POLYMERIC FLOCCULANTS:

SYNTHESIS, CHARACTERIZATION AND APPLICATIONS

A THESIS SUBMITTED TO

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UNDER THE GUIDANCE OF

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DECLARATION

I declare that the thesis entitled "**Polymeric flocculants: Synthesis, Characterization and Applications**" submitted by me for the degree of Doctor of Philosophy is the record of work carried out by me during the period form **02-05-2013** to **09-10-2019** under the guidance of **Dr. Manohar V. Badiger** and has not formed the basis for the award of any degree, diploma, associate ship, fellowship, titles in this or any other university or other institution of higher learning.

I further declare that the material obtained from other sources has been duly acknowledged in the thesis.

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TABLE OF CONTENTS

Chapter 1: Introduction

Chapter 3: Flocculation of kaolin using copolymers of acrylamide (AM) and diallyldimethylammonium chloride (DADMAC)

Chapter 4: Flocculation of kaolin using copolymers of acrylamide (AM) and 3-Acrylamidopropyltrimethylammonium chloride (APTMAC)

Chapter 5: Synthesis of chitosan graft copolymer flocculants

Abstract

The objective of this thesis is to synthesize and characterize an efficient flocculant for the separation of an industrially important mineral, kaolin. Flocculants are an integral part of many industrial separations and waste water treatment. Kaolin is a mineral clay which has wide applications in ceramics, paint, electronics and biomedical fields. In view of its wide range of applications, kaolin separation by flocculation is very important.

Flocculation is a phenomenon of colloidal destabilization. Flocculants act on a molecular level on the surface of particles to reduce the repulsive forces and increase the attractive forces. By the addition of flocculant (in ppm), finely divided or dispersed particles aggregate together to form flocs of a bigger size, which makes them to settle faster, effecting good separation. Various parameters that influence the efficiency of flocculation are polymer molecular weight (MW), charge density, polymer concentration, polymer dimension in solution, the presence of electrolytes etc. Depending on the source and nature of charge, flocculants are classified into organic and inorganic; synthetic and natural; anionic, cationic and neutral flocculants. There are different mechanisms proposed for the flocculation which include bridging, charge neutralization and electrostatic patch model. Although there are few reports on the flocculation of kaolin mineral, efforts are still being made to design and develop new, efficient flocculants for kaolin separation.

In this context, a research work was undertaken to synthesize and characterize efficient flocculants based on acrylamide (AM) and cationic monomers such as diallyldimethylammonium chloride (DADMAC) and 3-acrylamidopropyltrimethylammonium chloride (APTMAC) for kaolin flocculation. Further, in view of the environmental issues of synthetic flocculants, a biopolymer based flocculant namely chitosan-g-APTMAC graft copolymer was synthesized and evaluated for kaolin separation. The flocculation efficiency was correlated to the structural characteristics of the flocculants such as molecular weight, charge on the flocculant. The plausible mechanism for driving the flocculation were discussed.

In poly(AM-co-DADMAC) system, the content of DADMAC was varied in order to obtain flocculants with different molecular weights and charge densities. The

chemical structure of the copolymer was confirmed by ^{1}H and ^{13}C NMR spectroscopy. The charge on the polymer was analyzed by zeta sizer. The molecular weight was analyzed by GPC. The flocculation efficiency was studied by measuring the % transmittance of the supernatant liquid after flocculation. The zeta potential of the supernatant kaolin suspension was measured to correlate to the efficiency of flocculation. These flocculants showed good efficiency in flocculating kaolin suspensions. The flocs formed were characterized in terms of filter cake moisture content (FCMC), initial settling rate (ISR) and optical microscopy, which gve insight in understanding the flocculation process.

Since the reactivity of APTMAC monomer was higher, copolymers of AM and APTMAC were synthesized and examined for kaolin flocculation. The composition of APTMAC was varied in the copolymer to obtain flocculants with varying molecular weights and zeta potential. The flocculants were characterized by NMR, GPC and zeta potential. The flocculation efficiency was evaluated using kaolin suspension and the flocs were characterized in terms of FCMC, ISR and optical microscopy. Efficient flocculation of kaolin at lower dosages was demonstrated with poly (AM-co-APTMAC) cationic flocculant.

The use of chitosan as a backbone chain and grafting APTMAC onto it yields a partially biodegradable and environment friendly flocculant. The APTMAC content was varied in the reaction feed to get different graft copolymers with different molecular weights and charge densities. The grafted copolymers were characterized by NMR, GPC and zeta potential. The flocculation efficiency was analyzed using kaolin suspension and the flocs were characterized in terms of FCMC, ISR and optical microscopy.

The flocculation of kaolin could be achieved rapidly (~4 -10 min) with the lowest dosages of 2 - 4 ppm in the jar test method. All the flocculants synthesized and characterized in this thesis showed efficient flocculation for kaolin separation and have great potential in industrial separations.

List of tables

List of Schemes

List of figures

Abbreviations and symbols

AM	Acrylamide
PAM	Polyacrylamide
APTMAC	3-Acrylamidopropanetrimethylammonium chloride
AOETMAC	2-Acryloyloxyethyltrimethylammonium chloride
AM-co-DADMAC	copolymer of acrylamide and DADMAC
AM-co-APTMAC	copolymer of acrylamide and APTMAC
AD	acrylamide DADMAC
AA	Acrylamide APTMAC
Chi	Chitosan
CA	chitosan APTMAC
DADMAC	Diallyldimethylammonium chloride
D_2O	deuterium oxide
DI-water	deionized water
DSLR	Digital Single Lens Reflux
EO	Ethylene oxide
FCMC	Filter cake moisture content
GPC	Gel Permeation Chromatography
h	Hour
Hg	Mercury
ISR	Initial settling rate
KPS	potassium persulfate
KG	Kilogram

min	Minutes
M_w	weight average molecular weight
M_n	number average molecular weight
MW	Molecular weight
MOETMAC :	2-Methacryloyloxyethyltrimethylammonium chloride
mV	milli volts
mol %	mole percentage
ml	Millilitre
NMR	Nuclear Magnetic Resonance
nm	Nanometer
ppm	Parts Per Million
PDI	Polydispersity index
rpm	rotations per minute
UV	Ultraviolet
Vis	Visible
V-50	2, 2'-azobis(2-methylpropionamide) dihydrochloride
+ve	Positive

INTRODUCTION

CHAPTER-1

In this chapter we report on the literature survey of flocculants, factors affecting flocculation, mechanisms of flocculation, various flocculants synthesized so far, classification of flocculants. The characterization techniques for flocculants, characterization of flocs and other factors associated with flocculation are briefly explained.

1.1 Introduction

Polymeric flocculants are an important class of materials which have a wide range of applications such as mineral recovery[1–4], paper manufacturing[5–8], sugar cane juice clarification[9–11], protein recovery from marine waste water[12–15] and several other treatments of waste water in industries[16–27]. Flocculants act on a molecular level on the surface of particles to reduce the repulsive forces and increase the attractive forces. By the addition of flocculant (in ppm), finely divided or dispersed particles are aggregated together to form flocs of a bigger size, which makes them to settle speedily, effecting good separation. Various parameters that influence the efficiency of flocculation are polymer molecular weight (Mw), charge density, polymer concentration, polymer dimension in solution, the presence of electrolytes etc.

Depending on the source, the flocculants can be classified into inorganic and organic flocculants. The classification is shown in figure 1.1.

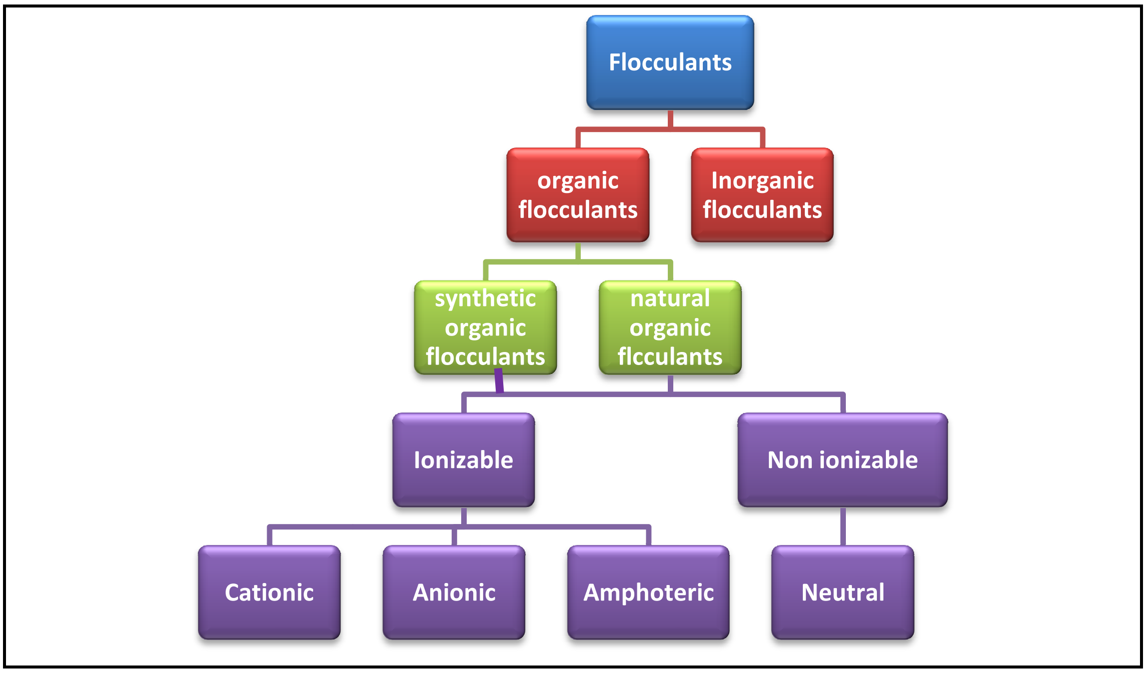

Figure-1.1: Classification of flocculants

Inorganic flocculants have been in use for a very long time and mostly include salts of multivalent metals such as, alum, ferric chloride etc[22,28,29]. The advantage of inorganic flocculants is that they are cheap and easily available, but they have several drawbacks. These are the requirement of large dosages to cause efficient flocculation, production of a large quantity of sludge as a by-product, which is difficult to dispose off. Further, inorganic flocculants are sensitive to pH and work for specific systems and do not flocculate very fine particles. Therefore, the use of inorganic flocculants is almost abandoned[30–32].

Table-1.1 gives the details of some of the inorganic flocculants along with dosages and working pH range.

Table-1.1: details of coagulant, dosage and working pH range

Coagulant	Dosage(ppm)	pH range
Alum ($KAl(SO_4)_2.12H_2O$)	75 -250	4.5 -7.0
$FeCl_3$	35 - 150	4.5 - 7.0
$FeSO_4\cdot 7H_2O$	70 - 200	4.0 - 7.0
Lime	150 - 500	9.0 - 11.0
Cationic poly electrolytes	2 - 5	---

Organic flocculants have a remarkable ability to flocculate at very low concentrations and have broad pH tolerance. Mostly, organic flocculants are polymeric and based on the source they can be classified into (i) synthetic organic flocculants which are synthesized from monomers such as acrylamide (AM), acrylic acid (Aa), ethylene oxide (EO), Diallyldimethylammonium chloride (DADMAC), etc. These synthetic polymers have advantages that they can be tailor-made to suit the end applications and exhibit longer shelf life with higher stability to microbial degradation. (ii) Natural flocculants are derived from biopolymers such as chitosan, cellulose, alginates and natural gums etc. Depending on the nature of the charge present on the polymeric chain, these flocculants are further classified into cationic, anionic and non-ionic flocculants. Therefore, many of the flocculants are polyelectrolyte in nature. The flocculants cause colloidal destabilization by adsorption onto a particle surface and extend beyond one particle. By virtue of their large molecular weights, the chains extend and bind to large number of particles. The correct choice of flocculant is key to efficient flocculation.

1.1.1 Mechanism of flocculation:

Flocculation is a process of bridging destabilized colloidal particles together to allow them to aggregate to a size where they will settle by gravity. When polyelectrolytes are added to the solution containing oppositely charged particles, the electrostatic attraction between them is considered to be the driving force for the adsorption and the flocculation. A few mechanisms postulated by John Gregory in 1972[33,34] are:

- Bridging
- Charge neutralization
- Electrostatic patch model

1.1.1.1 Bridging

Bridging flocculation occurs when the same polymer segment is bound to more than one particle thereby, bridging particles together; this kind of flocculation is found to be more efficient and effective in causing solid-liquid separation. The charged polymer will adsorb on fewer sites onto the particle surface, and the long loop or tails of the polymer is available for binding to neighbouring particles. Figure-1.2 depicts the bridging mechanism in the flocculation process.

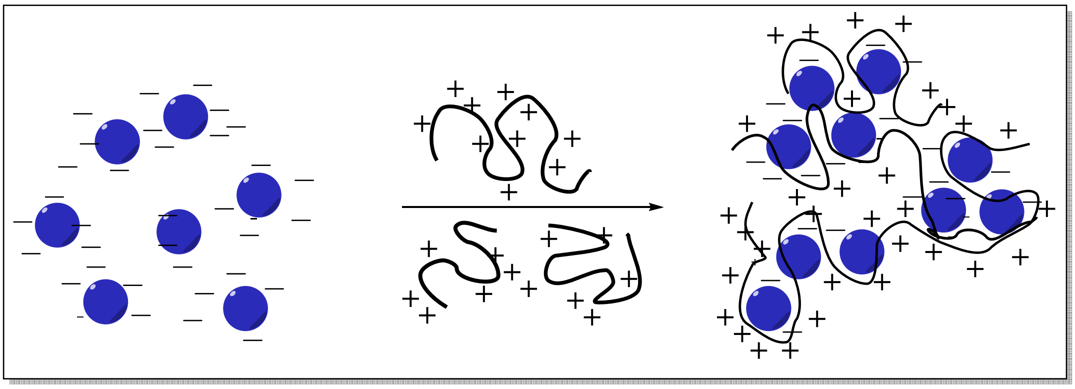

Figure-1.2: Bridging flocculation

For bridging to happen, the polymer chain should be so long that the extended loop should reach neighbouring particle, that is at least two electrical double layer lengths. The optimum dosage ranges from covering the 30 to 50% surface area of the particles; generally, it is 30 to 35% surface area covering.

1.1.1.2 Charge neutralization

Charge neutralization is caused by a reduction in electric double layer repulsion between particles due to the neutralization of charges on the particles by oppositely charged polyelectrolytes. Charge neutralization can be caused by multivalent metal ions such as, Al^{3+}, Ca^{2+} and Fe^{3+} or by low molecular weight polymer electrolytes. The mechanism of charge neutralization is shown in figure-1.3.

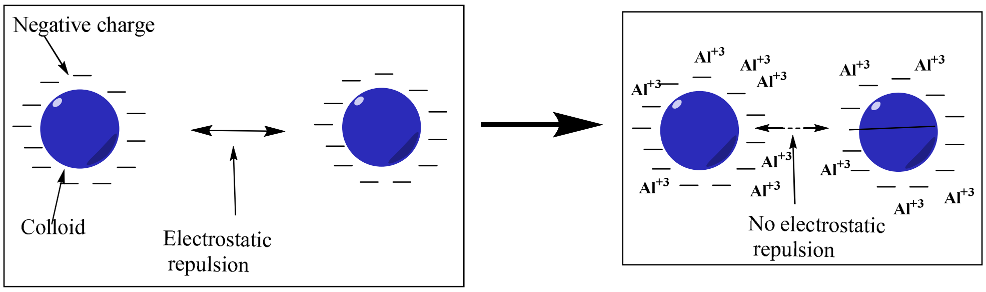

Figure-1.3: Charge neutralization flocculation

The amount of flocculant required would be higher here since the required weight of flocculant to neutralize is stoichiometric to the total available particle surface area.

1.1.1.3 Electrostatic patch model

In the electrostatic patch model, the highly charged polymer interacts with oppositely charged particles as a patch and the net residual charge on the patch on one particle surface can attach to the bare part of an oppositely charged particle again. This mechanism may operate independently or in association with bridging flocculation. The mechanism of electrostatic patch model is shown in figure-1.4

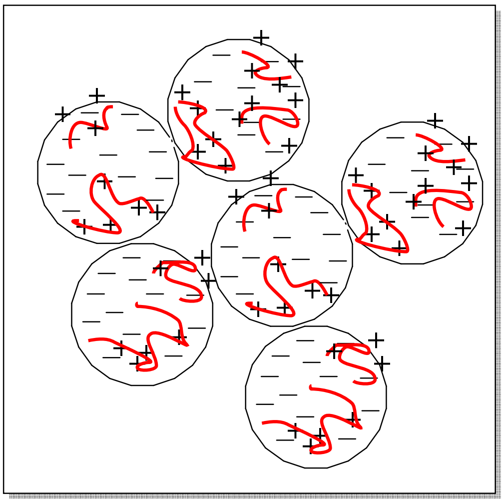

Figure-1.4: Electrostatic patch flocculation

The efficiency of any flocculation process will largely depend on several factors including, the choice of flocculant type, dosage, ionic strength, total dissolved solids, the size and distribution of colloidal particles in suspension. The effective flocculant must have an extended and flexible (elastic) configuration in the solution to achieve better particle bridging and to produce flocs capable of withstanding moderate shear force without rupturing. The floc strength can be estimated from the Bingham shear yield stress, which is a measure of the maximum force per unit area that the floc structure can withstand before rupturing. The parameters that influence the flocculation have been investigated and reported by N.J.D. Graham[35] and Zhou and Franks[34]. Amongst the several factors, Polymer molecular weight, Charge density, Chain dimensions in solution, Polymer concentration are the most important ones. These serve as the guiding parameters for efficient flocculation.

1.1.2 Polymer molecular weight:

Generally, high molecular weight polymer is desired for efficient flocculation. The molecular weight should be high enough to overcome the two particle's electrical double layer repulsion. The high molecular weight of flocculant leads to bridging flocculation. However, a very high molecular weight of a polymer can pose a problem in solubility. This can result in a highly viscous solution that is prone to damage to physical agitation. With very high molecular weight the filter cake moisture content will also increase. Therefore, the optimization of molecular weight needs to be considered.

1.1.3 Charge density on the flocculant:

Charge density on the flocculant is one of the main driving forces for binding or adsorption onto particle surfaces. Higher the charge density better is the binding. A very high charge density flocculant with low molecular weight can lead to flocculation by the mechanism of the electrostatic patch model. Excessive use of this very high charge density flocculant might lead to colloidal restabilization.

A linear polymer with a randomly distributed charge on the polymer surface can strongly bind to the particles with increased agitation and might yield dense flocs. For the graft copolymer, the binding can be weak and might yield loose flocs.

1.1.4 Polymer configuration in solution:

The molecular architecture of the polymer is very important in flocculation. The charge on the polymer stretches the chain due to repulsion and form loops and tails. The initial contact between particles occurs through these loops and tails. The number and size of these loops and tails will determine the efficiency of flocculation. A highly stretched polymer chain can cause flocculation through bridging.

1.1.5 Polymer concentration:

Polymer concentration for optimum flocculation is decided by the nature of the mechanism that is operating in flocculation. If the mechanism of flocculation is by charge neutralization, it might require concentration, which is stoichiometric to the total surface area of the particles. This is relatively higher and yields large flocs. If the mechanism of flocculation is by bridging, where the polymer is binding to more than one particle, then the concentration required is relatively very low. If the concentration is increased, flocculation might shift from bridging to electrostatic patch mechanism or to even to colloidal restabilization. Hence polymer concentration for flocculation is very important.

1.1.6 Methods of measuring flocculation

There are many methods used for measuring flocculation efficiency. Brostow et al[18]. Zheng et al[36] and Kumar et al[37], have reported the use of Jar test and settling test for measuring flocculation.

1.1.6.1 Jar test

In a typical Jar test, the solution of flocculant is added to the suspension of particles to be separated. The dosage is in ppm, and the system is stirred at high speed for the first 2 min and then followed by a slow stirring for 3 min. The stirring was done using an overhead stirrer with cross blades impeller to ensure uniform mixing. The timings of rapid and slow stirring vary from system to system. The rapid mixing was done to mix the flocculant with colloids to form flocs. Later the stirring was slowed down to prevent any possible damage to the polymer and flocs formed. Then the suspension was allowed to settle and the supernatant liquid was analyzed for turbidity either by turbidity meter or by transmittance using UV-spectroscopy. The transmittance method can be used to measure the clarity of the supernatant liquid with respect to time to obtain the kinetics of flocculation. The supernatant liquid is also tested for the changes in zeta potential; flocculation causes a shift in the zeta potential of the suspension. Figure 1.5 is a representative image of the jar test for mineral clay, kaolin separation.

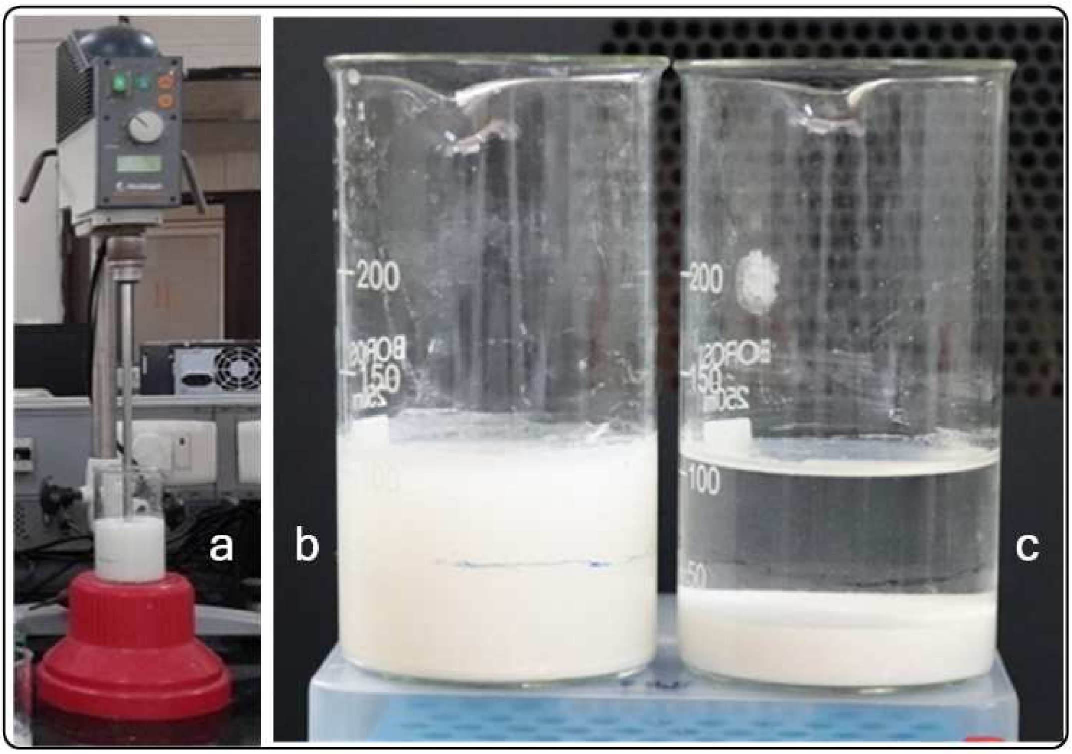

Figure-1.5: a) overhead stirring of kaolin suspension, b) kaolin blank, c) flocculated kaolin

1.1.6.2 Settling test

In the settling test, a graduated cylinder with the stopper is used. The suspension of the colloid is filled into the cylinder and to this solution, the flocculant is added. The mixing of the flocculant with particle is done by inverting the cylinder multiple times. The movement of interface, which separates the liquid and particles, which is also known as mud-line, is monitored with time. The height of the interface with reference to the graduations on the cylinder is recorded with time. This gives the velocity of the particle settling and the initial settling rate (ISR). The velocity increases with the increase in floc size. This test is also used to represent normalized mud-line height H_{t1}/H_{t0}, where H_{t1} is the height of mud-line at time t1 and H_{t0} is the height of the mud-line at time zero[19]. Figure 1.6 is a representative image to measure ISR.

Figure-1.6: Initial Settling Test 1) at time 0 and 2) after time t

Further, the flocs thus formed are also characterized by various techniques, Chen et al.[38] have studied Filter cake moisture content (FCMC), which is the measure of sludge conditioning efficiency. In this, the flocs formed after flocculation were filtered through a 0.45μ filter under a fixed vacuum for 30 min. Then the cakes formed were weighed before and after drying to calculate FCMC. Optical microscopy was also employed for studying flocs. Optical microscopy images can be analyzed[39] for floc size. The floc characterization is important and specific for industrial applications.

1.1.7 Nature of colloids:

Most of the naturally occurring minerals or particles and many industrial colloids and effluents which need to be separated or flocculated are anionic in nature and require cationic flocculants. Therefore, there is a great demand for cationic flocculants for efficient flocculation or separation processes. Table-1.2 gives examples of some of the colloidal systems along with suitable flocculants used for their separation.

Table 1.2: Nature of colloids and the type of flocculant used

Colloidal system	**Charge on colloid**	**Flocculant used**
protein	Anionic	Cationic
Kaolin clay	Anionic	Cationic
Water treatment	Anionic	Cationic
Copper floatation tailing	Cationic	Anionic
Mixed mineral Oxide tailing	Anionic	Cationic
Paper manufacturing	Anionic	Cationic and neutral

Lee et al[40]. have reviewed the use of various organic flocculants for the treatment of waste water. The details along with references are shown in table-1.3

Table-1.3: Application of different flocculants for waste water treatment

Type of water	**pH range**	**Flocculants**	**Reference**
Oily wastewater from refinery plant	-	Derivative of polyacrylamide (Poly1 and 3530S), polyacrylamide	Zhong et al[41].
Olive mill effluent	5.5-6.7	Four cationic (FO-4700-SH, FO-4490-SH, FO-4350-SHU and FO-4190-SH) and two anionic (FLOCAN 23 and AN 934-SH) polyelectrolytes	Sarika et al[42].
Aquaculture wastewater	6.9-7.7	Cationic polyamine (Magnafloc LT 7991), cationic organic polyelectrolytes (Magnafloc LT 7992 and 7995), cationic polyacrylamide (Hyperfloc CE 854 and CE 1950), copolymer of quaternary acrylate salt and acrylamide (Magnafloc 22S)	Ebeling et al[24].

Coal waste slurry	8.3	Polyacrylamide-based polymers (anionic: Praestol 2515, Praestol 2540, non-ionic: Magnofloc 351, cationic: Praestol 857 BS)	Sabah and Erkan[43]
Pulp and paper mill wastewater,	7.3-8.3	Cationic (Organopol 5415, Organopol 5020, Organopol 5470, Organopol 5450, Chemfloc 1515C) and anionic (Organopol 5540, Chemfloc 430A, AN 913, AN 913SH) polyacrylamides	Wong et al[44].
Simulated reactive dye wastewater, Simulated dye liquor wastewater, Actual printing and dyeing wastewater	7.0 6.6-7.8 11.2	Cationic polydiallyldimethylammonium chloride (PDADMAC) Cationic polyamine	Kang et al[45]. Yue et al[46].
Pulp and paper mill wastewater	7.0	Cationic polydiallyldimethylammonium chloride (polyDADMAC)	Razali et al[7].
Kaolin suspension	7.0	Cationic lignin polymers	Hasan et al[47].

1.1.8 Flocculation of Kaolin

Kaolin is an important mineral clay which has a lot of applications in ceramics, coatings, cement, manufacturing of paint thickeners, catalysis, chemical carriers, liquid barrier, paper coating, detergents etc[48–52]. Awad et al. have given comprehensive information about the applications kaolin[53]. In view of its importance and wide range of applications, flocculation of kaolin has become extremely important. Globally, large scale production of kaolin is made by IMERYS, BASF, Kamin, Thiele, AIMR, Sibelco and Smart stones.

Kaolin is anionic clay and consists of silica and alumina along with minor quantities of ferric oxide and titanium. The chemical composition of kaolin is $Al_2Si_2O_5(OH)_4$ and has a layered structure with alumina octahedral sheets and silica tetrahedral sheets stacked alternately. See figure-1.7 for the structure of kaolin. The layered lattice structure is inert over wide pH range[54].

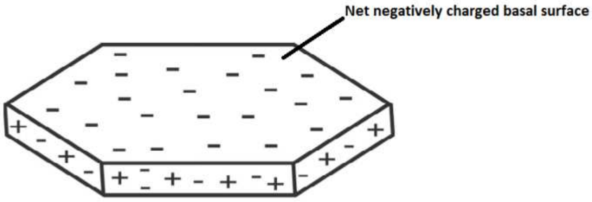

Fig-1.7: kaolin structure

1.1.9 Cationic flocculants:

Cationic flocculants can bind strongly to negatively charged particles and have a wide range of industrial applications in separation of anionic particles. There are quite a few cationic flocculants prepared from natural and synthetic polymers[55–60]. Many commercial flocculants are often based on poly (acrylamide) [PAM] and its derivatives since acrylamide [AM] is one of the most reactive monomers to undergo radical polymerization. AM has a high ratio of propagation to termination constant and as a result yields ultra-high molecular weight polymers. A large number of cationic flocculants are prepared from copolymerization of AM monomer with quaternary ammonium salt containing monomers such as Acryolyloxyethyltrimethylammonium chloride (AOETMAC), Methacryolyloxyethyltrimethylammonium chloride (MOETMAC), 3-acrylamidopropanetrimethylammonium chloride (APTMAC), Diallyldimethylammonium chloride (DADMAC) and vinylbenzyltrimethylammonium chloride (VBTMAC). Kumar et al. have reported on the amylopectin and acrylamide based cationic and amphoteric flocculants for the kaolin flocculation[37]

1.1.10 Chitosan

A large number of synthetic flocculants currently used for industrial separations are non-biodegradable and toxic in nature and pose severe environmental issues. Therefore, there is a major focus on design and development of natural polyelectrolytes or the modification of natural polyelectrolytes as flocculants for separation. In this context, biopolymers have emerged as promising materials to synthesize flocculants. Amongst the wide verity of biopolymers, chitosan, cellulose, guar gum, starch, sodium alginate, carrageenan, etc have become very important. For example, Hasan and Fatehi have prepared cationic lignin polymer for kaolin flocculation[47]. Starch-based flocculants have been prepared for the separation of kaolin[61–63] and hematite[62,64]. Particularly, chitosan is the second-largest biopolymer next to cellulose which is available abundantly. Further, chitosan being a non-food source for human beings and animals offer an advantage as a feed-stock for flocculant development.

Chitosan is a copolymer of D-glucosamine and N-acetyl-D-glucosamine, which is soluble in dilute acid solution[65]. Figure 1.8 shows the sources and structure of chitosan.

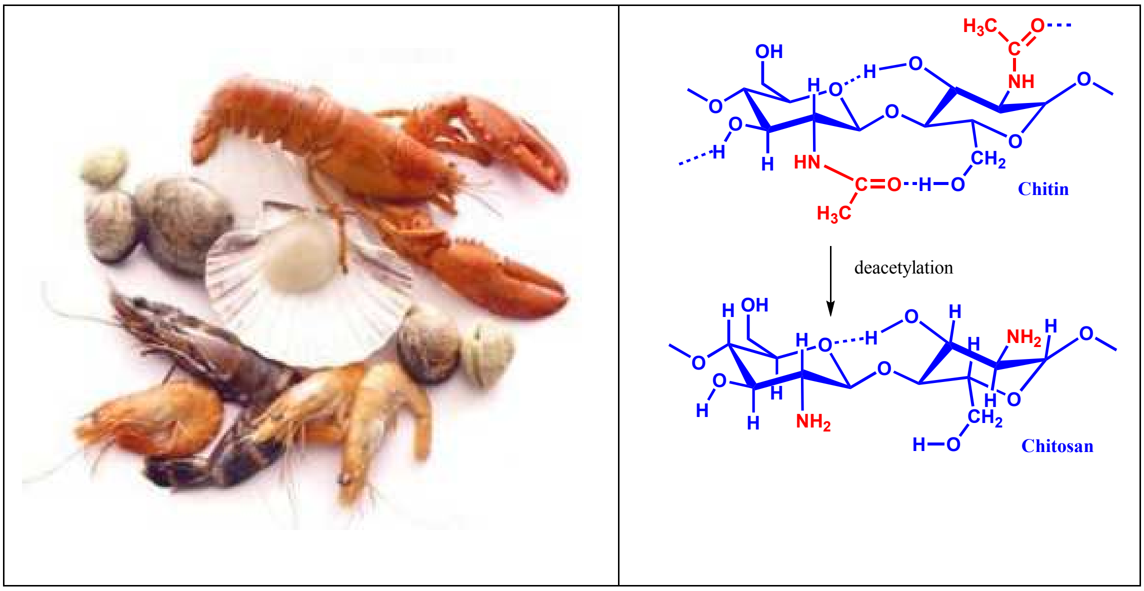

Figure-1.8: Source and structure of chitosan

Research on applications of chitosan in diverse areas such as pharmaceuticals, biomaterials, cosmetics, food processing, and chelation of heavy metals has grown phenomenally in recent years[65–78]. Among most of the modification methods, grafting has been proved to be a useful and convenient method for the synthesis of flocculants. Yang et al[39] have reported on the acrylamide grafted carboxymethyl chitosan for kaolin flocculation.

The graft copolymers generally combine the properties of both the backbone chain and the pendent grafted chain. A flexible chain grafted onto the rigid or semi-rigid backbone can increase the conformational freedom in solution and enhance the efficiency of flocculation.

Although there are a few cationic flocculants based on synthetic polymers and modified natural polymers for the kaolin flocculation. Still, there is a wide scope and demand for the development of newer efficient flocculants for kaolin mineral clay flocculation and industrial separation processes.

In this thesis work, the focus is given on the design and synthesis of cationic flocculants using copolymers of acrylamide and DADMAC / APTMAC and APTMAC grafted chitosan graft copolymer for kaolin flocculation.

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SCOPE AND OBJECTIVES

CHAPTER-2

In this chapter the scope and objectives of the thesis are discussed

Although there are a few flocculants used for the kaolin flocculation, still there is a great scope in designing and developing efficient cationic flocculants which have optimum molecular weight and charge density for separation of kaolin from aqueous streams, particularly at low dosages. Therefore, in this thesis work, efforts are made to synthesize cationic flocculants based on acrylamide (AM) monomer in combination with cationic monomers such as diallyldimethylammonium chloride (DADMAC) and 3-acrylamidopropyltrimethylammonium chloride (APTMAC). The composition of the monomers in the reaction feed was varied to get copolymers with different molecular weights and degree of charge. The chemical structures of all the copolymers were confirmed by ^{1}H and ^{13}C NMR spectroscopy. The molecular weights and degree of charge on the copolymers were determined using gel permeation chromatography (GPC) and zeta potential measurements. All the copolymers were used for kaolin flocculation using the established jar test method with the measurement of % transmission. The optimum dosages were identified for all the copolymers to obtain maximum kaolin flocculation. The efficiency of flocculation is correlated to the molecular weight and zeta potential of the copolymers and the plausible mechanisms, for the flocculation were proposed. The characterization of flocs in terms of Filter Cake Moisture Content (FCMC), Initial Settling Rate (ISR) and the optical microscopy of floc suspension were performed.

One of the most important anionic clay materials is kaolin, which is an anionic mineral clay consisting of silica and alumina along with minor quantities of ferric oxide and titanium. Kaolin has a lot of applications in coatings, manufacturing of paints, electronic ceramics and as a filler for several cosmetic formulations[1–5]. The extraction of kaolin from natural deposits involves a flocculation process[6].

Further, there has been a growing interest in developing flocculants from biopolymers because of their environmentally friendly nature[7]. In this context graft copolymerization of vinyl monomers onto chitosan can give desired properties to the obtained flocculants. In view of this, a cationic monomer, APTMAC was grafted onto chitosan and evaluated for the flocculation of kaolin. The structural characterization was performed on the graft copolymer by ^{1}H and ^{13}C NMR spectroscopy. Flocculation of kaolin suspension was carried out using the chitosan-g-APTMAC graft copolymers.

The objectives of the thesis are:

- To design and synthesize cationic flocculants based on acrylamide and cationic monomers namely, DADMAC and APTMAC
- To vary the composition of the monomers to obtain copolymers with higher molecular weight and higher zeta potential
- To characterize the obtained copolymers in terms of their chemical structure (by NMR spectroscopy), molecular weight (by GPC), and degree of charge (by zeta potential)
- To study the flocculation of kaolin using the above synthesized copolymers and to determine the optimum dosage levels for the maximum flocculation.
- To correlate the flocculation efficiency of the polymers to their molecular weight and charge density and to propose the mechanism of flocculation.
- To characterize the flocs in terms of FCMC, ISR and floc morphology by optical microscopy
- To synthesize chitosan-g-APTMAC graft copolymer and evaluate and study its performance for kaolin flocculation.

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FLOCCULATION OF KAOLIN USING COPOLYMER OF ACRYLAMIDE (AM) AND DIALLYLDIMETHYLAMMONIUM CHLORIDE (DADMAC)

CHAPTER-3

In this chapter we report on the syntheis of poly(AM-co-DADMAC) copolymers with varying content of AM and DADMAC. The copolymers were characterized by NMR, GPC and zeta potential analysis. The viscometric access to coil dimensions were studied by intrinsic viscosity and particle size by light scattering method. The flocculation efficiency was studied using kaolin suspensions and the flocs were characterized in tems of FCMC, ISR and optical microscopy. The optimum dosage was determined. The molecualr weight and charge density of the flocculant were correlated to the flocculation efficiency.

RSC Advances 5, 27674–27681 (2015)

3.1 Introduction

The use of organic polymeric flocculants for solid-liquid separations is known for a very long time[1]. Polymeric flocculants of only acrylamide (AM) were used in industrial solid-liquid separations, such as oil sand fine tailings separations and kaolin separation. The use of only polyacrylamide suffers from the drawback of forming gel like structures with high water retention in the flocs. This was attributed to the hydrogen bonding of the amide groups in acrylamide with positive ions in the slurry[2]. Hence use of only acrylamide is not advantageous. Copolymerization of acrylamide with cationic monomers such as Diallyldimethylammonium chloride (DADMAC) will have added advantage of including (+ve) charge on the copolymer for efficient flocculation. DADMAC is a cheaper monomer compared to many other cationic monomers and has a stable cationic structure with wide pH working range[3]. There are many synthesis methods for preparing copolymers of acrylamide and DADMAC, such as solution polymerization[4,5], γ-radiation techniques[6,7], dispersion and inverse emulsion polymerization[8] etc. Of all the methods, solution polymerization is a simple method, economically viable, safe and industrially convenient to operate. The use of template polymerization of AM and DADMAC in presence of polyacrylic acid is reported for flocculation kaolin[3]. However the approach proposed in our work is a simple copolymerization of AM and DADMAC in a single step. The flocculants showed better charge and molecular weights with efficient flocculation of kaolin suspension (3 wt%) at lower dosages (8 to 14 ppm).

In this work, we have synthesized cationic flocculant based on the combination of acrylamide (AM) and Diallyldimethylammonium chloride (DADMAC) for flocculation of kaolin suspension and demonstrated an efficient flocculation in small dosages (8-14ppm) of flocculants. The DADMAC monomer was selected here because of its low cost and commercial viability for flocculant production. But the drawback of this monomer in flocculant synthesis is its low reactivity ratio in copolymerization. Which will lead to lesser incorporation of the DADMAC into the flocculant and result in low zeta potential with low charge density and moderately high molecular weight. Therefore, our objective in this work was to balance the zeta potential and molecular weight by design and synthesizing different compositions of the copolymers and to obtain optimum composition of the flocculant for the efficient flocculation of kaolin using small dosages of flocculant. The flocculants thus synthesized were tested for their efficiency of kaolin separation. The chemical structure of copolymer was determined using ^{1}H and ^{13}C NMR spectroscopy. The intrinsic viscosity measurements and particle size measurements were done to understand coil dimensions in solution. The flocculation efficiency was correlated to the zeta potential and molecular weight of the copolymer. Floc characterizations like filter cake moisture content (FCMC), initial settling rate (ISR) and optical micrographs of flocs were studied and correlated to the flocculation and dosages.

3.2 Experimental

3.2.1 Materials and Methods

Acrylamide (AM) monomer was purchased from Fluka, USA and was used as such; diallyldimethylammonium chloride (DADMAC) monomer (65 wt% solution in water) was purchased from Aldrich, USA; ammonium persulphate, sodium metabisulphite and sodium chloride were purchased from SD-fine chemicals, Mumbai, India which were of analytical grade and used as received. Deionized water (conductivity 0.055 μS cm^{-1} at 25° C) was obtained in the lab (TKA, GmbH Stockland), Acetone was procured from Rankem, Mumbai, India. Kaolin was obtained from Thomas Baker Chemicals, Mumbai, India. Analytical grade Sodium nitrate was purchased from Merck, Mumbai, India and used as received.

3.2.2 Synthesis of cationic flocculant based on Acrylamide and DADMAC

Copolymers of acrylamide with DADMAC were synthesized by solution polymerization using ammonium persulphate and sodium metabisulphite as a redox initiator system. In a typical experiment, the calculated amounts of acrylamide and DADMAC solution (65%) were added to a 100 ml DI water in a double jacketed reaction vessel equipped with circulating water bath to maintain the desired reaction temperature. The stirring of the reaction mass was facilitated using an overhead stirrer with a cross blade impeller. The concentration of the monomers in the reaction mixture was 10 wt%. The DADMAC contents were varied to get different composition of copolymers. The reaction mixture was purged with nitrogen gas for 30 min to remove any dissolved oxygen and temperature was increased to 40˚ C. Then ammonium persulphate and sodium metabisulphite were added at an initiator concentration of 2 mol% and stirring was continued. The reaction mixture became viscous and the polymerization was further carried out for 6 h. Finally, the polymer was precipitated in acetone and dried in vacuum oven at 40˚ C. Three copolymers with different feed ratios (moles) of AM and DADMAC (AM: DADMAC; 80:20, 50:50 and 40:60) were synthesized and denoted as AD-8020, AD-5050 and AD-4060 respectively. The chemical structure of the copolymers was characterized using ^{1}H and ^{13}C NMR spectroscopy. The molecular weights of the copolymers were determined using gel permeation chromatography (GPC).

3.3 Characterizations

3.3.1 Gel permeation chromatography (GPC)

The molecular weight (MW) of the copolymers was determined using Agilent 1200 GPC with Shodex OH pak SB-800 series columns. The mobile phase used was 0.25 N $NaNO_3$, with a flow rate of 0.4 ml/min. 100 µl was the sample injection volume. The GPC column temperature was maintained at 40° C, and polyacrylamide standards were used for calibration.

