in the AA chains can form an additional complexing portion between the polymer and the inorganic coagulant. Many more carboxylic groups can increase interaction between the dye molecules and the CPFs. Therefore, increase in interactions between the dye molecules and complexed copolymer could be one reason for a better treatment. These interactions may be hydrophobic or hydrogen bonding. Hydrogen bonding was expected to occur between the amide and carboxyl groups on the monomer unit of crosslinked copolymer. Then, poly(AA-co-AM) has high water absorbency and dye adsorption than that of starch-g-poly(AA).

Efficiency of color reduction for the industrial wastewater containing textile dyes

The physical properties of textile dye from industry in Bangkok are shown in Table I. The complex polymeric flocculants that produced the high percentage of direct dye color reduction efficiency was selected and a quantity of 500 mg dm⁻³ was used. The CPF of poly(AA-co-AM) and Ca(OH)₂ in the ratio of 1 : 1 and 1 : 2 were used to compare with the CPF of starch-g-poly(AA) and Ca(OH)₂ in the ratio of 1 : 1 was used. Although the inorganic flocculants showed a higher percentage of color reduction, the CPF of poly(AA-co-AM)/Ca(OH)₂ at 1 : 2 ratio showed the similar efficiency for the color reduction by 95% for the direct dye and 76% for the dye from the industrial wastewater. The starch copolymer also showed some dye adsorption and color reduction, i.e., 74% for the direct dye, and 18% for the industrial wastewater (Table IV). One of the advantages of CPFs is the ease to remove the polymer flocculant from effluent stream by filtering. Absence of some toxic metal ions in the effluent is anticipated as another advantage for using complex polymer flocculant (see Fig. 8).

TABLE IV
Percentage Color Reduction of Wastewater After Treatment with Various Flocculants

Flocculants (500 mg dm ⁻³)	Color reduction (%)						
	Syn direct	A1/10 direct	A2/500 reactive	A2/1000 reactive	A3/2 mixed	B1/100 Acid	B2/2 mixed
Poly(AA-co-AM):Ca(OH) ₂ ; 1:1	53	22	3	1	ND	3	6
Poly(AA-co-AM):Ca(OH) ₂ ; 1:2	95	76	4	12	20	16	15
Starch-g-poly(AA):Ca(OH) ₂ ; 1:2	74	18	4	0.3	17	ND	ND
Al ₂ (SO ₄) ₃ ·18H ₂ O	99	100	77	69	35	18	ND
Ca(OH) ₂	99	96	19	30	92	ND	100
Fe ₂ (SO ₄) ₃	100	100	75	74	22	19	27
Initial dye concentrations, mg dm ⁻³	50	31	50	25	6	16	16

Properties of wastewater from the textile factory are described in Table I, ND = not detected. Measurement at $\lambda_{\max} = 585$ nm.

Reductions in COD and turbidity of the synthetic direct dye and industrial wastewater containing textile dyes

As shown in Table V, it was found that the Al₂(SO₄)₃·18H₂O, Ca(OH)₂, and Fe₂(SO₄)₃ solutions can reduce COD in almost all cases, except for the strong acid dye solutions (B1 and B2). Undoubtedly, there might be some specific complex formation reactions occurring in the diluted reactive dye solution A2/1000. In this work, the CPFs show significantly the COD reductions, which are better than the inorganic coagulants. Besides, the CPFs used in the treatment cannot effectively reduce turbidities (Table VI). Therefore, these CPFs are very useful for specific chemical

treatments and will probably be a potential cleaner technology to replace the classical chemical treatments in the future.

Efficiency dependence of the treatment on pH of the solution

Very importantly, the resulting pH values after the treatment of the synthetic direct dye are a major concern. The solution after the treatment was acidic when using CPF of poly(AA-co-AM) and Al₂(SO₄)₃·18H₂O, or Fe₂(SO₄)₃. The resulting pH value of the synthetic dye treated with the inorganic coagulants or the CPFs is shown in Table III. The pHs of the synthesized wastewater and industrial wastewater were alkaline after treatment with the CPF of starch-g-poly(AA)/Ca(OH)₂. The polymer/Ca(OH)₂ complexes were basic because of the nature of inorganic coagulant. The water samples became strongly acidic after the treatment with Al₂(SO₄)₃·18H₂O or Fe₂(SO₄)₃, as shown in Table VII. The basic effluent after being treated with the CPFs can be easily neutralized with a small amount of acid before draining.

