A STUDY ON THE EFFECT OF HYDROPHOBICALLY MODIFIED CATIONIC ACRYLAMIDE COPOLYMERS ON FLOCCULATION PROPERTIES OF KAOLIN SUSPENSION

by

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LIST OF SYMBOLS

mg/g	milligram per gram
mg/L	milligram per liter
^{o}C	degree Celsius
mmHg	millimeter mercury
M	molarity
n_c	mole of cationic comonomer
n_{AM}	mole of acrylamide
C	concentration of silver nitrate
V	volume of silver nitrate used
m	weight of the polymer
M_W	molecular weight of cationic monomer
M_{AM}	molecular weight of acrylamide
k	k constant
α	alpha constant
η	viscosity
A	calibration constant of the viscometer
ρ	density of solution
t	flow time
mol%	mole percent
$[\eta]$	intrinsic viscosity
g/mol	gram per mole

LIST OF ABBREVIATION

PAM	polyacrylamide
PDADMAC	polydiallyldimetylammonium chloride
NH_2	amine
VTMS	vinyl trimethoxysilane
PCA_5H_1	hexyloxypropyl
PCA_5D_1	decyloxypropyl
AHPTAAC	3-acrylamido-2-hydroxylypropyltrialkylammonium chloride
HPA	3-acrylamido-2-hydroxylypropyltrihexylammonium chloride
OPA	3-acrylamido-2-hydroxylypropyltrioctylammonium chloride
DPA	3-acrylamido-2-hydroxylypropyltridodecylammonium chloride
AM	acrylamide
P(HPA-co-AM)	poly(3-acrylamido-2-hydroxylypropyltrialkylammonium chloride-co-acrylamide)
P(OPA-co-AM)	poly(3-acrylamido-2-hydroxylypropyltrioctylammonium chloride-co-acrylamide)
P(DPA-co-AM)	poly(3-acrylamido-2-hydroxylypropyltridodecylammonium chloride-co-acrylamide)
FT-IR	Fourier Transform Infrared Spectrometry
TEM	Transmission Electron Miscroscope
SEM	Scanning Electron Microscope
ANOVA	analysis of variance
$Al_2Si_2O_5(OH)_4$	kaolin

Al_2O_3	octahedral alumina
-Si-O-Si-	siloxane
Si^{4+}	silicon ion
Al^{3+}	aluminium ion
Al-OH	aluminol
Si-OH	silanol
$FeCl_{3}.6H_2O$	hydrated ferric chloride
$Al_2(SO_4)_3 14H_2O$	hydrated alum
$CaCl_2$	calcium chloride
$Mg(NO_3)_2$	magnesium nitrate
$FeCl_3$	ferric chloride
NaCl	sodium chloride
PACl	polyaluminium chloride
$NaNO_3$	sodium nitrate
NTU	Nephelometric Turbidity Units
Ca^{2+}	calcium ion
Mg^{2+}	magnesium ion
Fe^{3+}	iron ion
$NaHCO_3$	sodium hydrogen carbonate
$CaCO_3$	calcium carbonate
PAM A	anionic polyacrylamide
PAM C	cationic polyacrylamide
PAM N	nonionic polyacrylamide
$MnCl_2$	manganese chloride
Ca(II)	calcium (II) ion

Mn(II)	manganese (II) ion
Da	Dalton
COO^-	carboxylate
PEO	Polyethylene oxide
$AlCl_3 \cdot 6H_2O$	hydrated aluminium chloride
$FeSO_4 \cdot 7H_2O$	hydrated ferric sulphate
$MgCl_2$	magnesium chloride
KCl	potassium chloride
NH_4Cl	ammonium chloride
$BaCl_2$	barium chloride
$ZnSO_4$	zinc sulphate
$Ca(NO_3)_2$	calcium nitrate
Na_2SO_4	sodium sulphate
PAAHTE	poly(acrylamide-co-3-acrylamido-2-hydroxylypropyltriethylammonium chloride)
PAAHTB	poly(acrylamide-co-3-acrylamido-2-hydroxylypropyltributylammonium chloride)
PAAHTO	poly(acrylamide-co-3-acrylamido-2-hydroxylypropyltrioctylammonium chloride)
SDS	sodium dodecyl sulphate
CTAB	Cetyl Trimethyl Ammonium Bromide

KAJIAN TERHADAP KESAN KATIONIK AKRILAMIDA KOPOLIMER HIDROFOBIK TERUBAH KE ATAS SIFAT PEMBERBUKUAN AMPAIAN KAOLIN

ABSTRAK

Satu siri kationik poliakrilamida hidrofobik terubah telah disintesis melalui larutan kopolimerasi radikal bebas dengan menggunakan ammonium persulfat/natrium hidrogen sulfit sebagai permula. Epiklorohidrin, akrilamida dan triakilamina telah digunakan untuk mensistesis monomer hidrofobik kationik 3-akrilamido-2-hidroksipropiltriakilammonium klorida yang mana kumpulan trialkil adalah triheksilamina (HPA), trioktilamina (OPA) and tridodesilamina (DPA). Monomer kationik dari kumpulan masing-masing yang berkepekatan rendah (1 – 6 mol%) dikopolimerasi dengan akrilamida untuk mendapatkan poliakrilamida kationik hidrofobik terubah. Kopolimer yang diperolehi pada kepekatan monomer yang tinggi adalah tidak larut dalam cecair akues disebabkan sifat hidrofobik yang tinggi dan kesan pengikatan rantai. Keputusan menunjukkan bahawa kelikatan intrinsik dan jisim molekul bagi kopolimer menurun dengan peningkatan kepekatan kumpulan kationik hidrofobik, manakala ketumpatan cas menunjukkan sifat yang songsang. Inframerah Jelmaan Fourier (FTIR) dan Mikroskopi Elektron Transmisi (TEM) telah digunakan untuk menerangkan kumpulan kimia dan struktur dalam kopolimer tersebut. Korelasi telah dibuat di antara jisim molekul dengan ketumpatan cas kopolimer. Didapati bahawa terdapat satu hubungan korelasi songsang yang signifikan dalam kajian ini. Kesan poliakrilamida kationik hidrofobik terubah mempunyai jisim molekul dan ketumpatan cas yang berbeza ke atas pemberbukuan campuran kaolin telah dikaji. Jisim molekul yang tinggi didapati berkesan dalam pemberbukuan campuran kaolin. Perbandingan kumpulan hidrofobik yang berbeza dan penggantian nisbah monomer ke atas penurunan kekeruhan telah dijalankan.