3.3.2 Zeta potential measurements

Zeta potential measurements were carried out at 25° C using Brookhaven 90 plus particle size analyzer, USA. The polymer concentration used was 0.1 g dL^{-1}. The data reported is the average value of 10 cycles and 10 runs.

3.3.3 Hydrodynamic radii

Hydro dynamic radii were measured using Brookhaven 90 plus particle size analyzer, USA. The experiments were performed at 90˚, monitoring the variation in the intensity of the scattered light caused by the Brownian motion of the particles. The polymer solutions of known concentrations in deionized water were filtered through 0.22 µ filters (Millipore syringe filter)

3.3.4 Viscosity measurements

Viscosity measurements were conducted using an Ubbelohde capillary viscometer with capillary diameter 0.63 mm with AVS 479 (SCHOTT Gerate, Mainze, Germany). The measurements were done either in deionized water or in NaCl solutions (0.0003 to 1 M). The temperature was maintained at 25° C ± 0.05° C. For only deionized water the polymer concentration range was 0.01 to 0.05 weight %. For NaCl solutions the concentrations varied from 0.1 to 0.5 weight % due to decrease in viscosity of the solution.

3.3.5 NMR studies

The ^{1}H and ^{13}C NMR spectra of copolymers were recorded on Bruker AV 500 MHz spectrometer. The copolymer samples were prepared in D_2O.

3.3.6 Flocculation test for kaolin

Kaolin (particle size 1μ) suspension in water (3.0 wt-%) was used for the flocculation test. Kaolin suspension was prepared by stirring kaolin solution using overhead stirrer at 400 rpm for 30 min. In a typical flocculation study, to a 100 ml kaolin suspension, a known volume of flocculant solution (1g L^{-1}) was added and stirred for 5 min (with 300 rpm for first 2 min and at 100 rpm for 3 min) using an overhead stirrer, Heidolph RZR 2012, Germany with cross blade impeller. After 5 min, stirring was stopped and immediately, 1 ml aliquot was drawn from the central portion of the solution. The transmittance (%) was measured for this solution using Shimadzu UV-PC 1601 UV-Vis spectrophotometer, Japan, in the kinetic mode at 700 nm. This value of the transmittance was taken as zero minute reading. The solution was allowed to settle and the aliquots were drawn at predefined interval of time till 40 min and transmittance was measured. Then transmittance vs. time was plotted to find out the time required for maximum transmittance to occur. For the zeta potential measurement, the supernatant liquid was taken after 40 min flocculation with different dosages of flocculant.

The optimum dosage of the flocculant for each composition was determined. Different dosages were tested for kaolin suspension flocculation, the dosage at which the transmittance is 90% or more was considered as optimum dosage for that composition. This 90% transmittance was higher than what was reported earlier[9]

3.3.7 Floc characterization

3.3.7.1 Initial settling rate (ISR)

The initial settling rate (ISR) of kaolin suspension for the AD-4060, AD-5050 and AD-8020 flocculants was evaluated by adding a known volume of flocculant (Concentration, 1g L^{-1}) to a 100 ml of 3.0 Wt % kaolin suspension in a stoppered measuring cylinder. The flocculant was uniformly mixed by inverting the cylinder 10 times up-down. The height of the kaolin liquid interface was recorded as a function of time for AD-4060, AD-5050 and AD-8020.

3.3.7.2 Filter Cake Moisture Content (FCMC)

The property of kaolin flocs after the flocculation was evaluated in terms of Filter Cake Moisture Content (FCMC)[10,11]. The FCMC is an important index used to characterize the floc state. It is intuitive and is widely used method. The flocculants are also used as a filtration aid, with the objective of increasing filtration rate and to reduce the filter cake moisture content. FCMC is important in such industrial separations where the floc is the product of interest such as kaolin separation, protein separation form marine fish processing industry etc. Lesser the moisture content faster will be the drying process. A 3.0 Wt % kaolin suspension was used for FCMC study. The flocculation was performed by adding a known volume of AD-4060, AD-5050 and AD-8020 flocculants (Concentration, 1g L^{-1}) and stirring at 300 rpm for 2 min followed by 100 rpm for 3 min. Then the suspension was allowed to stand for 40 min to reach equilibrium settling; this floc was filtered using a 0.45 µm Millipore filter paper in a sintered funnel at 450 mm of Hg vacuum for 30 min. The filter cake was transferred to a crucible, weighed and dried in an oven at 100˚ C for 24 h and FCMC was calculated using the following equation.

$$FCMC = \frac{W_1 - W_2}{W_1 - W_0} X\ 100$$

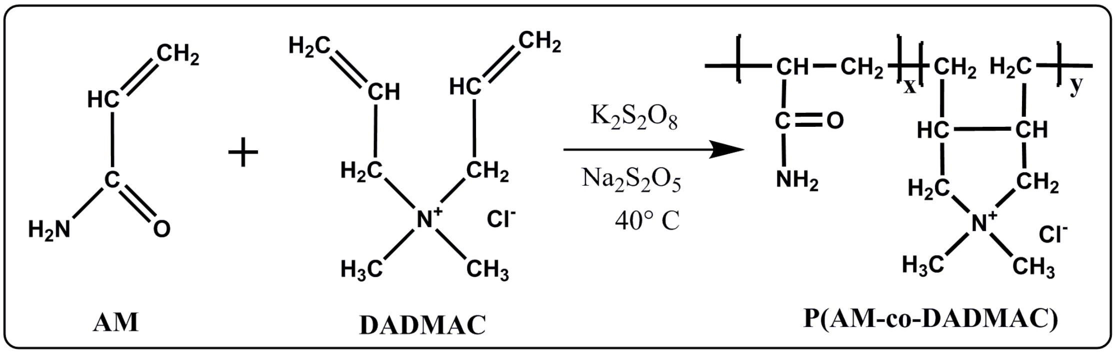
Where W_0 is the weight of the crucible, W_1 is the total weight of crucible + filter cake before drying and W_2 is the total weight of crucible + cake after drying to constant weight. With this FCMC study, one can get information about the role of polymer in moisture retention in flocs.

The flocculation was monitored by using optical microscopy (Leica, Germany) and the filter cakes were photographed with a DSLR camera (Canon EOS 77D, USA)

3.4 Results and Discussion

3.4.1 Synthesis and characterization of flocculants

Amongst a few cationic monomers available, DADMAC was chosen considering its high utility in commercial flocculants and it is available at a cheaper price than many cationic monomers. Synthesizing an efficient cationic flocculant lies in obtaining high molecular weight and high zeta potential copolymer. The acrylamide monomer, with its high ratio of propagation to termination constant, gives high molecular weight to the polymer. Whereas, the cationic monomer provides an overall charge density to the copolymer. Therefore, it is very important to critically balance both the monomer contents to obtain high molecular weight and high zeta potential polymer for efficient flocculation. Accordingly, three copolymers, with varying AM and DADMAC contents were prepared.. The copolymers were coded as AD-8020, AD-5050 and AD-4060, respectively. The quantitative yields of the copolymers AD-8020, AD-5050 and AD-4060 were determined to be 88, 74, and 69% respectively. The reaction scheme for the synthesis of poly (AM-co-DADMAC) is shown in scheme-3.1. The structural characterization of the copolymers was carried out using ^{1}H and ^{13}C NMR spectroscopy.



Scheme 3.1: Reaction scheme for the synthesis of poly (AM-co-DADMAC)

3.4.2 Chemical structure by NMR spectroscopy

We show in figure-3.1, the ^{1}H NMR spectra of representative poly (AM-co-DADMAC) [AD-8020] and a homopolymer of polyacrylamide. The methyl ($-CH_3$) proton peaks of DADMAC appear in the range of 3.0 to 3.3 ppm and the methylene ($-CH_2-$) protons of DADMAC attached to nitrogen atom give peaks at 3.78 ppm. The methylene ($-CH_2-$) proton peaks of the backbone chain of AM and DADMAC appear in the range of 1.5 - 1.8 ppm. The methine protons of the AM backbone appear at 2.0 to 2.4 ppm. All the characteristic peaks of the copolymer assigned, agree with those reported in the literature[3,12,13].

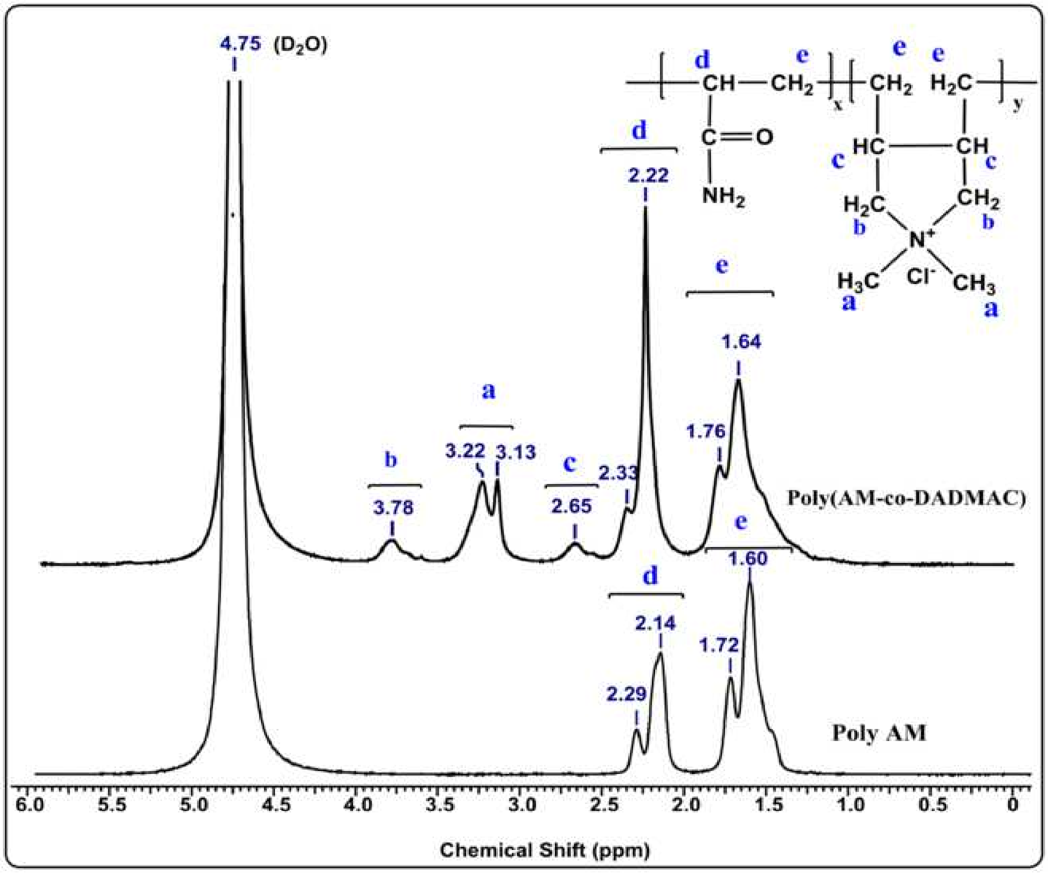


Figure-3.1: 500 MHz ^{1}H NMR spectrum for Polyacrylamide and Poly (AM-co-DADMAC) [AD-8020]

The mol fractions of DADMAC in the copolymers were obtained by NMR spectroscopy. The ^{1}H NMR spectrum of the copolymer shows the AM peak at 2.3 ppm and that of DADAMAC at 2.78 ppm. The area under the peak for single protons of AM and DADMAC was calculated, which yields the moles of AM and DADMAC.

Taking the molecular weights of AM (71.08 g mol^{-1}) and DADMAC (161.67g mol^{-1}) into consideration, the mol fraction of the DADMAC was calculated to be 0.12, 0.32 and 0.44 respectively for AD-8020, AD-5050 and AD-4060.

We also show in Figure-3.2, the ^{13}C NMR spectrum (Bruker, AV 500 MHz, D_2O) of poly (AM-co-DADMAC) [AD-4060]. The methyl ($-CH_3$) carbon peaks of DADMAC appear at 54.4 ppm and methylene ($-CH_2-$) carbon of the backbone chain of AM and DADMAC appear at 34.9 ppm. The methylene ($-CH_2-$) carbon of DADMAC attached to nitrogen gives a peak at 66 to 70 ppm and peak for methine (-CH-) carbon next to carbon attached to nitrogen of DADMAC and methine (-CH-) carbon of acrylamide backbone appear at 41.7 ppm. Both the ^1H and ^{13}C NMR spectra confirm the chemical structure of the copolymer.

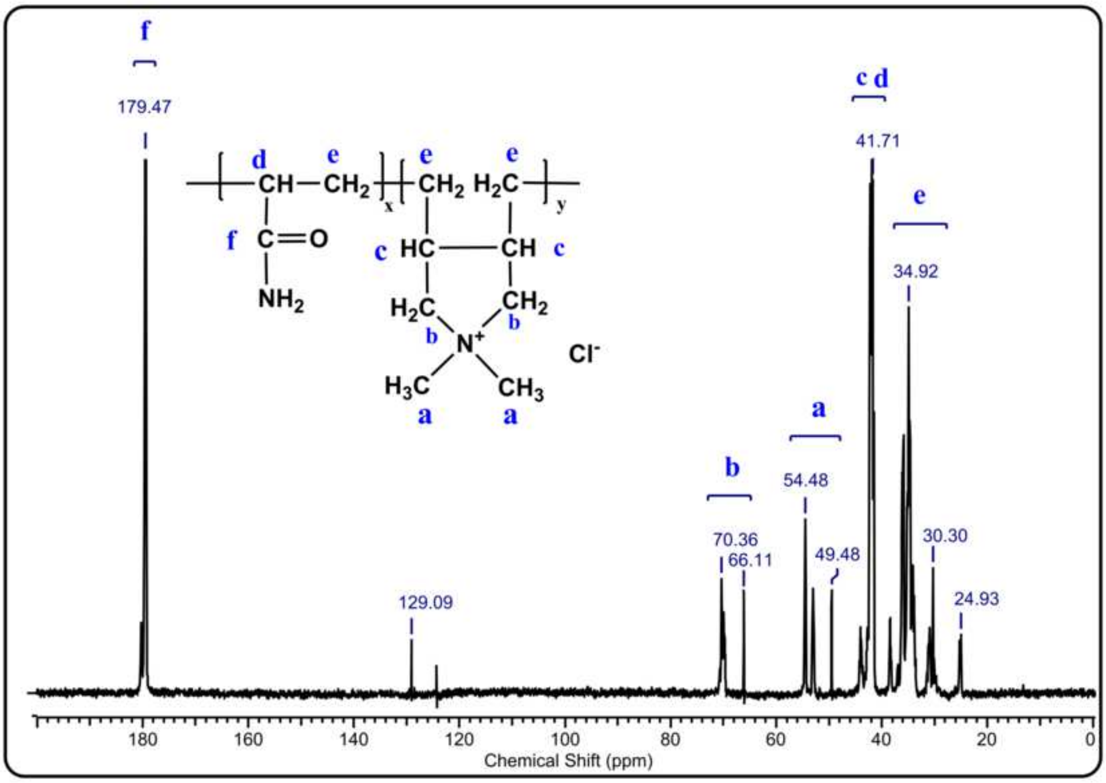


Figure-3.2: 400 MHz ^{13}C NMR spectrum for Poly (AM-co-DADMAC)

In figure 3.3 and 3.4 we show the ^1H and ^{13}C stacked NMR spectra of all the three compositions AD-8020, AD-5050 and AD-4060 respectively. The NMR spectra of all the compositions clearly show the peaks for both AM and DADMAC. Further, it can be clearly seen that the intensity of peaks for AM increases as the AM content increases form AD-4060 to AD-8020 and Vice versa was observed for DADMAC.

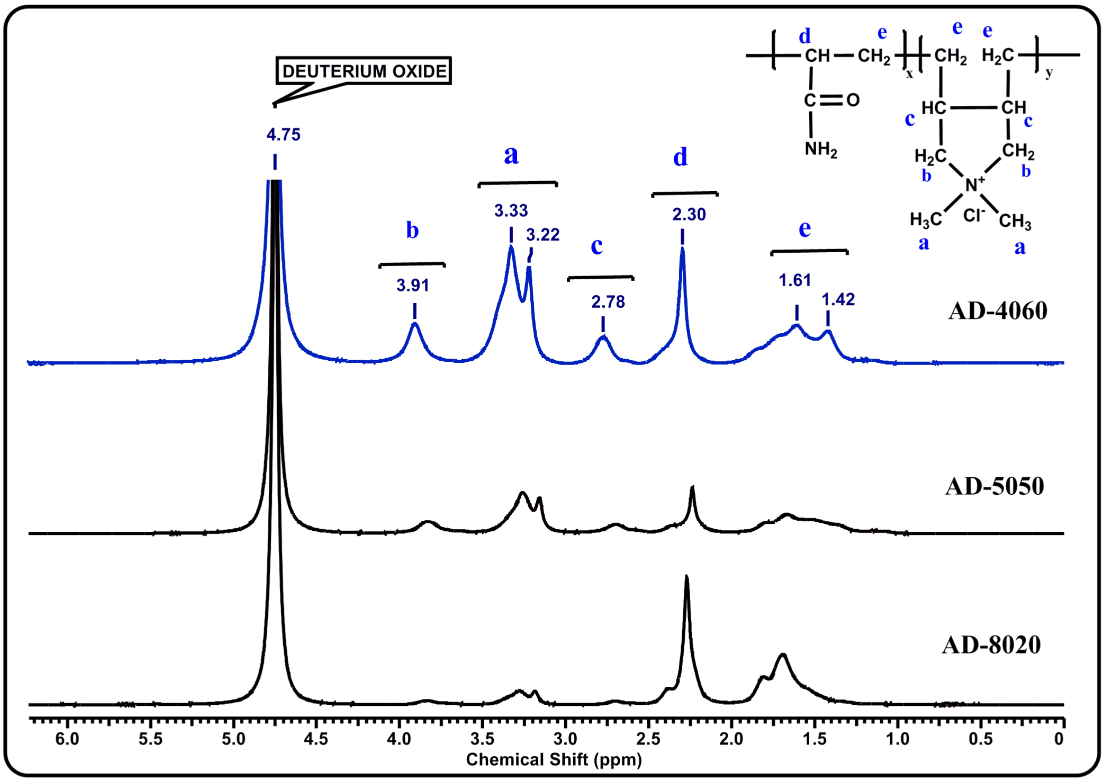


Figure-3.3: 500 MHz ^{1}H NMR spectrum for Poly (AM-co-DADMAC) [AD-4060, AD-5050 and AD-8020]

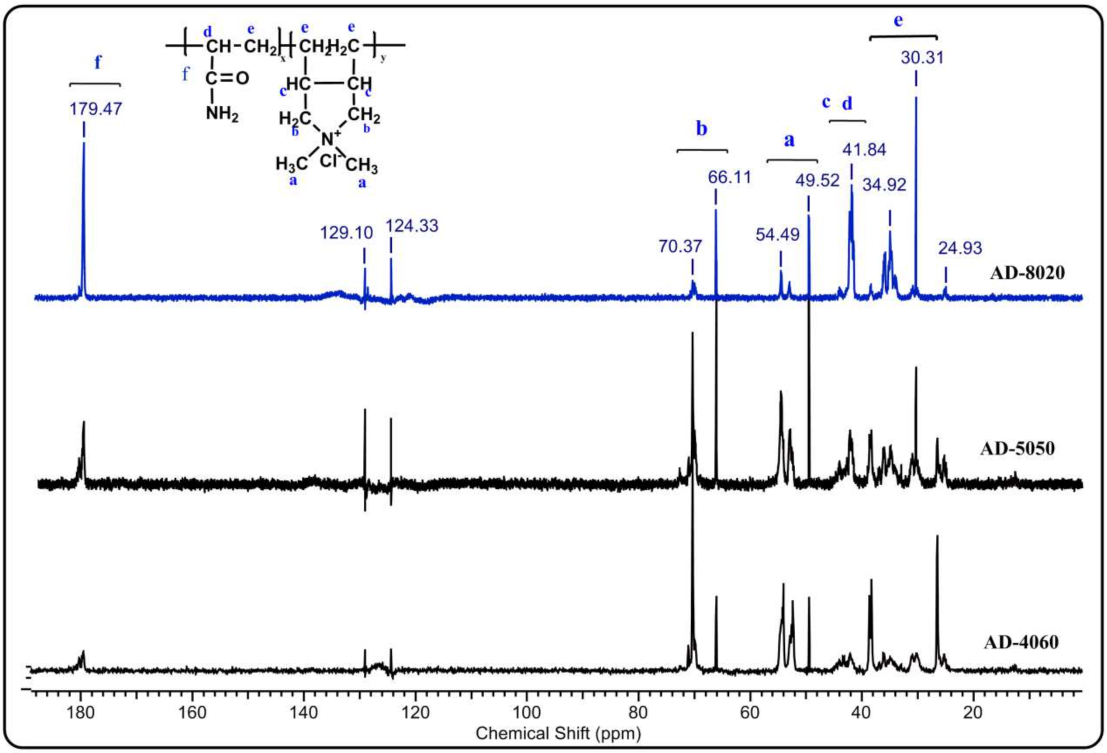


Figure-3.4: 400 MHz ^{13}C NMR spectrum for Poly (AM-co-DADMAC) [AD-4060, AD-5050 and AD-8020]

3.4.3 Study of coil dimensions of the flocculant in solution

The coil dimensions of the flocculant in solution was studied in the presence and absence of salt. The hydrodynamic radii and intrinsic viscosity were studied using particle size analyzer and Ubbelohde capillary viscometer respectively. In only water and at low salt concentrations the polymer coils shrink upon an increase of polymer concentration. For sufficiently high salinity of the solvent the polymer coils expand, this behaviour is due to the unfavourable thermodynamic quality of solvents containing much salt. Such a situation leads to an increase in the number of intersegmental contacts and to higher friction. At a certain characteristic salinity of the solvent, the dimensions become independent of polymer concentration. Figure-3.5 shows the changes in hydrodynamic radii and intrinsic viscosity with the change in polymer concentration. Figure-3.6 represents the coil dimensions at no salt, less salt and sufficient salt conditions.

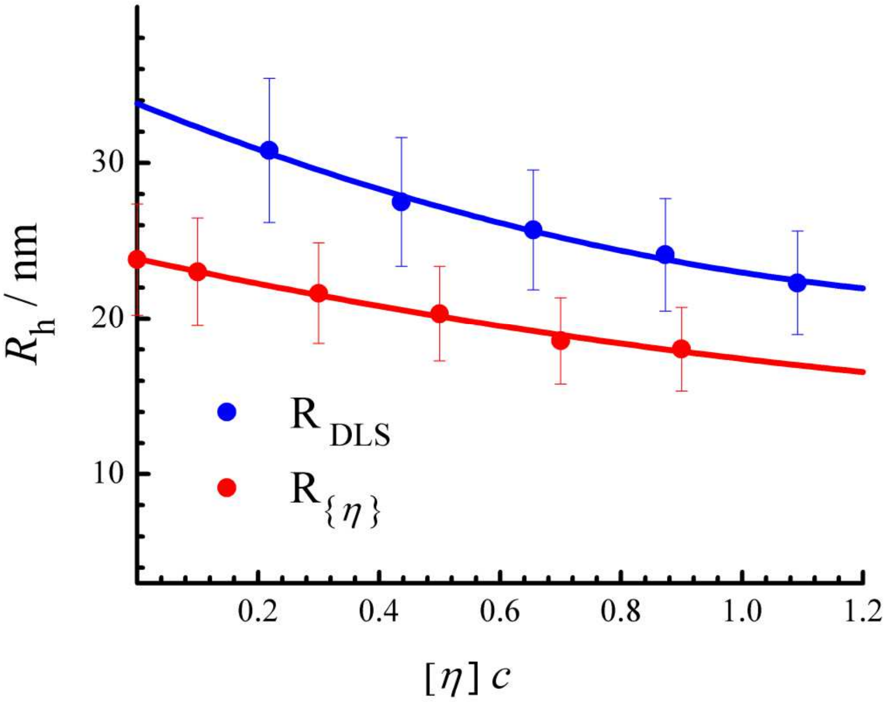


Figure-3.5: Comparison of the hydrodynamic radii of the polyelectrolyte coils (AD-8020) as a function of the reduced polymer concentration obtained from Dynamic Light Scattering and viscometry in 0.25 mol NaCl.

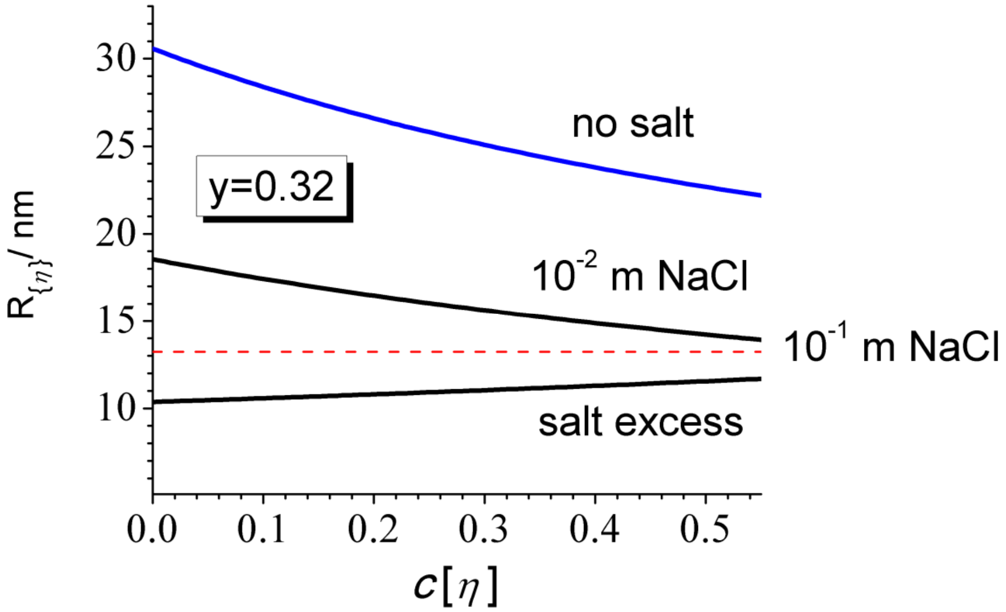


Figure-3.6: Coil dimensions as a function of the reduced polymer concentration for the polymer sample AD-5050. The salt contents of the solvents are indicated in the graph.

It is clear from the figures that the coil dimensions dependent on the molecular weight, charge and salt concentration in the solution. The free coil dimensions is important parameter for efficient flocculation. The coil dimensions reduce with increase in the concentrations. This implies that the optimum dosage of the flocculant should be at lower concentrations where the coil dimensions are higher. Same phenomenon was observed even at low salt concentrations.

3.4.4 Molecular weight and zeta potential

The molecular weight and zeta potential of the copolymers were determined using GPC and particle size analyzer, respectively. We show in table-3.1 the molecular weights and zeta potential of AD-8020, AD-5050 and AD-4060 samples.

Table-3.1: Molecular weight and Zeta potential of copolymers

Samples	**M_w** **(Kg mol^{-1})**	**M_n** **(Kg mol^{-1})**	**PDI** **(M_w/M_n)**	**Mol fraction DADMAC**	**pH**	**Zeta potential (mV)**
AD-8020	227.0	87.7	2.6	0.12	6.0-7.5	(+) 20.0 - 22.0
AD-5050	93.4	42.5	2.2	0.32	6.5-7.5	(+) 26.5 - 28.5
AD-4060	52.3	35.8	1.5	0.44	6.5-7.8	(+)39.5 - 41.3
Kaolin	-	-	-	-	6.5-7.0	(-)18.0 - 20.0

It can be readily seen that when the acrylamide content in the copolymer is high, the copolymer yields high molecular weight but gives low zeta potential (AD-8020). Whereas, the high content of cationic comonomer, DADMAC (AD-4060) gives higher zeta potential due to the presence of high charge density on the polymer and yields low molecular weight copolymer. The copolymer with equal feed ratio shows the values in between both the AD-8020 and AD-4060. These observations for composition are further evidenced by NMR studies. The particle size of the polymer also increases with the increase in DADMAC content. This can be attributed to the fact that the increased DADMAC content will increase the charge on the polymer which leads to intra molecular charge repulsion and open coil confirmation of polymer resulting into increase in size. This open coil confirmation is favourable for effective binding to cause efficient flocculation.

3.4.5 Flocculation of Kaolin

The flocculation efficiency of copolymers, AD-8020, AD-5050 and AD-4060 on kaolin aqueous suspension was examined by measuring the transmittance on kaolin suspension after the equilibrium flocculation (~40 min). The kaolin bears a negative charge on the surface in the pH range of 6.5 - 7.5 and exhibits the zeta potential of (-) 18 - 20.0 mV. The average size of the kaolin particles was ~1.0 µm. The efficiency of flocculation of kaolin suspension (3.0 wt %) was investigated at different dosages of flocculants.

We show in figure-3.7, a typical setup for the flocculation of Kaolin suspension. The flocculation setup consists of an overhead stirrer with a cross blade impeller and a beaker. Figure-3.7a shows the kaolin suspension before the addition of flocculant which is stable and looks milky. Upon addition of cationic flocculant and initial stirring the milky suspension turns into a clear solution after stopping the stirring (figure-3.7b). The initial stirring was 300 rpm for first 2 min, followed by stirring at 100 rpm for 3 min. This stirring cycle was followed because, during initial rapid stirring, mixing of particles and polymer occur which is the most desired. During the slow stirring at 100 rpm the floc size increase and begin to settle at the bottom. The transmittance of the clear solution was measured. Similar experiments were carried out for different dosages of flocculants.

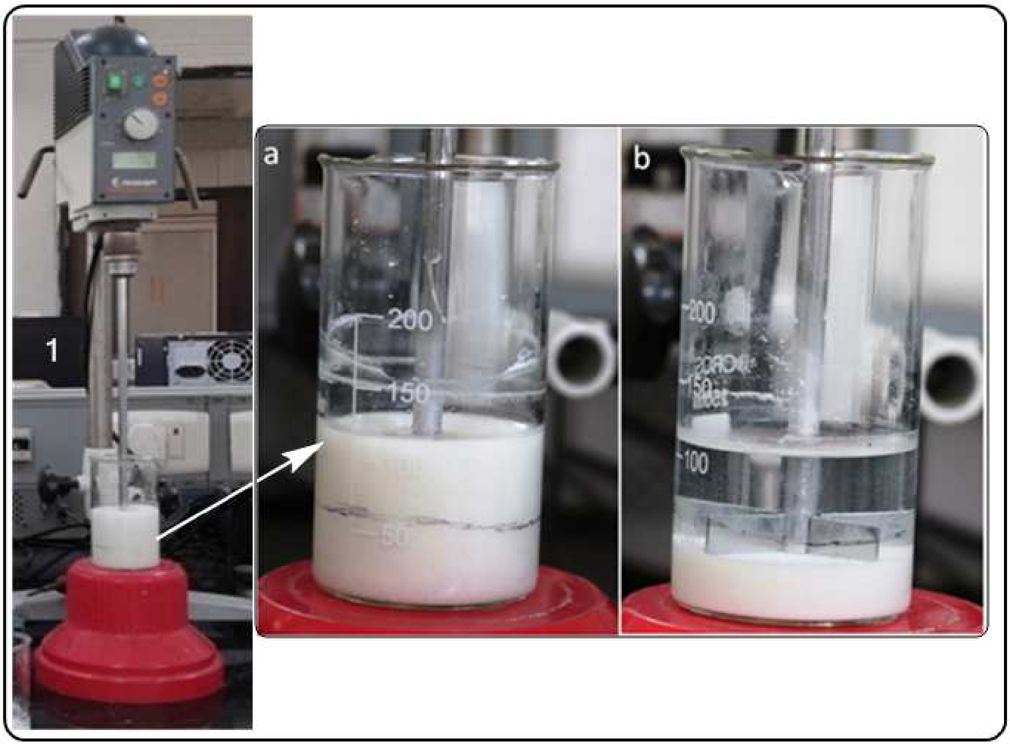


Figure-3.7: Flocculation of Kaolin aqueous suspension (1) flocculation setup, (a) Before flocculation and (b) after flocculation

Figure-3.8 shows the percentage transmittance of kaolin supernatant liquid vs. different dosage of flocculants, AD-8020, AD-5050 and AD-4060 taken at pH 7 and at equilibrium flocculation time of ~ 40 min.

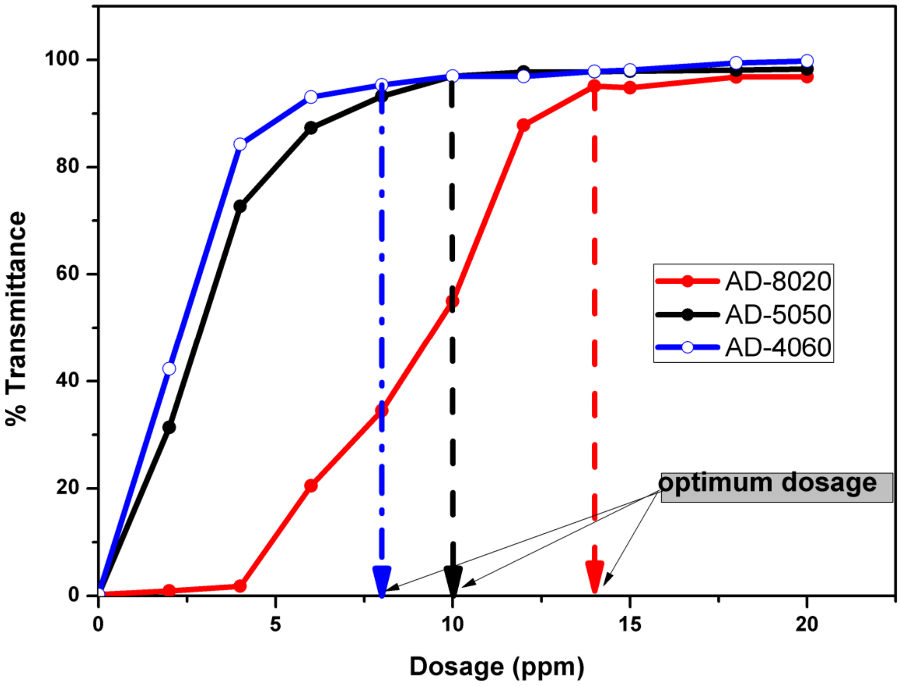


Figure-3.8: Transmittance of kaolin supernatant vs. dosage of flocculants after 40 min of equilibrium flocculation

It can be revealed from the figure that, AD-4060 shows nearly 95-98 % transmittance at the dosage range of 8 - 10 ppm and remains constant till 20 ppm. The AD-5050 showed 95 -98% transmittance at the dosage range of 10 - 12 ppm. Whereas, AD-8020 flocculant showed 95-98 % transmittance at the dosage range of about 14 - 16 ppm. Therefore, the optimum dosage levels for AD-4060, AD-5050 and AD-8020 flocculants for kaolin flocculation can be considered as 8.0 ppm, 10.0 ppm and 14.0 ppm, respectively. These flocculants showed efficient flocculation and the optimum dosages were found to be quite low compared to the values reported earlier.[10]

The AD-4060 flocculant contains more of cationic polymer and exhibits a high degree of charge with high zeta potential (+ 41.3 mV). In this case, the mechanism of flocculation could be due to the charge neutralization followed by bridging. In the case of flocculant AD-5050, the charge is moderate with moderate zeta potential (+ 28.5 mV) and moderate molecular weight (93.4 Kg mol^{-1}). The mechanism of flocculation is also can be due to charge neutralization and bridging. For the flocculant AD-8020, a higher dosage was required (~14.0 ppm) to get 95-98% transmittance in the flocculation. In AD-8020 flocculant, the charge density is low (zeta potential + 22mV) but the molecular weight is high (227 Kg mol^{-1}). Because of the high molecular weight, the long polymer chain can get attached to a large number of kaolin particles and the flocculation can occur through the bridging mechanism. The requirement of more number of polymer chains for bridging leads to high optimum dosage for AD-8020. These observations clearly indicate that charge density on the polymer plays a dominant role in the kaolin flocculation.

We also measured the zeta potential of kaolin supernatant solution as a function of different dosage of flocculants AD-8020, AD-5050 and AD-4060. The results are shown in figure-3.9.

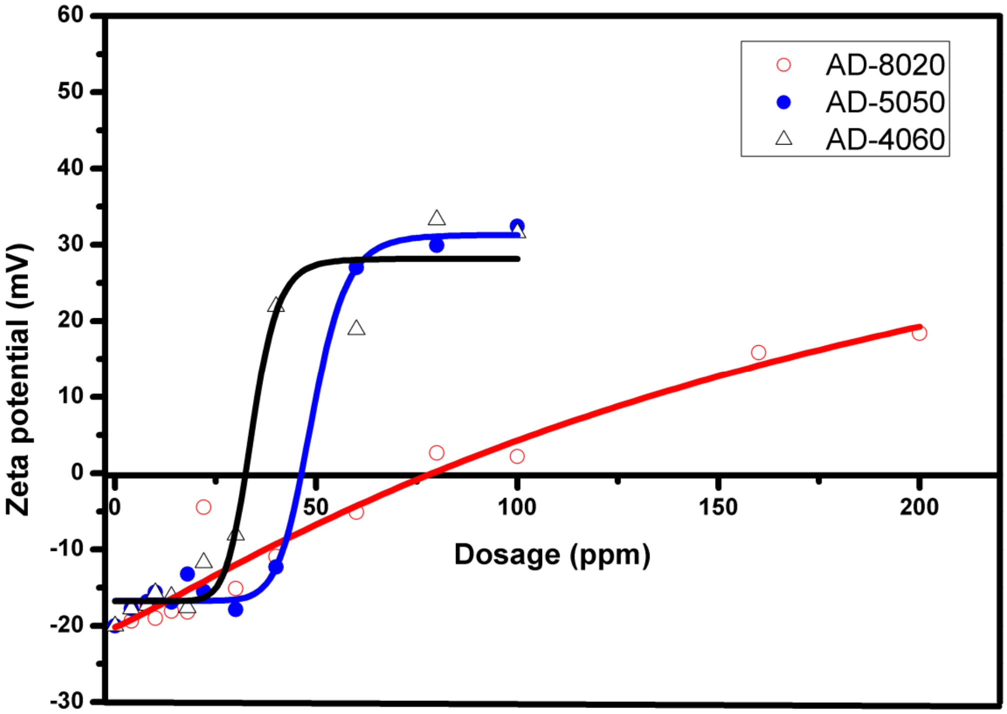


Figure-3.9: Zeta potential of kaolin suspension supernatant at different dosages after equilibrium flocculation using AD-8020, AD-5050 and AD-4060

It is observed that, the zeta potential of kaolin solution changed from (-) 20 mV to (+) 35 mV with an increase in the dosage of flocculants. This is due to the fact that the oppositely charged flocculants neutralize and diminish the surface charge of the suspended kaolin particles resulting into the formation of kaolin flocs. However, it is interesting to note from the figure-3.9 that the zeta potential of the kaolin supernatant did not reach zero value at 95% transmittance for the optimum dosage of AD-8020, AD-5050 and AD-4060 flocculants. The zeta potential values remained at (-) 15 to

(-) 10 mV. This could be due to the presence of still some very fine particles of unneutralized kaolin present in the supernatant liquid. Further, the kaolin fine particles are partially or heterogeneously bound by flocculants to form micro flocs that cannot settle down and hence they float and show reduced zeta potential value.

At higher dosage content, the zeta potential values crossed the zero value and attained a positive value of zeta potentials. This is because; the higher concentration of flocculant is available to bind to all the finely dispersed particles and the heterogeneously bound kaolin particles. These observations clearly indicate that there seems to be a broad flocculation regime and the possibility of both charge neutralization and bridging mechanism for driving the flocculation.

It is also observed form the figure, that the dosages at which the zeta potential value is zero for AD-8020, AD-5050 and AD-4060 were ~ 80, 48 and 30 ppm respectively. These values are more than 5 times higher than the optimum dosages. At optimum dosage, more than 95 % clarity of suspension was achieved or most of the kaolin was flocculated and that supernatant water can be reused to suspend the kaolin for next cycle of kaolin mining. This will improve the economy and efficiency of the kaolin recovery process enormously.

3.4.6 Kinetics of flocculation

In order to understand the kinetics of flocculation, the percentage transmittance of kaolin suspension as a function of time was measured for flocculants, AD-8020, AD-5050 and AD-4060 at different dosages and at their optimum dosages. Figure-3.10 shows the results of % transmittance vs. time for three flocculants at optimum dosages. Figure-3.11 to 3.13 shows the results of % transmittance vs. time for three flocculants at different dosages.