Residual metal ion concentrations of CPFs and inorganic coagulants in the synthetic dye wastewater treatment

Figure 8 shows the residual metal ions after treatments of the synthetic wastewater. Although the color reduction of the inorganic coagulants was much higher than the CPFs, one can observe that the residual concentrations of inorganic coagulants are much higher than the CPFs due to their higher solubility in water. Ca(OH)₂ gives the highest residual calcium ion concentration than the other two ions of Al³⁺ and Fe³⁺. Considering the two CPFs at the ratio of 1:2, starch complex/Ca(OH)₂ releasing less Ca²⁺ ion concentration in water could be presumed that the a higher amount of ion has been incorporated in the complexes and the com-

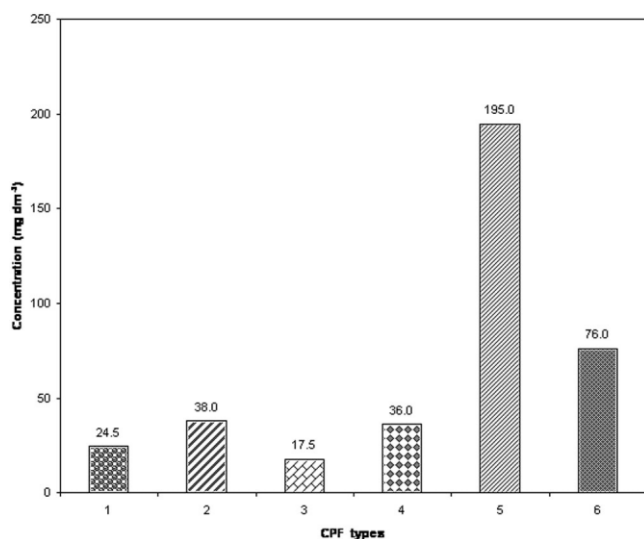


Figure 8 The residual metal ion concentrations in the synthetic dye wastewater after treatments with 500 mg dm⁻³ of CPFs and inorganic coagulants: (1) Poly(AA-co-AM)/Ca(OH)₂, ratio 1 : 1; (2) Poly(AA-co-AM)/Ca(OH)₂, ratio 1 : 2; (3) Starch-g-poly(AA)/Ca(OH)₂, ratio 1 : 2; (4) Al₂(SO₄)₃·18H₂O; (5) Ca(OH)₂; (6) Fe₂(SO₄)₃.

TABLE V
Percentage COD Reduction of Wastewater After Treatment with Various Flocculants

Flocculants (500 mg dm ⁻³)	COD reduction (%)						
	Syn direct	A1/10 direct	A2/500 reactive	A2/1000 reactive	A3/2 mixed	B1/100 acid	B2/2 mixed
Poly(AA-co-AM) : Ca(OH) ₂ ; 1 : 1	29	ND	3	44	19	ND	2
Poly(AA-co-AM) : Ca(OH) ₂ ; 1 : 2 (250 mg dm ⁻³)	ND	6	14	56	14	ND	1
Poly(AA-co-AM) : Ca(OH) ₂ ; 1 : 2	55	ND	9	67	13	16	5
Starch-g-poly(AA) : Ca(OH) ₂ ; 1 : 2	ND	ND	0	ND	15	ND	ND
Al ₂ (SO ₄) ₃ ·18H ₂ O	81	44	77	44	21	18	45
Ca(OH) ₂	79	44	19	22	19	ND	23
Fe ₂ (SO ₄) ₃	84	67	75	89	26	19	45
Initial COD (mg dm ⁻³)	29	92	78	21	478	213	502

Syn. = The synthesized dye in an aqueous solution of 50.0 mg dm⁻³ as a model dye solution.

A1, A2, A3, B1, and B2 = Waste water from the textile factory as described in Table I.

NA = no data available.

plex stability is also higher. However, the use of CPFs in wastewater treatment could be safer than the pure inorganic coagulant even though one has to sacrifice the high treatment efficiency.