Kopolimer kumpulan heksil yang mempunyai jisim molekul sebanyak 2.13×10^6g/mol menunjukkan aktiviti pemberbukuan terbaik sebanyak 99%. Kepekatan monomer hidrofobik kationik sebanyak 1 mol% dalam kopolimer didapati sebagai sistem terbaik dalam pemberbukuan campuran kaolin. ‘Bridging’ merupakan mekanisma utama dalam pemberbukuan campuran kaolin. Kopolimer dengan kumpulan dodecil mempunyai kandungan air yang paling sedikit dalam mendakan berbanding dengan kumpulan oktil dengan heksil.

A STUDY ON THE EFFECT OF HYDROPHOBICALLY MODIFIED CATIONIC ACRYLAMIDE COPOLYMERS ON FLOCCULATION PROPERTIES OF KAOLIN SUSPENSION

ABSTRACT

A series of hydrophobically modified cationic polyacrylamides were synthesized via free radical solution copolymerization using ammonium persulphate/sodium hydrogen sulphite as the redox initiator. Epichlorohydrin, acrylamide and trialkylamine were used to synthesize the hydrophobic cationic monomer 3-acrylamido-2-hydroxypropyltriakylammonium chloride (AHPTAAC) in which the trialkyl group was trihexylamine, trioctylamine and tridodecylamine. Low concentration (1-6 mol %) of cationic monomer from each group were copolymerized with acrylamide to obtain hydrophobically modified cationic polyacrylamides. Copolymer obtained at high concentration of cationic monomer was insoluble in the aqueous medium due to its high hydrophobicity and entanglement effect. Results show that the intrinsic viscosity and molecular weight of the copolymers decreases with the increase in concentration of the hydrophobic cationic group, whereas charge density indicates the reverse behaviour. Fourier Transform Infrared (FTIR) and Transmission Electron Microscopy (TEM) were also carried out to elucidate the functional groups and structures of the copolymer respectively. A correlation analysis has been done between molecular weight and charge density of the copolymers. It was found that there is a significant inverse correlationship between molecular weight and charge density in this study. The effect of hydrophobically modified cationic polyacrylamide of varying molecular weight and charge density on flocculation of a kaolin suspension has been investigated. High molecular weight was found to be ideal in flocculating kaolin suspension. Comparison of different hydrophobic groups and monomer substitution ratio on turbidity removal was done. Hexyl group copolymer which had the highest molecular weight of 2.13×10^6g/mol shows the best flocculation activity and reduced turbidity by 99%. 1 mol % of hydrophobic cationic monomer concentration in copolymers was found to be the best system in flocculating the kaolin suspension. Bridging was the dominant mechanism in flocculating the kaolin suspension. Copolymer with a dodecyl group had the least water retention in the flocculated sludge compared to octyl and hexyl groups.

CHAPTER 1

INTRODUCTION

1.1 Colloids Dispersion

Colloids such as organic matters, microbes, clays and oil droplets, pose a settling problem when disperse in aqueous medium. Dispersion is defined to be a structure developed according to the nature of the operative particles interactions and surface forces. The origin of the interaction forces is attributed to electrostatic repulsion, polarization and covalent interactions. Colloidal sizes are too small to be influenced by an external gravitational force and hence form stable colloid in aqueous medium. Stable dispersion resists to aggregation where a net repulsive force dominates between particle surfaces (Lyklema, 1978; Addai-Mensah and Prestidge, 2005). Thus, an aggregation force is needed to be introduced in order to clump the colloids together to form agglomerate which will settle and filter in subsequent steps.

1.2 Mineral Industry (Kaolin) in Malaysia

Malaysia produces bauxite, coal, feldspar, gold, ilmenite, iron ore, kaolin, mica, monazite, natural gas, oil, sand and gravel struverite, tin and zircon. There are 21 kaolin mines in Johor and Perak. 83% of kaolin in Perak productions is from Bidor and Tapah. Kaolin clay production is important in the mineral industry of Malaysia. Table 1.1 shows the production of kaolin clay in Malaysia from the year 1996 to the year 2005. Locally produced kaolin clay is used in the production of cement, ceramics, chemicals, paint, paper filler, and rubber. Kaolin produced from Malaysia’s mineral industry is mainly exported to Japan, Taiwan and Thailand (Wu, 2000; Tse, 2005). The environmental aspects of mine development are regulated by the Environmental Quality Act (Prescribed Activities) (Environmental Impact Assessment) Order 1987, which was an amended to the Environmental Quality Act of 1987 (Wu, 2000).