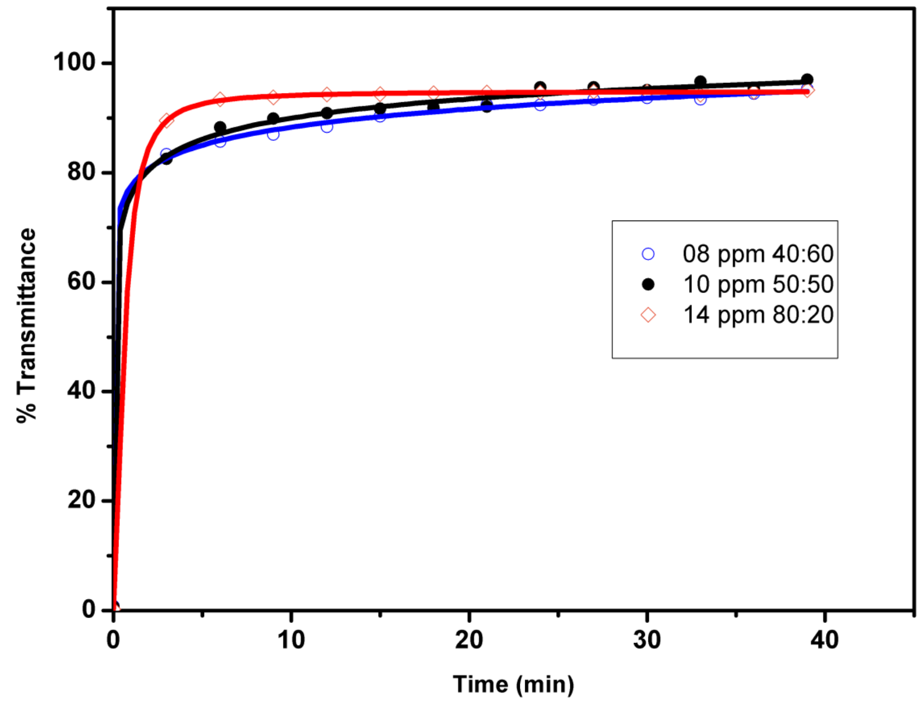


Figure-3.10: Kinetics of flocculation of AD-8020, AD-5050 and AD-4060 at optimum dosage

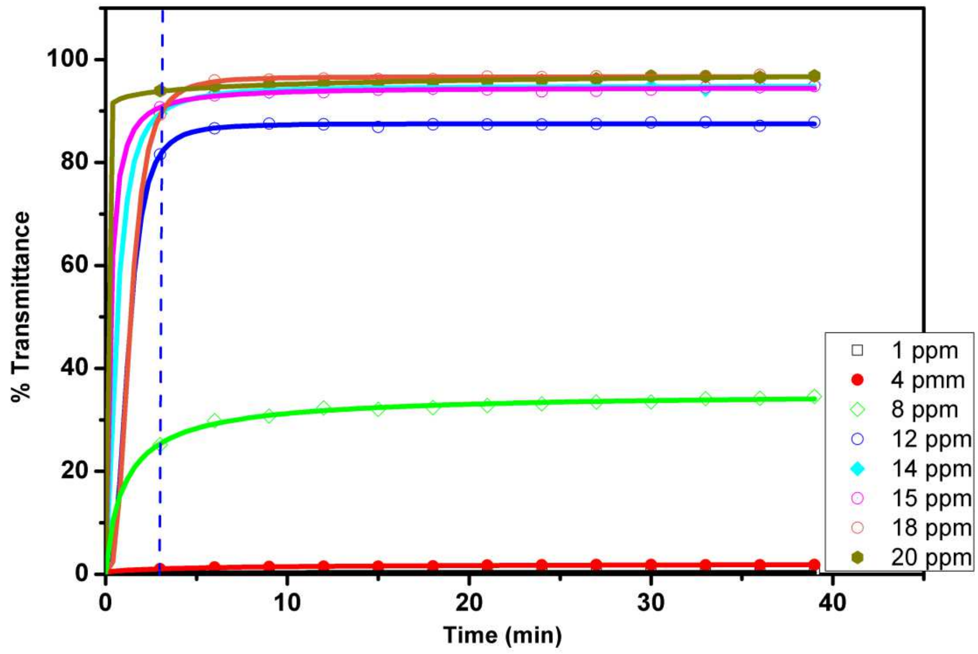


Figure-3.11: Transmittance of kaolin supernatant vs. time of AD-8020

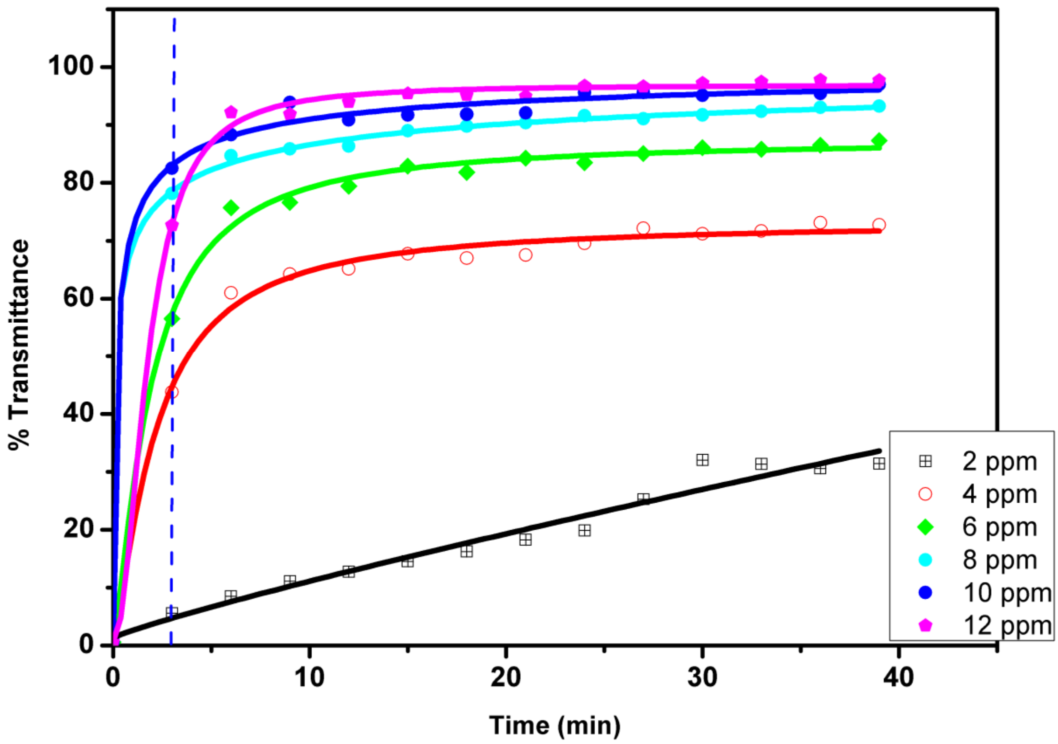


Figure-3.12: Transmittance of kaolin supernatant vs. time of AD-5050

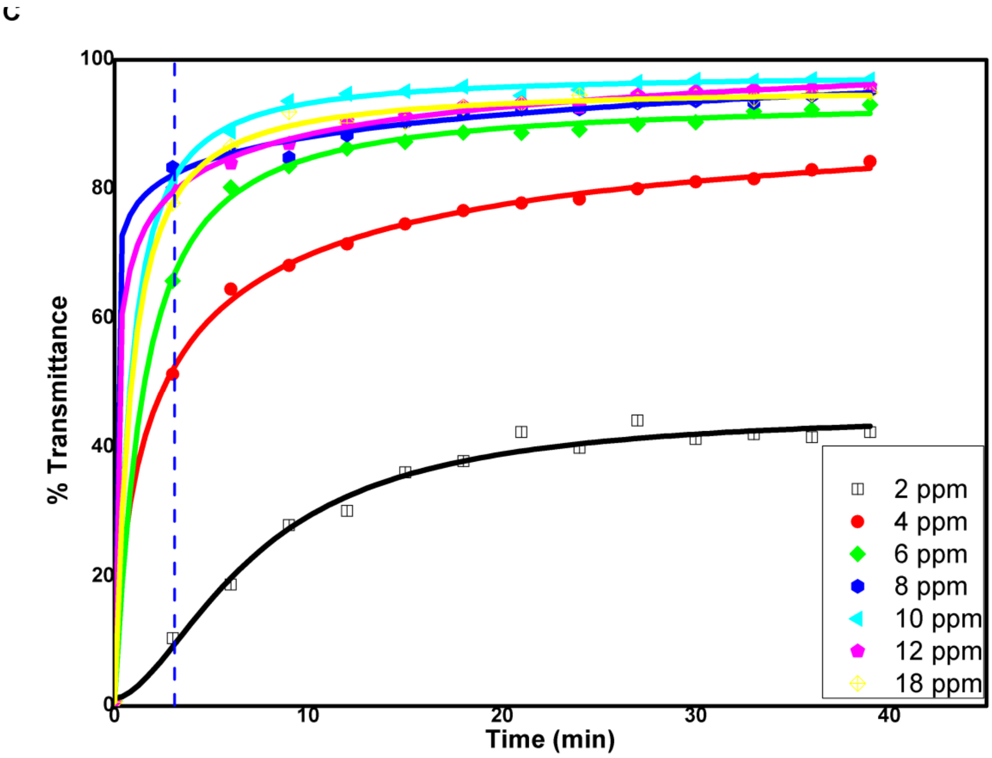


Figure-3.13: Transmittance of kaolin supernatant vs. time of AD-4060

It is clearly seen that 80 - 85% transmittance could be achieved within 3 min of flocculant addition to the kaolin suspension at their respective optimum dosages. This shows that the flocculant separates kaolin rapidly. The AD-4060 flocculant gave maximum % transmittance at optimum dosage of 8 ppm. These studies indicate that the charge on the flocculant (zeta potential) plays a dominant role compared to molecular weight for the efficient flocculation of Kaolin suspension.

From figure-3.11 to 3.13, it can be seen that the dosages prior to the optimum dosage also shows reasonably good % transmittance, which indicates that the flocculants have a broader flocculation range.

3.4.7 Floc characterization

3.4.7.1 Initial settling rate (ISR)

Figure 3.14 shows the interface height vs. time for flocculants AD-4060, AD-5050 and AD-8020 at their optimum dosages of 8, 10 and 14 ppm respectively. It can be readily seen that, the interface height decreases rapidly within the first 100 seconds and remains almost constant after 300 seconds for all the flocculants. This predicts the initial settling rate of ~0.01cm s^{-1} for the flocculants. These observations clearly reveal that AD-4060, AD-5050 and AD-8020 flocculate kaolin suspension very rapidly. It can also be seen that the AD-8020 has fastest and the AD-5050 has faster initial settling rate compared to AD-4060. This could be due to the difference in their floc size, wherein for AD-8020, the floc size formed is bigger by virtue of its higher molecular weight. Whereas for AD-4060, the lower molecular weight forms a smaller floc size, which will take more time to settle.

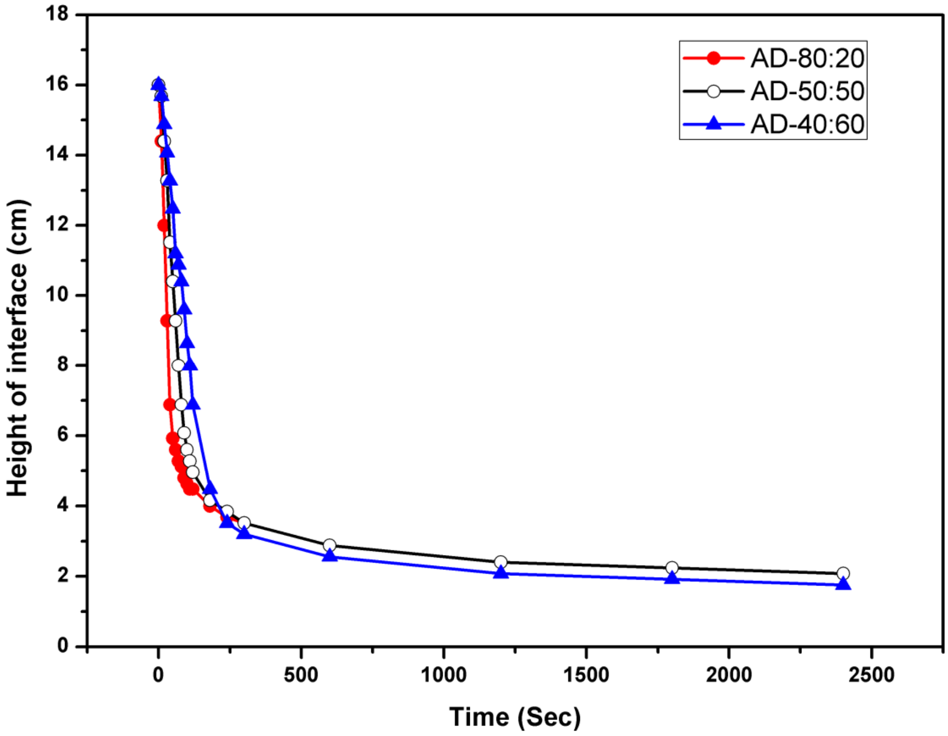


Figure-3.14: Initial settling rate of CP-4060 and CP-8020

3.4.7.2 Filter Cake Moisture Content (FCMC)

FCMC is an important parameter to characterize the floc state. Flocculants were also employed as filtration aids, where the flocs formed will help in faster filtration and reduced moisture in the flocs. Which helps in faster drying of the final floc product. Figure-3.15 shows the results of FCMC for AD-4060, AD-5050 and AD-8020 at different dosages. The FCMC of AD-4060, AD-5050 and AD-8020 remained independent with respect to dosage in the range of 10 to 20 ppm used in this work. However, the earlier reports indicate a decrease in FCMC with an increase in dosage levels when the dosage levels are quite high (~40 to 50 ppm). We observed a very small change in FCMC with these low dosage levels. Nevertheless, these lower dosages (10-20 ppm) were found to be efficient in flocculation and gave more than 95 % transmittance in the flocculation process. The filter cakes of AD-8020 showed slightly higher FCMC compared to AD-4060 and AD-5050 which could be attributed to the higher molecular weight of the polymer that results into increased hydrophilicity of flocculant and absorbs more moisture. The cakes of AD-5050 showed less FCMC value than both AD-8020 and AD-4060; this could be due to lower molecular weight and charge density.

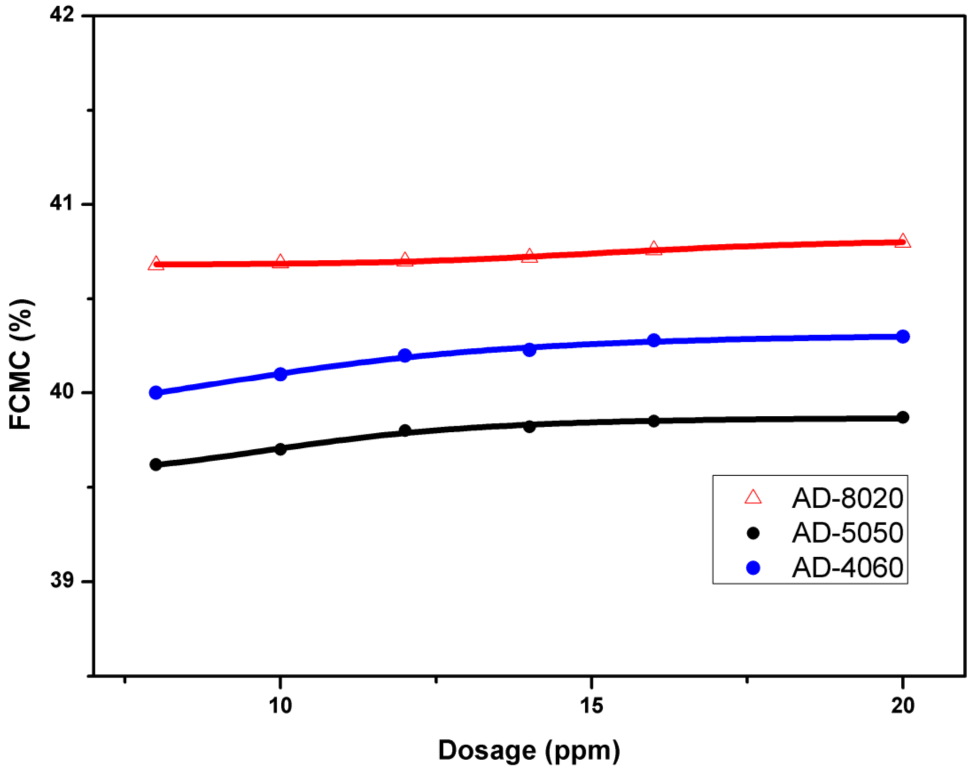


Figure-3.15: Filter cake moisture content study of CP-4060 and CP-8020 at different dosages

The visual observation of the filter cakes after the flocculation using AD-4060, AD-5050 and AD-8020 at different dosages was made and photographs are shown in figure-3.16.

Figure-3.16: Photographs of filter cakes after flocculation and drying for AD-8020 (a-d) AD-5050 (e - h) and AD-4060 (i-l)

It is observed that, as the dosage increase, the surface of the filter cake becomes more smoother and softer. This could be due to the formation of dense flocs at higher dosages of flocculant.

3.4.7.3 Optical microscopic studies

The optical microscopy was performed on kaolin suspensions obtained under different dosages of AD-4060, AD-5050 and AD-8020 flocculants. The optical micrographs are shown in figure-3.17. Kaolin suspension without any flocculant does not show the flocs and one can see a uniform suspension [figure-3.17 (a)]

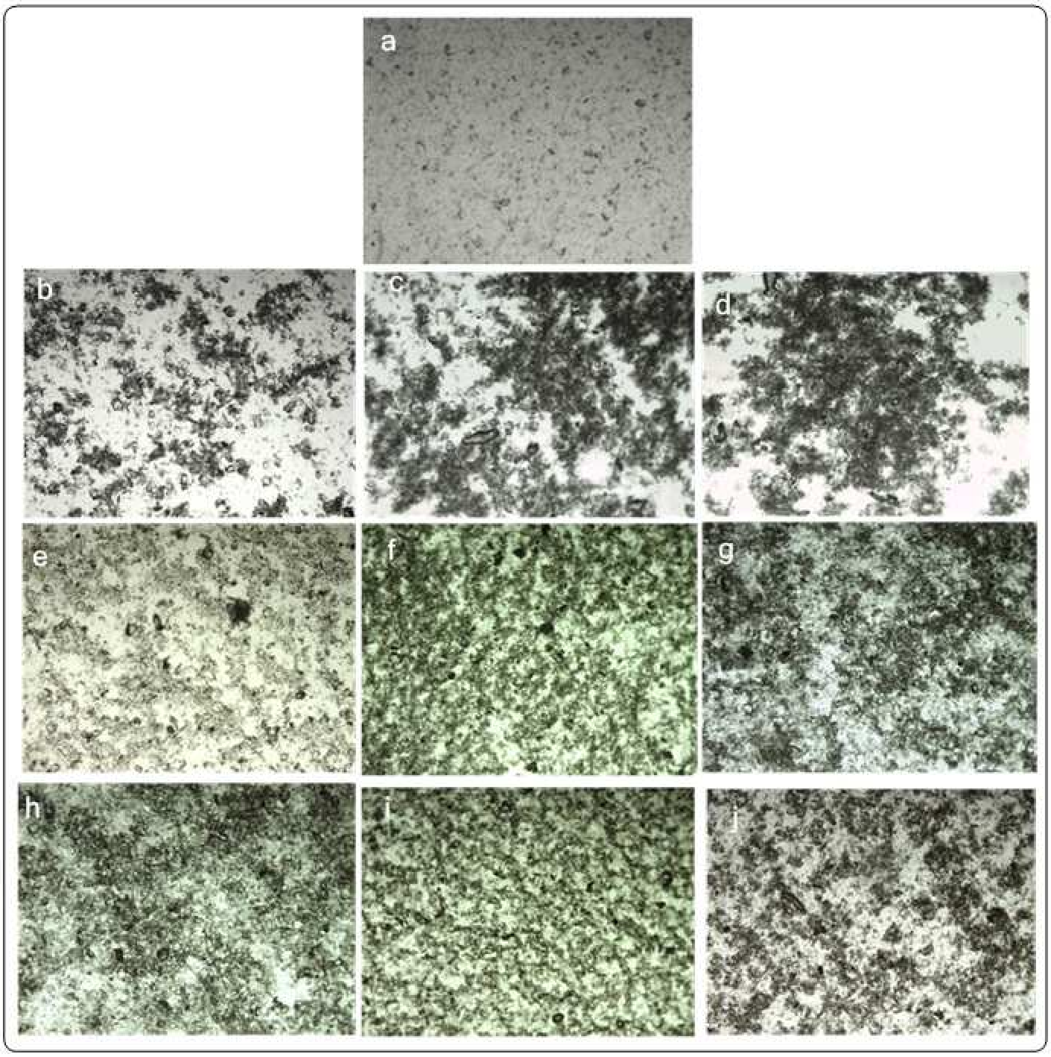


Figure-3.17: Optical micrographs of kaolin flocculation at different dosages, Kaolin (a), AD-4060 (b-d), AD-5050 (e-g) and AD-8020 (h-j)

However, upon flocculation, kaolin flocs are observed very clearly and the floc size increases with the dosage of flocculant. The observed optimum dosages of 8, 10 and 14 ppm for flocculants AD-4060, AD-5050 and AD-8020 respectively, show more than 95 % transmittance in the supernatant liquid after the floc formation. This is visible in the micrographs of figure-3.17 (b), (e) and (j).

3.5 Conclusions

In conclusion, we have shown that the cationic flocculants based on the copolymer of acrylamide (AM) and diallyldimethylammonium chloride (DADMAC) efficiently flocculates kaolin from its aqueous suspensions. Depending on the ratio of monomers incorporated, the copolymers could be obtained with different molecular weights and zeta potentials which are very important properties required for efficient flocculation. The mole fraction of the DADMAC was determined by proton NMR spectroscopy. It was inferred form the viscosity and particle size measurements that the intrinsic viscosity and hydrodynamic radii decreases with an increase in polymer concentration. This means the hydrodynamic radii is higher at low polymer concentrations. Similar phenomenon was observed at very low salt concentrations also. The optimum dosages for maximum flocculation were found to be 8.0, 10.0 and 14.0 ppm for AD-4060, AD-5050 and AD-8020 copolymers, respectively. The minimum time required for maximum flocculation was determined to be ~ 3-4 minutes investigated as per the laboratory scale. The copolymer (AD-4060) with high zeta potential gave the best flocculation efficiency. The floc characterization was performed interms of floc size and FCMC. Based on the results it was proposed that, the charge neutralization and bridging are the main mechanisms for driving the flocculation. These copolymers show great promise in the flocculation of kaolin from aqueous streams in industries.

3.6 References

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FLOCCULATION OF KAOLIN USING COPOLYMER OF ACRYLAMIDE (AM) AND (3-ACRYLAMIDOPROPYL) TRIMETHYLAMMONIUM CHLORIDE (APTMAC)

CHAPTER-4

In this chapter we report on the synthesis of poly (AM-co-APTMAC) copolymers. The compositoin of APTMC was varied to obtain different copolymers. The polymers were characterized by NMR, GPC and Zeta potential. The flocculation efficiency was studied using kaolin suspensions. The flocs were characterized in terms of FCMC, ISR and optical microscopic analysis. Correlation was drawn between the flocculation efficiency and the molecular weight and charge of the flocculants.

J Appl Polym Sci **47286 (2018). doi:10.1002/app.47286**

4.1 Introduction

Polyelectrolyte flocculants continue to attract major attention due to their importance in solid-liquid separations in a wide range of industries. Large numbers of cationic flocculants have been utilized for the flocculation of kaolin. Divakaran and Pillai [1,2] have used chitosan for flocculation of kaolin. Haijiany Li etal [3] have used starch based cationic polymer for kaolin flocculation. Hasan etal[4] have used cationic lignin polymers for kaolin flocculation. Kumar etal[5] have used cationic amylopectin based flocculant for kaolin separation. Flocculation and dewatering of kaolin suspension was performed using polyacrylamide in the presence of surfactants [6–8]. A few cationic monomers such as Diallyldimethylammonium chloride (DADMAC), 2-Acryloyloxyethyltrimethylammonium chloride (AOETMAC), 2-Methacryloyloxyethyltrimethylammonium chloride (MOETMAC), 3-Acrylamidopropyltrimethylammonium chloride (APTMAC) etc., have been copolymerized with acrylamide to synthesize cationic flocculants. Among these cationic monomers, APTMAC has a high reactivity ratio with acrylamide[9,10]. This higher reactivity ratio will result in higher incorporation of APTMAC into copolymer resulting in higher charge and molecular weight on the flocculant. A judicious combination of APTMAC along with acrylamide can yield cationic flocculants with desired properties.

In this work, we have synthesized cationic flocculant based on the combination of acrylamide (AM) and (3-Acrylamidopropyl) trimethylammonium chloride (APTMAC) for flocculation of kaolin suspension and demonstrated an efficient flocculation in very small dosages (3-10ppm) of flocculants. The chemical structure of copolymer was determined using ^{1}H and ^{13}C NMR spectroscopy. The flocculation efficiency is correlated to the zeta potential and molecular weight of the copolymer. Floc characterizations like filter cake moisture content (FCMC), initial settling rate (ISR) and optical micrographs of floc were studied and correlated to the flocculation with an increase in dosage.

4.2 Experimental

4.2.1 Materials and Methods

Acrylamide (AM), 3-Acrylamidopropyltrimethylammonium chloride (APTMAC) (75 wt-% aqueous solution), 2, 2'-azobis(2-methylpropionamide) dihydrochloride (V-50) were procured from Aldrich, USA and were used as received. Deionized water (conductivity 0.055 µS cm^{-1} at 25° C) was used for all the reactions. Acetone was purchased from Rankem, Mumbai, India. Kaolin was procured from Thomas Baker chemicals, Mumbai, India. Analytical grade Sodium nitrate was obtained from Merck, Mumbai, India and used as received.

4.2.2 Synthesis of cationic flocculant based on Acrylamide and APTMAC

Cationic flocculants were prepared by copolymerization of acrylamide and APTMAC monomer using solution polymerization technique. V-50 was used as a thermal initiator. In a typical reaction, 5 g AM and 3.64 g (4.85 ml) APTMAC were dissolved in 90 ml of DI water in a flange type double jacketed reaction vessel equipped with an overhead stirrer, nitrogen gas inlet, and a thermowell. The initial total concentration of the monomers in the reaction mixture was 10 Wt %. The reaction mixture was purged with nitrogen gas for 30 minutes to remove any dissolved oxygen. The temperature of the reaction mixture was increased to 56° C. Then, 0.475 g V-50 initiator was added to the reaction mixture with continuous stirring and nitrogen gas purging for 6 h. The viscosity of the reaction mixture increased rapidly, indicating the formation of the copolymer. After 6 h, the polymer was precipitated in acetone and dried in an oven at 40° C under vacuum. Three copolymers with different feed ratios (moles) of AM and APTMAC (AM: APTMAC; 80:20, 50:50 and 40:60) were prepared and denoted as AA-8020, AA-5050 and AA-4060, respectively. The chemical structure of the copolymers was characterized using ^{1}H and ^{13}C NMR spectroscopy. The molecular weights of the copolymers were determined using gel permeation chromatography (GPC).

4.3 characterizations

4.3.1 Gel permeation chromatography (GPC)

The molecular weight (MW) of the copolymers was determined using Agilent 1200 GPC with Shodex OH pak SB-800 series columns. The mobile phase used was 0.25 N $NaNO_3$, with a flow rate of 0.4 ml/min. 100 µl was the sample injection volume. The GPC column temperature was maintained at 40° C, and polyacrylamide standards were used for calibration.

4.3.2 Zeta potential measurements

Zeta potential and Particle size measurements were carried out at 25° C using Brookhaven 90 plus particle size analyzer, USA. The polymer concentration used was 0.1 g dL^{-1}.

4.3.3 NMR studies

The ^1H and ^{13}C NMR spectra of copolymers were recorded on Bruker AV 500 MHz and Bruker AV 400 MHz spectrometer respectively. The copolymer samples were prepared in D_2O.

4.3.4 Flocculation test for kaolin

Kaolin (particle size 1µ) suspension in water (3.0 wt-%) was used for the flocculation test. Kaolin suspension was prepared by stirring kaolin solution using overhead stirrer at 400 rpm for 30 min. In a typical flocculation study, to a 100 ml kaolin suspension, a known volume of flocculant solution (1g L^{-1}) was added and stirred for 5 min (with 300 rpm for first 2 min and at 100 rpm for 3 min) using an overhead stirrer, Heidolph RZR 2012, Germany with cross blade impeller. After 5 min, stirring was stopped and immediately 1 ml aliquot was drawn from the central portion of the solution. The transmittance (%) was measured for this solution using Shimadzu UV-PC 1601 UV-Vis spectrophotometer, Japan in the kinetic mode at 700 nm. This value of the transmittance was taken as zero minute reading. The solution was allowed to settle and the aliquots were drawn every 3 min for ~40 min and transmittance was measured. Then transmittance vs time was plotted to find out the time required for maximum flocculation to occur. For the zeta potential measurement, the supernatant liquid was taken after 40 min flocculation with different dosages of flocculant.

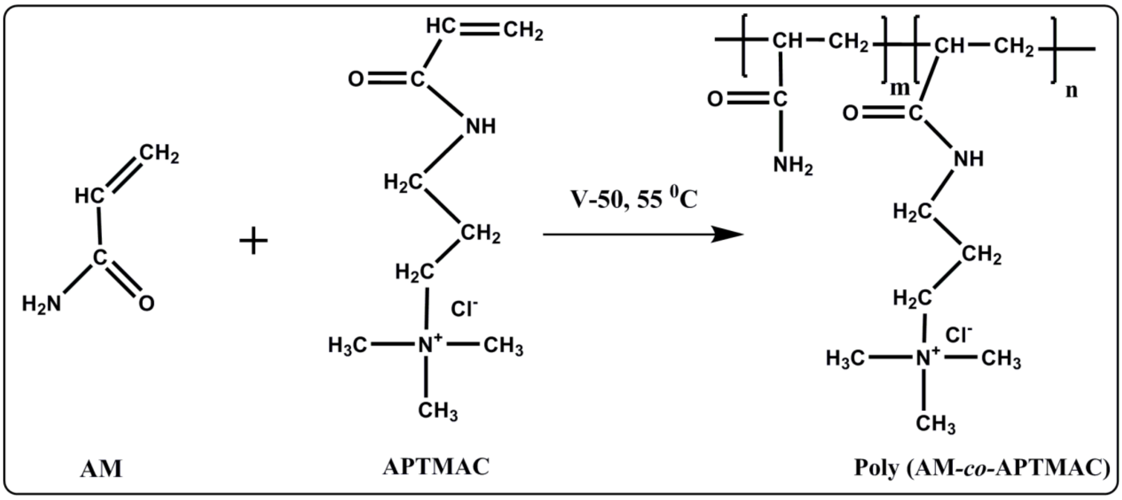
4.3.5 Floc characterization

The procedures for floc characterizations were reported earlier in chapter-3 under section **3.3.7** ***(Initial settling rate (ISR) 3.3.7.1, Filter Cake Moisture Content (FCMC) and optical microscopy studies 3.3.7.2)***

4.4 Results and Discussion

4.4.1 Synthesis and characterization of flocculants

Cationic flocculants were prepared using acrylamide and APTMAC at three different mole ratios (AM: APTMAC; 80:20, 5050 and 40:60). Amongst a few cationic monomers available, APTMAC was chosen considering its high reactivity ratio with AM. Synthesizing an efficient cationic flocculant lies in obtaining high molecular weight and high zeta potential copolymer. The acrylamide monomer with its high ratio of propagation to termination constant, gives high molecular weight to the polymer. Whereas, the cationic monomer provides an overall charge density to the copolymer. Therefore, it is very important to critically balance both the monomer contents to obtain high molecular weight and high zeta potential polymer for efficient flocculation. Accordingly, three copolymers, with varying AM and APTMAC content were prepared. The quantitative yields of the copolymers AA-8020, AA-5050 and AA-4060 were determined to be 91, 92, and 93% respectively. The copolymers were coded as AA-8020, AA-5050 and AA-4060, respectively. The reaction scheme for the synthesis of poly (AM-co-APTMAC) is shown in scheme-4.1. The structural characterization of the copolymers was carried out using ^{1}H and ^{13}C NMR spectroscopy.



Scheme-4.1: Reaction scheme for the synthesis of poly (AM-co-APTMAC)

4.4.2 Chemical structure by NMR spectroscopy

We show in figure-4.1, the ^{1}H NMR spectra of poly (AM-co-APTMAC) [AA-4060] and a homopolymer of polyacrylamide. The methyl ($-CH_3$) proton peaks of APTMAC appear at 3.4 ppm and the methylene ($-CH_2-$) protons of APTMAC attached to nitrogen atom give peaks in the range of 3.2 - 3.3 ppm. The methylene ($-CH_2-$) proton peaks of the backbone chain of AM and APTMAC appear in the range of 1.6 - 1.7 ppm. All the characteristic peaks of the copolymer assigned, agree with those reported in the literature. [11,12]

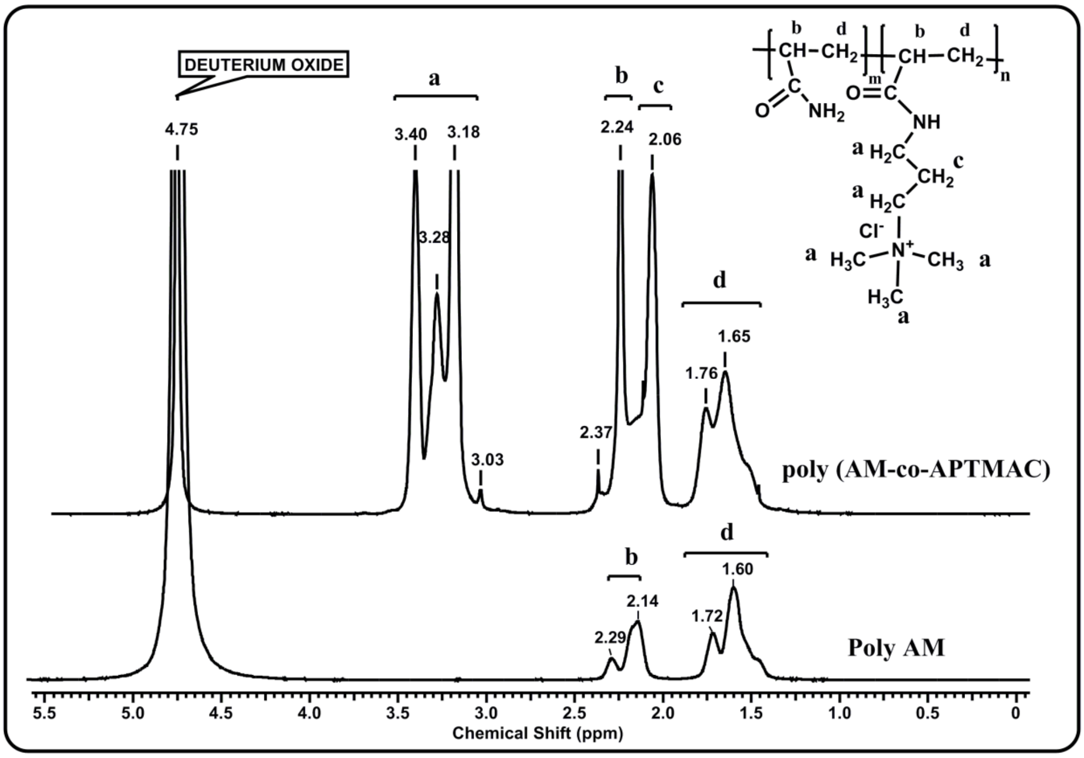


Figure-4.1: 500 MHz ^{1}H NMR spectra for Polyacrylamide and Poly (AM-co-APTMAC) [AA-4060]

We also show in Figure-4.2, the ^{13}C NMR spectrum of poly (AM-co-APTMAC) [AA-4060]. The methyl (-CH_3) carbon peaks of APTMAC appear at 53.17 ppm and the peaks for methylene (-CH_2-) carbon of APTMAC attached to amide nitrogen appear at 36.45 ppm and methylene (-CH_2-) carbon of backbone chain of AM and APTMAC appear at 35.01 ppm. The methylene (-CH_2-) carbon of APTMAC attached to nitrogen gives a peak at 64.22 ppm and the peak for methylene (-CH_2-) carbon next to carbon attached to nitrogen appears at 22.58 ppm. All the characteristic peaks of the copolymer assigned agree with the earlier reported values[13]. Both the ^{1}H and ^{13}C NMR spectra confirm the chemical structure of the copolymer.

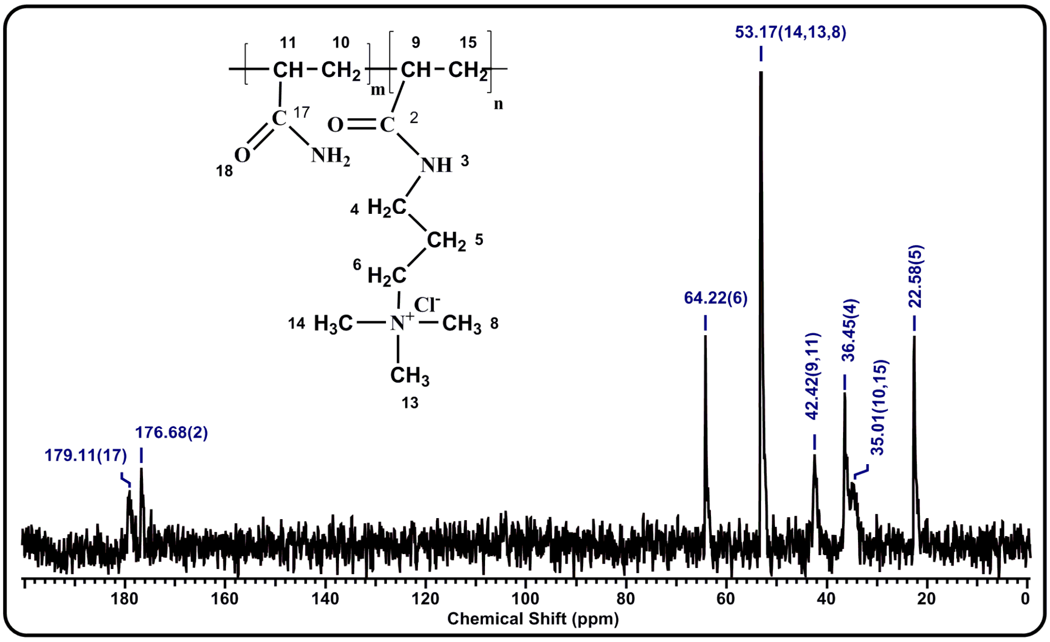


Figure-4.2: 400 MHz ^{13}C NMR spectra for Poly (AM-co-APTMAC) [AA-4060]

Figure-4.3 and 4.4 represent the ^{1}H and ^{13}C stacked NMR spectra for all the three compositions AA-8020, AA-5050 and AA-4060 respectively. It can be clearly seen that the intensity of peaks for APTMAC increases from AA-8020 to AA-4060, indicating increased incorporation of APTMAC with increasing feed ratio.

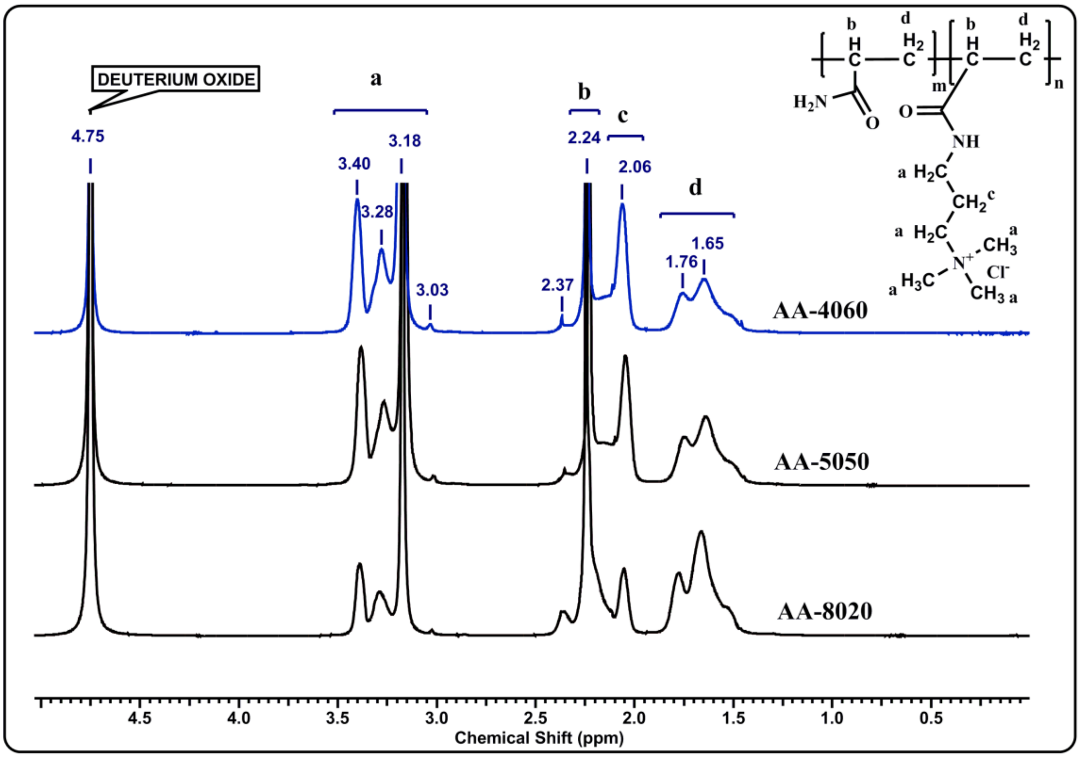


Figure-4.3: 500 MHz ^{1}H NMR spectra for AA-8020, AA-5050 and AA-4060

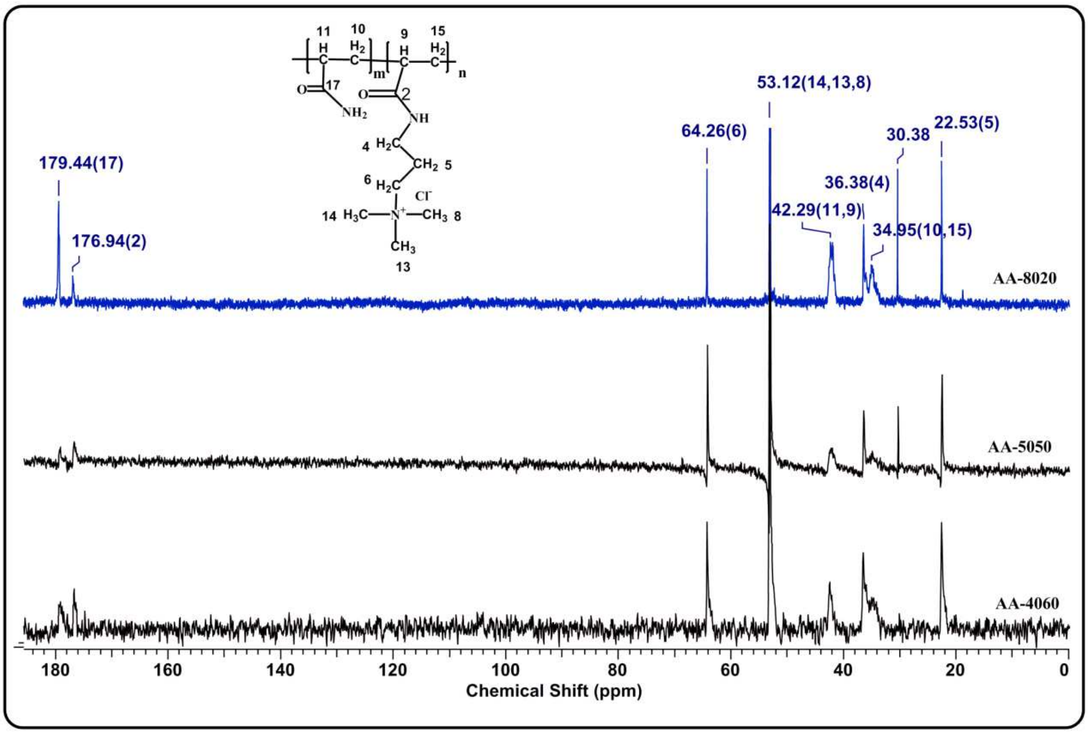


Figure-4.4: 400 MHz ^{13}C NMR spectra for AA-8020, AA-5050 and AA-4060

4.4.3 Molecular weight and zeta potential

The molecular weight and zeta potential of the copolymers were determined using GPC and particle size analyzer, respectively. We show in table-4.1 the molecular weights and zeta potential of AA-8020, AA-5050 and AA-4060 samples.