CONCLUSIONS

Poly(AA-co-AM) and starch-g-poly(AA) were prepared by radical copolymerization in water using ammonium peroxide/TEMED initiator with N-MBA crosslinker. The water absorption capacity of the starch-g-poly(AA-co-AM) was higher than that of starch-g-poly(AA), and the CPFs had the lowest water absorption. The metal ion densities obtained by SEM/EDX technique along with water absorbency of the CPFs revealed that a higher amount of metal ion of the inorganic coagulant is necessary for a better color reduction. The complex superabsorbent polymer flocculants with inorganic coagulants of Al₂(SO₄)₃·18H₂O, Ca(OH)₂, or Fe₂(SO₄)₃ in various ratios of copolymer to inorganic material exhibited different performances as flocculating agents in terms of color reduction, re-

duced turbidity, pH, and COD reduction of the synthetic dye and mixed dyes from the textile industry. The dye adsorption was studied with the synthetic aqueous solution of direct dye, Sirius blue K-CFN. It was found that the CPF of poly(AA-co-AM) with Ca(OH)₂ with a 1:2 ratio can reduce Sirius blue K-CFN color by 95 and 76% for the textile industrial wastewater. The adsorptions of the dyes increased with the increasing content of Ca(OH)₂ in the superabsorbent. The percentage COD reduction of the CFP was satisfactory (not less than 67% in A2 reactive dye). Turbidity of the wastewater for A2/500 and A2/1000 was not good but the pH values of these two concentrations were relatively alkaline. As a whole, the performance of the polymer complex flocculating agent of poly(AA-co-AM) and starch-g-poly(AA)/Ca(OH)₂ is good enough for dye wastewater treatment from the textile industry.

We thank Ms. W. Supasuk for carrying some part of the experimental work in the wastewater treatment. Many thanks are due to Chulalongkorn University's graduate School on partial support of research chemicals.

TABLE VI
Turbidity of the Wastewater after Treatment with Various Flocculants

Flocculants (500 mg dm ⁻³)	Turbidity (NTU)						
	Syn direct	A1/10 direct	A2/500 reactive	A2/1000 reactive	A3/2 mixed	B1/100 acid	B2/2 mixed
Poly(AA-co-AM) : Ca(OH) ₂ ; 1 : 1	ND	9.99	3.33	1.58	9.15	0.54	9.99
Poly(AA-co-AM) : Ca(OH) ₂ ; 1 : 2	4.1	9.99	6.11	1.44	9.99	1.32	9.99
Starch-g-poly(AA) : Ca(OH) ₂ ; 1 : 2	0.6	9.99	2.53	1.86	9.25	3.27	9.99
Al ₂ (SO ₄) ₃ ·18H ₂ O	1.1	1.66	9.99	0.48	8.70	2.31	1.82
Ca(OH) ₂	3.2	2.06	1.60	7.81	3.81	9.99	9.99
Fe ₂ (SO ₄) ₃	2.9	2.26	9.99	9.99	9.99	9.99	2.42
Initial turbidity (NTU)	ND	5.89	0.18	0.17	8.39	0.32	9.99

Properties of wastewater from the textile factory are described in Table I.

ND = not detected.

TABLE VII
pH After Treatment with Various Flocculants

Flocculants (500 mg dm ⁻³)	pH						
	Syn direct	A1/10 direct	A2/500 reactive	A2/1000 reactive	A3/2 mixed	B1/100 Acid	B2/2 mixed
Poly(AA-co-AM):Ca(OH) ₂ ; 1 : 1	11.1	10.0	9.5	10.5	9.2	10.0	9.8
Poly(AA-co-AM):Ca(OH) ₂ ; 1 : 2	11.7	11.3	10.5	11.2	10.5	10.7	10.5
Starch-g-poly(AA):Ca(OH) ₂ ; 1 : 2	11.0	10.0	10.6	10.4	10.2	10.0	9.7
Al ₂ (SO ₄) ₃ ·18H ₂ O	4.0	3.6	3.7	3.8	4.1	3.8	4.2
Ca(OH) ₂	12.2	11.4	11.2	11.4	11.2	11.0	11.4
Fe ₂ (SO ₄) ₃	2.8	2.5	2.3	2.4	2.7	2.3	2.5
No flocculants (Initial pH)	7.0	7.8	9.4	9.3	10.8	4.2	7.0

ND, not detected.

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