Table 1.1 The production of kaolin clay in Malaysia from the year 1996 to the year 2005. (Source: Wu, 2000; Tse, 2005)

Year	Kaolin Production in Malaysia (metric tons)
1996	324,578
1997	221,769
1998	198,930
1999	208,187
2000	233,885
2001	364,458
2002	323,916
2003	425,942
2004	326,928
2005	494,511

1.3 Environmental Problems that Arise from the Mineral Industry (Kaolin)

Kaolin is a mineral that has a wide variety of applications in industry, particularly as paper filler and coating pigments. It is used as an extender in water-based paints and ink, and as a functional additive that can improve the properties of the material in which it forms a stable dispersion (Tekin et al., 2005). Kaolin clay constitutes a common yet problematic mineral for waste tailings treatment and disposal from hydrometallurgical and mineral processing operations. Moreover, waste residues produced from the mineral and paper processing industries need to be disposed off in an environmental friendly manner. Mineral industrial wastes consisting of mineral such as kaolin is difficult to settle and consolidate due to its colloidal size, anisotropic shape and permanently negatively charged basal faces. When disperse in water, kaolin often forms a turbid suspension. Besides, kaolin invariably poses a significant problem to dewatering since the flocs structures formed through flocculant assisted gravity thickening, typically retain a great deal of water due to its underlying interfacial chemistry and particles interactions (McFarlene et al., 2005b). Hence, removal of these particles from effluents before discharging into the environment becomes a problem encountered by the clay processing industry (Divakaran and Pillai, 2001; McFarlene et al., 2005a; Nasser and James, 2006, 2007).

1.4 Coagulation-Flocculation Method

Coagulation-flocculation is one of the physico-chemical methods employed in industries to destabilize particles that are dispersed in water. Coagulation-flocculation process involves adding floc-forming chemical reagent to water or wastewater to enmesh or agglomerate non-settleable colloidal solids and slow settling suspended solids to produce rapid settling flocs. The flocs are subsequently removed by sedimentation prior to discharge (Reynolds and Richards, 1996). Figure 1.1 depicts a coagulation-flocculation treatment process. Coagulation-flocculation process takes place after pH adjustment to an optimal pH. Coagulated and flocculated sludge is allowed to settle and dewater; treated supernatant will be filtered and discharged.

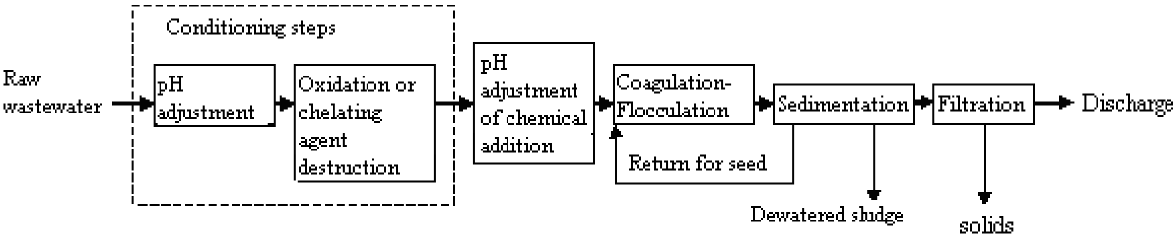

Figure 1.1 Model of coagulation-flocculation treatment facility (Woodard, 2006)

1.5 Overview of Hydrophobically Modified Polymers in Coagulation-Flocculation Process

Hydrophobically modified polymers have recently become the subject of extensive research due to their unique characteristics and applications. It is able to improve the efficiency in solid-liquid separation, making it important in water and wastewater application. The introduction of hydrophobic group into the chain backbone will eventually reduce its solubility in water and increase polymer's hydrophobicity (Vorchheimer, 1981). With the association of hydrophobic group, polymers have exhibited a very interesting rheological property and enhanced stability compared to the unmodified polymers (Zhu et al., 2007).

Studies on some hydrophobically modified polymers synthesis for special applications had been carried out. Hydrophobic modification of synthetic polymers can be performed through chemical grafting or copolymerization procedure. Several kinds of hydrophobically modified polymers have been developed such as hydrophobically modified polyacrylamide (Candau and Selb, 1999), hydrophobically modified chitosan (Bratskaya et al., 2006), hydrophobically modified polycation (Dragan et al., 2002), hydrophobically modified starch (Nilsson and Bergenståhl, 2007), hydrophobically modified PDADMAC (Zhao et al., 2002), and among them hydrophobically modified polyacrylamides received the most attention (Candau and Selb, 1999).

1.5.1 Hydrophobically Modified Polyacrylamides

There are various types of polyelectrolytes available in the market and the commonly used polyelectrolytes are acrylamide and its derivatives. Polyacrylamides are the most common type of polymeric flocculant due to their effectiveness as flocculants (Wong et al., 2006) and ability to produce good settling performance with relatively low cost (Nasser and James, 2006). Acrylamide and its derivatives have been extensively used in industrial water treatment as a flocculant (Besra et al., 2003; Qian et al., 2004; Wong et al., 2006). Various techniques have been used to improve the performance and to obtain cost effective polyacrylamide derivatives in flocculating contaminants. Adsorption of polyacrylamide on solids from aqueous solutions is essential in stabilization of colloids and this mechanism is determined by the nature of the polymers (Somoshina et al., 2003). Hydrophobically modification techniques were done by changing the structures of the polyacrylamides. These polymers are tailored on the basis of a hydrophilic structure by introducing a relatively small amount of hydrophobic monomer into a hydrophilic macromolecular chain (Candau and Selb, 1999).

Copolymerization of hydrophobically modified polyacrylamides can be done by adding a relatively low amount (1-5 mol%) of hydrophobic comonomer into the polymer chain (Biggs et al., 1992; Volpert et al., 1997).The presence of hydrophobic moieties in the hydrophilic chain exhibits high surface and interfacial activities hence enhances ability to adsorb at an interface (Yahaya et al., 2001). The domains consisting of hydrophobic groups of different polymer chains play a role of intermolecular entanglement which can lead to a significant increase of viscosity and eventually to the formation of physical gel that is extensively exploited for blocking water in enhanced oil recovery (Shaskina et al., 2003). The increase of solution viscosity is directly related to the size of the hydrophobic group due to the increase in hydrophobic interactions (Candau and Selb, 1999). Addition of hydrophobic group in the polyacrylamide chain has promoted application in enhanced oil recovery, drilling fluids, coatings, or cosmetics drag reduction, flocculation, super absorbency, latex paints, hydraulic fluids, protein separations, industrial thickeners, controlled drug release, biological/medical purposes and typically in wastewater treatment (Daughton, 1998; Yahaya et al., 2001; Wei et al., 2004; Zhu et al., 2007).