Table-4.1: Molecular weight and Zeta potential of copolymers

Samples	M_w (Kg mol^{-1})	M_n (Kg mol^{-1})	PDI (M_w/M_n)	pH	Zeta potential (mV)
AA-8020	275	166	1.6	6.5-7.0	(+) 52.0 - 55.0
AA-5050	207	169	1.22	6.5-7.0	(+) 62.0 - 66.0
AA-4060	185	162	1.1	6.5-7.0	(+) 90.0 - 93.0
Kaolin	-	-	-	6.5-7.0	(-) 18.0 - 20.0

It can be readily seen that when the acrylamide content in the copolymer is high, the copolymer yields high molecular weight but low zeta potential (AA-8020). Whereas, the high content of cationic comonomer, APTMAC (AA-4060) gives higher zeta potential due to the presence of high charge density on the polymer and yields low molecular weight copolymer. The copolymer with equal feed ratio shows the values in between both the AA-8020 and AA-4060. The particle size of the polymer also increases with the increase in APTMAC content. This is because the increased APTMAC content will increase the charge on the polymer. This leads to charge repulsion and open coil confirmation of polymer making it to increase in size. This open coil confirmation is favourable for effective binding to cause flocculation.

4.4.4 Flocculation of Kaolin

The flocculation efficiency of copolymers, AA-8020, AA-5050 and AA-4060 on kaolin aqueous suspension was examined by measuring the transmittance on kaolin suspension after the equilibrium flocculation (~40 min). The kaolin bears a negative charge on the surface in the pH range of 6.5 - 7.5 and exhibits the zeta potential of (-) 18 - 20.0 mV. The average size of kaolin particles was ~1.0 µm. The efficiency of flocculation of kaolin suspension (3.0 wt %) was investigated at different dosages of flocculants.

A typical set-up for the kaolin flocculation is shown in figure 3.7 of chapter-3. Figure-3.7a shows the kaolin suspension before the addition of flocculant which is stable and looks milky. Upon addition of cationic flocculant and initial stirring milky suspension turns into a clear solution after stopping the stirring (figure-3.7b). The kaolin particles begin to settle at the bottom the transmittance of the clear solution was measured. Similar experiments were carried out for different dosages of flocculants.

Figure-4.5 shows the percentage transmittance of kaolin supernatant liquid vs different dosage of flocculants, AA-8020, AA-5050 and AA-4060 taken at pH 7 and at equilibrium flocculation time of ~ 40 min.

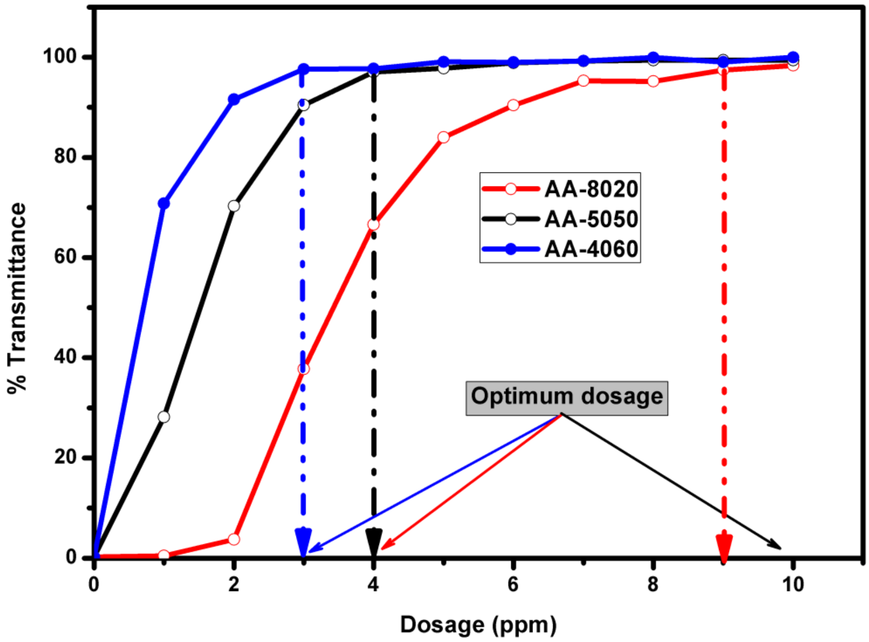


Figure-4.5: Transmittance of kaolin supernatant vs dosage of flocculants after 40 min of equilibrium flocculation

It can be revealed from the figure that, AA-4060 shows nearly 95-98 % transmittance at the dosage range of 3 - 5 ppm and remains constant till 10 ppm. The AA-5050 showed 95 -98% transmittance at the dosage range of 4 - 6 ppm. Whereas, AA-8020 flocculant showed 95-98 % transmittance at the dosage range of about 9 - 10 ppm. Therefore, the optimum dosage levels for AA-4060, AA-5050 and AA-8020 flocculants for kaolin flocculation can be considered as 3.0 ppm, 4 ppm and 9.0 ppm, respectively. These flocculants showed efficient flocculation and the optimum dosages were found to be quite low compared to the values reported earlier.[14]

The AA-4060 flocculant contains more of cationic polymer and exhibits a high degree of charge with high zeta potential (+ 93 mV). In this case, the driving force for the flocculation could be attributed to the charge neutralization followed by bridging. However, because of the high charge content of the polymer (AA-4060), the possibility of some contribution of patch mechanism for flocculation cannot be ruled out. In case of flocculant AA-5050 where, the charge is moderate with moderate zeta potential (+ 66 mV) has moderate molecular weight (207 Kg mol^{-1}). Here the driving force for flocculation is charge neutralization followed by bridging. For the flocculant AA-8020, higher dosage level (~9.0 ppm) was required to get 95-98% transmittance in the flocculation. In AA-8020 flocculant, the charge density is low (zeta potential + 55mV) but the molecular weight is high (275 Kg mol^{-1}). Because of the high molecular weight, the long polymer chain can get attached to a large number of kaolin particles and the flocculation can occur through the bridging mechanism. The requirement of more number of polymer chains for bridging leads to high optimum dosage for AA-8020. These observations clearly indicate that charge density on the polymer plays a dominant role in the flocculation of kaolin suspension studied here.

We also measured the zeta potential of kaolin supernatant solution as a function of different dosage of flocculants AA-8020, AA-5050 and AA-4060. The results are shown in figure-4.6.

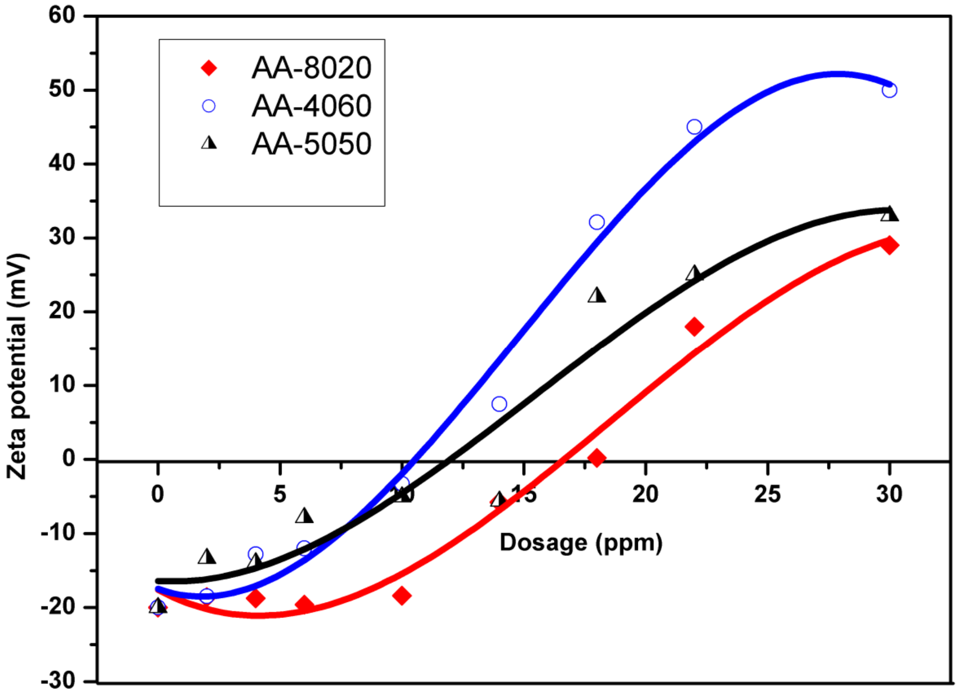


Figure-4.6: Zeta potential of kaolin suspension supernatant at different dosages after equilibrium flocculation using AA-8020, AA-5050 and AA-4060

It is observed that, the zeta potential of kaolin solution changed from (-) 20 mV to (+) 50 mV with an increase in the dosage of flocculants. This is due to the fact that the oppositely charged flocculants neutralized and diminished the surface charge of the suspended kaolin particles resulting into the formation of kaolin flocs. However, it is surprising to see from the figure-4.6 that the zeta potential of the kaolin supernatant did not reach zero value at 95% transmittance for the optimum dosage of AA-8020, AA-5050 and AA-4060 flocculants. The zeta potential values remained at (-) 10 to (-) 20 mV. This could be due to the presence of still some very fine particles of unneutralized kaolin present in the supernatant liquid. Further, the kaolin fine particles are partially or heterogeneously bound by flocculants to form micro flocs that cannot settle down and hence they float and show reduced zeta potential value.

At higher dosage content, the zeta potential values crossed the zero value and attained positive zeta potentials. These observations clearly indicate that there seems to be a broad flocculation regime and the possibility of both charge neutralization and bridging mechanism followed for the flocculation.

It is also observed form the figure, that the dosages at which the zeta potential is zero for AA-8020, AA-5050 and AA-4060 were 16, 12 and 10 ppm respectively. These dosages are more than 3-4 times higher than the optimum dosage. At optimum dosage more than 95 % clarity or kaolin was flocculated and that supernatant water can be reused to suspend kaolin for the next cycle of kaolin mining. This will enormously improve the economy and efficiency of the recovery process.

4.4.5 Kinetics of flocculation

In order to understand the kinetics of flocculation, we measured the percentage transmittance of kaolin suspension as a function of time for flocculants, AA-8020, AA-5050 and AA-4060 at their optimum dosage and at different dosages. Figure-4.7 shows the results of % transmittance vs time for three flocculants at their optimum dosage. The figures 4.8 to 4.10 shows the results of % transmittance vs time for three flocculants at different dosages.

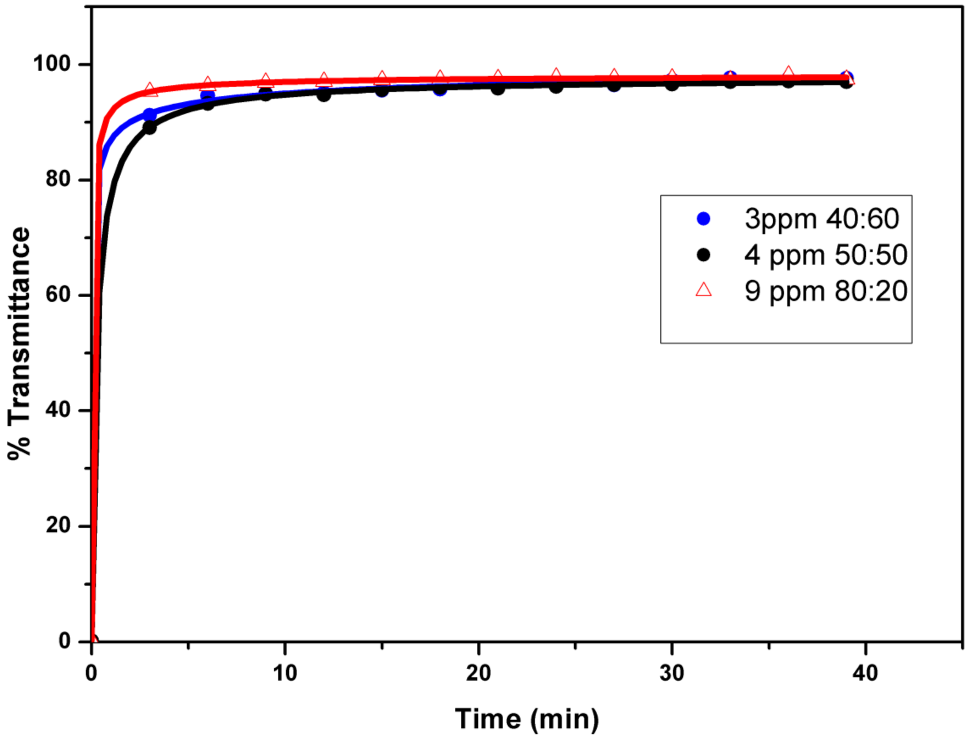


Figure-4.7: Kinetics of flocculation at optimum dosage

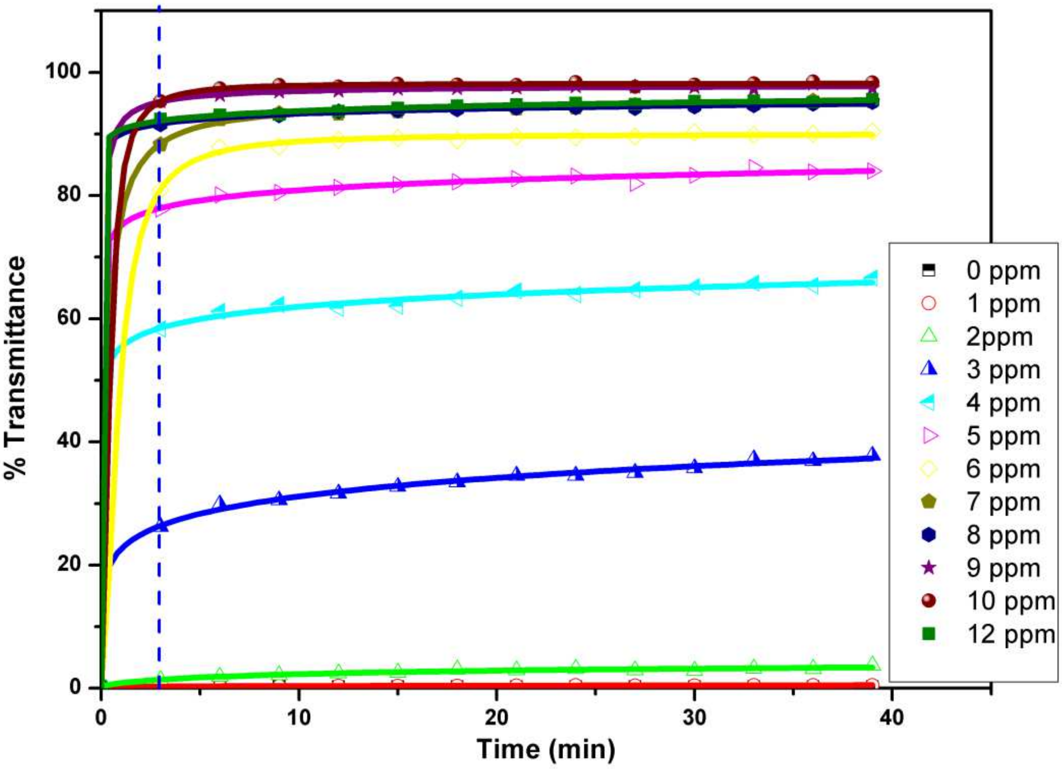


Figure-4.8: Kinetics of flocculation at different dosages of AA-8020

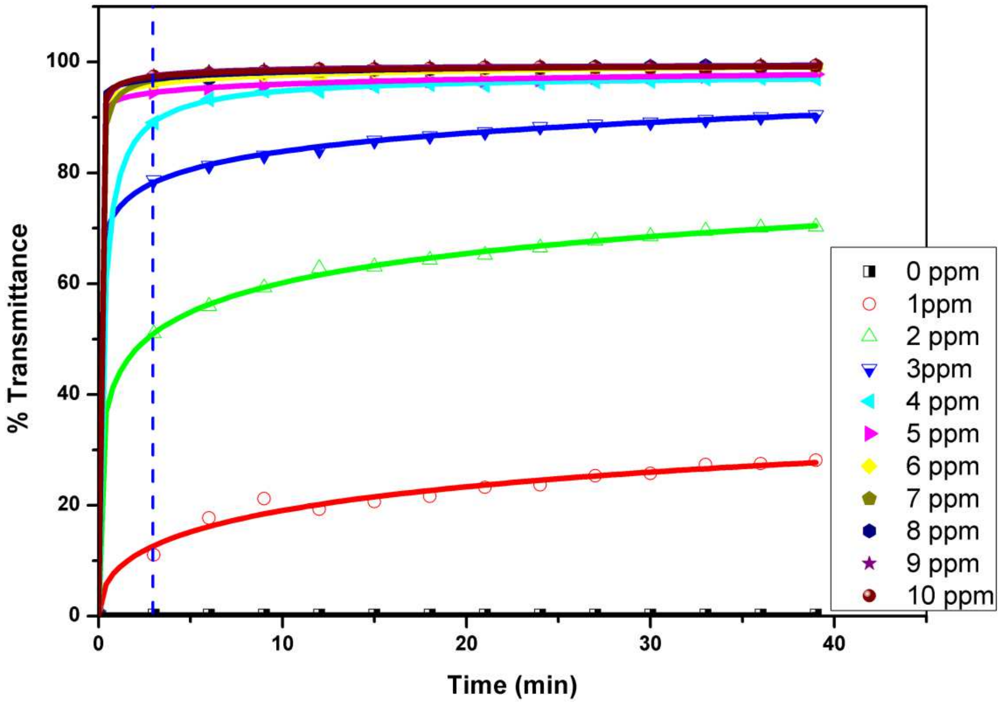


Figure-4.9: Kinetics of flocculation at different dosages of AA-5050

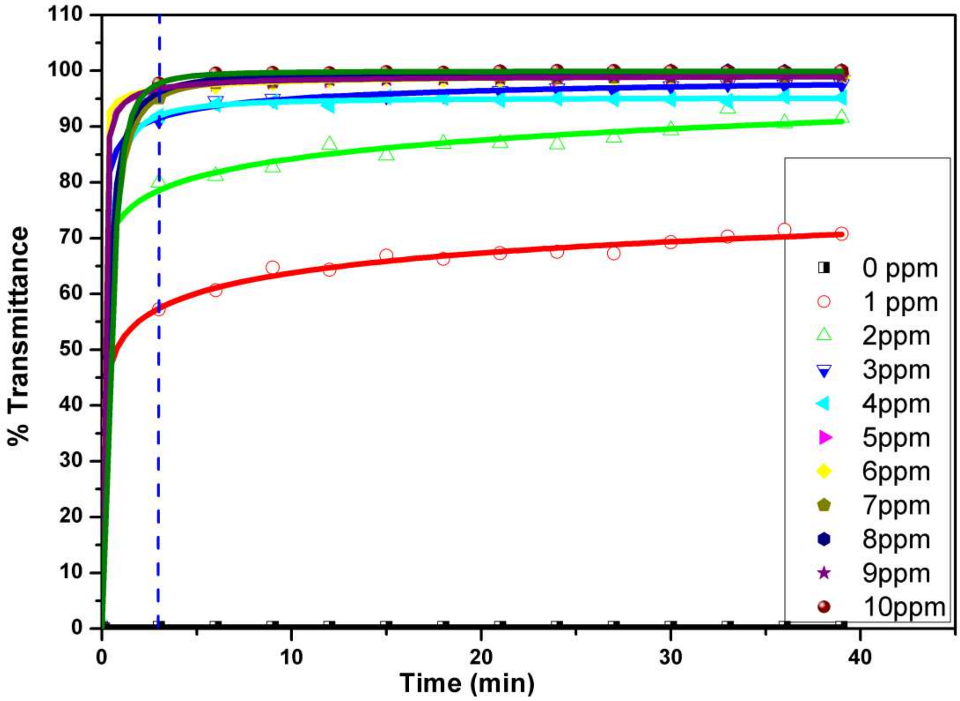


Figure-4.10: Kinetics of flocculation at different dosages of AA-4060

It is clearly seen that 95 - 98% transmittance could be achieved within 3 min of flocculant addition to the kaolin suspension at their respective optimum dosages of flocculants. The AA-4060 flocculant gave maximum % transmittance at an optimum dosage of 3 ppm. These studies indicate that the charge on the flocculant (zeta potential) plays a dominant role compared to molecular weight for the efficient flocculation of Kaolin suspension.

From figure-4.8 to 4.10, it can be seen that the dosages prior to the optimum dosage also shows reasonably good % transmittance, which indicates that the flocculants have a broader flocculation range.

4.4.6 Floc characterization

4.4.6.1 Initial settling rate (ISR)

Figure 4.11 shows the interface height vs time for flocculants AA-4060, AA-5050 and AA-8020 at their optimum dosage levels of 3, 4 and 9 ppm respectively. It can be readily seen that, the interface height decreases rapidly within the first 100 seconds and remains almost constant after 250 seconds for all the flocculants. This predicts the initial settling rate of ~0.1cm s^{-1} for the flocculants. These observations clearly reveal that AA-4060, AA-5050 and AA-8020 flocculate kaolin suspension very rapidly.

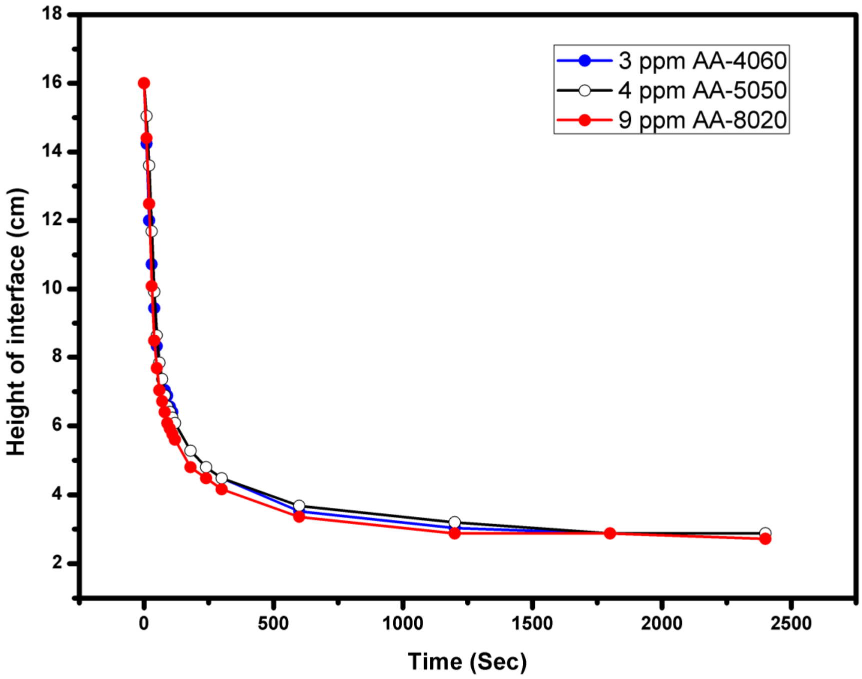


Figure-4.11: Initial settling rate of AA-4060, AA-5050 and AA-8020

4.4.6.2 Filter Cake Moisture Content (FCMC)

Figure-4.12 shows the results of FCMC for AA-4060, AA-5050 and AA-8020 at different dosages. The FCMC of AA-4060, AA-5050 and AA-8020 remained independent with respect to dosage in the range of 2 to 10 ppm used in this work. However, the earlier reports indicate a decrease in FCMC with an increase in dosage levels when the dosage levels are quite high (~40 to 50 ppm). We observed a very small change in FCMC with these low dosage levels. Nevertheless, these small dosages (2-10 ppm) were found to be efficient in flocculation and gave more than 95 % transmittance in the flocculation process. The FCMC of AA-4060 showed slightly higher FCMC to AA-8020 and AA-5050, which could be attributed to the high charge in the polymer which results into increased hydrophilicity of flocculant and absorbs more moisture. The AA-5050 showed less FCMC value than both AA-8020 and AA-4060; this may be because AA-5050 has lesser molecular weight than AA-8020 and lesser charge than AA-4060 hence the water retention is less.

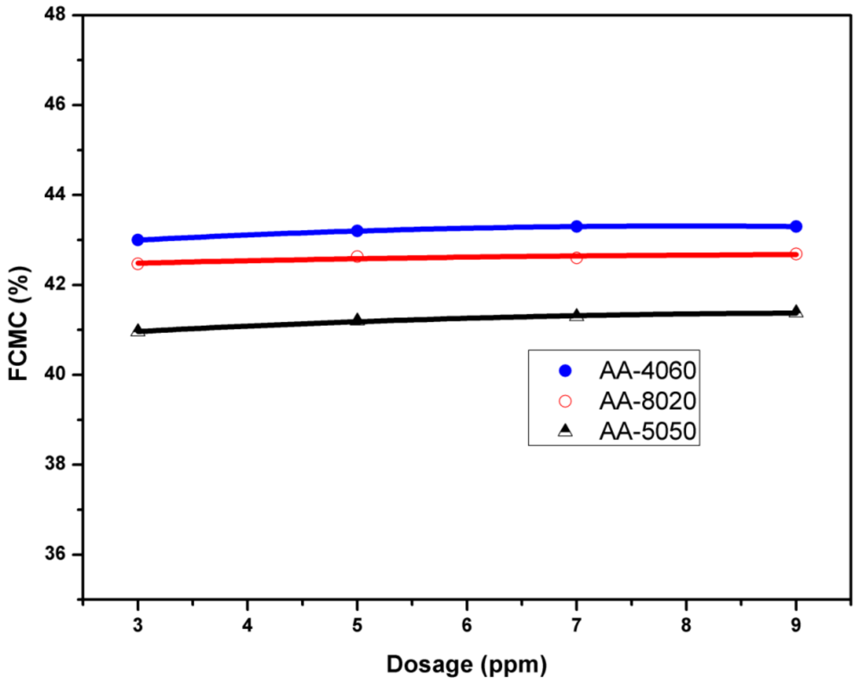


Figure-4.12: Filter cake moisture content study of AA-4060, AA-5050 and AA-8020 at different dosages

The visual observation of the filter cakes after the flocculation using AA-4060, AA-5050 and AA-8020 at different dosages was made and photographs are shown in figure-4.13.

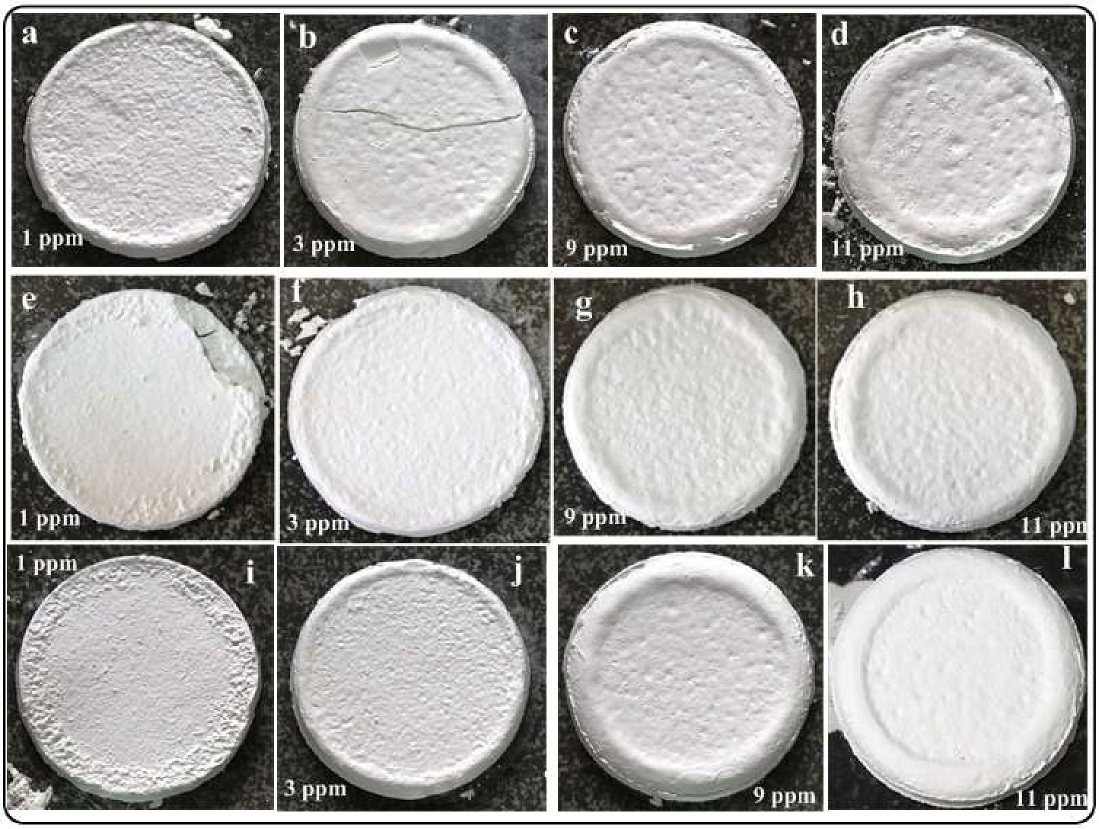


Figure-4.13: Photographs of filter cakes after flocculation and drying for AA-4060 (a-d) AA-5050 (e - h) and AA-8020 (i-l)

It is observed that, as the dosage increase, the surface of the filter cake becomes smoother and softer. This could be due to the formation of dense flocs at higher dosages of flocculant.

4.4.6.3 Optical microscopic studies

The optical microscopy was performed on kaolin flocs obtained under different dosages of AA-4060, AA-5050 and AA-8020 flocculants. The optical micrographs are shown in figure-4.14. Kaolin suspension without any flocculant does not show the flocs and one can see a uniform suspension [figure-4.14 (a)]

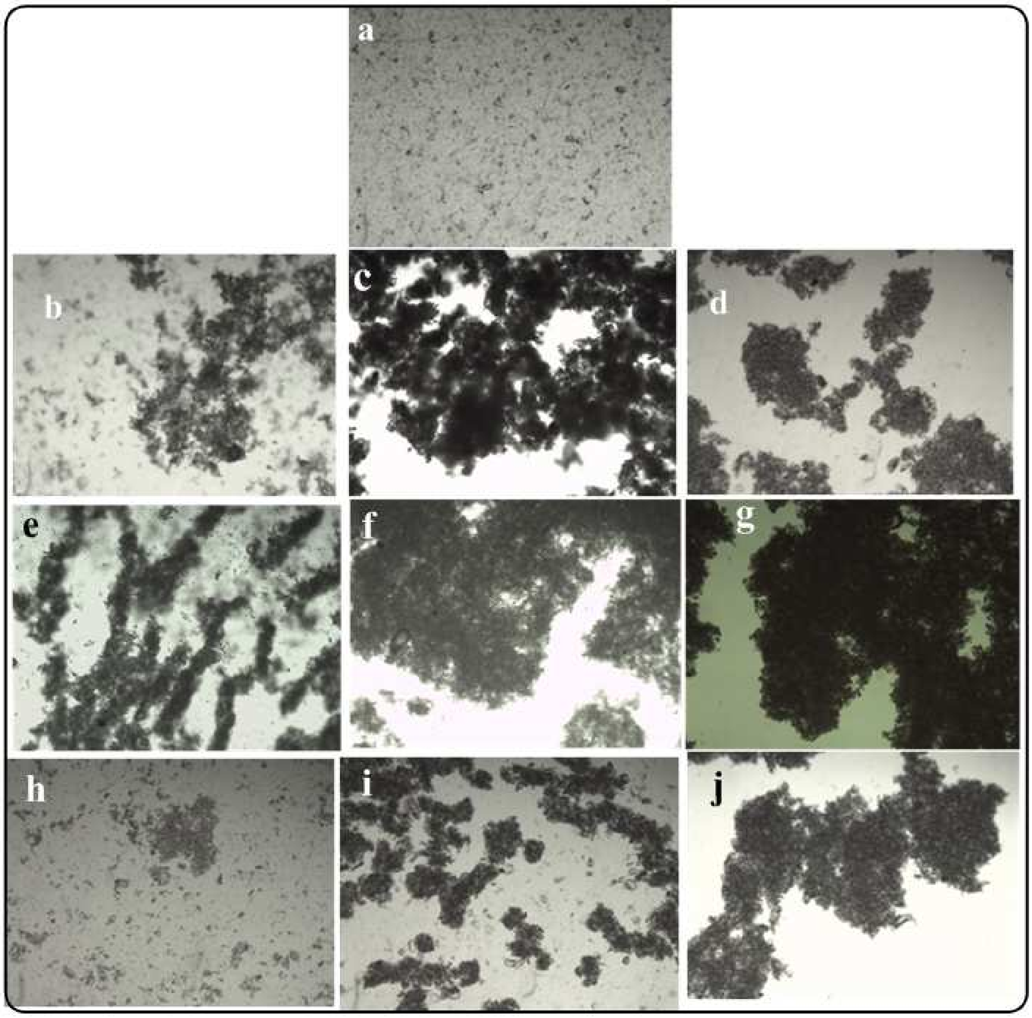


Figure-4.14: Optical micrographs of kaolin flocculation at different dosages Kaolin (a), AA-4060 (b-d), AA-5050 (e-g) and AA-8020 (h-j)

However, upon flocculation, kaolin flocs are observed very clearly and the floc size increases with the dosage of flocculant. The observed optimum dosages of 3, 4 and 9 ppm for flocculants AA-4060, AA-5050 and AA-8020 respectively show more than 95 % transmittance in the supernatant liquid after the floc formation. This is visible in the micrographs of figure-4.14 (b), (e) and (j).

4.5 Conclusions

In conclusion, we have shown that the cationic flocculants based on the copolymer of acrylamide (AM) and 3-acrylamidopropyltrimethylammonium chloride (APTMAC) efficiently flocculates kaolin from aqueous solution. Depending on the ratio of monomers, the copolymers could be obtained with different molecular weight and zeta potentials which are very important properties required for good flocculation. The optimum dosages for maximum flocculation were found to be 3.0, 4.0 and 9.0 ppm for AA-4060, AA-5050 and AA-8020 copolymers, respectively. The minimum time required for maximum flocculation was determined to be 3-4 minutes in the laboratory scale. The copolymer (AA-4060) with high zeta potential gave the best flocculation efficiency. The floc characterization was performed interms of floc size and FCMC. Based on the results it was proposed that the charge neutralization and bridging are the main mechanisms for driving the flocculation. These copolymers show great promise in the flocculation of kaolin from aqueous streams in industries.

4.6 References

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SYNTHESIS OF CHITOSAN GRAFT COPOLYMER FLOCCULANTS

CHAPTER-5

In this chapter we report on the graft polymerization of chitosan with APTMAC. The feed weight ratio of APTMAC was varied to get different graft copolymers. The characterization of graft copolymer was done using NMR, GPC and zeta potential measurements. The flocculation efficiency was studied using kaolin suspensions. The flocs were characterized by FCMC, ISR and optical microscopic analysis. The flocculation efficiency was correlated to charge and molecular weight of the polymer.

5.1 Introduction

The use of biopolymers for flocculation applications has been practiced since many decades. The bio polymer based flocculants mostly use polymers such as starch[1–5], cellulose[6–9], chitosan[10–15], Pullulan[16,17], guar gum[18–21], natural gums[22–24] etc. The advantage of using chitosan over other biopolymers is that it is not a feedstock for humans and animals and hence will not deplete the food source. The other advantages of using chitosan are, it is biodegradable, non-toxic and environmental friendly[25–30]. Chitosan is the second largest available carbohydrate polymer on earth next only to cellulose and is available in plenty at lesser cost. The use of chitosan alone as flocculant is not very effective for flocculating kaolin because of working pH limitations and also due to low molecular weight[12,31]. One of the major drawbacks of using chitosan is its solubility, because of inter and intra molecular hydrogen bonding, chitosan dissolves only in acidic solution of pH less than 5. At this acidic pH, there is a possibility of increased degradation of chitosan which results in reduction of its molecular weight and hence the flocculation efficiency[12]. The flocculant based on chitosan graft polymer which is also soluble in pH 6 and above is preferred to avoid its degradation and loss of flocculation efficiency. Chemical modification of chitosan by grafting, using vinyl monomers and monomers with cationic charge has been reported[10,14,27,32–35]. The grafting improves the solubility of chitosan by interrupting the inter and intra molecular hydrogen bonds. This addresses the issue of solubility and charge on chitosan for efficient flocculation. The graft polymers are partially biodegradable because of the polysaccharide backbone and are stable for shearing since the presence of flexible synthetic polymer chain is grafted onto a rigid or semi-rigid polysaccharide backbone. This flexible grafted chain helps in adsorption to the colloidal particles, improving the flocculation efficiency. There are many methods to graft chitosan but potassium persulfate induced free radical polymerization yields better grafted chitosan flocculants which are easily soluble in water. The other methods such as gamma radiation induced grafting results in graft polymers having lesser solubility in water[12]. There are many cationic monomers grafted onto chitosan. The use of (2-methacryloyloxyethyl)trimethylammonium chloride (MOETMAC) has been reported by Jian-Ping Wang et al[13,36]. The chitosan grafted MOETMAC shows broader pH flocculation range but has a limited solubility in water. The grafting of both acrylamide and MOETMAC was also reported[31] wherein, the acrylamide monomer contributes to increase the molecular weight and the MOETMAC enhances the charge density. The use of 3-acrylamidopropanetrimethylammonium chloride (APTMAC) for grafting onto chitosan and its application for kaolin recovery is not reported to the best of our knowledge.

In this work, we have synthesized cationic chitosan flocculants based on the graft copolymerization of chitosan (Chi) with cationic monomer (3-Acrylamidopropyl) trimethylammonium chloride (APTMAC) for flocculation of kaolin suspension and demonstrated an efficient flocculation in very small dosages (2-4 ppm) of flocculants. The chemical structure of the graft copolymer was determined using ^{1}H and ^{13}C NMR spectroscopy. The flocculation efficiency was correlated to the zeta potential and molecular weight of the copolymer. The characterizations of flocculants in terms of filter cake moisture content (FCMC), initial settling rate (ISR) and optical micrographs of kaolin suspension were studied and correlated to the flocculation of kaolin suspensions.

5.2 Experimental

5.2.1 Materials and Methods

Chitosan (Chi), 3-Acrylamidopropyltrimethylammonium chloride (APTMAC) (75 wt-% aqueous solution), potassium persulfate were procured from Aldrich, USA and were used as received. Deionized water (conductivity 0.055 µS cm^{-1} at 25° C) (TKA instruments, GmbH Stockland) was used for all the reactions. Laboratory grade acetone was purchased from Rankem, Mumbai, India. Kaolin was procured from Thomas Baker Chemicals, Mumbai, India. Chromatography grade acetic acid was obtained from Sisco Research Laboratory, Mumbai, India. Analytical grade sodium acetate was procured from Sd-fine chemicals, Mumbai, India and was used as received.

5.2.2 Synthesis of cationic flocculant: chitosan grafted with APTMAC

Cationic flocculants were prepared by grafting APTMAC onto chitosan using Potassium persulfate as an initiator. The free radical was generated on the chitosan backbone, which eventually polymerizes the APTMAC monomer into a graft chain. In a typical reaction, 3 g accurately weighed chitosan was transferred to a 500 ml capacity flanged double jacketed reactor, equipped with an overhead stirrer and a temperature controlled circulating water bath. To this 300 ml of 1% acetic acid aqueous solution was added (to obtain 1 Wt% chitosan solution). The solution was stirred till chitosan was completely dissolved. The argon gas was purged into the solution for 30 min to remove any dissolved oxygen. Then the temperature was increased to 56º C and 120 mg of $K_2S_2O_8$ was added with continuous stirring with continuous purging of argon gas. After 5 minutes of the addition of $K_2S_2O_8$, required amount of APTMAC monomer solution was added drop wise[37]. This delayed addition was performed to avoid possible homo polymerization of APTMAC. The reaction continued for 3 hours. The copolymer was recovered by precipitation in acetone and dried in a vacuum oven at 40° C. Three graft copolymers with different feed ratios (wt %) of APTMAC and chitosan (Chi: APTMAC; 1:3, 1:5 and 1:8) were prepared and denoted as CA-1:3, CA-1:5 and CA-1:8, respectively. The chemical structure of the copolymers was characterized using ^1H and ^{13}C NMR spectroscopy. The molecular weights of the copolymers were determined using gel permeation chromatography (GPC).

5.3 Characterizations

5.3.1 Gel permeation chromatography (GPC)

The molecular weight (MW) of copolymers was determined using Agilent 1200 GPC with Shodex OH pak SB-800 series columns. The mobile phase used was 0.3 N CH_3COOH and 0.2 N CH_3COONa with a flow rate of 0.8 ml/min. 100 µl was the sample injection volume. The GPC column temperature was maintained at 40° C, and Pullulan standards were used for calibration.

5.3.2 Zeta potential and Particle size measurements

Zeta potential and Particle size measurements were carried out at 25° C using Brookhaven 90 plus particle size analyzer, USA. The polymer concentration used was 0.1 g dL^{-1}.

5.3.3 NMR studies

The ^{1}H and ^{13}C NMR spectra of copolymers were recorded on Bruker AV 400 MHz spectrometer. The samples were prepared in D_2O.