1.5.2 Hydrophobically Modified Chitosan

Chitosan can be described as an amino-polysaccharide which is produced by deacetylation of chitin. It is a polymer of D-glucosamine with an NH_2 group in place of the OH group on carbon-2-of D-glucose. It poses cationic charge and establishes to coagulate negatively charged suspended particles in aqueous medium (Divakaran and Pillai, 2001; Pinotti et al., 2001; Roussy et al., 2005; Guibal and Roussy, 2007;). It has been widely employed as biopolymer in wastewater treatment for dyes (Guibal and Roussy 2007), kaolinite suspensions (Divakaran and Pillai 2001), bentonite suspensions, metal cations, inorganic anionic solutes, latex particles, microorganisms and pesticides (Roussy et al., 2005).

The presence of amine functional group in chitosan has induced effective binding of metal cations in near neutral condition and adsorption on anionic solutes in acidic medium (Guibal and Roussy, 2007). The performance of chitosan was reported to be highly dependent on pH in treating kaolinite suspensions (Divakaran and Pillai, 2001) and reactive dye (Guibal and Roussy, 2007). The highly pH dependence thus invokes additional chemicals in optimizing the pH which eventually increases the treatment cost.

In view of improvement of wastewater treatment efficiency, modification of molecules to become more hydrophobic was seen to have greater ability to penetrate and react (Roussy et al., 2005). A hydrophobically modified chitosan derivative was synthesized in treating oil-water emulsions (Bratskaya et al., 2006). By incorporating hydrophobic substitutes into chitosan backbone, synergetic effect of cationic and hydrophobic groups is formed, thus, increasing the efficiency in oil and water separation. The hydrophobically modified chitosan has gained the advantage of requiring low dosages; therefore it contributes to higher efficiency of turbidity reduction in comparison with the ordinary chitosan.

Considering its non toxic characteristic, hydrophobically modified chitosan poses its advantage as an environmental friendly flocculant in treating wastewater. Sludge produced from the treated wastewater can be safely disposed off in municipal landfills due to its biodegradable properties.

1.5.3 Hydrophobically Modified Polydiallyldimetylammonium Chloride (PDADMAC)

Cationic quaternary ammonium polyelectrolytes have been employed in diverse application in wastewater treatment industry recently. Polydiallyldimetylammonium chloride acts as an excellent water-soluble cationic ammonium polymer. PDADMAC is characterized with its cationic nature, high charge density and low molecular weight (Yu et al., 2006). However, high cationicity of PDADMAC poses a problem of difficulty in forming high molecular weight during polymerization due to the presence of allyl monomers in the molecular chain (Tian et al., 2006). Bridging mechanism thus becomes less prominent for PDADMAC.

To enhance bridging mechanism and reduce treatment cost, PDADMAC therefore undertakes some modification, grafted action, addition of hydrophobic or hydrophilic monomers and polyelectrolyte complexes during polymerization (Tian et al., 2007). According to Zhao et al., (2002), a hydrophobic monomer vinyl trimethoxysilane (VTMS) was polymerized with DADMAC to form hydrophobically modified polymer poly(diallyldimethylammonium chloride-vinyl- trimethoxysilane) [P(DADMAC-VTMS)]. Attempts to apply this hydrophobically modified P(DADMAC-VTMS) in treating negatively charged kaolinite, dye liquor and oily wastewater have shown an improvement in turbidity reduction, decolourization and oil removal.

However, higher dosages were required to treat wastewaters mentioned above. It was attributed to the decrease of cationicity due to addition of VTMS and it needs higher dosage to neutralize the surface charge. In spite of the higher dosages required, bulky and fluffy P(DADMAC-VTMS) have enhanced the interaction between hydrophobic kaolinite particles with its improved hydrophobicity. The hydrolysis of VTMS produces P(DADMAC-VTMS) with relatively low contents of hydroxyl groups. Hydrophobic and hydroxyl functionalities thus enhance coulombic attraction, hydrogen bonding and hydrophobic association in dye treatments. For oil removal, the addition of VTMS group has induced expansion of polymer and improved its solubility in solution therefore improves the attractive interaction between oil droplets.

The synergism effects between cationic functionality and hydrophobic group have shown an outstanding performance in treating negatively charged wastewater. Furthermore, the existence of VTMS in PDADMAC also plays a role similar to a surfactant in an aqueous solution (Zhao et al., 2002). Polydiallyldimetylammonium chloride (PDADMAC) has been reported to be a common polymer as flocculant or flocculant aid in the destabilization of colloidal suspensions, clarification of industrial wastewater, solid-liquid separation, sewage treatment and so forth (Zhao et al., 2002; Tian et al., 2007). Chemical structure of PDADMAC is illustrated in

Figure 1.2. Polydiallyldimetylammonium chloride is a cationic and high charge density polyelectrolyte used in treating negatively charged colloids. Its allyl monomers are hard to polymerize, thus yielding relative low molecular weight in comparison with other common vinyl monomers (Tian et al., 2006). Charge neutralization is proven to be the primary mechanism of PDADMAC in the destabilization of colloids due to its optimal dosage in treating oppositely charged particles occurred near the point of zero in zeta potential measurement. However, there is less probability for bridging mechanism to occur due to highly charged and short chain of PDADMAC that tends to adsorb particles in a flat state. PDADMAC is described to have narrow range of optimal dosage ascribed to maximize treatment, where the particle surface is neutralized by positive charge of PDADMAC; further increase of dosage caused charge reversal thus inducing restabilization of particles (Yu et al., 2006).

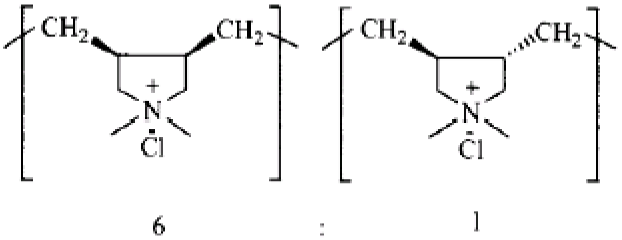

Figure 1.2 Chemical Structure of PDADMAC (Tian et al., 2007)

1.5.4 Hydrophobically Modified Polycations

Cationic polyelectrolytes with quaternary ammonium salts are commonly used as flocculants in treating negatively charged wastewater. Their chain flexibility, molecular weight, and charge density are the main factors in determining the application of the cationic polymers in the treatment of drinking water; removal of coal, biological mashes, or waste dye from industrial wastewaters, paper processing and thickening of sludges (Dragan et al., 2002).

The presence of a low content of hydrophobic chains in the polycation structure may improve their affinity toward hydrophobic organic molecules and colloidal suspension. Dragan et al. (2002) synthesized hydrophobically modified polycation by performing condensation polymerization using quaternary ammonium salt group and hydrophobic chains e.g. hexyloxypropyl, PCA_5H_1 and PCA_5H_2; and decyloxypropyl, PCA_5D_1. Hydrophobically modified polycations with long hydrophobic chain decyloxypropyl group was effective in removing montmorillonite from the aqueous suspensions.

1.6 Significance of Study

Various derivatives of polyacrylamide have been explored over the past decades in order to improve flocculation performance in solid-liquid separation. Polyacrylamide based flocculants have become the most popular polyelectrolytes among others in the water treatment industries due to its economical reason and high performance in treating wastewater. Despite a great variety and availability of commercially available flocculants, there is still a need for improvement of their efficiency and development of products for special applications (Bratskaya et al., 2006). Hence, improvement to acrylamide-based polyelectrolytes is necessary to achieve cost reduction and to enhance current solid-liquid separation performance..

Ren et al. (2007) has studied the copolymerization of acrylamide with 3-acrylamido-2-hydroxylypropyltrialkylammonium chloride (AHPTAAC). The hydrophobic quaternary ammonium salt containing trietylamine, tributylamine and trioctylamine groups shows the enhancement in flocculation performance. It was found that increase in the chain length had enhanced the efficiency of the flocculation and decreased the weight of sludge produced. However, previous work done by Ren *et al*. (2007) was not extended to the higher homologous series of trialkylamine. Thus, the aim of the present work is to copolymerize higher homologous series such as trihexylamine, trioctylamine and tridodecylamine with the quaternary ammonium salt in order to investigate their effectiveness in flocculating kaolin suspension.

1.7 Objectives

Specific objectives of the present study include:

1 To synthesize and to characterize the hydrophobically modified cationic polyacrylamide;

2 To determine the effects of hydrophobically modified cationic polyacrylamide on kaolin flocculation;

3 To compare the performance of the copolymers between hydrophobic group and within hydrophobic group of different ratio on turbidity removal.

1.8 Scope of the Study

The main focus of this research is the synthesis of hydrophobically modified cationic polyacrylamide with different hydrophobic group chain lengths. 3-acrylamido-2-hydroxypropyltriakylammonium chloride (AHPTAAC) in which trialkyl group is to be substituted by trihexylamine (HPA), trioctylamine (OPA) and tridodecylamine (DPA) will be synthesized with acrylamide (AM). P(HPA-co-AM), P(OPA-co-AM) and P(DPA-co-AM) copolymers will be synthesized using free-radical solution copolymerization.

Intrinsic viscosity and molecular weight, FT-IR, charge density, solution behaviour of copolymer solution and TEM images are to be used to characterize the copolymer produced. Flocculation test on kaolin suspension will be done in order to investigate the effect of hydrophobically modified cationic polyacrylamide on solid-liquid separation performance. The main parameter in this study is turbidity. Copolymers from each group and different ratios will be applied in flocculating kaolin suspension. The weight of sludge produced using different group of copolymers is to be studied.

CHAPTER 2

LITERATURE REVIEW

2.1 Coagulation-Flocculation of Kaolin Suspension

Kaolin $Al_2Si_2O_5(OH)_4$ suspension was used as a representative of colloidal materials because kaolin is a widespread thickening agent and a key component in various industrial fluid formulations. The crystallographic structure of kaolin corresponds to the 1:1 layer structure as show in Figure 2.1 where the principal building elements are single silica tetrahedral sheet and single octahedral alumina (Al_2O_3) sheet oriented, so that the tips of the silica tetrahedrons and one of the layers of the octahedral alumina sheet form common layer. The basal face, displaying an inert siloxane (-Si-O-Si-) structure carries a permanent negative charge as a result of isomorphous substitution of Si^{4+} by Al^{3+} groups. At the edge of the crystal, the octahedral alumina and tetrahedral silica sheets are disrupted and broken bonds exposing aluminol (Al-OH) and silanol (Si-OH) groups occur. The edge face may be charged as a result of protonation and deprotonation of the surface hydroxyl group depending on pH (Nasser and James, 2006, 2007).