5.3.4 Flocculation test for kaolin

Kaolin (particle size 1μ) suspension in water (3.0 wt-%) was used for the flocculation test. Kaolin suspension was prepared by stirring kaolin solution using overhead stirrer at 400 rpm for 30 min. In a typical flocculation study, to a 100 ml kaolin suspension, a known volume of flocculant solution (1g L^{-1}) was added and stirred for 5 min (with 300 rpm for first 2 min and at 100 rpm for 3 min) using an overhead stirrer, Heidolph RZR 2012, Germany with cross blade impeller. After 5 min, stirring was stopped and immediately, 1 ml aliquot was drawn from the central portion of the solution. The transmittance (%) was measured for this solution using Shimadzu UV-PC 1601 UV-Vis spectrophotometer, Japan, in the kinetic mode at 700 nm. This value of the transmittance was taken as zero minute reading. The solution was allowed to settle and the aliquots were drawn at a predetermined time till 40 min and transmittance was measured. Then transmittance vs time was plotted to find out the time required for maximum transmission to occur. For the zeta potential measurement, the supernatant liquid was taken after 40 min of flocculation. Solutions with different dosages of flocculant were examined.

5.3.5 Floc characterization

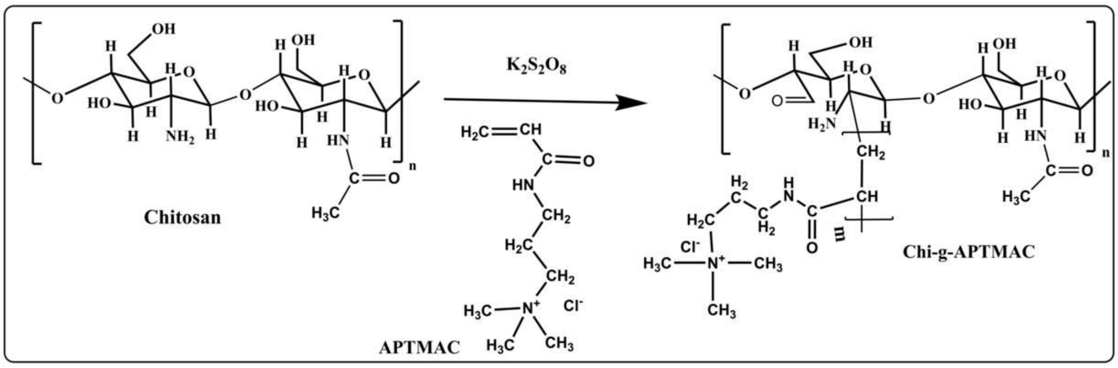
The procedures for floc characterizations were reported earlier in chapter-3 under section 3.3.7 (***Initial settling rate (ISR) 3.3.7.1, Filter Cake Moisture Content (FCMC)*** *and* ***optical microscopy studies 3.3.7.2)***

5.4 Results and Discussion

5.4.1 Synthesis and characterization of flocculants

Chitosan is structurally similar to cellulose, but it has amino (-NH_2) groups and acetamido (-$NHCOCH_3$) groups at the C_2 position of the anhydroglucose unit (AGU). These functional groups help in the chemical modification of chitosan to improve its solubility and widen its applications. Among various methods, graft copolymerization is the most attractive and a large number of vinyl monomers have been graft copolymerized onto chitosan using free radical initiation or γ-irradiation techniques. In the chitosan grafted copolymers, the rigid nature of chitosan can give a more extended conformation in solution along with a high charge density. On the other hand, the grafted polymer chain gives flexibility to the overall polymer. Chitosan is a unique polysaccharide with a positive charge in its structure in the acidic medium and helps in synthesizing cationic flocculants.

Grafting of cationic monomers onto chitosan can enhance the charge density of the copolymer which is generally a desired parameter for an efficient flocculant. In this work, a cationic monomer namely 3-acrylamidopropanetrimethylammonium chloride (APTMAC) was chosen to graft copolymerize onto chitosan due to its high reactivity ratio[38,39]. Copolymers with different contents of APTMAC (Chitosan: APTMAC Wt% 1:3; 1:5 and 1:8) were synthesized and denoted as CA-1:3, CA-1:5 and CA-1:8 respectively. The reaction pathway for the synthesis of chitosan-g-APTMAC is shown in scheme-5.1. The quantitative yields of the graft copolymers CA-1:3, CA-1:5 and CA-1: 8 were 42, 43, and 56% respectively.



Scheme-5.1: Reaction scheme for the synthesis of chitosan-g-APTMAC copolymers

5.4.2 Chemical structure by NMR spectroscopy

We show in figure-5.1, the ^{1}H NMR spectrum of representative CA-1:8 and chitosan. The methyl (-CH_3) proton peaks of APTMAC appear at 3.3 ppm and the methylene (-CH_2-) protons of APTMAC attached to nitrogen atom give peaks in the range of 3.2–3.3 ppm. The methyl (-CH_3) proton peak of the acetyl group of N-acetyl glucosamine appears at 2 ppm, the proton peak for H_2 of chitosan appear at 3.0 ppm and the proton peaks for ring H_3 to H_6 of chitosan appear at 3.5 - 3.8 ppm. All the characteristic peaks of the graft copolymer assigned match with those reported in the literature[16,40,41].

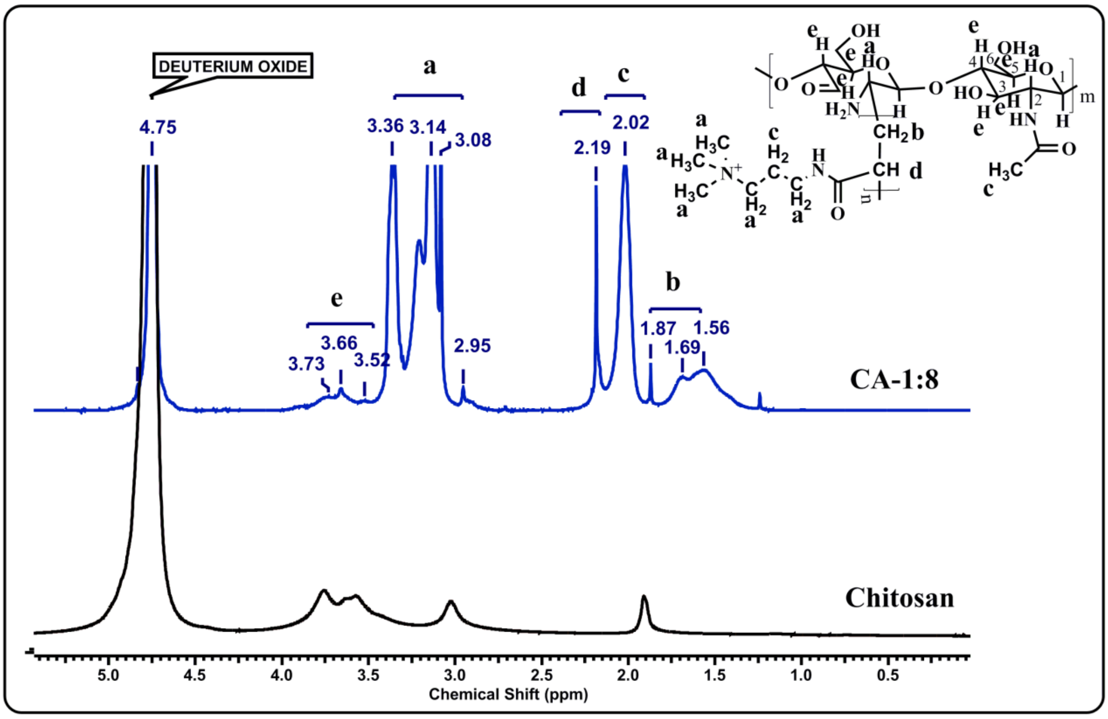


Figure-5.1: 400 MHz ^{1}H NMR spectrum for chitosan and CA-1:8

Figure-5.2 shows the representative ^{13}C NMR spectrum of CA-1:5 and chitosan. The methyl (-CH_3) carbons of APTMAC appear at 53.1 ppm and the peaks for methylene (-CH2-) carbons of APTMAC attached to amide nitrogen appear at 36.5 ppm and methylene (-CH_2-) carbon of backbone chain of APTMAC appears at 36.0 ppm. The methylene (-CH_2-) carbon of APTMAC attached to nitrogen gives a peak at 64.1 ppm and peak for methylene (-CH_2-) carbon next to carbon attached to nitrogen, appear at 22.5 ppm. The carbons of the chitosan ring C5, C8 and C9 appear at 56.1, 71.7 and at 74.8 ppm respectively. The C6 carbon appears at 60.1 ppm. Both the ^{1}H and ^{13}C NMR spectra confirm the chemical structure of the graft copolymer in comparison with chitosan.

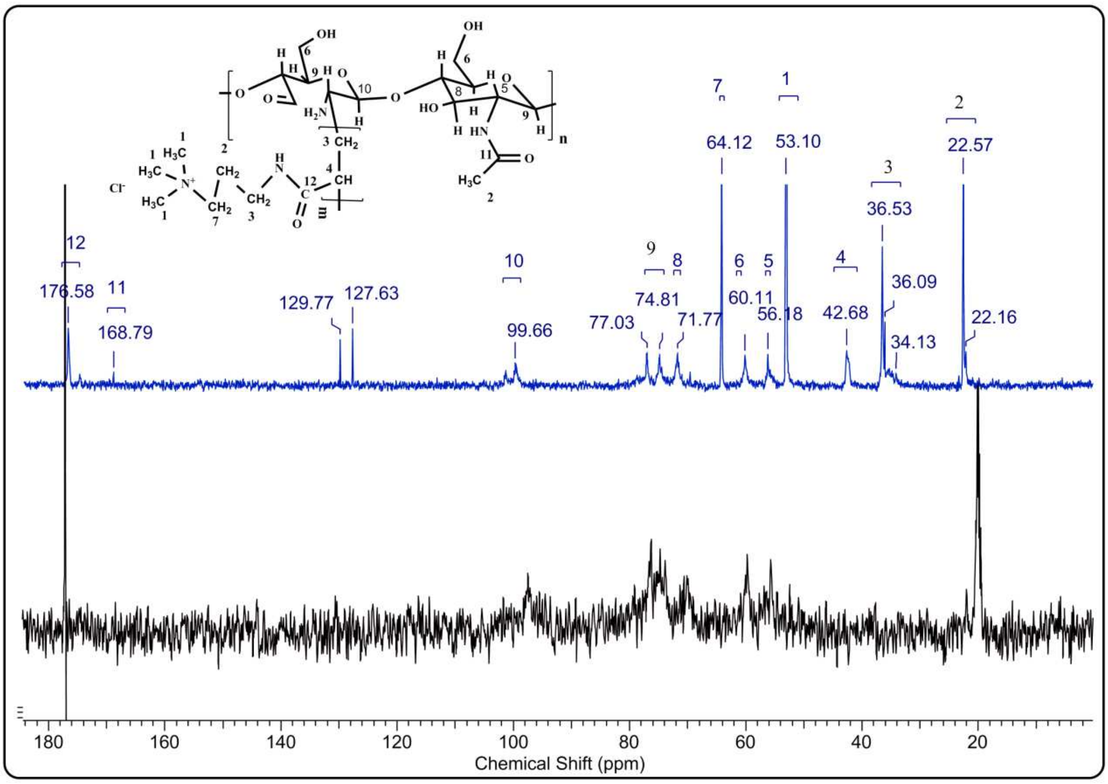


Figure-5.2: 400 MHz ^{13}C NMR spectrum of chitosan and CA-1:5

Figures 5.3 and 5.4 show the ^{1}H and ^{13}C stacked NMR spectra of all the three compositions respectively (CA-1:3, CA-1:5 and CA-1:8). The combined stack plots of the NMR spectra clearly indicate the successive increase in the intensities of the peaks for APTMAC with increase in its feed weight %.

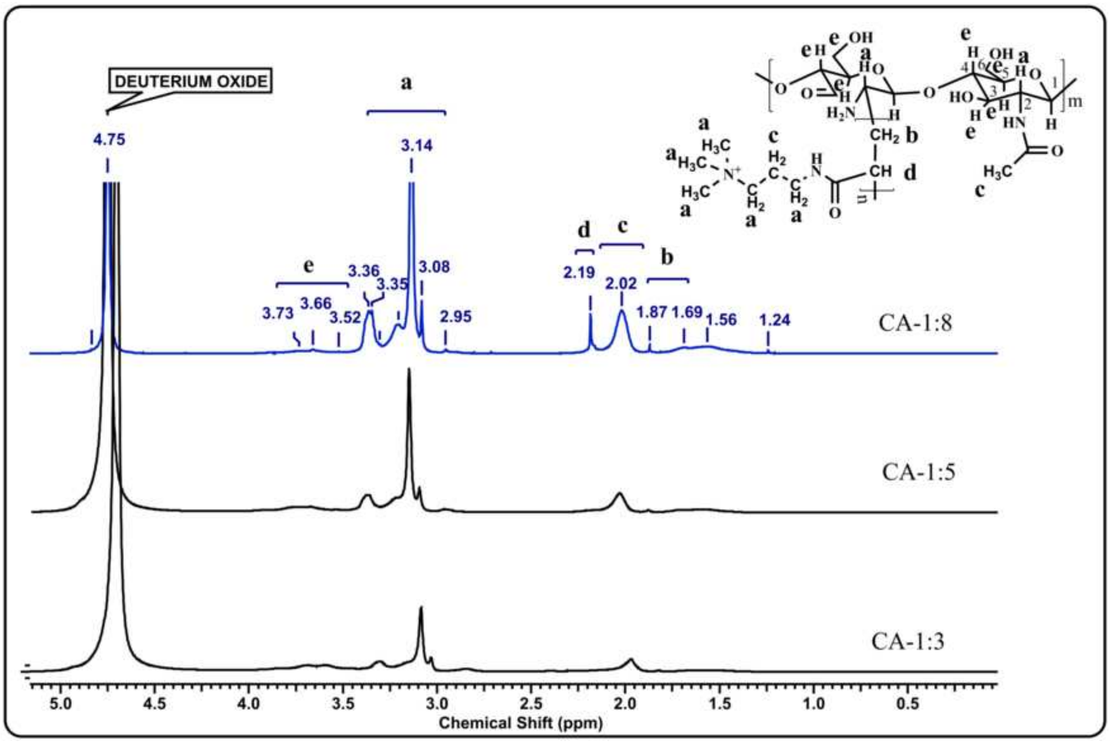


Figure-5.3: 400 MHz ^{1}H NMR spectra of CA-1:3, 1:5 and 1:8

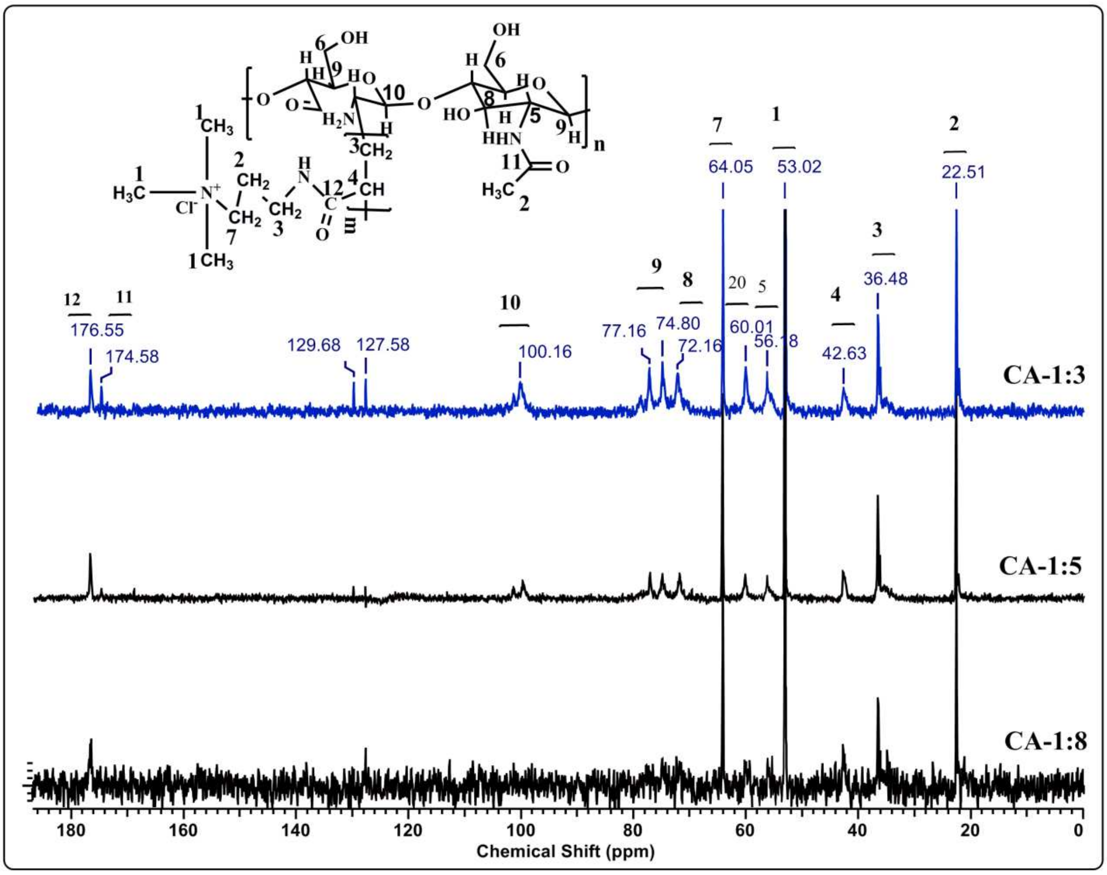


Figure-5.4: 400 MHz ^{13}C NMR spectrum of CA-1:3, 1:5 and 1:8

5.4.3 Molecular weight and zeta potential

The molecular weight and zeta potential of the graft copolymers were determined using GPC and particle size analyzer, respectively. Table-5.1 shows the molecular weights and zeta potential of CA-1:3, CA-1:5 and CA-1:8 samples.

Table-5.1: Molecular weight and Zeta potential of copolymers

Samples	**M_w (Kg mol^{-1})**	**M_n (Kg mol^{-1})**	**PDI (M_w/M_n)**	**pH**	**Zeta potential (mV)**
CA-1:3	408	285	1.4	6.0-7.0	(+) 32.0 - 35.0
CA-1:5	790	229	3.4	6.0-7.0	(+) 50.0 - 53.0
CA-1:8	826	316	2.6	6.0-7.0	(+) 55.0 - 58.0
Kaolin	-	-	-	6.0-7.0	(-) 18.0 - 20.0
Chitosan	375	-	-	-	-

It can be seen from table-5.1 that when the APTMAC content in the graft copolymer increases, the molecular weight and zeta potential increases from CA-1:3 to CA-1:8. The higher content of APTMAC in graft copolymer (CA-1:8) shows higher zeta potential value. The particle size of the polymer also increased with the increase in APTMAC content. This can be attributed to the extended coil conformation as a result of the repulsion in the like charges of the polymer arrangement by the presence of APTMAC. This extended coil confirmation is favourable for effective binding to cause efficient flocculation.

5.4.4 Flocculation of Kaolin

The flocculation efficiency of graft copolymers, CA-1:3, CA-1:5 and CA-1:8 on kaolin aqueous suspension was examined by measuring the transmittance on kaolin suspension after the equilibrium flocculation (∼40 min). The kaolin bears a negative charge on the surface in the pH range of 6.5 - 7.5 and exhibits the zeta potential of (-) 18 - 20.0 mV. The average size of kaolin particles was ∼1.0 µm. The efficiency of flocculation of kaolin suspension (3.0 wt %) was investigated at different dosages of flocculants.

A typical set-up for the kaolin flocculation is shown in figure 3.7 of chapter-3. Figure-3.7a shows the kaolin suspension before the addition of flocculant, which is stable and looks milky. Upon addition of cationic flocculant and initial stirring, milky suspension turns into a clear solution after stopping the stirring (figure-3.7b). The kaolin particles begin to settle at the bottom. The transmittance of the clear solution was measured. Similar experiments were carried out for different dosages of flocculants.

Figure-5.5 shows the percentage transmittance of kaolin supernatant liquid vs different dosages of flocculants, CA-1:3, CA-1:5 and CA-1:8 taken at pH 7 and at equilibrium flocculation time of ~ 40 min.

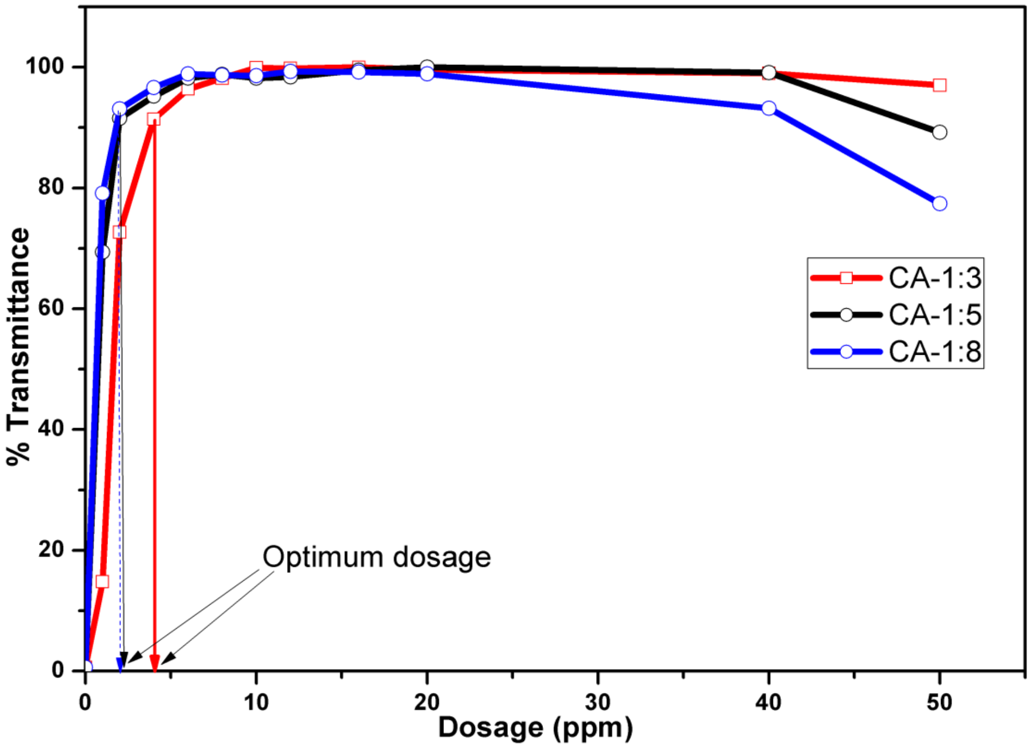


Figure-5.5: Transmittance of kaolin supernatant vs. dosage of flocculants after 40 min of equilibrium flocculation

It can be clearly observed from the figure that, CA-1:8 shows more than 90 % transmittance at the dosage range of 2 - 6 ppm and remains constant till 20 ppm. After 20 ppm, the % transmittance reduced with the further increase in flocculant dosage. This is due to the colloidal restabilization. CA-1:5 also shows more than 90% transmittance at the dosage range of 2 - 6 ppm and remains constant till 40 ppm.

The % transmittance decreases after 40 ppm which is due to colloidal restabilization. Whereas, CA-1:3 flocculant showed more than 90 % transmittance in the dosage range of about 4 - 10 ppm and remains constant till 50 ppm and showed no colloidal restabilization. This could be attributed to lesser charge on the CA-1:3. These observations clearly show that the charge on the polymer is directly proportional to the feed weight ratio of APTMAC, which is further evidenced by NMR studies. The optimum dosage levels for CA-1:3, CA-1:5 and CA-1:8 flocculants for kaolin flocculation could be considered as 2.0 ppm, 2.0 ppm and 4.0 ppm, respectively. These flocculants showed efficient flocculation and the optimum dosages were found to be significantly lower compared to the values reported earlier[13,36].

The CA-1:8 and CA-1:5 flocculants contain more of APTMAC polymer and exhibit a high degree of charge with high zeta potential (+ 50 to 60 mV). In this case, the driving force for the flocculation could be attributed to the charge neutralization followed by bridging. However, the possibility of electrostatic patch mechanism in flocculation cannot be ruled out as there is a colloidal restabilization at higher dosage.

For the flocculant CA-1:3, higher dosage level (~4.0- 8.0 ppm) was required to get 95-98% transmittance in the flocculation. In CA-1:3 flocculant, the charge density is low (zeta potential + 32 mV) and also the molecular weight is low (408 Kg mol^{-1}). Because of the lower charge density and low molecular weight more flocculant is needed to cause flocculation. These observations clearly indicate that charge density on the polymer plays a dominant role in the kaolin flocculation.

We also measured the zeta potential of kaolin supernatant solution as a function of different dosage of flocculants CA-1:3, CA-1:5 and CA-1:8. The results are shown in figure-5.6.

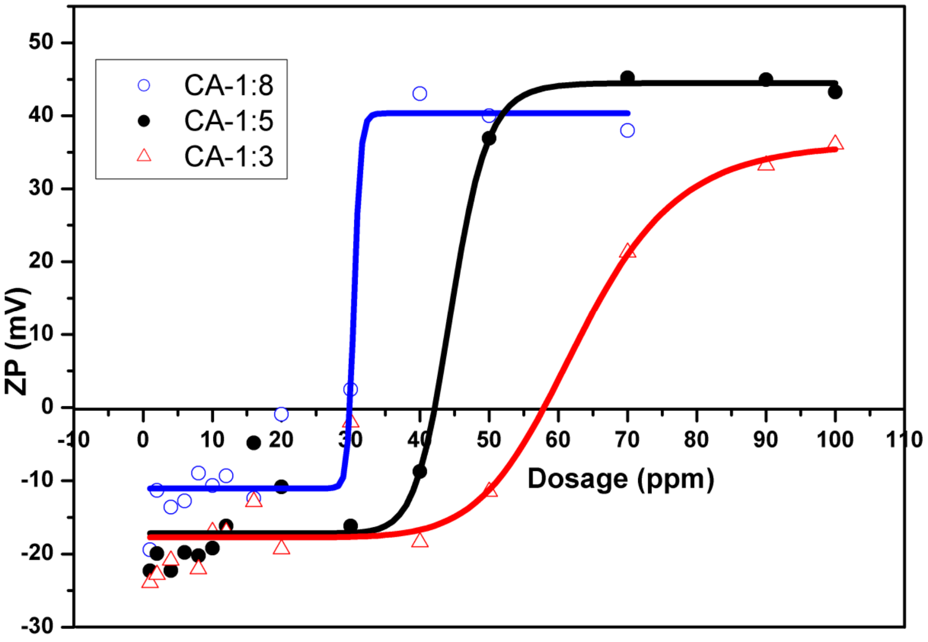


Figure-5.6: Zeta potential of kaolin suspension supernatant at different dosages after equilibrium flocculation using CA-1:8, CA-1:5 and CA-1:3

It is observed that the zeta potential of kaolin solution changed from (-) 20 mV to (+) 50 mV with an increase in the dosage of flocculants. This is due to the fact that the oppositely charged flocculants neutralize and diminish the surface charge of the suspended kaolin particles resulting into the formation of kaolin flocs. However, it is interesting to note from the figure-5.8 that the zeta potential of the kaolin supernatant did not reach zero value at 95% transmittance for the optimum dosage of CA-1:8, CA-1:5 and CA-1:3 flocculants. The zeta potential values remained at (-) 10 to (-) 20 mV. This could be attributed to the presence of small quantities of very fine particles of unneutralized kaolin present in the supernatant liquid. Further, the kaolin fine particles are partially or heterogeneously bound by flocculants to form micro flocs that cannot settle down and hence float and show reduced zeta potential value.

At higher dosage content, the zeta potential values crossed the zero value and attained positive values of zeta potential. These observations clearly indicate that there seems to be a broad flocculation regime and the possibility of both charge neutralization and bridging mechanism for driving the flocculation.

It is also observed form the figure that the dosages at which the zeta potential is zero for CA-1:8, CA-1:5 and CA-1:3 were 30, 40 and 58 ppm respectively. These dosages are more than 10 times higher than the optimum dosage. At optimum dosage, more than 95 % clarity or kaolin was flocculated and that supernatant water can be reused to suspend kaolin for next cycle of kaolin mining. This can enormously improve the economy and efficiency of the recovery process.

5.4.5 Kinetics of flocculation

In order to understand the kinetics of flocculation, the percentage transmittance of kaolin suspension as a function of time were measured for flocculants, CA-1:8, CA-1:5 and CA-1:3 at different doses and also at their optimum dosage. Figure-5.7 shows the results of % transmittance vs time for three flocculants at their optimum dosage and figure-5.8 to 5.10 shows the % transmittance vs time for three flocculants at different dosages.

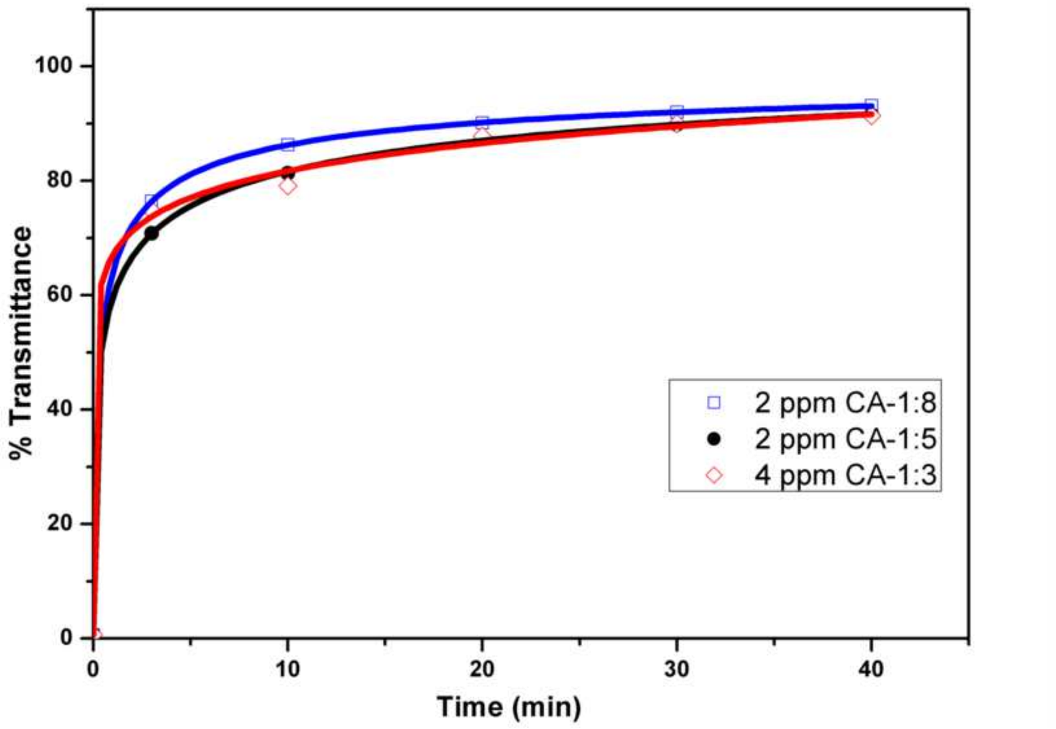


Figure-5.7: Kinetics of flocculation of CA-1:8, CA-1:5 and CA-1:3 at optimum dosage

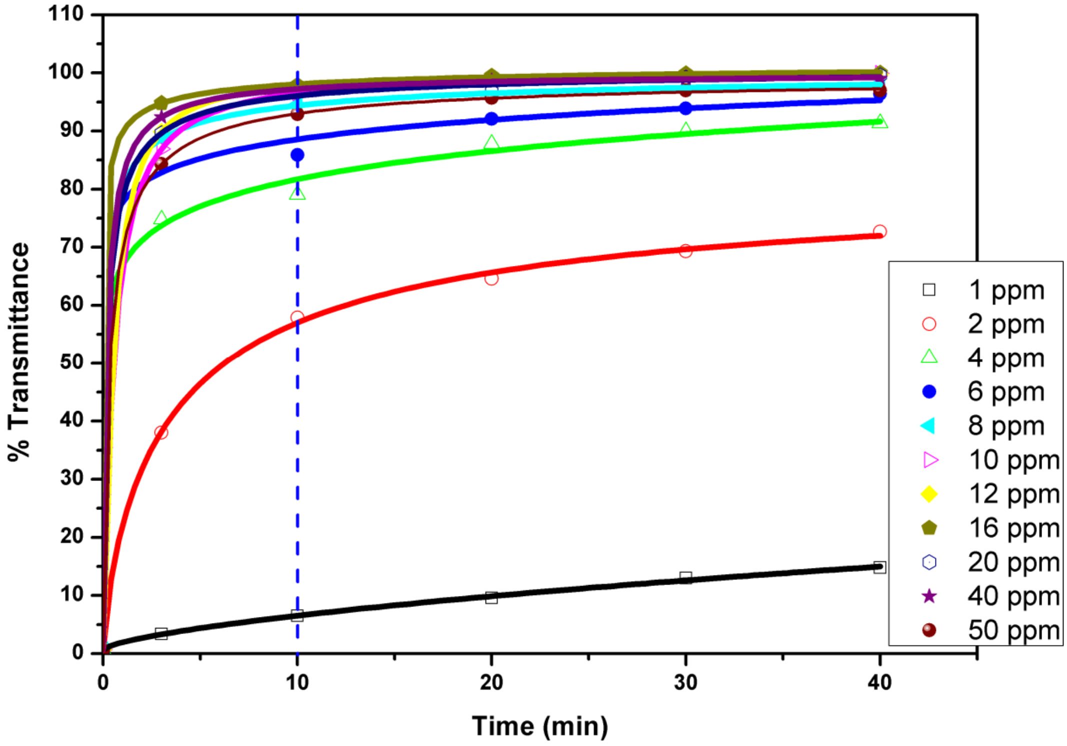


Figure-5.8: Transmittance of kaolin supernatant vs. time of CA-1:3

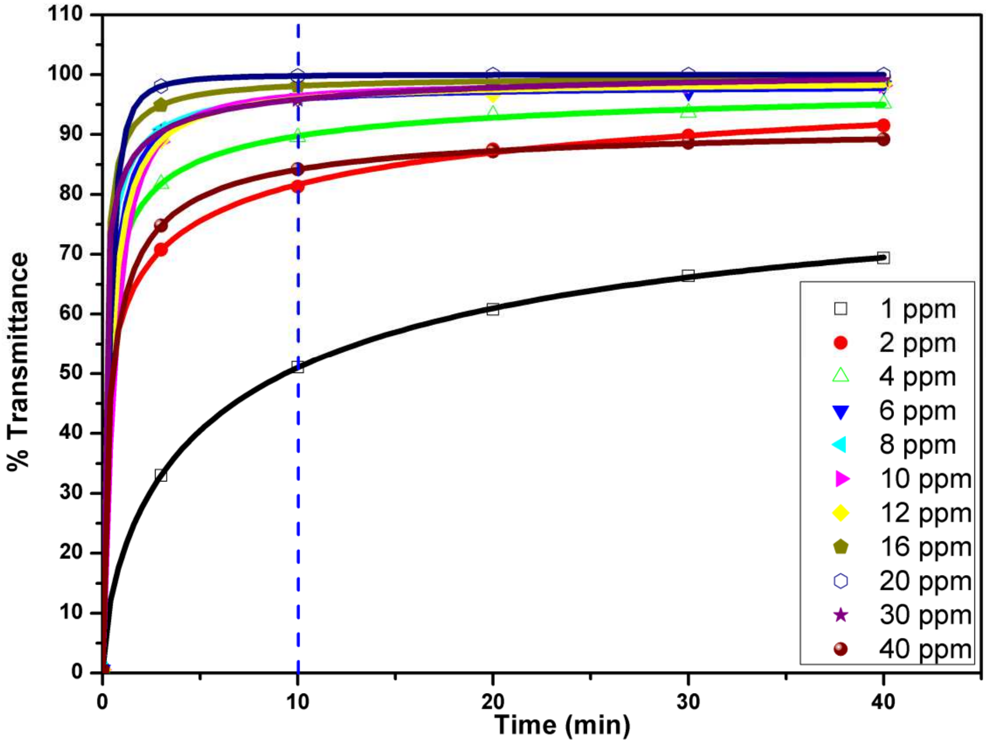


Figure-5.9: Transmittance of kaolin supernatant vs. time of CA-1:5

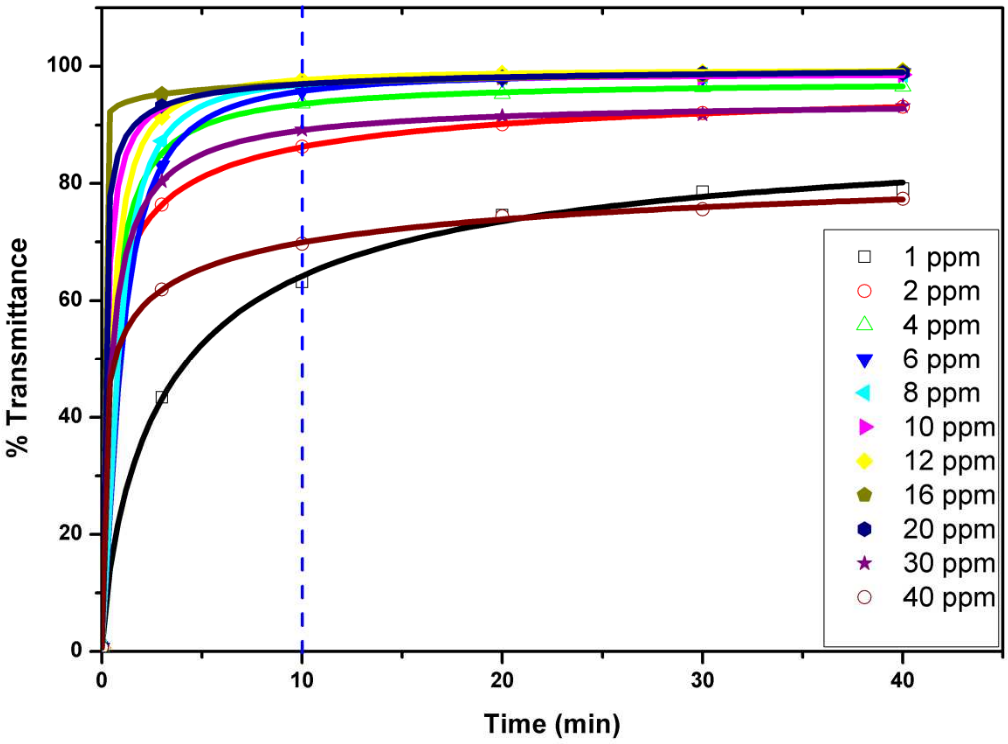


Figure-5.10: Transmittance of kaolin supernatant vs. time of CA-1:8

It is clearly seen that, 80 - 85% transmittance could be achieved within 10 min of flocculant addition to the kaolin suspension at their respective optimum dosages of flocculants. At the end of 40 min, the % transmittance reached to 90%, which indicated a bridging mechanism for the flocculation. The initial phase of time during flocculation is involved in charge neutralization and later the bridging occurs for the effective flocculation. The % transmittance increases with time indicating that bridging occurs with time. Further the high molecular weight of the polymer also contributes to the bridging. Both CA-1:8 and CA-1:5 gave maximum % transmittance of more than 90% at an optimum dosage of 2 ppm. This is because the charge required to neutralize the kaolin particles is just sufficient in CA-1:5 and the bridging mechanism causes the increase in % transmittance. The increased charge density in CA-1:8 resulted in 90 % transmittance in a short time. These studies indicate that both charge and molecular weight play important role in the efficient flocculation.

5.4.6 Floc characterization

5.4.6.1 Initial settling rate (ISR)

Figure-5.11 shows the interface height vs. time for flocculants CA-1:8, CA-1:5 and CA-1:3 at their optimum dosage levels of 2, 2 and 4 ppm respectively. It can be readily seen that the interface height decreases rapidly within the first 100 seconds and remains almost constant after 250 seconds for all the flocculants. This predicts the initial settling rate of ~0.1cm s^{-1} for the flocculants. These observations clearly reveal that CA-1:8, CA-1:5 and CA-1:3 flocculate kaolin suspension very rapidly.

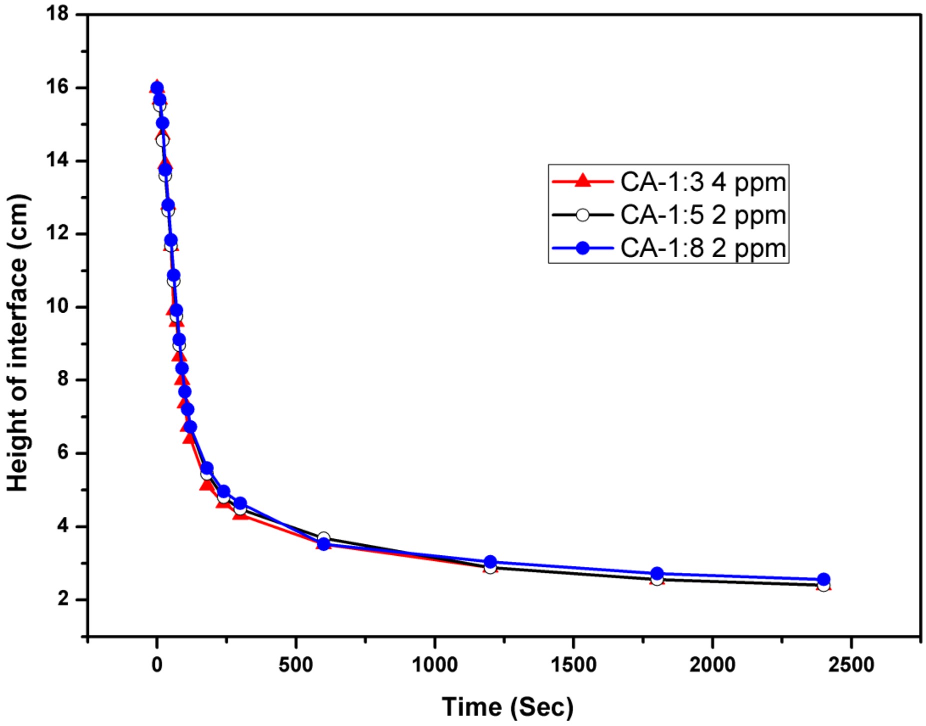


Figure-5.11: Initial settling rate of CA-1:8, CA-1:5 and CA-1:3

5.4.6.2 Filter Cake Moisture Content (FCMC)

Figure-5.12 shows the results of FCMC for CA-1:8, CA-1:5 and CA-1:3 at different dosages. The FCMC of CA-1:8, CA-1:5 and CA-1:3 remained independent of dosages in the range of 2 to 10 ppm. However, the earlier reports indicate a decrease in FCMC with an increase in dosage levels when the dosage levels are quite high (~40 to 50 ppm). We observed a very small change in FCMC with these low dosage levels. Nevertheless, these small dosages (2-10 ppm) were found to be efficient in flocculation and gave more than 95 % transmittance in the flocculation process. The FCMC of CA-1:8 showed slightly higher FCMC to CA-1:5 and CA-1:3 which could be attributed to the high charge and molecular weight in the polymer which results into increased hydrophilicity of flocculant and absorbs more moisture. Further, the FCMC is in the decreasing order with decreasing APTMAC content. This clearly shows that charge on the polymer and molecular weight influences the FCMC.