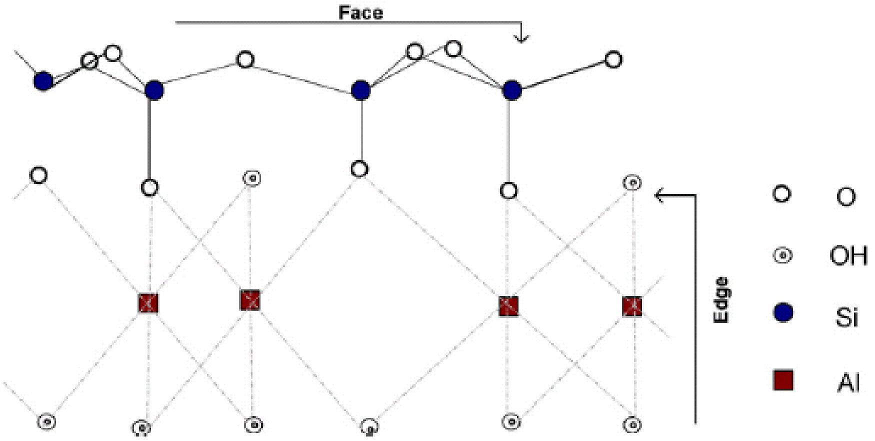

Figure 2.1 Atom arrangement in a unit cell of kaolin (Source: Nasser, M. S. and James, A.E. (2007).

Due to kaolin's colloidal size, anisotropic shape and permanently negatively charged basal faces, it tends to form a turbid and stable dispersion when it disperses in aqueous medium. Thus an addition of aggregation force is needed to induce settling of particles. Coagulation-flocculation method has become the common method in solid-liquid separation. Materials used to induce coagulation-flocculation of kaolin suspension have been extensively explored by researchers. Various materials that consist of inorganic coagulant, synthetic polymeric flocculants, bio-based flocculants and modified-flocculants have been studied to improve the kaolin/aqueous medium separating system. Table A1 summarizes some of the materials used in coagulation-flocculation of kaolin suspension.

Polymeric flocculants have been discovered to be useful materials in agglomerating particles in the wastewater treatment system. Polymer added as flocculants or coagulant aid induces coagulation-flocculation process by binding colloids in the aqueous medium. The addition of polymeric flocculants enables the formation of heavier and denser flocs that facilitate the settling of aggregates. Various flocculants such as inorganic flocculants, organic flocculants, bio-flocculant, grafted flocculants and hydrophobically modified flocculants have been developed. The properties of the polymeric flocculants are characterized according to their molecular weight, ionic nature, charge density, hydrophobicity and chemical composition. Different kinds and properties were employed in treating different wastewater in order to get an efficient treatment performance.

Various kinds of polymer have been applied in kaolin removal. However they still draw some disadvantages since some materials do not function on their own. The polymers still require additional chemicals such as metal based coagulant, pH adjustment to induce the kaolin separation process. Inorganic coagulants used have produced high volumes of metal hydroxides sludge which is difficult to dewater, resulting in serious problem to the mineral processing industry. Kaolin poses a dewatering problem since the flocs structures formed through flocculant assisted gravity thickening typically retain a great deal of water due to its underlying interfacial chemistry and particles interactions (McFarlene et al., 2005b). To overcome this problem, according to Besra et al., (2002a, 2002b, 2003, 2004), surfactants was added to reduce the moisture contained in the sludge cakes. Another measure that can be done to overcome this problem is by hydrophobically modifying the polyacrylamide to improve the flocculation properties by reducing the water retention in the sludge (Ren et al., 2007).

2.2 Hydrophobically Modified Polyacrylamide

Acrylamide-based polymers are highly utilized in the industry due to their useful monomer for obtaining water-soluble high molecular weight polymers (Chagas et al., 2004). Polyacrylamides have been widely used due to their low costs. Acrylamide (C_3H_5NO) appears as an odourless, white crystalline solid with molecular weight of 71.08; density of 1.122g/mL at 30°C, melting point 84.5±0.3°C boiling point 125-136°C at 25 mm Hg. In pure form, acrylamide readily polymerizes at its melting point 84.5°C (Daughton, 1998). In addition, acrylamide is a polyfunctional molecule that contains a vinylic carbon-carbon double bond and an amine group. The electron deficient double bond of acrylamide is susceptible to a wide range of chemical reactions including nucleophilic additions. Acrylamide also exhibits relatively high stability where it is soluble in water and many organic solvents (Wong *et al.*, 2006). Acrylamide performance can be enhanced by varying its conformation and copolymerization with other monomers by introducing functional group that has a high affinity for a particular mineral phase or adding charged groups that allow the polymer to take on an extended conformation in solution (Owen *et al.*, 2002).

Despite a great variety of commercially available flocculants, there is still a need for improvement on their efficiency and on the development of products for special applications. Hydrophobic modification of synthetic polyacrylamides which can be performed through chemical grafting or copolymerization procedure was suggested as a new innovation to enhance the performance of the polymers (Bratskaya et al., 2006). Hydrophobically modified polyacrylamides generally consists of a hydrophilic main chain (charged or uncharged) and a hydrophobic group at the polymer backbone (Grassl et al., 2001; Penott-Chang et al., 2006). Associations of hydrophobic groups with the polymer chains play a role of intermolecular crosslinks, which can lead to a significant increase of viscosity. The ability of hydrophobically associating polymers to enhance viscosity of aqueous solutions is extensively exploited in a variety of practical applications (Shakina et al., 2003). In aqueous solutions, the hydrophobic groups have a strong tendency to associate together yielding intra- and intermolecular networks (Feng et al., 2002, 2005). Owing to intermolecular cross-linking of hydrophobic units, hydrophobically modified polyacrylamides is found to be capable of minimizing their exposure to water by blocking water and increasing the viscosity of the solution at high hydrophobic units concentrations; hence hydrophobically modified polyacrylamide can be used as thickeners (Shakina et al., 2003; Wu et al., 2006).

2.3 Synthesis of Hydrophobically Modified Polyacrylamide

Several processes that have been proposed to synthesize hydrophobically modified polymer are: (1) homogenous copolymerization (dispersion in organic solvent) (Grassl et al., 2001); (2) condensation copolymerization (byproduct produced at the end product) (Ghimici et al., 2001); (3) micellar copolymerization (addition of surfactant) (Candau & Selb, 1999); (4) solution copolymerization (Ren et al., 2007).