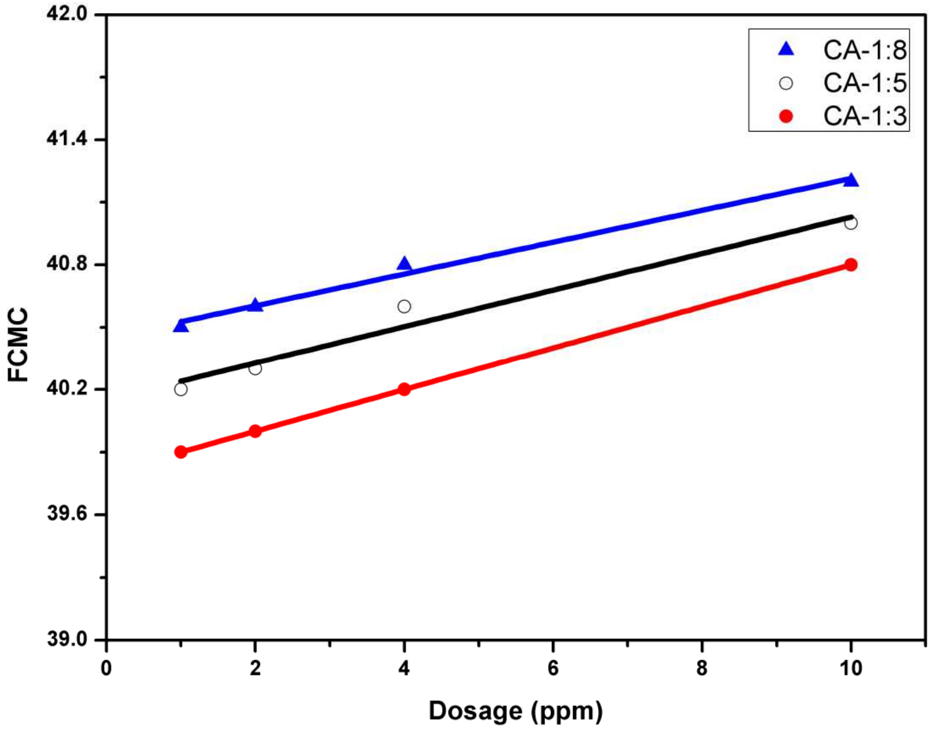


Figure-5.12: Filter cake moisture content study of CA-1:8, CA-1:5 and CA-1:3 at different dosages

The visual observation of the filter cakes after the flocculation using CA-1:8, CA-1:5 and CA-1:3 at different dosages was made and photographs are shown in figure-5.13

Figure-5.13: Photographs of filter cakes after flocculation and drying for CA-1:3 (a-d) CA-1:5 (f - i) and CA-1:8 (j-m)

It is observed that, as the dosage increase, the surface of the filter cake becomes smoother and softer. This could be due to the formation of dense flocs at higher dosages of flocculant.

5.4.6.3 Optical microscopic studies

The optical microscopy was performed on kaolin flocs obtained under different dosages of CA-1:8, CA-1:5 and CA-1:3 flocculants. The optical micrographs are shown in figure-5.14. Kaolin suspension without any flocculant does not show the flocs and one can see a uniform suspension [figure-5.14 (a)]

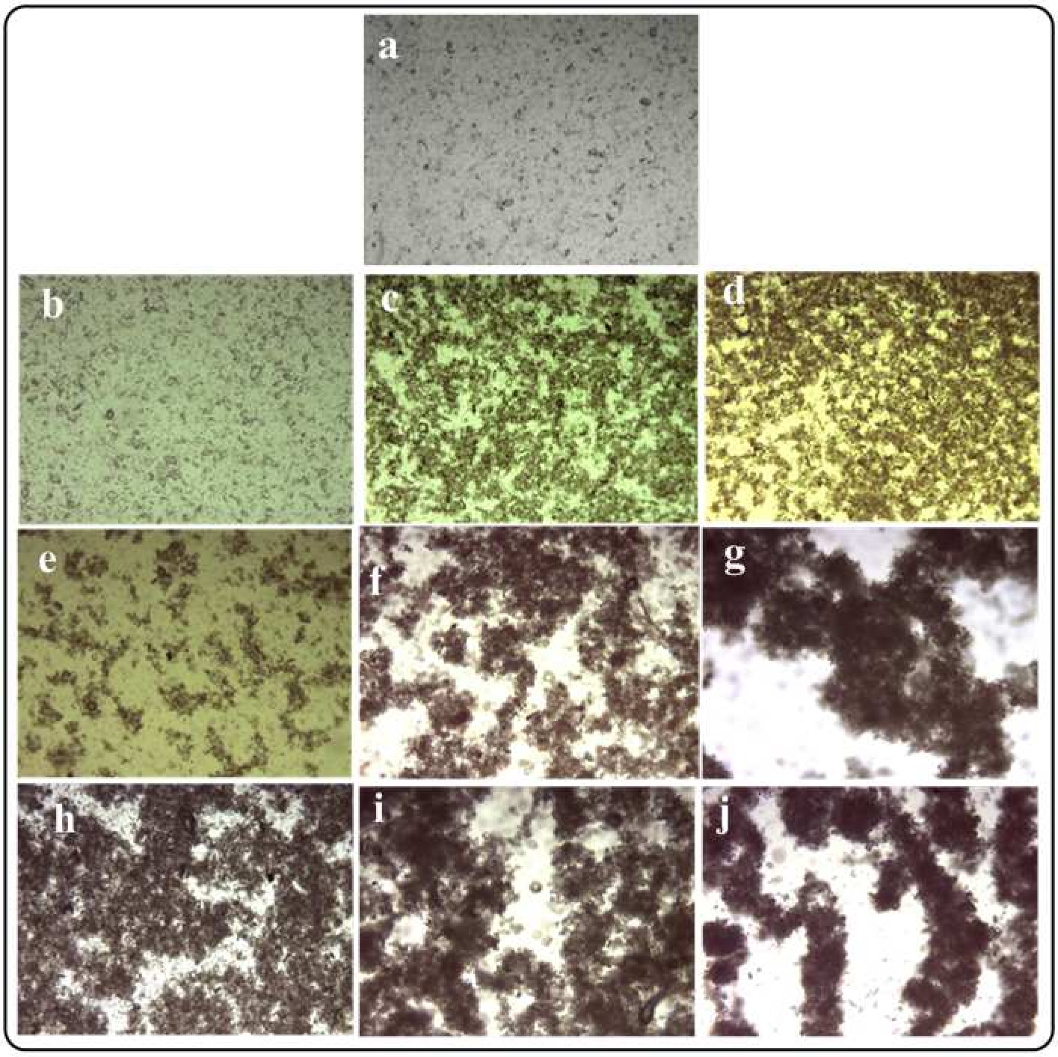


Figure-5.14: Optical micrographs of kaolin flocculation at different dosages Kaolin (a), CA-1:3 (b-d), CA-1:5 (e-g) and CA-1:8 (h-j)

However, upon flocculation, kaolin flocs are observed very clearly and the floc size increases with the dosage of flocculant. The observed optimum dosages of 2, 2 and 4 ppm for flocculants CA-1:8, CA-1:5 and CA-1:3 respectively show more than 95 % transmittance in the supernatant liquid after the floc formation. This is visible in the micrographs of figure-5.16 (c), (f) and (i).

5.5 Conclusions

In conclusion, we have shown that the cationic flocculants based on the graft copolymer of chitosan and 3-acrylamidopropyltrimethylammonium chloride (APTMAC) efficiently flocculates kaolin from aqueous solution. Depending on the ratio of monomers, the graft copolymers could be obtained with different molecular weight and zeta potentials, which are very important properties required for efficient flocculation. The optimum dosages for maximum flocculation were found to be 2.0, 2.0 and 4.0 ppm for CA-18, CA-1:5 and CA-1:3 graft copolymers, respectively. The minimum time required for maximum flocculation was determined to be 4-10 minutes in the laboratory scale. Both the copolymers CA-1:8 and CA-1:5 gave the best flocculation efficiency. The floc characterization was performed in terms of floc size and FCMC. Based on the results it was proposed that the charge neutralization and bridging are the main mechanisms for driving the flocculation. These graft copolymers show great promise in the flocculation of kaolin from aqueous streams in industries and are biodegradable and environmental friendly.

5.6 References

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SUMMARY AND CONCLUSIONS

CHAPTER-6

In this chapter summary and conclusions of the thesis work are discussed.

The main objective of this thesis work was to synthesize and characterize efficient flocculants for kaolin flocculation. Accordingly, flocculants based on copolymers of acrylamide and cationic functional monomers such as DADMAC and APTMAC and graft copolymers of chitosan and APTMAC were synthesized and evaluated for kaolin flocculation. Acrylamide monomer was selected because of its inherent property of yielding high molecular weight and the cationic monomers impart cationic charge to the flocculant, which are the most essential parameters for an efficient flocculant. Chitosan, a biopolymer grafted with APTMAC yielded partially biodegradable flocculant. These flocculants were tested for their molecular weights and charge density and examined for flocculation of kaolin suspensions. Kaolin is an important industrial mineral which has wide applications in industry. This was the motivation behind synthesizing efficient flocculants for kaolin separation.

In the first chapter a detailed literature survey on flocculants, importance of flocculants in industrial separations is presented. Various mechanisms which drives the flocculation and factors which influence the flocculation were explained. Classification of flocculants based on their structure and source was given. Major focus was given on flocculants used for kaolin separation. In view of the environmental issues, the importance and use of biopolymer based flocculants were discussed. Particular emphasis was given on chitosan based flocculants. Different methods used to study flocculation such as jar test and settling test was explained, and also the floc characterization methods such as FCMC and ISR were elaborated.

In the second chapter, the scope and objectives of the work in terms of design and synthesis of new and efficient flocculants for kaolin flocculation were given.

The third chapter dealt with synthesis of copolymers of acrylamide and DADMAC at different molar composition. The characterizations in terms of chemical structure and composition was performed using ^{1}H and ^{13}C NMR spectroscopy. The molecular weights and zeta potentials were determined using GPC and Zeta sizer. The flocculation efficiency was tested on kaolin suspension and the optimum dosages were evaluated. The optimum dosages of flocculants AD-4060, AD-5050 and AD-8020 were found to be 8 , 10 and 14 ppm, respectively. The flocs were characterized in terms of FCMC and optical microscopy. The flocculation efficiency was correlated to the molecular weight and charge on the flocculant.

In the fourth chapter, the copolymerization of acrylamide and APTMAC was discussed and copolymers with three different monomer compositions were synthesized. The chemical structure of the copolymers was confirmed by ^{1}H and ^{13}C NMR spectroscopy. The molecular weight and zeta potential were determined by GPC and zetasizer. The flocculation efficiency was tested on kaolin suspension and the optimum dosages were determined. The optimum dosages for flocculants, AA-4060, AA-5050 and AA-8020 were found to be 3 , 4 and 9 ppm respectively. The flocs were characterized in terms of FCMC and optical microscopy. The flocculation efficiency was correlated to the molecular weight and charge on the flocculant, the mechanism of flocculation was discussed in terms of charge neutralization and bridging. To the best of our knowledge this copolymer system was used for the first time for the kaolin flocculation and found to be efficient.

The fifth chapter dealt with the synthesis of biopolymer chitosan grafted APTMAC copolymers. The composition of APTMAC was varied and three graft copolymers with different APTMAC content were synthesized. The chemical structure of the graft copolymers was characterized by ^{1}H and ^{13}C NMR spectroscopy. The molecular weight and zeta potential values were determined. The flocculation efficiency was tested on kaolin suspension and the optimum dosages were determined. The optimum dosage of flocculants CA-1:8, CA-1:5 and CA-1:3 were found to be 2 , 2 and 4 ppm respectively. The flocs were characterized in terms of FCMC and optical microscopy. The flocculation efficiency was correlated to the molecular weight and charge on the flocculant.

We have successfully synthesized and characterized flocculants based on acrylamide copolymers and chitosan graft copolymers and demonstrated their applications in kaolin separation. Besides kaolin these flocculants also have a great potential in other industrial solid liquid separations by flocculation.

List of publications

1. ***Suresha P. Ranganath*** *and Manohar V. Badiger,* Flocculation of kaolin from aqueous suspension using low dosage of acrylamide based cationic flocculants, Journal of Applied Polymer Science. 47286 (2018*). Doi:10.1002/app.47286*
2. ***Suresha P. R****, Manohar V. Badiger And Bernhard Wolf,* Polyelectrolytes in dilute solution: viscometric access to coil dimensions and salt effects, RSC Advances., 5 (35), 27674 - 27681 (2015), DOI:10.1039/c5ra01376c.
3. **Suresha P. R.** and Manohar V. Badiger; Synthesis and characterization of biodegradable chitosan graft copolymers for kaolin separation. Manuscript under preparation.
4. **Suresha P. R.** and Manohar V. Badiger, polyelectrolytes based on chitosan for wound healing applications. Manuscript under preparation.
5. *Venkatakrishnan Balasubramanian, Brindha Velappan, Sandhya Kurvilla Vijayan, Hepzibah Jabamani, Vedaraman Nagarajan, John Sundar Victor,* ***Suresha P. Ranganath****, Manohar V Badiger, Velappan Kandukalpatti Chinnaraj And Muralidharan Chellappa,* Studies on the use of sodium polyacrylate (SPA) for low-salt animal skin preservation, Environmental Science and Pollution Research., 2019.
6. *Rupali Shaligram Mehare,* ***Suresha P. Ranganath****, Vikash Chaturvedi, Manohar V. Badiger and Manjusha V. Shelke, In Situ* Synthesis of Nitrogen and Sulfur enriched Hierarchical Porous Carbon for high-Performance Supercapacitor, Energy and Fuels., 32, 908 - 915 (2017), DOI:10.1021/acs.energyfuels.7b02305.

Conferences

1. *Participated in* ***Asian Polymer Association international Conference*** *on polymers on the frontiers of science and technology held during February 2013 at Punjab university, Chandigarh and presented a poster titled "****Synthesis and characterization of cationic polyelectrolytes for flocculation****" and received* ***best poster award.***

2. *Received* ***best poster award*** *for the poster titled "* ***Synthesis and Characterization of polymeric flocculants for protein separation****" at APA International conference on Polymers : Vision and innovations, February 2014, held at India Habitat Centre, New Delhi, India.*

3. *Represented CSIR-NCL, Pune and RGSTC, Mumbai at* ***India International Science Festival(IISF)*** *held at NPL, New Delhi, Dec 2016. Polymers for industrial application exhibition pavilion for separation of fish proteins from waste waters of marine fish industries using flocculants.*

4. *Presented poster titled "Flocculants for industrial separations" at* ***Plastivision*** *a polymer exhibition and trade show held at exhibition ground, Mumbai. This poster was presented in innovation pavilion of the exhibition.*

5. *Participated and presented a poster titled "****Design and synthesis of efficient polymeric flocculants for industrial separations****" at conference on advancements in polymer science and technology* ***APA-2015*** *held at Saurashtra university, Rajkot, Gujarat, India.*

"POLYMERIC FLOCCULANTS:
SYNTHEIS, CHARACTERIZATION AND APPLICATIONS"

A THESIS SUBMITTED TO

SAVITRIBAI PHULE PUNE UNIVERSITY

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CHEMISTRY

SUBMITTED BY

SURESHA P. R.

UNDER THE GUIDANCE OF

Dr. MANOHAR V. BADIGER

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OCTOBER 2019

DECLARATION

I declare that the thesis entitled "**polymeric flocculants: synthesis, characterization and applications**" submitted by me for the degree of Doctor of Philosophy is the record of work carried out by me during the period form **02-05-2013** to **09-10-2019** under the guidance of **Dr. Manohar V. Badiger** and has not formed the basis for the award of any degree, diploma, associate ship, fellowship, titles in this or any other university or other institution of higher learning.

I further declare that the material obtained from other sources has been duly acknowledged in the thesis.

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Place : Pune

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Suresha P. R.

TABLE OF CONTENTS

Chapter 1: Introduction

Chapter 3: Flocculation of kaolin using copolymers of acrylamide (AM) and diallyldimethylammonium chloride (DADMAC)

Chapter 4: Flocculation of kaolin using copolymers of acrylamide (AM) and 3-Acrylamidopropyltrimethylammonium chloride (APTMAC)

Chapter 5: Synthesis of chitosan graft copolymer flocculants

Abstract

The objective of this thesis is to synthesize and characterize an efficient flocculant for the separation of an industrially important mineral, kaolin. Flocculants are an integral part of many industrial separations and waste water treatment. Kaolin is a mineral clay which has wide applications in ceramics, paint, electronics and biomedical fields. In view of its wide range of applications, kaolin separation by flocculation is very important.

Flocculation is a phenomenon of colloidal destabilization. Flocculants act on a molecular level on the surface of particles to reduce the repulsive forces and increase the attractive forces. By the addition of flocculant (in ppm), finely divided or dispersed particles aggregate together to form flocs of a bigger size, which makes them to settle faster, effecting good separation. Various parameters that influence the efficiency of flocculation are polymer molecular weight (MW), charge density, polymer concentration, polymer dimension in solution, the presence of electrolytes etc. Depending on the source and nature of charge, flocculants are classified into organic and inorganic; synthetic and natural; anionic, cationic and neutral flocculants. There are different mechanisms proposed for the flocculation which include bridging, charge neutralization and electrostatic patch model. Although there are few reports on the flocculation of kaolin mineral, efforts are still being made to design and develop new, efficient flocculants for kaolin separation.

In this context, a research work was undertaken to synthesize and characterize efficient flocculants based on acrylamide (AM) and cationic monomers such as diallyldimethylammonium chloride (DADMAC) and 3-acrylamidopropyltrimethylammonium chloride (APTMAC) for kaolin flocculation. Further, in view of the environmental issues of synthetic flocculants, a biopolymer based flocculant namely chitosan-g-APTMAC graft copolymer was synthesized and evaluated for kaolin separation. The flocculation efficiency was correlated to the structural characteristics of the flocculants such as molecular weight, charge on the flocculant. The plausible mechanism for driving the flocculation were discussed.

In poly(AM-co-DADMAC) system, the content of DADMAC was varied in order to obtain flocculants with different molecular weights and charge densities. The

chemical structure of the copolymer was confirmed by ^{1}H and ^{13}C NMR spectroscopy. The charge on the polymer was analyzed by zeta sizer. The molecular weight was analyzed by GPC. The flocculation efficiency was studied by measuring the % transmittance of the supernatant liquid after flocculation. The zeta potential of the supernatant kaolin suspension was measured to correlate to the efficiency of flocculation. These flocculants showed good efficiency in flocculating kaolin suspensions. The flocs formed were characterized in terms of filter cake moisture content (FCMC), initial settling rate (ISR) and optical microscopy, which gve insight in understanding the flocculation process.

Since the reactivity of APTMAC monomer was higher, copolymers of AM and APTMAC were synthesized and examined for kaolin flocculation. The composition of APTMAC was varied in the copolymer to obtain flocculants with varying molecular weights and zeta potential. The flocculants were characterized by NMR, GPC and zeta potential. The flocculation efficiency was evaluated using kaolin suspension and the flocs were characterized in terms of FCMC, ISR and optical microscopy. Efficient flocculation of kaolin at lower dosages was demonstrated with poly (AM-co-APTMAC) cationic flocculant.

The use of chitosan as a backbone chain and grafting APTMAC onto it yields a partially biodegradable and environment friendly flocculant. The APTMAC content was varied in the reaction feed to get different graft copolymers with different molecular weights and charge densities. The grafted copolymers were characterized by NMR, GPC and zeta potential. The flocculation efficiency was analyzed using kaolin suspension and the flocs were characterized in terms of FCMC, ISR and optical microscopy.

The flocculation of kaolin could be achieved rapidly (∼4 -10 min) with the lowest dosages of 2 - 4 ppm in the jar test method. All the flocculants synthesized and characterized in this thesis showed efficient flocculation for kaolin separation and have great potential in industrial separations.

List of tables

List of Schemes

List of figures

Abbreviations and symbols

AM	Acrylamide
PAM	Polyacrylamide
APTMAC	3-Acrylamidopropanetrimethylammonium chloride
AOETMAC	2-Acryloyloxyethyltrimethylammonium chloride
AM-co-DADMAC	copolymer of acrylamide and DADMAC
AM-co-APTMAC	copolymer of acrylamide and APTMAC
AD	acrylamide DADMAC
AA	Acrylamide APTMAC
Chi	Chitosan
CA	chitosan APTMAC
DADMAC	Diallyldimethylammonium chloride
D_2O	deuterium oxide
DI-water	deionized water
DSLR	Digital Single Lens Reflux
EO	Ethylene oxide
FCMC	Filter cake moisture content
GPC	Gel Permeation Chromatography
h	Hour
Hg	Mercury
ISR	Initial settling rate
KPS	potassium persulfate
KG	Kilogram

min	Minutes
M_w	weight average molecular weight
M_n	number average molecular weight
MW	Molecular weight
MOETMAC :	2-Methacryloyloxyethyltrimethylammonium chloride
mV	milli volts
mol %	mole percentage
ml	Millilitre
NMR	Nuclear Magnetic Resonance
nm	Nanometer
ppm	Parts Per Million
PDI	Polydispersity index
rpm	rotations per minute
UV	Ultraviolet
Vis	Visible
V-50	2, 2'-azobis(2-methylpropionamide) dihydrochloride
+ve	Positive

INTRODUCTION

CHAPTER-1

In this chapter we report on the literature survey of flocculants, factors affecting flocculation, mechanisms of flocculation, various flocculants synthesized so far, classification of flocculants. The characterization techniques for flocculants, characterization of flocs and other factors associated with flocculation are briefly explained.

1.1 Introduction

Polymeric flocculants are an important class of materials which have a wide range of applications such as mineral recovery[1–4], paper manufacturing[5–8], sugar cane juice clarification[9–11], protein recovery from marine waste water[12–15] and several other treatments of waste water in industries[16–27]. Flocculants act on a molecular level on the surface of particles to reduce the repulsive forces and increase the attractive forces. By the addition of flocculant (in ppm), finely divided or dispersed particles are aggregated together to form flocs of a bigger size, which makes them to settle speedily, effecting good separation. Various parameters that influence the efficiency of flocculation are polymer molecular weight (Mw), charge density, polymer concentration, polymer dimension in solution, the presence of electrolytes etc.

Depending on the source, the flocculants can be classified into inorganic and organic flocculants. The classification is shown in figure 1.1.

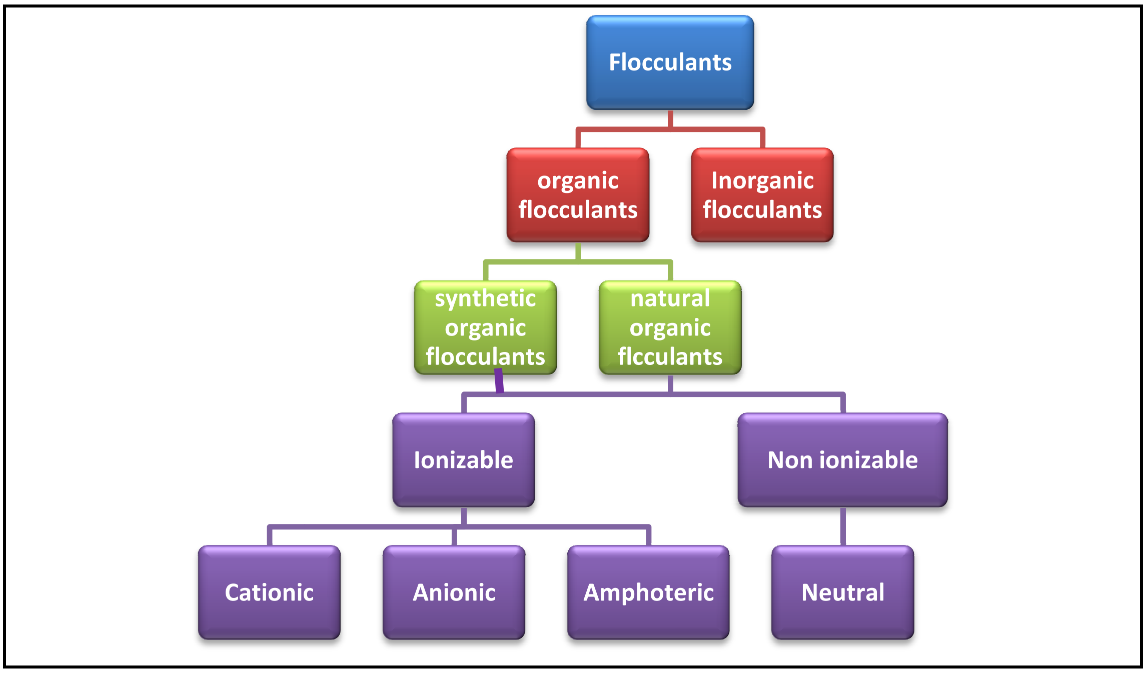

Figure-1.1: Classification of flocculants

Inorganic flocculants have been in use for a very long time and mostly include salts of multivalent metals such as, alum, ferric chloride etc[22,28,29]. The advantage of inorganic flocculants is that they are cheap and easily available, but they have several drawbacks. These are the requirement of large dosages to cause efficient flocculation, production of a large quantity of sludge as a by-product, which is difficult to dispose off. Further, inorganic flocculants are sensitive to pH and work for specific systems and do not flocculate very fine particles. Therefore, the use of inorganic flocculants is almost abandoned[30–32].

Table-1.1 gives the details of some of the inorganic flocculants along with dosages and working pH range.

Table-1.1: details of coagulant, dosage and working pH range

Coagulant	Dosage(ppm)	pH range
Alum ($KAl(SO_4)_2.12H_2O$)	75 -250	4.5 -7.0
$FeCl_3$	35 - 150	4.5 - 7.0
$FeSO_4 \cdot 7H_2O$	70 - 200	4.0 - 7.0
Lime	150 - 500	9.0 - 11.0
Cationic poly electrolytes	2 - 5	---

Organic flocculants have a remarkable ability to flocculate at very low concentrations and have broad pH tolerance. Mostly, organic flocculants are polymeric and based on the source they can be classified into (i) synthetic organic flocculants which are synthesized from monomers such as acrylamide (AM), acrylic acid (Aa), ethylene oxide (EO), Diallyldimethylammonium chloride (DADMAC), etc. These synthetic polymers have advantages that they can be tailor-made to suit the end applications and exhibit longer shelf life with higher stability to microbial degradation. (ii) Natural flocculants are derived from biopolymers such as chitosan, cellulose, alginates and natural gums etc. Depending on the nature of the charge present on the polymeric chain, these flocculants are further classified into cationic, anionic and non-ionic flocculants. Therefore, many of the flocculants are polyelectrolyte in nature. The flocculants cause colloidal destabilization by adsorption onto a particle surface and extend beyond one particle. By virtue of their large molecular weights, the chains extend and bind to large number of particles. The correct choice of flocculant is key to efficient flocculation.

1.1.1 Mechanism of flocculation:

Flocculation is a process of bridging destabilized colloidal particles together to allow them to aggregate to a size where they will settle by gravity. When polyelectrolytes are added to the solution containing oppositely charged particles, the electrostatic attraction between them is considered to be the driving force for the adsorption and the flocculation. A few mechanisms postulated by John Gregory in 1972[33,34] are:

- Bridging
- Charge neutralization
- Electrostatic patch model

1.1.1.1 Bridging

Bridging flocculation occurs when the same polymer segment is bound to more than one particle thereby, bridging particles together; this kind of flocculation is found to be more efficient and effective in causing solid-liquid separation. The charged polymer will adsorb on fewer sites onto the particle surface, and the long loop or tails of the polymer is available for binding to neighbouring particles. Figure-1.2 depicts the bridging mechanism in the flocculation process.

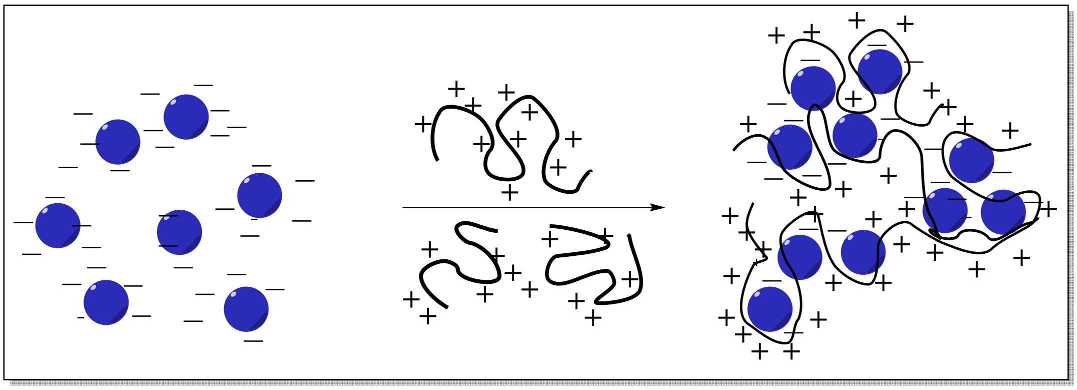

Figure-1.2: Bridging flocculation

For bridging to happen, the polymer chain should be so long that the extended loop should reach neighbouring particle, that is at least two electrical double layer lengths. The optimum dosage ranges from covering the 30 to 50% surface area of the particles; generally, it is 30 to 35% surface area covering.

1.1.1.2 Charge neutralization

Charge neutralization is caused by a reduction in electric double layer repulsion between particles due to the neutralization of charges on the particles by oppositely charged polyelectrolytes. Charge neutralization can be caused by multivalent metal ions such as, Al^{3+}, Ca^{2+} and Fe^{3+} or by low molecular weight polymer electrolytes. The mechanism of charge neutralization is shown in figure-1.3.

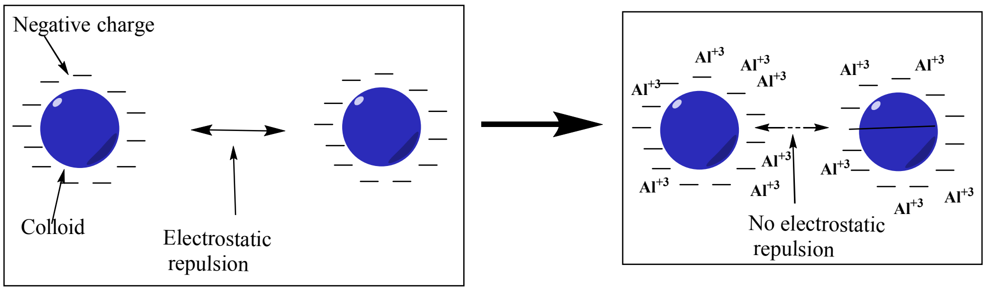

Figure-1.3: Charge neutralization flocculation

The amount of flocculant required would be higher here since the required weight of flocculant to neutralize is stoichiometric to the total available particle surface area.

1.1.1.3 Electrostatic patch model

In the electrostatic patch model, the highly charged polymer interacts with oppositely charged particles as a patch and the net residual charge on the patch on one particle surface can attach to the bare part of an oppositely charged particle again. This mechanism may operate independently or in association with bridging flocculation. The mechanism of electrostatic patch model is shown in figure-1.4

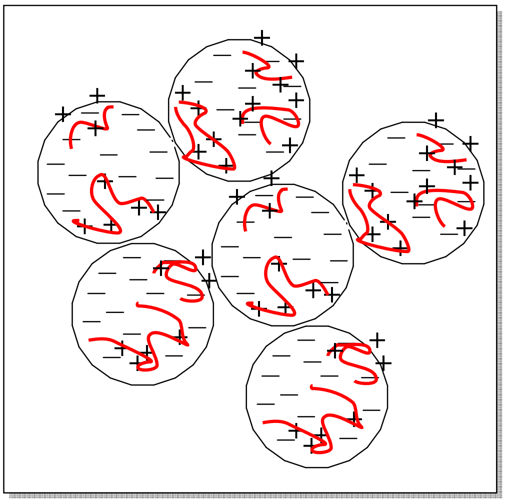

Figure-1.4: Electrostatic patch flocculation

The efficiency of any flocculation process will largely depend on several factors including, the choice of flocculant type, dosage, ionic strength, total dissolved solids, the size and distribution of colloidal particles in suspension. The effective flocculant must have an extended and flexible (elastic) configuration in the solution to achieve better particle bridging and to produce flocs capable of withstanding moderate shear force without rupturing. The floc strength can be estimated from the Bingham shear yield stress, which is a measure of the maximum force per unit area that the floc structure can withstand before rupturing. The parameters that influence the flocculation have been investigated and reported by N.J.D. Graham[35] and Zhou and Franks[34]. Amongst the several factors, Polymer molecular weight, Charge density, Chain dimensions in solution, Polymer concentration are the most important ones. These serve as the guiding parameters for efficient flocculation.

1.1.2 Polymer molecular weight:

Generally, high molecular weight polymer is desired for efficient flocculation. The molecular weight should be high enough to overcome the two particle's electrical double layer repulsion. The high molecular weight of flocculant leads to bridging flocculation. However, a very high molecular weight of a polymer can pose a problem in solubility. This can result in a highly viscous solution that is prone to damage to physical agitation. With very high molecular weight the filter cake moisture content will also increase. Therefore, the optimization of molecular weight needs to be considered.

1.1.3 Charge density on the flocculant:

Charge density on the flocculant is one of the main driving forces for binding or adsorption onto particle surfaces. Higher the charge density better is the binding. A very high charge density flocculant with low molecular weight can lead to flocculation by the mechanism of the electrostatic patch model. Excessive use of this very high charge density flocculant might lead to colloidal restabilization.

A linear polymer with a randomly distributed charge on the polymer surface can strongly bind to the particles with increased agitation and might yield dense flocs. For the graft copolymer, the binding can be weak and might yield loose flocs.

1.1.4 Polymer configuration in solution:

The molecular architecture of the polymer is very important in flocculation. The charge on the polymer stretches the chain due to repulsion and form loops and tails. The initial contact between particles occurs through these loops and tails. The number and size of these loops and tails will determine the efficiency of flocculation. A highly stretched polymer chain can cause flocculation through bridging.

1.1.5 Polymer concentration:

Polymer concentration for optimum flocculation is decided by the nature of the mechanism that is operating in flocculation. If the mechanism of flocculation is by charge neutralization, it might require concentration, which is stoichiometric to the total surface area of the particles. This is relatively higher and yields large flocs. If the mechanism of flocculation is by bridging, where the polymer is binding to more than one particle, then the concentration required is relatively very low. If the concentration is increased, flocculation might shift from bridging to electrostatic patch mechanism or to even to colloidal restabilization. Hence polymer concentration for flocculation is very important.

1.1.6 Methods of measuring flocculation

There are many methods used for measuring flocculation efficiency. Brostow et al[18]. Zheng et al[36] and Kumar et al[37], have reported the use of Jar test and settling test for measuring flocculation.

1.1.6.1 Jar test

In a typical Jar test, the solution of flocculant is added to the suspension of particles to be separated. The dosage is in ppm, and the system is stirred at high speed for the first 2 min and then followed by a slow stirring for 3 min. The stirring was done using an overhead stirrer with cross blades impeller to ensure uniform mixing. The timings of rapid and slow stirring vary from system to system. The rapid mixing was done to mix the flocculant with colloids to form flocs. Later the stirring was slowed down to prevent any possible damage to the polymer and flocs formed. Then the suspension was allowed to settle and the supernatant liquid was analyzed for turbidity either by turbidity meter or by transmittance using UV-spectroscopy. The transmittance method can be used to measure the clarity of the supernatant liquid with respect to time to obtain the kinetics of flocculation. The supernatant liquid is also tested for the changes in zeta potential; flocculation causes a shift in the zeta potential of the suspension. Figure 1.5 is a representative image of the jar test for mineral clay, kaolin separation.

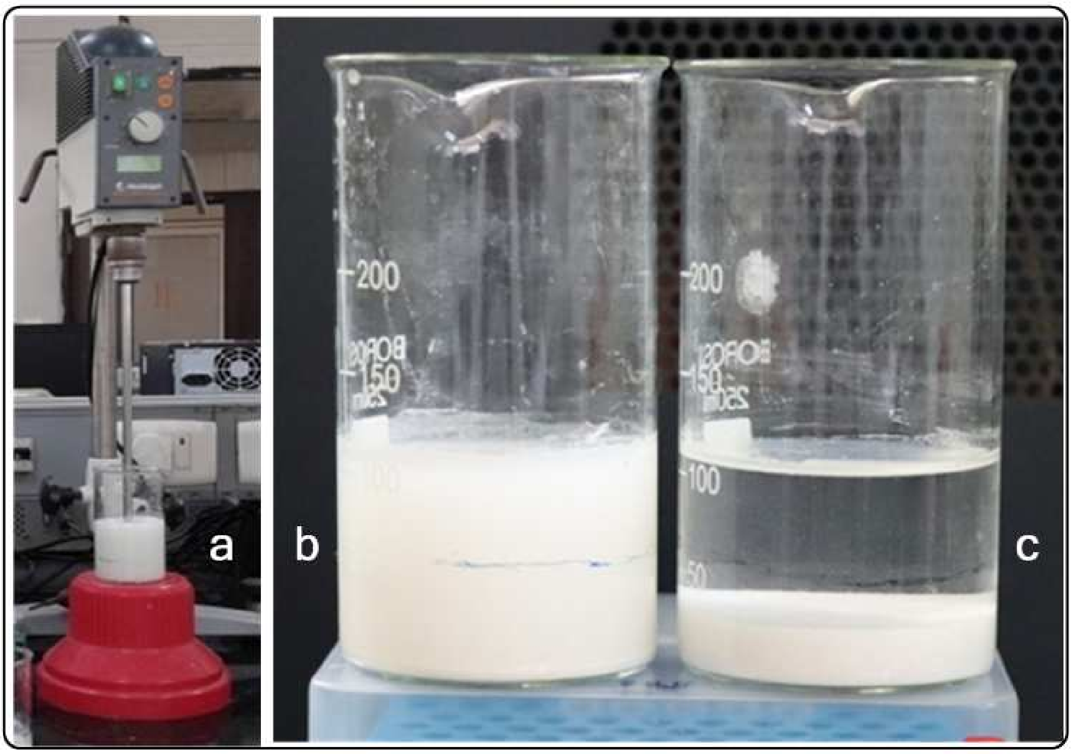

Figure-1.5: a) overhead stirring of kaolin suspension, b) kaolin blank, c) flocculated kaolin

1.1.6.2 Settling test

In the settling test, a graduated cylinder with the stopper is used. The suspension of the colloid is filled into the cylinder and to this solution, the flocculant is added. The mixing of the flocculant with particle is done by inverting the cylinder multiple times. The movement of interface, which separates the liquid and particles, which is also known as mud-line, is monitored with time. The height of the interface with reference to the graduations on the cylinder is recorded with time. This gives the velocity of the particle settling and the initial settling rate (ISR). The velocity increases with the increase in floc size. This test is also used to represent normalized mud-line height H_{t1}/H_{t0}, where H_{t1} is the height of mud-line at time t1 and H_{t0} is the height of the mud-line at time zero[19]. Figure 1.6 is a representative image to measure ISR.

Figure-1.6: Initial Settling Test 1) at time 0 and 2) after time t

Further, the flocs thus formed are also characterized by various techniques, Chen et al.[38] have studied Filter cake moisture content (FCMC), which is the measure of sludge conditioning efficiency. In this, the flocs formed after flocculation were filtered through a 0.45µ filter under a fixed vacuum for 30 min. Then the cakes formed were weighed before and after drying to calculate FCMC. Optical microscopy was also employed for studying flocs. Optical microscopy images can be analyzed[39] for floc size. The floc characterization is important and specific for industrial applications.

1.1.7 Nature of colloids:

Most of the naturally occurring minerals or particles and many industrial colloids and effluents which need to be separated or flocculated are anionic in nature and require cationic flocculants. Therefore, there is a great demand for cationic flocculants for efficient flocculation or separation processes. Table-1.2 gives examples of some of the colloidal systems along with suitable flocculants used for their separation.

Table 1.2: Nature of colloids and the type of flocculant used

Colloidal system	**Charge on colloid**	**Flocculant used**
protein	Anionic	Cationic
Kaolin clay	Anionic	Cationic
Water treatment	Anionic	Cationic
Copper floatation tailing	Cationic	Anionic
Mixed mineral Oxide tailing	Anionic	Cationic
Paper manufacturing	Anionic	Cationic and neutral

Lee et al[40]. have reviewed the use of various organic flocculants for the treatment of waste water. The details along with references are shown in table-1.3

Table-1.3: Application of different flocculants for waste water treatment

Type of water	**pH range**	**Flocculants**	**Reference**
Oily wastewater from refinery plant	-	Derivative of polyacrylamide (Poly1 and 3530S), polyacrylamide	Zhong et al[41].
Olive mill effluent	5.5-6.7	Four cationic (FO-4700-SH, FO-4490-SH, FO-4350-SHU and FO-4190-SH) and two anionic (FLOCAN 23 and AN 934-SH) polyelectrolytes	Sarika et al[42].
Aquaculture wastewater	6.9-7.7	Cationic polyamine (Magnafloc LT 7991), cationic organic polyelectrolytes (Magnafloc LT 7992 and 7995), cationic polyacrylamide (Hyperfloc CE 854 and CE 1950), copolymer of quaternary acrylate salt and acrylamide (Magnafloc 22S)	Ebeling et al[24].