It has been reported in many research papers that micellar copolymerization is the common method to synthesize hydrophobically modified polyacrylamide (Candau & Selb, 1999). However, the addition of surfactants in the copolymerization medium, which causes a decrease in molecular weight, and the difficulty in removing the surfactants from the medium, draw the disadvantages of the method. Table 2.1 shows the summary of the monomers used in the synthesis of hydrophobically modified polyacrylamides.

Table 2.1 Summary of monomers that are used in the synthesis of hydrophobically modified polyacrylamides.

Hydrophobically Modified Comonomers	Copolymerization method	Reference
N-(4-ethyl-phenyl)acrylamide	Micellar	Biggs et al., 1992
N-*n*-dodecylacrylamide *N*-*n*-tetradecylacrylamide	Micellar	Li and Kwak, 2003
N,*N*-dihexylacrylamide	Micellar	Volpert et al., 1997
di-*n*-propylacrylamide *di*-*n*-octylacrylamide	Micellar	Wei et al., 2004
n-decylarylamide *t*-octylacrylamide	Micellar	Penott-Chang et al., 2006
N-octadecylacrylamide	Micellar	Zhu et al., 2007
N-nonylacrylamide *N*-dodecylacrylamide	Micellar	Blagodatskikh et al., 2004
N-phenethylacrylamide	Miecellar	Abu-Sharkh et al., 2001
2-ethyl-hexyl-methacrylate (EHMA)	Micellar	Somashina et al., 2003
N,N-dipentylacryamide	Micellar	Ren et al., 2008
N-benzylacrylamide	Micellar	Yahaya et al., 2001
n-nonylacrylamide	Micellar	Shaskina et al., 2003
N-arylalkylacrylamide	Micellar	Ma et al., 2002
Sodium 2-acrylamido-tetradecane sulfonate	Micellar	Gao et al., 2007
(Dimethylammonioethoxy)dicyanoethenolate)propylmethacrylamide	Homogeneous Micellar	Gassl et al., 2001
Epichlorohydrin with dimetylamine, N,N-dimethyl-1,3-diaminopropane (DMDAP), hexyloxypropylamine polymer, decyloxypropylamine polymer	Condensation	Ghimici et al., 2001
3-acrylamido-2-hydroxypropyltriethylammonium chloride 3-acrylamido-2-hydroxypropyltributhylammonium chloride 3-acrylamido-2-hydroxypropyltriocthylammonium chloride	Solution	Ren et al., 2007

2.4 Coagulation- Flocculation Process

Coagulation-flocculation of colloidal suspensions are important process in many industries, such as pulp and paper making, mineral and ceramics processing, and water treatment. Coagulation of dissolved and colloidal substances in wastewater is essentially understood in light of Derjaguin-Landau-Verwey-Overbeek theory (DLVO theory). Coagulation decreases and neutralizes the electric charge on the suspended particles by using inorganic salts such as aluminium and ferric salts (Maximova & Dahl, 2006). Flocculation plays a major role also in the fate and transport of contaminants in aquatic environments by bringing the aggregated flocs to form large agglomerates in the presence of polymers (Somasundran et al., 2005; Maximova & Dahl, 2006).

Flocculation has been proven in many researches to be effective in solid-liquid separation process by its advantage in reduction of sludge volume and rapid separation of solids from liquids (Besra et al., 2003). It plays an important role in adsorbing the fine particle and colloid using high molecular weight polymeric flocculants under physical mixing. This physico-chemical process has been adopted in many mineral processing, hydrometallurgical operation, and wastewater treatment and so on.

It primarily involves two basic steps:

(i) Transport of a particle to another adjacent particle leading to collision.

(ii) Adhesion of the particles resulting in aggregation (Besra et al., 2004).

2.4.1 Mechanisms of Flocculation

Polymeric flocculant induces colloids destabilization and structure modification which lead to polymer-particle interactions, floc structure characteristics and sediment dewatering behaviour. There are four major mechanisms of destabilization of the colloids particles by polymers:

(a) Charge neutralization

(b) Electrostatic patch

(c) Bridging

(d) Depletion flocculation (Addai-Mensah and Prestidge, 2005; Maximova & Dahl, 2006; Yu et al., 2006)

However, more than one mechanism may operate concurrently, depending on the nature of the particle surface and the flocculant conformation at the solid-liquid interface (Runkana et al., 2004).

2.4.1.1 Charge neutralization

Charged particles tend to repulse each other in the dilute suspension, forming dispersion. Disperse particles pose settling problem and remain stable in the suspension. In order to adsorb and aggregate colloids, thus optimizing removal of colloids from water, charge neutralization mechanism is required. Charge neutralization of the surface charge leads to destabilization and agglomerate into big flocs (Bratskaya et al., 2006).

Charge neutralization of insoluble dispersed material surface charge would require addition of a metallic salt coagulant, or charged (usually low molecular-weight) organic polyelectrolyte with rapid mixing in order to lower the potential energy of repulsion between adjacent colloids (Walzer, 1981; Cill, 1985). Polymers of high charge density are favored for charge neutralization (Fan et al., 2000). During charge neutralization, counter charged polyelectrolytes destabilize colloids surface charge by adsorbing on the colloidal surface. Attraction between counter charged polyelectrolyte and colloid results in neutralization of charge towards zero. However, the restabilization of colloids will occur with continuous addition of counter charged polyelectrolyte. Restabilization can be due to excessive chemical dosages resulted in deterioration where the surfaces beyond point of zero charge. (Penniman, 1981). Charge neutralization by adsorption infers that the colloid-water interface is changed, and thus, so are its physiochemical properties (Schwoyer, 1981). Figure 2.2 shows charge neutralization mechanism.