Coal waste slurry	8.3	Polyacrylamide-based polymers (anionic: Praestol 2515, Praestol 2540, non-ionic: Magnofloc 351, cationic: Praestol 857 BS)	Sabah and Erkan[43]
Pulp and paper mill wastewater,	7.3-8.3	Cationic (Organopol 5415, Organopol 5020, Organopol 5470, Organopol 5450, Chemfloc 1515C) and anionic (Organopol 5540, Chemfloc 430A, AN 913, AN 913SH) polyacrylamides	Wong et al[44].
Simulated reactive dye wastewater, Simulated dye liquor wastewater, Actual printing and dyeing wastewater	7.0 6.6-7.8 11.2	Cationic polydiallyldimethylammonium chloride (PDADMAC) Cationic polyamine	Kang et al[45]. Yue et al[46].
Pulp and paper mill wastewater	7.0	Cationic polydiallyldimethylammonium chloride (polyDADMAC)	Razali et al[7].
Kaolin suspension	7.0	Cationic lignin polymers	Hasan et al[47].

1.1.8 Flocculation of Kaolin

Kaolin is an important mineral clay which has a lot of applications in ceramics, coatings, cement, manufacturing of paint thickeners, catalysis, chemical carriers, liquid barrier, paper coating, detergents etc[48–52]. Awad et al. have given comprehensive information about the applications kaolin[53]. In view of its importance and wide range of applications, flocculation of kaolin has become extremely important. Globally, large scale production of kaolin is made by IMERYS, BASF, Kamin, Thiele, AIMR, Sibelco and Smart stones.

Kaolin is anionic clay and consists of silica and alumina along with minor quantities of ferric oxide and titanium. The chemical composition of kaolin is $Al_2Si_2O_5(OH)_4$ and has a layered structure with alumina octahedral sheets and silica tetrahedral sheets stacked alternately. See figure-1.7 for the structure of kaolin. The layered lattice structure is inert over wide pH range[54].

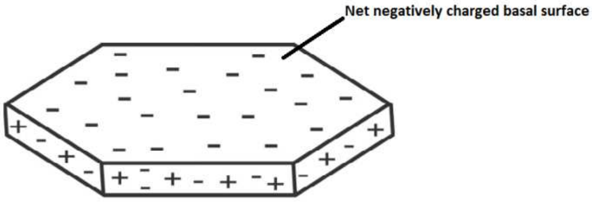

Fig-1.7: kaolin structure

1.1.9 Cationic flocculants:

Cationic flocculants can bind strongly to negatively charged particles and have a wide range of industrial applications in separation of anionic particles. There are quite a few cationic flocculants prepared from natural and synthetic polymers[55–60]. Many commercial flocculants are often based on poly (acrylamide) [PAM] and its derivatives since acrylamide [AM] is one of the most reactive monomers to undergo radical polymerization. AM has a high ratio of propagation to termination constant and as a result yields ultra-high molecular weight polymers. A large number of cationic flocculants are prepared from copolymerization of AM monomer with quaternary ammonium salt containing monomers such as Acryolyloxyethyltrimethylammonium chloride (AOETMAC), Methacryolyloxyethyltrimethylammonium chloride (MOETMAC), 3-acrylamidopropanetrimethylammonium chloride (APTMAC), Diallyldimethylammonium chloride (DADMAC) and vinylbenzyltrimethylammonium chloride (VBTMAC). Kumar et al. have reported on the amylopectin and acrylamide based cationic and amphoteric flocculants for the kaolin flocculation[37]

1.1.10 Chitosan

A large number of synthetic flocculants currently used for industrial separations are non-biodegradable and toxic in nature and pose severe environmental issues. Therefore, there is a major focus on design and development of natural polyelectrolytes or the modification of natural polyelectrolytes as flocculants for separation. In this context, biopolymers have emerged as promising materials to synthesize flocculants. Amongst the wide verity of biopolymers, chitosan, cellulose, guar gum, starch, sodium alginate, carrageenan, etc have become very important. For example, Hasan and Fatehi have prepared cationic lignin polymer for kaolin flocculation[47]. Starch-based flocculants have been prepared for the separation of kaolin[61–63] and hematite[62,64]. Particularly, chitosan is the second-largest biopolymer next to cellulose which is available abundantly. Further, chitosan being a non-food source for human beings and animals offer an advantage as a feed-stock for flocculant development.

Chitosan is a copolymer of D-glucosamine and N-acetyl-D-glucosamine, which is soluble in dilute acid solution[65]. Figure 1.8 shows the sources and structure of chitosan.

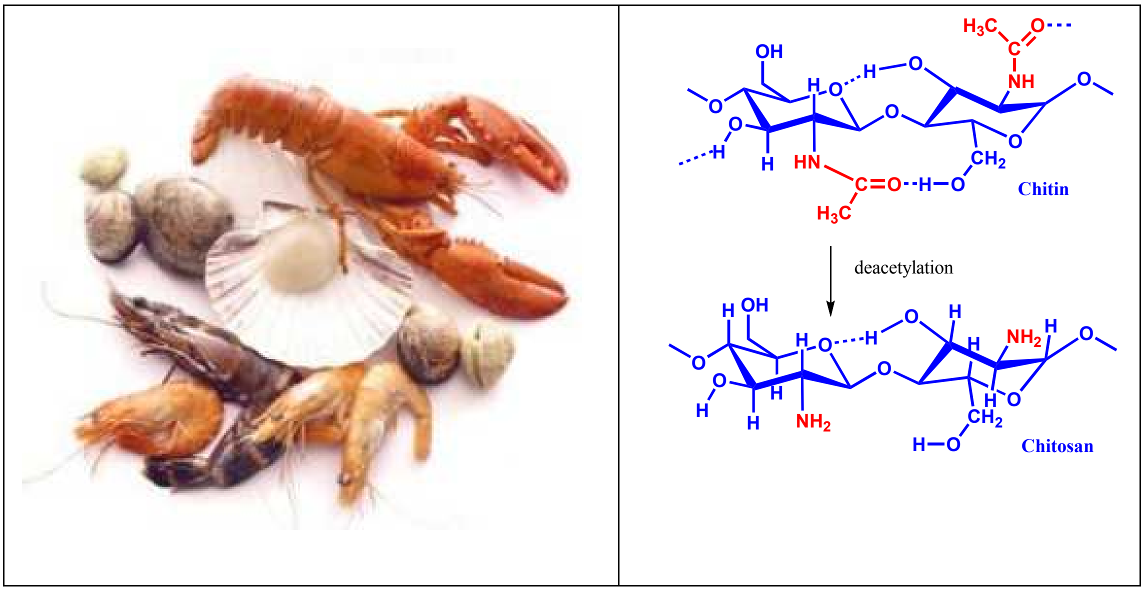

Figure-1.8: Source and structure of chitosan

Research on applications of chitosan in diverse areas such as pharmaceuticals, biomaterials, cosmetics, food processing, and chelation of heavy metals has grown phenomenally in recent years[65–78]. Among most of the modification methods, grafting has been proved to be a useful and convenient method for the synthesis of flocculants. Yang et al[39] have reported on the acrylamide grafted carboxymethyl chitosan for kaolin flocculation.

The graft copolymers generally combine the properties of both the backbone chain and the pendent grafted chain. A flexible chain grafted onto the rigid or semi-rigid backbone can increase the conformational freedom in solution and enhance the efficiency of flocculation.

Although there are a few cationic flocculants based on synthetic polymers and modified natural polymers for the kaolin flocculation. Still, there is a wide scope and demand for the development of newer efficient flocculants for kaolin mineral clay flocculation and industrial separation processes.

In this thesis work, the focus is given on the design and synthesis of cationic flocculants using copolymers of acrylamide and DADMAC / APTMAC and APTMAC grafted chitosan graft copolymer for kaolin flocculation.

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SCOPE AND OBJECTIVES

CHAPTER-2

In this chapter the scope and objectives of the thesis are discussed

Although there are a few flocculants used for the kaolin flocculation, still there is a great scope in designing and developing efficient cationic flocculants which have optimum molecular weight and charge density for separation of kaolin from aqueous streams, particularly at low dosages. Therefore, in this thesis work, efforts are made to synthesize cationic flocculants based on acrylamide (AM) monomer in combination with cationic monomers such as diallyldimethylammonium chloride (DADMAC) and 3-acrylamidopropyltrimethylammonium chloride (APTMAC). The composition of the monomers in the reaction feed was varied to get copolymers with different molecular weights and degree of charge. The chemical structures of all the copolymers were confirmed by ^{1}H and ^{13}C NMR spectroscopy. The molecular weights and degree of charge on the copolymers were determined using gel permeation chromatography (GPC) and zeta potential measurements. All the copolymers were used for kaolin flocculation using the established jar test method with the measurement of % transmission. The optimum dosages were identified for all the copolymers to obtain maximum kaolin flocculation. The efficiency of flocculation is correlated to the molecular weight and zeta potential of the copolymers and the plausible mechanisms, for the flocculation were proposed. The characterization of flocs in terms of Filter Cake Moisture Content (FCMC), Initial Settling Rate (ISR) and the optical microscopy of floc suspension were performed.

One of the most important anionic clay materials is kaolin, which is an anionic mineral clay consisting of silica and alumina along with minor quantities of ferric oxide and titanium. Kaolin has a lot of applications in coatings, manufacturing of paints, electronic ceramics and as a filler for several cosmetic formulations[1–5]. The extraction of kaolin from natural deposits involves a flocculation process[6].

Further, there has been a growing interest in developing flocculants from biopolymers because of their environmentally friendly nature[7]. In this context graft copolymerization of vinyl monomers onto chitosan can give desired properties to the obtained flocculants. In view of this, a cationic monomer, APTMAC was grafted onto chitosan and evaluated for the flocculation of kaolin. The structural characterization was performed on the graft copolymer by ^{1}H and ^{13}C NMR spectroscopy. Flocculation of kaolin suspension was carried out using the chitosan-g-APTMAC graft copolymers.

The objectives of the thesis are:

- To design and synthesize cationic flocculants based on acrylamide and cationic monomers namely, DADMAC and APTMAC
- To vary the composition of the monomers to obtain copolymers with higher molecular weight and higher zeta potential
- To characterize the obtained copolymers in terms of their chemical structure (by NMR spectroscopy), molecular weight (by GPC), and degree of charge (by zeta potential)
- To study the flocculation of kaolin using the above synthesized copolymers and to determine the optimum dosage levels for the maximum flocculation.
- To correlate the flocculation efficiency of the polymers to their molecular weight and charge density and to propose the mechanism of flocculation.
- To characterize the flocs in terms of FCMC, ISR and floc morphology by optical microscopy
- To synthesize chitosan-g-APTMAC graft copolymer and evaluate and study its performance for kaolin flocculation.

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FLOCCULATION OF KAOLIN USING COPOLYMER OF ACRYLAMIDE (AM) AND DIALLYLDIMETHYLAMMONIUM CHLORIDE (DADMAC)

CHAPTER-3

In this chapter we report on the syntheis of poly(AM-co-DADMAC) copolymers with varying content of AM and DADMAC. The copolymers were characterized by NMR, GPC and zeta potential analysis. The viscometric access to coil dimensions were studied by intrinsic viscosity and particle size by light scattering method. The flocculation efficiency was studied using kaolin suspensions and the flocs were characterized in tems of FCMC, ISR and optical microscopy. The optimum dosage was determined. The molecualr weight and charge density of the flocculant were correlated to the flocculation efficiency.

***RSC Advances* 5, 27674–27681 (2015)**

3.1 Introduction

The use of organic polymeric flocculants for solid-liquid separations is known for a very long time[1]. Polymeric flocculants of only acrylamide (AM) were used in industrial solid-liquid separations, such as oil sand fine tailings separations and kaolin separation. The use of only polyacrylamide suffers from the drawback of forming gel like structures with high water retention in the flocs. This was attributed to the hydrogen bonding of the amide groups in acrylamide with positive ions in the slurry[2]. Hence use of only acrylamide is not advantageous. Copolymerization of acrylamide with cationic monomers such as Diallyldimethylammonium chloride (DADMAC) will have added advantage of including (+ve) charge on the copolymer for efficient flocculation. DADMAC is a cheaper monomer compared to many other cationic monomers and has a stable cationic structure with wide pH working range[3]. There are many synthesis methods for preparing copolymers of acrylamide and DADMAC, such as solution polymerization[4,5], γ-radiation techniques[6,7], dispersion and inverse emulsion polymerization[8] etc. Of all the methods, solution polymerization is a simple method, economically viable, safe and industrially convenient to operate. The use of template polymerization of AM and DADMAC in presence of polyacrylic acid is reported for flocculation kaolin[3]. However the approach proposed in our work is a simple copolymerization of AM and DADMAC in a single step. The flocculants showed better charge and molecular weights with efficient flocculation of kaolin suspension (3 wt%) at lower dosages (8 to 14 ppm).

In this work, we have synthesized cationic flocculant based on the combination of acrylamide (AM) and Diallyldimethylammonium chloride (DADMAC) for flocculation of kaolin suspension and demonstrated an efficient flocculation in small dosages (8-14ppm) of flocculants. The DADMAC monomer was selected here because of its low cost and commercial viability for flocculant production. But the drawback of this monomer in flocculant synthesis is its low reactivity ratio in copolymerization. Which will lead to lesser incorporation of the DADMAC into the flocculant and result in low zeta potential with low charge density and moderately high molecular weight. Therefore, our objective in this work was to balance the zeta potential and molecular weight by design and synthesizing different compositions of the copolymers and to obtain optimum composition of the flocculant for the efficient flocculation of kaolin using small dosages of flocculant. The flocculants thus synthesized were tested for their efficiency of kaolin separation. The chemical structure of copolymer was determined using ^{1}H and ^{13}C NMR spectroscopy. The intrinsic viscosity measurements and particle size measurements were done to understand coil dimensions in solution. The flocculation efficiency was correlated to the zeta potential and molecular weight of the copolymer. Floc characterizations like filter cake moisture content (FCMC), initial settling rate (ISR) and optical micrographs of flocs were studied and correlated to the flocculation and dosages.

3.2 Experimental

3.2.1 Materials and Methods

Acrylamide (AM) monomer was purchased from Fluka, USA and was used as such; diallyldimethylammonium chloride (DADMAC) monomer (65 wt% solution in water) was purchased from Aldrich, USA; ammonium persulphate, sodium metabisulphite and sodium chloride were purchased from SD-fine chemicals, Mumbai, India which were of analytical grade and used as received. Deionized water (conductivity 0.055 μS cm^{-1} at 25° C) was obtained in the lab (TKA, GmbH Stockland), Acetone was procured from Rankem, Mumbai, India. Kaolin was obtained from Thomas Baker Chemicals, Mumbai, India. Analytical grade Sodium nitrate was purchased from Merck, Mumbai, India and used as received.

3.2.2 Synthesis of cationic flocculant based on Acrylamide and DADMAC

Copolymers of acrylamide with DADMAC were synthesized by solution polymerization using ammonium persulphate and sodium metabisulphite as a redox initiator system. In a typical experiment, the calculated amounts of acrylamide and DADMAC solution (65%) were added to a 100 ml DI water in a double jacketed reaction vessel equipped with circulating water bath to maintain the desired reaction temperature. The stirring of the reaction mass was facilitated using an overhead stirrer with a cross blade impeller. The concentration of the monomers in the reaction mixture was 10 wt%. The DADMAC contents were varied to get different composition of copolymers. The reaction mixture was purged with nitrogen gas for 30 min to remove any dissolved oxygen and temperature was increased to 40˚ C. Then ammonium persulphate and sodium metabisulphite were added at an initiator concentration of 2 mol% and stirring was continued. The reaction mixture became viscous and the polymerization was further carried out for 6 h. Finally, the polymer was precipitated in acetone and dried in vacuum oven at 40˚ C. Three copolymers with different feed ratios (moles) of AM and DADMAC (AM: DADMAC; 80:20, 50:50 and 40:60) were synthesized and denoted as AD-8020, AD-5050 and AD-4060 respectively. The chemical structure of the copolymers was characterized using ^{1}H and ^{13}C NMR spectroscopy. The molecular weights of the copolymers were determined using gel permeation chromatography (GPC).

3.3 Characterizations

3.3.1 Gel permeation chromatography (GPC)

The molecular weight (MW) of the copolymers was determined using Agilent 1200 GPC with Shodex OH pak SB-800 series columns. The mobile phase used was 0.25 N $NaNO_{3,}$ with a flow rate of 0.4 ml/min. 100 µl was the sample injection volume. The GPC column temperature was maintained at 40° C, and polyacrylamide standards were used for calibration.

3.3.2 Zeta potential measurements

Zeta potential measurements were carried out at 25° C using Brookhaven 90 plus particle size analyzer, USA. The polymer concentration used was 0.1 g dL^{-1}. The data reported is the average value of 10 cycles and 10 runs.

3.3.3 Hydrodynamic radii

Hydro dynamic radii were measured using Brookhaven 90 plus particle size analyzer, USA. The experiments were performed at 90˚, monitoring the variation in the intensity of the scattered light caused by the Brownian motion of the particles. The polymer solutions of known concentrations in deionized water were filtered through 0.22 µ filters (Millipore syringe filter)

3.3.4 Viscosity measurements

Viscosity measurements were conducted using an Ubbelohde capillary viscometer with capillary diameter 0.63 mm with AVS 479 (SCHOTT Gerate, Mainze, Germany). The measurements were done either in deionized water or in NaCl solutions (0.0003 to 1 M). The temperature was maintained at 25˚ C ± 0.05˚ C. For only deionized water the polymer concentration range was 0.01 to 0.05 weight %. For NaCl solutions the concentrations varied from 0.1 to 0.5 weight % due to decrease in viscosity of the solution.

3.3.5 NMR studies

The ^{1}H and ^{13}C NMR spectra of copolymers were recorded on Bruker AV 500 MHz spectrometer. The copolymer samples were prepared in D_2O.

3.3.6 Flocculation test for kaolin

Kaolin (particle size 1μ) suspension in water (3.0 wt-%) was used for the flocculation test. Kaolin suspension was prepared by stirring kaolin solution using overhead stirrer at 400 rpm for 30 min. In a typical flocculation study, to a 100 ml kaolin suspension, a known volume of flocculant solution (1g L^{-1}) was added and stirred for 5 min (with 300 rpm for first 2 min and at 100 rpm for 3 min) using an overhead stirrer, Heidolph RZR 2012, Germany with cross blade impeller. After 5 min, stirring was stopped and immediately, 1 ml aliquot was drawn from the central portion of the solution. The transmittance (%) was measured for this solution using Shimadzu UV-PC 1601 UV-Vis spectrophotometer, Japan, in the kinetic mode at 700 nm. This value of the transmittance was taken as zero minute reading. The solution was allowed to settle and the aliquots were drawn at predefined interval of time till 40 min and transmittance was measured. Then transmittance vs. time was plotted to find out the time required for maximum transmittance to occur. For the zeta potential measurement, the supernatant liquid was taken after 40 min flocculation with different dosages of flocculant.

The optimum dosage of the flocculant for each composition was determined. Different dosages were tested for kaolin suspension flocculation, the dosage at which the transmittance is 90% or more was considered as optimum dosage for that composition. This 90% transmittance was higher than what was reported earlier[9]

3.3.7 Floc characterization

3.3.7.1 Initial settling rate (ISR)

The initial settling rate (ISR) of kaolin suspension for the AD-4060, AD-5050 and AD-8020 flocculants was evaluated by adding a known volume of flocculant (Concentration, 1g L^{-1}) to a 100 ml of 3.0 Wt % kaolin suspension in a stoppered measuring cylinder. The flocculant was uniformly mixed by inverting the cylinder 10 times up-down. The height of the kaolin liquid interface was recorded as a function of time for AD-4060, AD-5050 and AD-8020.

3.3.7.2 Filter Cake Moisture Content (FCMC)

The property of kaolin flocs after the flocculation was evaluated in terms of Filter Cake Moisture Content (FCMC)[10,11]. The FCMC is an important index used to characterize the floc state. It is intuitive and is widely used method. The flocculants are also used as a filtration aid, with the objective of increasing filtration rate and to reduce the filter cake moisture content. FCMC is important in such industrial separations where the floc is the product of interest such as kaolin separation, protein separation form marine fish processing industry etc. Lesser the moisture content faster will be the drying process. A 3.0 Wt % kaolin suspension was used for FCMC study. The flocculation was performed by adding a known volume of AD-4060, AD-5050 and AD-8020 flocculants (Concentration, 1g L^{-1}) and stirring at 300 rpm for 2 min followed by 100 rpm for 3 min. Then the suspension was allowed to stand for 40 min to reach equilibrium settling; this floc was filtered using a 0.45 µm Millipore filter paper in a sintered funnel at 450 mm of Hg vacuum for 30 min. The filter cake was transferred to a crucible, weighed and dried in an oven at 100° C for 24 h and FCMC was calculated using the following equation.

$$FCMC = \frac{W_1 - W_2}{W_1 - W_0} X\ 100$$

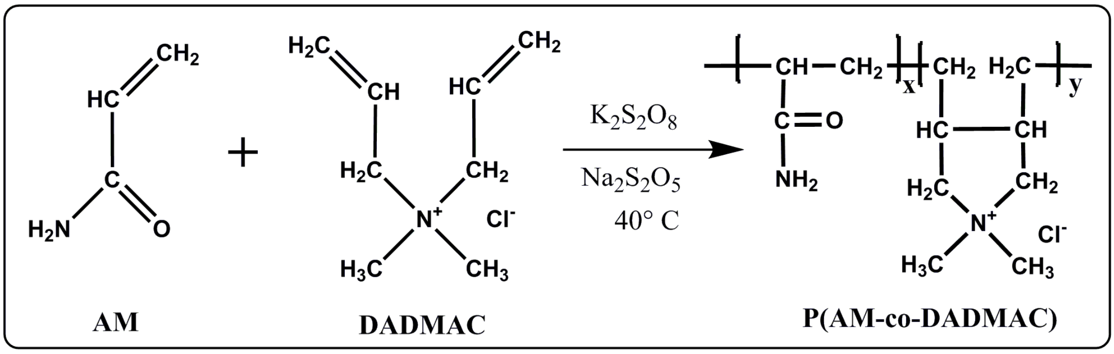
Where W_0 is the weight of the crucible, W_1 is the total weight of crucible + filter cake before drying and W_2 is the total weight of crucible + cake after drying to constant weight. With this FCMC study, one can get information about the role of polymer in moisture retention in flocs.

The flocculation was monitored by using optical microscopy (Leica, Germany) and the filter cakes were photographed with a DSLR camera (Canon EOS 77D, USA)

3.4 Results and Discussion

3.4.1 Synthesis and characterization of flocculants

Amongst a few cationic monomers available, DADMAC was chosen considering its high utility in commercial flocculants and it is available at a cheaper price than many cationic monomers. Synthesizing an efficient cationic flocculant lies in obtaining high molecular weight and high zeta potential copolymer. The acrylamide monomer, with its high ratio of propagation to termination constant, gives high molecular weight to the polymer. Whereas, the cationic monomer provides an overall charge density to the copolymer. Therefore, it is very important to critically balance both the monomer contents to obtain high molecular weight and high zeta potential polymer for efficient flocculation. Accordingly, three copolymers, with varying AM and DADMAC contents were prepared.. The copolymers were coded as AD-8020, AD-5050 and AD-4060, respectively. The quantitative yields of the copolymers AD-8020, AD-5050 and AD-4060 were determined to be 88, 74, and 69% respectively. The reaction scheme for the synthesis of poly (AM-co-DADMAC) is shown in scheme-3.1. The structural characterization of the copolymers was carried out using ^{1}H and ^{13}C NMR spectroscopy.



Scheme 3.1: Reaction scheme for the synthesis of poly (AM-co-DADMAC)

3.4.2 Chemical structure by NMR spectroscopy

We show in figure-3.1, the ^1H NMR spectra of representative poly (AM-co-DADMAC) [AD-8020] and a homopolymer of polyacrylamide. The methyl ($-CH_3$) proton peaks of DADMAC appear in the range of 3.0 to 3.3 ppm and the methylene ($-CH_2-$) protons of DADMAC attached to nitrogen atom give peaks at 3.78 ppm. The methylene ($-CH_2-$) proton peaks of the backbone chain of AM and DADMAC appear in the range of 1.5 - 1.8 ppm. The methine protons of the AM backbone appear at 2.0 to 2.4 ppm. All the characteristic peaks of the copolymer assigned, agree with those reported in the literature[3,12,13].

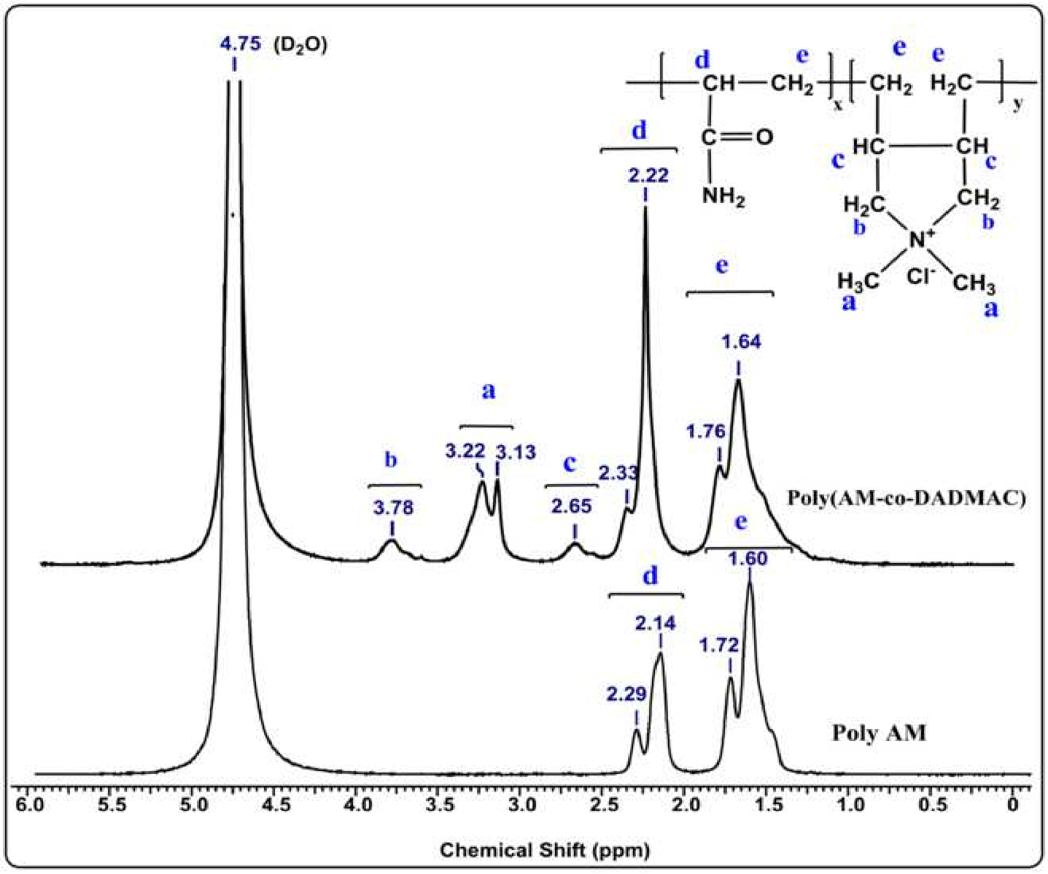


Figure-3.1: 500 MHz ^1H NMR spectrum for Polyacrylamide and Poly (AM-co-DADMAC) [AD-8020]

The mol fractions of DADMAC in the copolymers were obtained by NMR spectroscopy. The ^1H NMR spectrum of the copolymer shows the AM peak at 2.3 ppm and that of DADAMAC at 2.78 ppm. The area under the peak for single protons of AM and DADMAC was calculated, which yields the moles of AM and DADMAC.

Taking the molecular weights of AM (71.08 g mol^{-1}) and DADMAC (161.67g mol^{-1}) into consideration, the mol fraction of the DADMAC was calculated to be 0.12, 0.32 and 0.44 respectively for AD-8020, AD-5050 and AD-4060.

We also show in Figure-3.2, the ^{13}C NMR spectrum (Bruker, AV 500 MHz, D_2O) of poly (AM-co-DADMAC) [AD-4060]. The methyl ($-CH_3$) carbon peaks of DADMAC appear at 54.4 ppm and methylene ($-CH_2-$) carbon of the backbone chain of AM and DADMAC appear at 34.9 ppm. The methylene ($-CH_2-$) carbon of DADMAC attached to nitrogen gives a peak at 66 to 70 ppm and peak for methine (-CH-) carbon next to carbon attached to nitrogen of DADMAC and methine (-CH-) carbon of acrylamide backbone appear at 41.7 ppm. Both the ^{1}H and ^{13}C NMR spectra confirm the chemical structure of the copolymer.

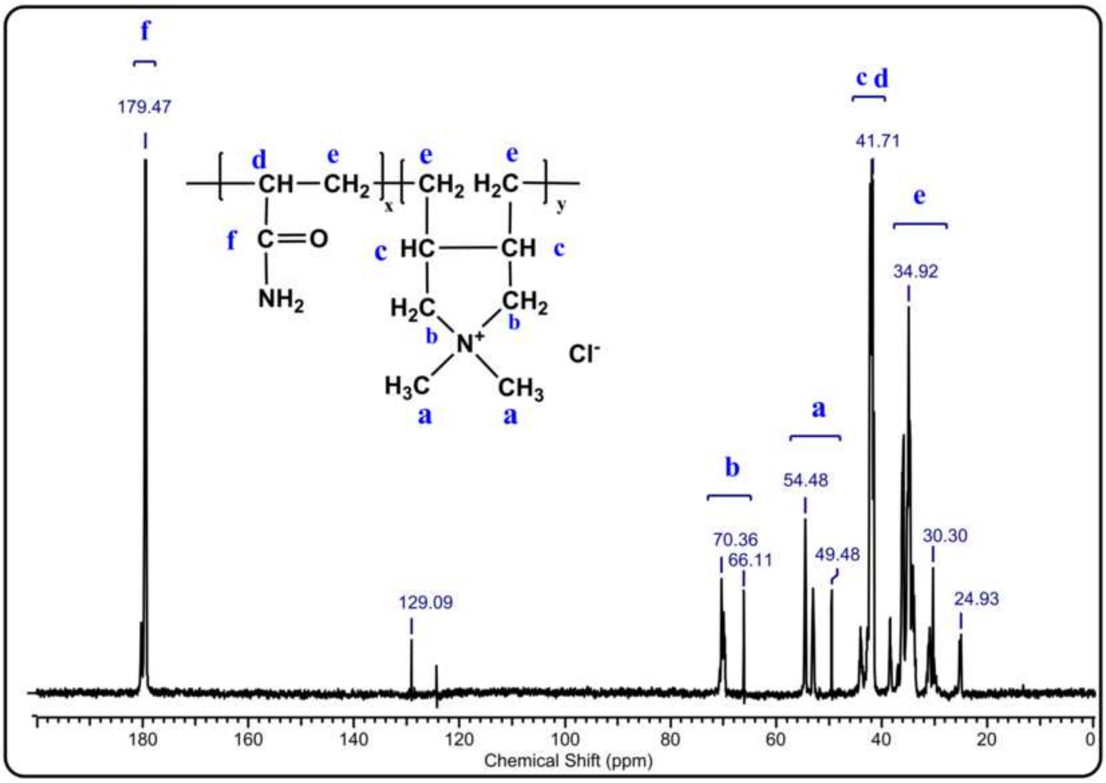


Figure-3.2: 400 MHz ^{13}C NMR spectrum for Poly (AM-co-DADMAC)

In figure 3.3 and 3.4 we show the ^{1}H and ^{13}C stacked NMR spectra of all the three compositions AD-8020, AD-5050 and AD-4060 respectively. The NMR spectra of all the compositions clearly show the peaks for both AM and DADMAC. Further, it can be clearly seen that the intensity of peaks for AM increases as the AM content increases form AD-4060 to AD-8020 and Vice versa was observed for DADMAC.

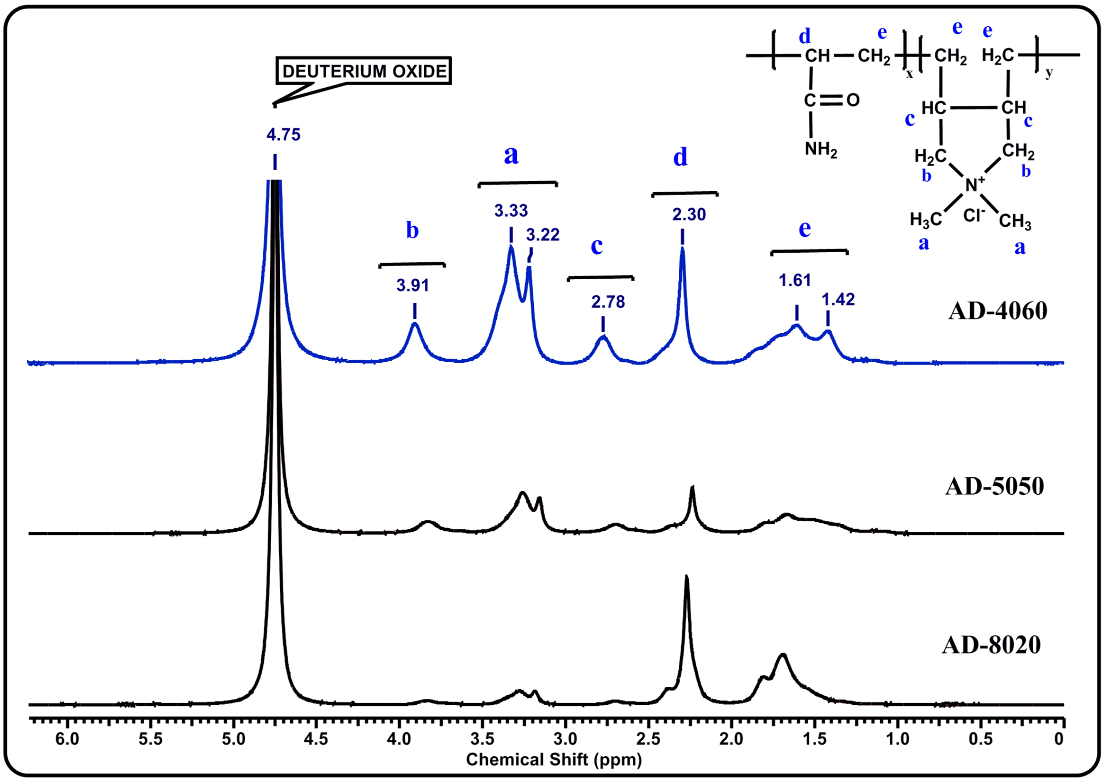


Figure-3.3: 500 MHz ^{1}H NMR spectrum for Poly (AM-co-DADMAC) [AD-4060, AD-5050 and AD-8020]

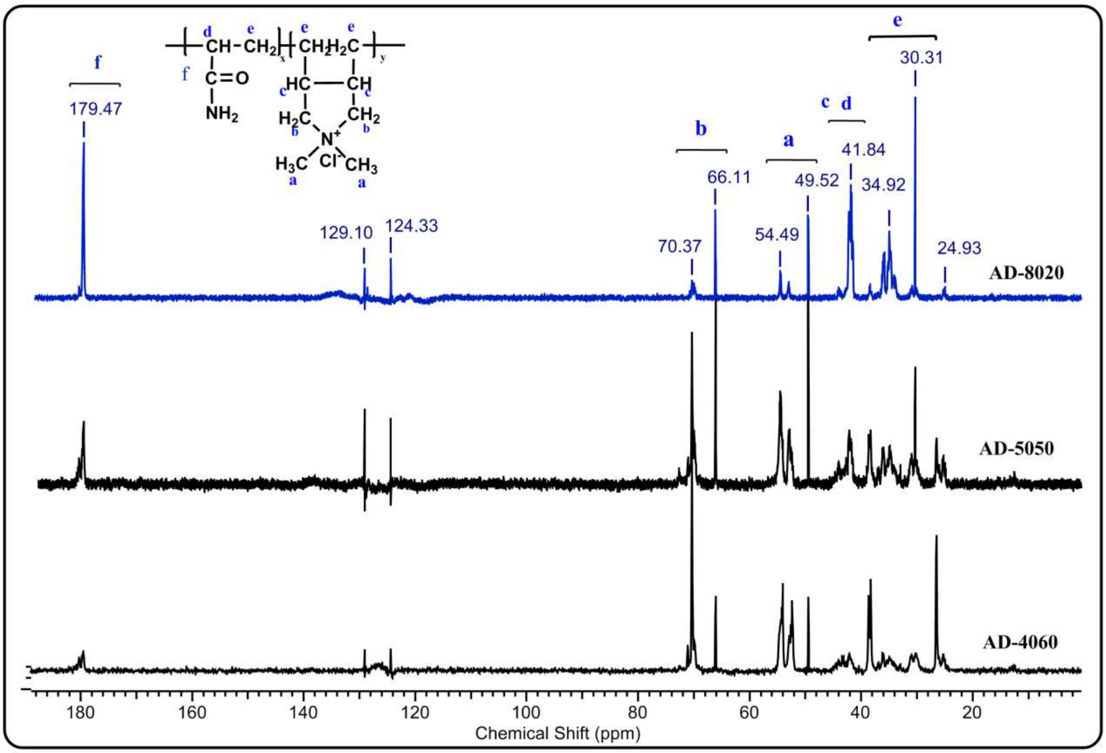


Figure-3.4: 400 MHz ^{13}C NMR spectrum for Poly (AM-co-DADMAC) [AD-4060, AD-5050 and AD-8020]

3.4.3 Study of coil dimensions of the flocculant in solution

The coil dimensions of the flocculant in solution was studied in the presence and absence of salt. The hydrodynamic radii and intrinsic viscosity were studied using particle size analyzer and Ubbelohde capillary viscometer respectively. In only water and at low salt concentrations the polymer coils shrink upon an increase of polymer concentration. For sufficiently high salinity of the solvent the polymer coils expand, this behaviour is due to the unfavourable thermodynamic quality of solvents containing much salt. Such a situation leads to an increase in the number of intersegmental contacts and to higher friction. At a certain characteristic salinity of the solvent, the dimensions become independent of polymer concentration. Figure-3.5 shows the changes in hydrodynamic radii and intrinsic viscosity with the change in polymer concentration. Figure-3.6 represents the coil dimensions at no salt, less salt and sufficient salt conditions.

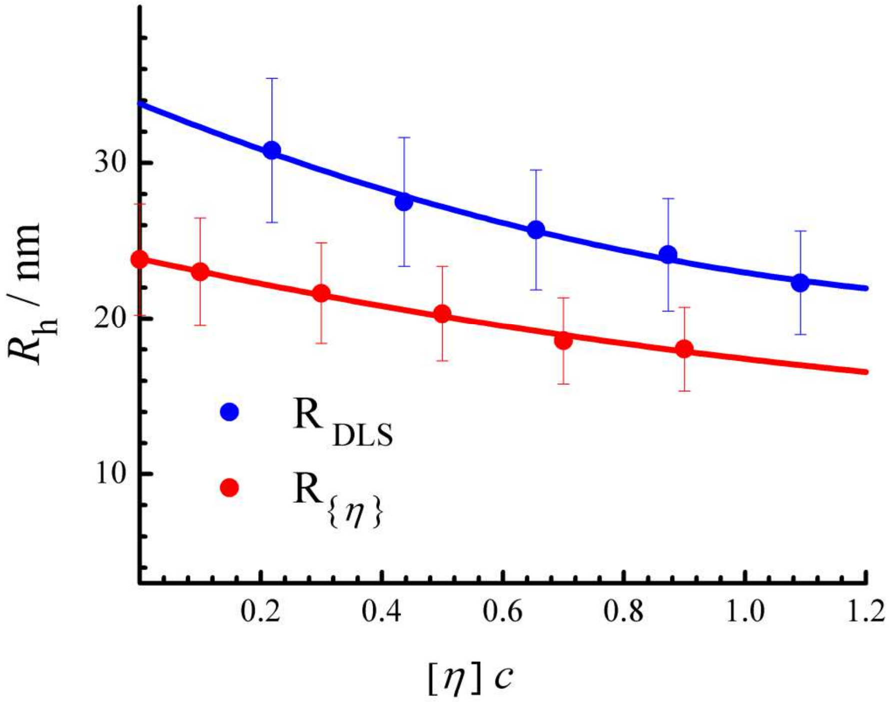


Figure-3.5: Comparison of the hydrodynamic radii of the polyelectrolyte coils (AD-8020) as a function of the reduced polymer concentration obtained from Dynamic Light Scattering and viscometry in 0.25 mol NaCl.

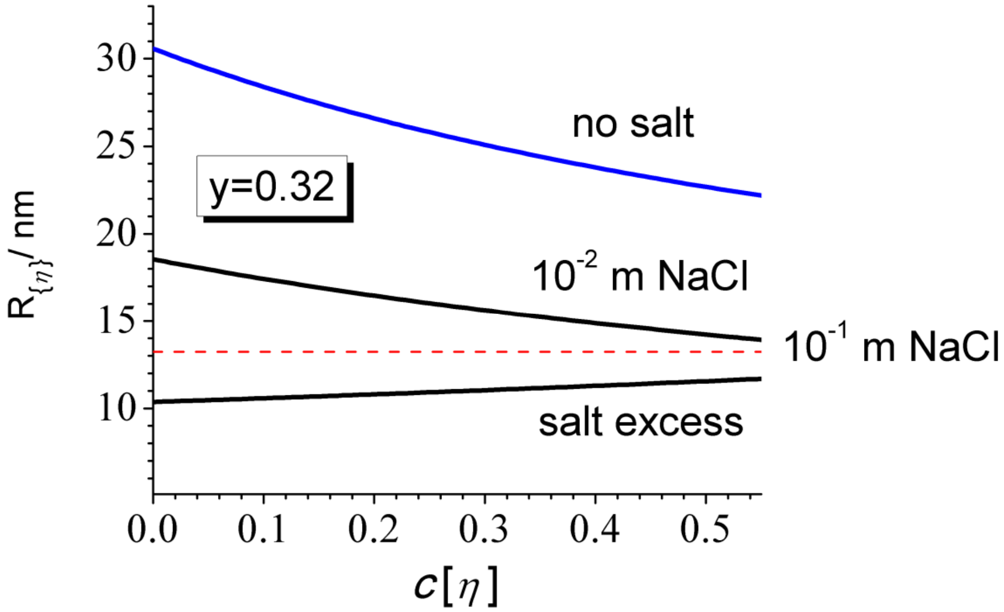


Figure-3.6: Coil dimensions as a function of the reduced polymer concentration for the polymer sample AD-5050. The salt contents of the solvents are indicated in the graph.