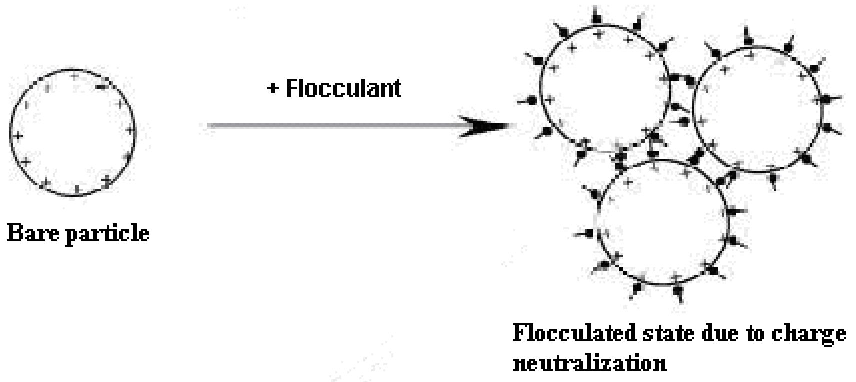

Figure 2.2 Charge neutralization mechanism (Furusawa et al., 2002)

2.4.1.2 Electrostatic Patch

An electrostatic patch model was developed for a system containing particles having a fairly low density of immobile surface charge and the adsorbing polymer having a high charge density (Fan et al., 2000). The net residual charge of the polymer patch on one particle surface can attach to the bare part of an oppositely charged particle (Yu et al., 2006). In this instance, it is not physically possible for each charged group on the polymer chain to be adjacent to a charged surface site and regions of excess electrically neutral. Particles having this mosaic type of charge distribution may interact in such a way that positive and negative patches come into contact, giving quite strong attachment (Addai-Mensah and Prestidge, 2005). A mosaic of positive patches on the surface is formed and results in initial patchwise adsorption followed by bridging. In the case of patch neutralization, both polymer molecular weight and charge density are important (Fan et al., 2000).

2.4.1.3 Bridging

Bridging is defined as adsorption of individual polymer chains onto several particles simultaneously; such binding forms molecular bridges between adjoining particles in the floc (Addai-Mensah and Prestidge, 2005). Via the connectivity mediate attractive interactions, bridging by organic and inorganic polymers enables the destabilization of particles by which the molecules of the added chemical attach onto two or more particles causing aggregation (Podgornik and Licer, 2006).

There are two kinds of bridging, i.e. bridging between similar and dissimilar charged materials. Bridging of negatively charged colloids by high molecular weight cationic and anionic polyelectrolytes are examples of the first and second kinds, respectively (Schwoyer, 1981).

Generally, bridging mechanism can be explained in four stages:

(i) Dispersion of the polymer in the colloid suspension – Disentanglement of polymer chain after addition of polymer solution into wastewater. The polymer structure opens wide enough to bind on particle surface.

(ii) Adsorption of the polymer at the solid-liquid interface – Polymer attaches on colloid surface with the bulk of the chain projecting into the surrounding solution for contact and adherence.

(iii) Compression of the adsorbed molecule – Attached particles are brought close together with its polymer chain.

(iv) Collision of the partially coated particles leading to the formation of bridge – Adjacent adsorbed particles collide and hence the buildup of a three dimensional flocs comprising the particle polymer network (Cill, 1985).

To induce bridging, slow mixing is required to contribute collision among polymer chains and particles. Only adequate slow mixing will produce large and dense flocs. The factors controlling effective flocculation induced by interparticle bridging include flocculant characteristics such as molecular weight, charge density, functionality and dosage, mineral particle zeta potential, particle size and surface area and solid concentration, presence of simple and hydrolysable metal ions, pH, temperature, and the degree of shear and compression (Addai-Mensah and Prestidge, 2005). However, strong adsorption is not favorable in the flocculation process, because strong adsorption can cause surface saturation, preventing effective bridging and restabilising fine particles (Nasser and James, 2006). Thus, polymers of high molecular weight are favored for polymer bridging (Fan et al., 2000). Bridging mechanism with polymer chain is illustrated in Figure 2.3.

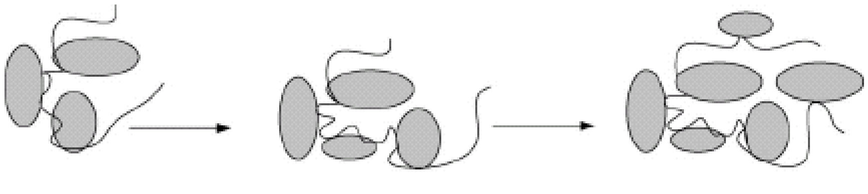

Figure 2.3 Bridging with polymer chain. (Nasser and James 2006)

2.4.1.4 Depletion Flocculation

Depletion flocculation is induced by the low adsorption polymers with high concentrations, where the osmotic pressure present between polymer-rich and particle-rich phases due to the difference of polymer concentration (Yu et al., 2006). When the free polymers are eliminated from the interparticle region in which polymer molecules cannot exist without deformation, the depletion effect is induced by their osmotic pressure, due to the difference of polymer concentration between the inside and outside regions, and brings the particles together. The depletion effect operates after saturation adsorption by the excess polymer molecules (Furusawa et al., 1999).

2.4.2 Factors Affecting Flocculation

It has been well established that the effectiveness of flocculation by polymeric flocculants lies on various aspects related to the surface chemistry of the particles as well as on the sort of flocculant, ionic nature, molecular weight, charge density, bulk properties of the flocculants in the solution, solids content and type of wastewater (Besra et al., 2004; Qian et al., 2004). The chain flexibility, the molecular weight, the solubility, the charge density are also the factors that determine the applications of these polymers in the wastewater and surface water purification process (Ghimici et al., 2001).

2.4.2.1 pH

pH affects coagulation-flocculation of kaolin. Kaolin dispersion in aqueous solution has a negative charge on the surface. At pH 2.2, the zeta potential of the kaolin surface is near to zero, indicating the point of zero charge (pzc) for kaolin. At