It is clear from the figures that the coil dimensions dependent on the molecular weight, charge and salt concentration in the solution. The free coil dimensions is important parameter for efficient flocculation. The coil dimensions reduce with increase in the concentrations. This implies that the optimum dosage of the flocculant should be at lower concentrations where the coil dimensions are higher. Same phenomenon was observed even at low salt concentrations.

3.4.4 Molecular weight and zeta potential

The molecular weight and zeta potential of the copolymers were determined using GPC and particle size analyzer, respectively. We show in table-3.1 the molecular weights and zeta potential of AD-8020, AD-5050 and AD-4060 samples.

Table-3.1: Molecular weight and Zeta potential of copolymers

Samples	**M_w** **($Kg\ mol^{-1}$)**	**M_n** **($Kg\ mol^{-1}$)**	**PDI** **(M_w/M_n)**	**Mol fraction DADMAC**	**pH**	**Zeta potential (mV)**
AD-8020	227.0	87.7	2.6	0.12	6.0-7.5	(+) 20.0 - 22.0
AD-5050	93.4	42.5	2.2	0.32	6.5-7.5	(+) 26.5 - 28.5
AD-4060	52.3	35.8	1.5	0.44	6.5-7.8	(+)39.5 - 41.3
Kaolin	-	-	-	-	6.5-7.0	(-)18.0 - 20.0

It can be readily seen that when the acrylamide content in the copolymer is high, the copolymer yields high molecular weight but gives low zeta potential (AD-8020). Whereas, the high content of cationic comonomer, DADMAC (AD-4060) gives higher zeta potential due to the presence of high charge density on the polymer and yields low molecular weight copolymer. The copolymer with equal feed ratio shows the values in between both the AD-8020 and AD-4060. These observations for composition are further evidenced by NMR studies. The particle size of the polymer also increases with the increase in DADMAC content. This can be attributed to the fact that the increased DADMAC content will increase the charge on the polymer which leads to intra molecular charge repulsion and open coil confirmation of polymer resulting into increase in size. This open coil confirmation is favourable for effective binding to cause efficient flocculation.

3.4.5 Flocculation of Kaolin

The flocculation efficiency of copolymers, AD-8020, AD-5050 and AD-4060 on kaolin aqueous suspension was examined by measuring the transmittance on kaolin suspension after the equilibrium flocculation (~40 min). The kaolin bears a negative charge on the surface in the pH range of 6.5 - 7.5 and exhibits the zeta potential of (-) 18 - 20.0 mV. The average size of the kaolin particles was ~1.0 µm. The efficiency of flocculation of kaolin suspension (3.0 wt %) was investigated at different dosages of flocculants.

We show in figure-3.7, a typical setup for the flocculation of Kaolin suspension. The flocculation setup consists of an overhead stirrer with a cross blade impeller and a beaker. Figure-3.7a shows the kaolin suspension before the addition of flocculant which is stable and looks milky. Upon addition of cationic flocculant and initial stirring the milky suspension turns into a clear solution after stopping the stirring (figure-3.7b). The initial stirring was 300 rpm for first 2 min, followed by stirring at 100 rpm for 3 min. This stirring cycle was followed because, during initial rapid stirring, mixing of particles and polymer occur which is the most desired. During the slow stirring at 100 rpm the floc size increase and begin to settle at the bottom. The transmittance of the clear solution was measured. Similar experiments were carried out for different dosages of flocculants.

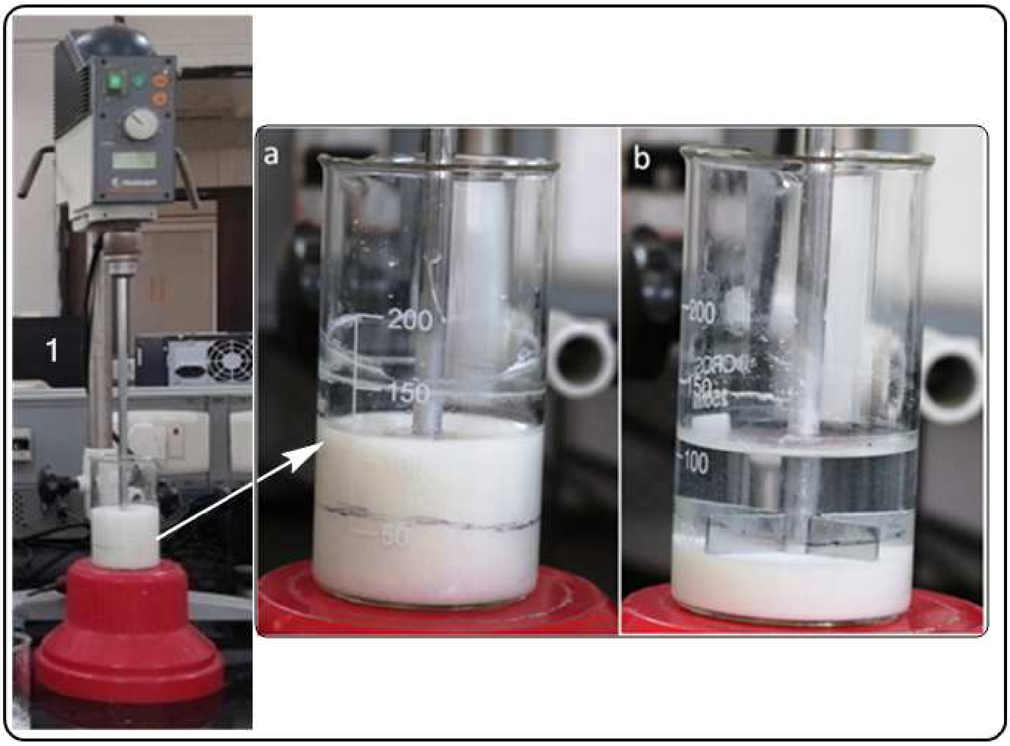


Figure-3.7: Flocculation of Kaolin aqueous suspension (1) flocculation setup, (a) Before flocculation and (b) after flocculation

Figure-3.8 shows the percentage transmittance of kaolin supernatant liquid vs. different dosage of flocculants, AD-8020, AD-5050 and AD-4060 taken at pH 7 and at equilibrium flocculation time of ~ 40 min.

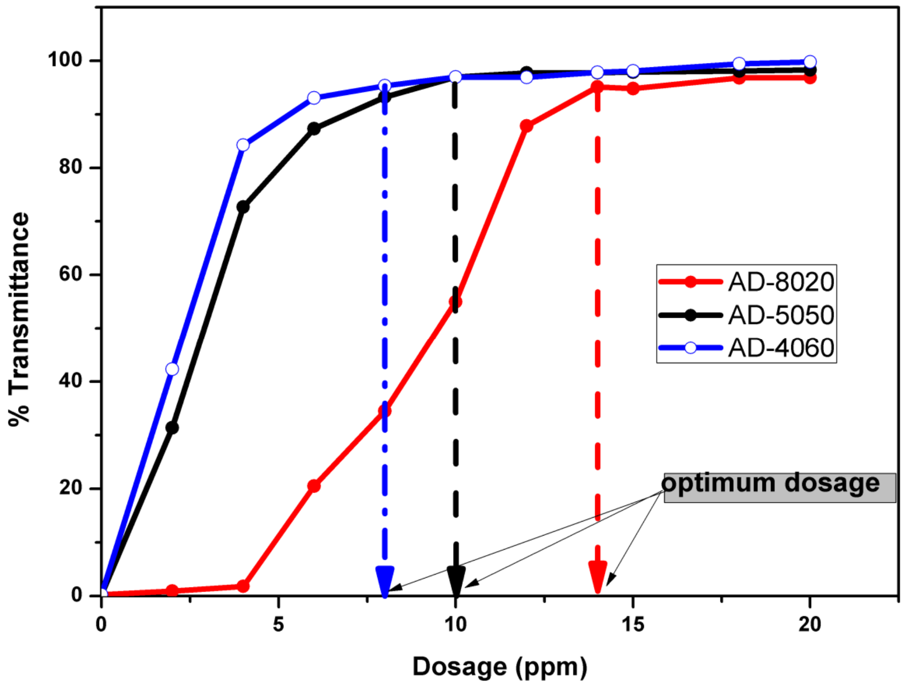


Figure-3.8: Transmittance of kaolin supernatant vs. dosage of flocculants after 40 min of equilibrium flocculation

It can be revealed from the figure that, AD-4060 shows nearly 95-98 % transmittance at the dosage range of 8 - 10 ppm and remains constant till 20 ppm. The AD-5050 showed 95 -98% transmittance at the dosage range of 10 - 12 ppm. Whereas, AD-8020 flocculant showed 95-98 % transmittance at the dosage range of about 14 - 16 ppm. Therefore, the optimum dosage levels for AD-4060, AD-5050 and AD-8020 flocculants for kaolin flocculation can be considered as 8.0 ppm, 10.0 ppm and 14.0 ppm, respectively. These flocculants showed efficient flocculation and the optimum dosages were found to be quite low compared to the values reported earlier.[10]

The AD-4060 flocculant contains more of cationic polymer and exhibits a high degree of charge with high zeta potential (+ 41.3 mV). In this case, the mechanism of flocculation could be due to the charge neutralization followed by bridging. In the case of flocculant AD-5050, the charge is moderate with moderate zeta potential (+ 28.5 mV) and moderate molecular weight (93.4 Kg mol^{-1}). The mechanism of flocculation is also can be due to charge neutralization and bridging. For the flocculant AD-8020, a higher dosage was required (~14.0 ppm) to get 95-98% transmittance in the flocculation. In AD-8020 flocculant, the charge density is low (zeta potential + 22mV) but the molecular weight is high (227 Kg mol^{-1}). Because of the high molecular weight, the long polymer chain can get attached to a large number of kaolin particles and the flocculation can occur through the bridging mechanism. The requirement of more number of polymer chains for bridging leads to high optimum dosage for AD-8020. These observations clearly indicate that charge density on the polymer plays a dominant role in the kaolin flocculation.

We also measured the zeta potential of kaolin supernatant solution as a function of different dosage of flocculants AD-8020, AD-5050 and AD-4060. The results are shown in figure-3.9.

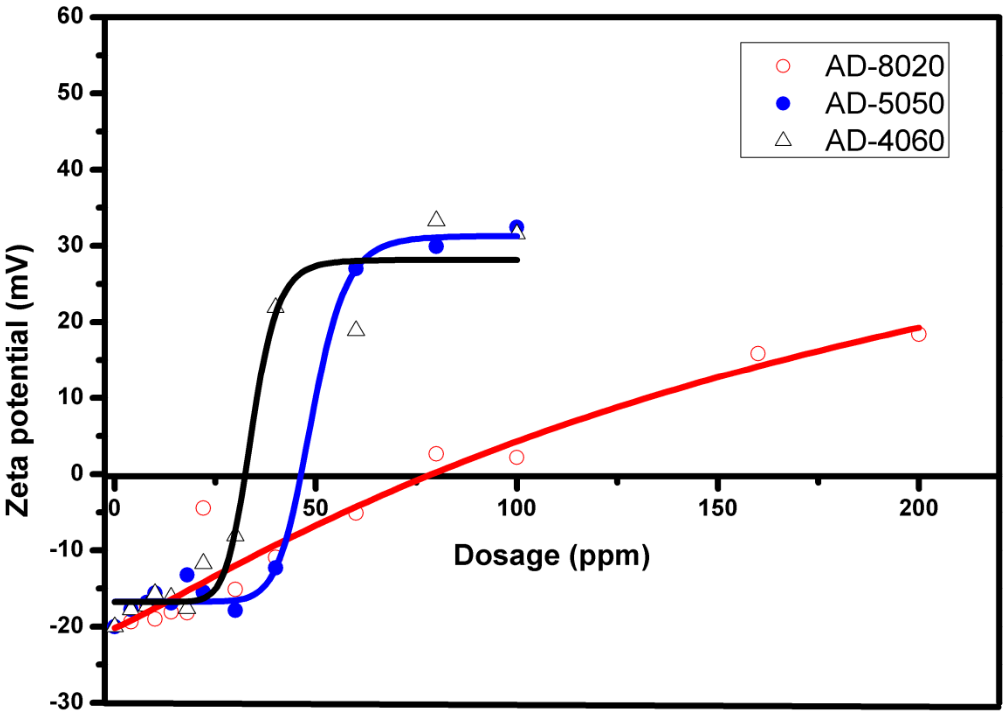


Figure-3.9: Zeta potential of kaolin suspension supernatant at different dosages after equilibrium flocculation using AD-8020, AD-5050 and AD-4060

It is observed that, the zeta potential of kaolin solution changed from (-) 20 mV to (+) 35 mV with an increase in the dosage of flocculants. This is due to the fact that the oppositely charged flocculants neutralize and diminish the surface charge of the suspended kaolin particles resulting into the formation of kaolin flocs. However, it is interesting to note from the figure-3.9 that the zeta potential of the kaolin supernatant did not reach zero value at 95% transmittance for the optimum dosage of AD-8020, AD-5050 and AD-4060 flocculants. The zeta potential values remained at (-) 15 to

(-) 10 mV. This could be due to the presence of still some very fine particles of unneutralized kaolin present in the supernatant liquid. Further, the kaolin fine particles are partially or heterogeneously bound by flocculants to form micro flocs that cannot settle down and hence they float and show reduced zeta potential value.

At higher dosage content, the zeta potential values crossed the zero value and attained a positive value of zeta potentials. This is because; the higher concentration of flocculant is available to bind to all the finely dispersed particles and the heterogeneously bound kaolin particles. These observations clearly indicate that there seems to be a broad flocculation regime and the possibility of both charge neutralization and bridging mechanism for driving the flocculation.

It is also observed form the figure, that the dosages at which the zeta potential value is zero for AD-8020, AD-5050 and AD-4060 were ~ 80, 48 and 30 ppm respectively. These values are more than 5 times higher than the optimum dosages. At optimum dosage, more than 95 % clarity of suspension was achieved or most of the kaolin was flocculated and that supernatant water can be reused to suspend the kaolin for next cycle of kaolin mining. This will improve the economy and efficiency of the kaolin recovery process enormously.

3.4.6 Kinetics of flocculation

In order to understand the kinetics of flocculation, the percentage transmittance of kaolin suspension as a function of time was measured for flocculants, AD-8020, AD-5050 and AD-4060 at different dosages and at their optimum dosages. Figure-3.10 shows the results of % transmittance vs. time for three flocculants at optimum dosages. Figure-3.11 to 3.13 shows the results of % transmittance vs. time for three flocculants at different dosages.

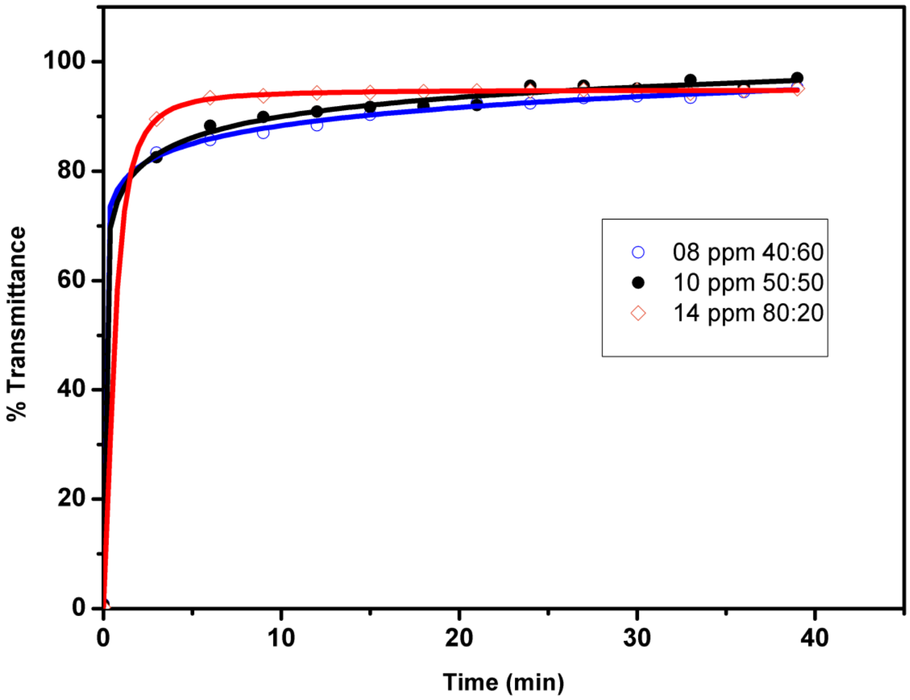


Figure-3.10: Kinetics of flocculation of AD-8020, AD-5050 and AD-4060 at optimum dosage

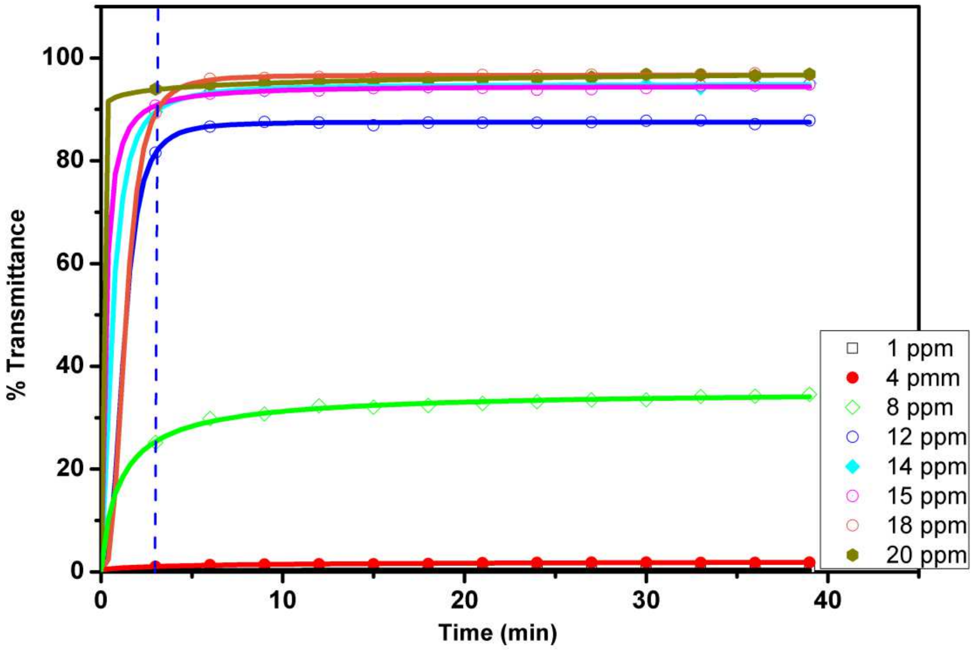


Figure-3.11: Transmittance of kaolin supernatant vs. time of AD-8020

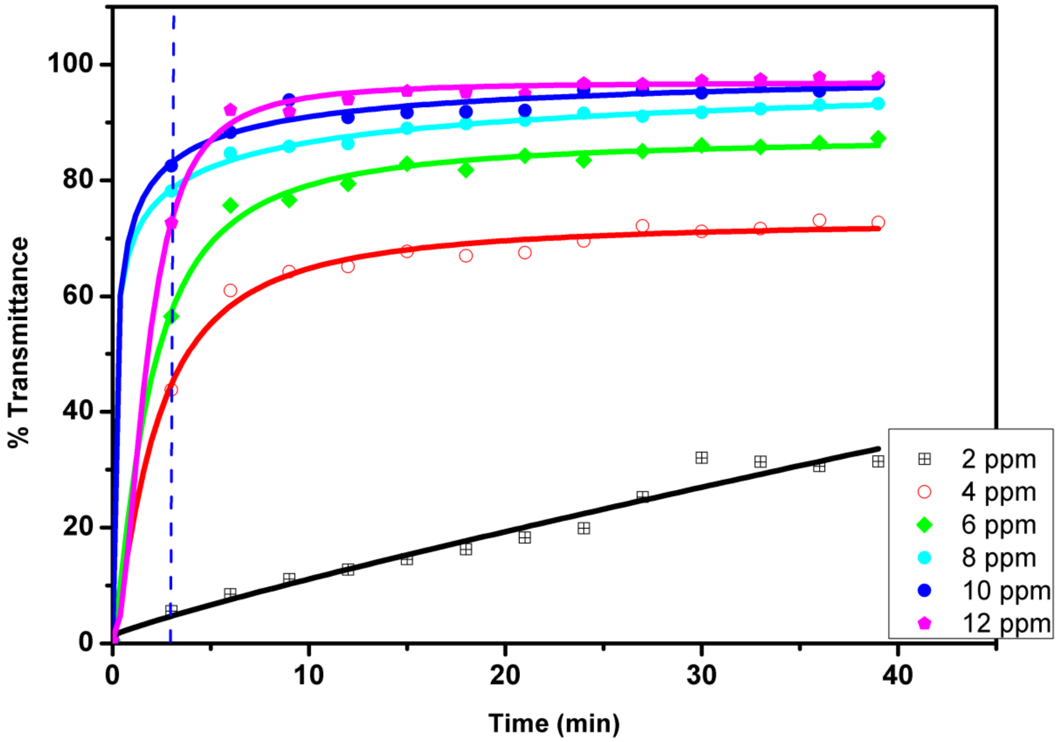


Figure-3.12: Transmittance of kaolin supernatant vs. time of AD-5050

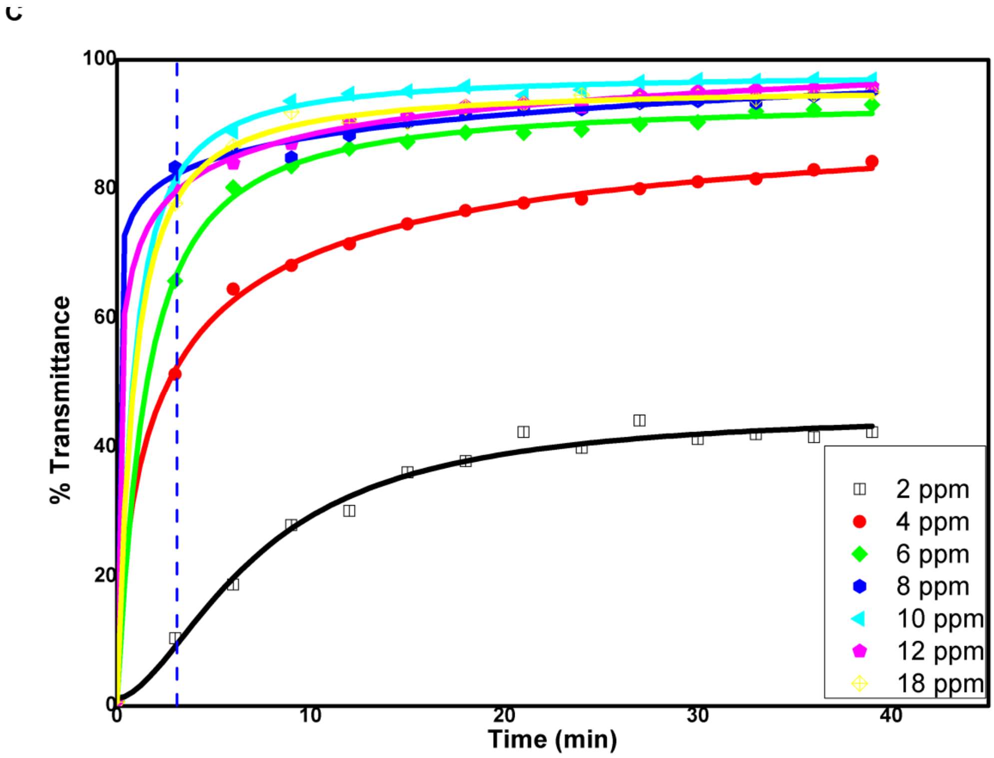


Figure-3.13: Transmittance of kaolin supernatant vs. time of AD-4060

It is clearly seen that 80 - 85% transmittance could be achieved within 3 min of flocculant addition to the kaolin suspension at their respective optimum dosages. This shows that the flocculant separates kaolin rapidly. The AD-4060 flocculant gave maximum % transmittance at optimum dosage of 8 ppm. These studies indicate that the charge on the flocculant (zeta potential) plays a dominant role compared to molecular weight for the efficient flocculation of Kaolin suspension.

From figure-3.11 to 3.13, it can be seen that the dosages prior to the optimum dosage also shows reasonably good % transmittance, which indicates that the flocculants have a broader flocculation range.

3.4.7 Floc characterization

3.4.7.1 Initial settling rate (ISR)

Figure 3.14 shows the interface height vs. time for flocculants AD-4060, AD-5050 and AD-8020 at their optimum dosages of 8, 10 and 14 ppm respectively. It can be readily seen that, the interface height decreases rapidly within the first 100 seconds and remains almost constant after 300 seconds for all the flocculants. This predicts the initial settling rate of $\sim$0.01cm s^{-1} for the flocculants. These observations clearly reveal that AD-4060, AD-5050 and AD-8020 flocculate kaolin suspension very rapidly. It can also be seen that the AD-8020 has fastest and the AD-5050 has faster initial settling rate compared to AD-4060. This could be due to the difference in their floc size, wherein for AD-8020, the floc size formed is bigger by virtue of its higher molecular weight. Whereas for AD-4060, the lower molecular weight forms a smaller floc size, which will take more time to settle.

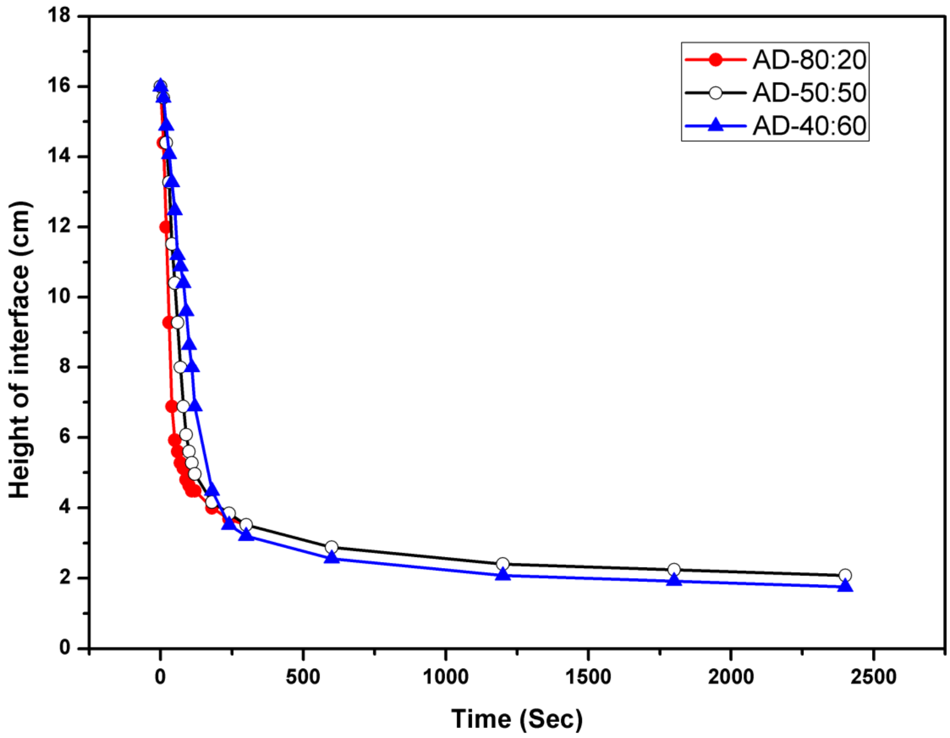


Figure-3.14: Initial settling rate of CP-4060 and CP-8020

3.4.7.2 Filter Cake Moisture Content (FCMC)

FCMC is an important parameter to characterize the floc state. Flocculants were also employed as filtration aids, where the flocs formed will help in faster filtration and reduced moisture in the flocs. Which helps in faster drying of the final floc product. Figure-3.15 shows the results of FCMC for AD-4060, AD-5050 and AD-8020 at different dosages. The FCMC of AD-4060, AD-5050 and AD-8020 remained independent with respect to dosage in the range of 10 to 20 ppm used in this work. However, the earlier reports indicate a decrease in FCMC with an increase in dosage levels when the dosage levels are quite high (~40 to 50 ppm). We observed a very small change in FCMC with these low dosage levels. Nevertheless, these lower dosages (10-20 ppm) were found to be efficient in flocculation and gave more than 95 % transmittance in the flocculation process. The filter cakes of AD-8020 showed slightly higher FCMC compared to AD-4060 and AD-5050 which could be attributed to the higher molecular weight of the polymer that results into increased hydrophilicity of flocculant and absorbs more moisture. The cakes of AD-5050 showed less FCMC value than both AD-8020 and AD-4060; this could be due to lower molecular weight and charge density.

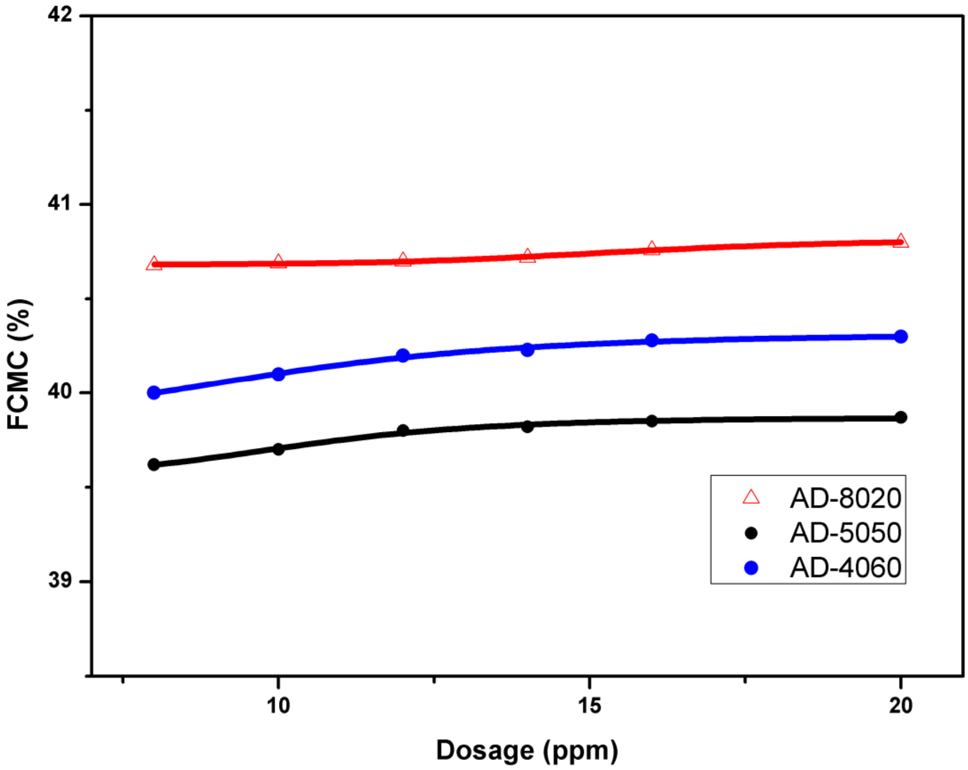


Figure-3.15: Filter cake moisture content study of CP-4060 and CP-8020 at different dosages

The visual observation of the filter cakes after the flocculation using AD-4060, AD-5050 and AD-8020 at different dosages was made and photographs are shown in figure-3.16.

Figure-3.16: Photographs of filter cakes after flocculation and drying for AD-8020 (a-d) AD-5050 (e - h) and AD-4060 (i-l)

It is observed that, as the dosage increase, the surface of the filter cake becomes more smoother and softer. This could be due to the formation of dense flocs at higher dosages of flocculant.

3.4.7.3 Optical microscopic studies

The optical microscopy was performed on kaolin suspensions obtained under different dosages of AD-4060, AD-5050 and AD-8020 flocculants. The optical micrographs are shown in figure-3.17. Kaolin suspension without any flocculant does not show the flocs and one can see a uniform suspension [figure-3.17 (a)]

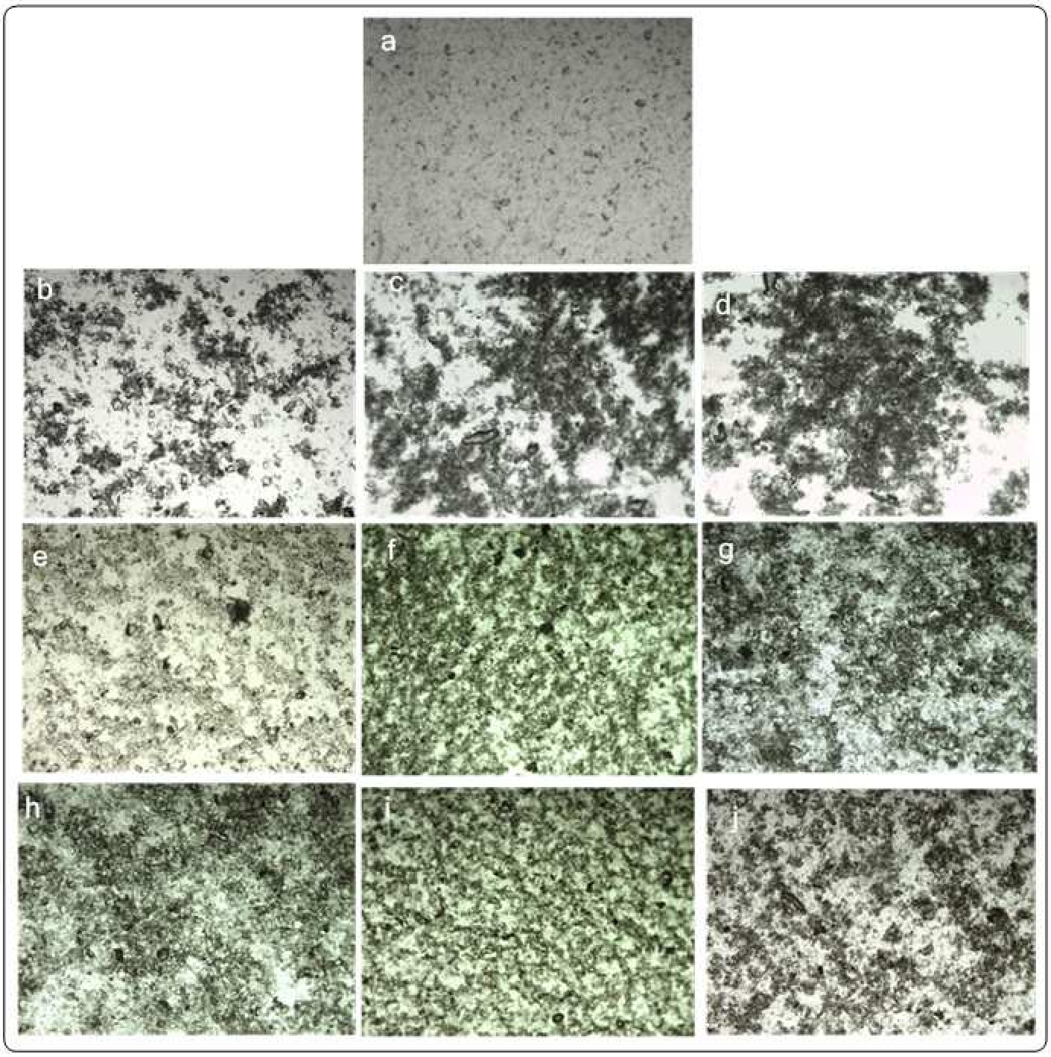


Figure-3.17: Optical micrographs of kaolin flocculation at different dosages, Kaolin (a), AD-4060 (b-d), AD-5050 (e-g) and AD-8020 (h-j)

However, upon flocculation, kaolin flocs are observed very clearly and the floc size increases with the dosage of flocculant. The observed optimum dosages of 8, 10 and 14 ppm for flocculants AD-4060, AD-5050 and AD-8020 respectively, show more than 95 % transmittance in the supernatant liquid after the floc formation. This is visible in the micrographs of figure-3.17 (b), (e) and (j).

3.5 Conclusions

In conclusion, we have shown that the cationic flocculants based on the copolymer of acrylamide (AM) and diallyldimethylammonium chloride (DADMAC) efficiently flocculates kaolin from its aqueous suspensions. Depending on the ratio of monomers incorporated, the copolymers could be obtained with different molecular weights and zeta potentials which are very important properties required for efficient flocculation. The mole fraction of the DADMAC was determined by proton NMR spectroscopy. It was inferred form the viscosity and particle size measurements that the intrinsic viscosity and hydrodynamic radii decreases with an increase in polymer concentration. This means the hydrodynamic radii is higher at low polymer concentrations. Similar phenomenon was observed at very low salt concentrations also. The optimum dosages for maximum flocculation were found to be 8.0, 10.0 and 14.0 ppm for AD-4060, AD-5050 and AD-8020 copolymers, respectively. The minimum time required for maximum flocculation was determined to be ~ 3-4 minutes investigated as per the laboratory scale. The copolymer (AD-4060) with high zeta potential gave the best flocculation efficiency. The floc characterization was performed interms of floc size and FCMC. Based on the results it was proposed that, the charge neutralization and bridging are the main mechanisms for driving the flocculation. These copolymers show great promise in the flocculation of kaolin from aqueous streams in industries.

3.6 References

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FLOCCULATION OF KAOLIN USING COPOLYMER OF ACRYLAMIDE (AM) AND (3-ACRYLAMIDOPROPYL) TRIMETHYLAMMONIUM CHLORIDE (APTMAC)

CHAPTER-4

In this chapter we report on the synthesis of poly (AM-co-APTMAC) copolymers. The compositoin of APTMC was varied to obtain different copolymers. The polymers were characterized by NMR, GPC and Zeta potential. The flocculation efficiency was studied using kaolin suspensions. The flocs were characterized in terms of FCMC, ISR and optical microscopic analysis. Correlation was drawn between the flocculation efficiency and the molecular weight and charge of the flocculants.

J Appl Polym Sci 47286 (2018). doi:10.1002/app.47286

4.1 Introduction

Polyelectrolyte flocculants continue to attract major attention due to their importance in solid-liquid separations in a wide range of industries. Large numbers of cationic flocculants have been utilized for the flocculation of kaolin. Divakaran and Pillai [1,2] have used chitosan for flocculation of kaolin. Haijiany Li etal [3] have used starch based cationic polymer for kaolin flocculation. Hasan etal[4] have used cationic lignin polymers for kaolin flocculation. Kumar etal[5] have used cationic amylopectin based flocculant for kaolin separation. Flocculation and dewatering of kaolin suspension was performed using polyacrylamide in the presence of surfactants [6–8]. A few cationic monomers such as Diallyldimethylammonium chloride (DADMAC), 2-Acryloyloxyethyltrimethylammonium chloride (AOETMAC), 2-Methacryloyloxyethyltrimethylammonium chloride (MOETMAC), 3-Acrylamidopropyltrimethylammonium chloride (APTMAC) etc., have been copolymerized with acrylamide to synthesize cationic flocculants. Among these cationic monomers, APTMAC has a high reactivity ratio with acrylamide[9,10]. This higher reactivity ratio will result in higher incorporation of APTMAC into copolymer resulting in higher charge and molecular weight on the flocculant. A judicious combination of APTMAC along with acrylamide can yield cationic flocculants with desired properties.

In this work, we have synthesized cationic flocculant based on the combination of acrylamide (AM) and (3-Acrylamidopropyl) trimethylammonium chloride (APTMAC) for flocculation of kaolin suspension and demonstrated an efficient flocculation in very small dosages (3-10ppm) of flocculants. The chemical structure of copolymer was determined using ^{1}H and ^{13}C NMR spectroscopy. The flocculation efficiency is correlated to the zeta potential and molecular weight of the copolymer. Floc characterizations like filter cake moisture content (FCMC), initial settling rate (ISR) and optical micrographs of floc were studied and correlated to the flocculation with an increase in dosage.

4.2 Experimental

4.2.1 Materials and Methods

Acrylamide (AM), 3-Acrylamidopropyltrimethylammonium chloride (APTMAC) (75 wt-% aqueous solution), 2, 2'-azobis(2-methylpropionamide) dihydrochloride (V-50) were procured from Aldrich, USA and were used as received. Deionized water (conductivity 0.055 µS cm^{-1} at 25° C) was used for all the reactions. Acetone was purchased from Rankem, Mumbai, India. Kaolin was procured from Thomas Baker chemicals, Mumbai, India. Analytical grade Sodium nitrate was obtained from Merck, Mumbai, India and used as received.

4.2.2 Synthesis of cationic flocculant based on Acrylamide and APTMAC

Cationic flocculants were prepared by copolymerization of acrylamide and APTMAC monomer using solution polymerization technique. V-50 was used as a thermal initiator. In a typical reaction, 5 g AM and 3.64 g (4.85 ml) APTMAC were dissolved in 90 ml of DI water in a flange type double jacketed reaction vessel equipped with an overhead stirrer, nitrogen gas inlet, and a thermowell. The initial total concentration of the monomers in the reaction mixture was 10 Wt %. The reaction mixture was purged with nitrogen gas for 30 minutes to remove any dissolved oxygen. The temperature of the reaction mixture was increased to 56° C. Then, 0.475 g V-50 initiator was added to the reaction mixture with continuous stirring and nitrogen gas purging for 6 h. The viscosity of the reaction mixture increased rapidly, indicating the formation of the copolymer. After 6 h, the polymer was precipitated in acetone and dried in an oven at 40° C under vacuum. Three copolymers with different feed ratios (moles) of AM and APTMAC (AM: APTMAC; 80:20, 50:50 and 40:60) were prepared and denoted as AA-8020, AA-5050 and AA-4060, respectively. The chemical structure of the copolymers was characterized using ^{1}H and ^{13}C NMR spectroscopy. The molecular weights of the copolymers were determined using gel permeation chromatography (GPC).

4.3 characterizations

4.3.1 Gel permeation chromatography (GPC)

The molecular weight (MW) of the copolymers was determined using Agilent 1200 GPC with Shodex OH pak SB-800 series columns. The mobile phase used was 0.25 N $NaNO_{3,}$ with a flow rate of 0.4 ml/min. 100 µl was the sample injection volume. The GPC column temperature was maintained at 40° C, and polyacrylamide standards were used for calibration.

4.3.2 Zeta potential measurements

Zeta potential and Particle size measurements were carried out at 25° C using Brookhaven 90 plus particle size analyzer, USA. The polymer concentration used was 0.1 g dL^{-1}.

4.3.3 NMR studies

The ^1H and ^{13}C NMR spectra of copolymers were recorded on Bruker AV 500 MHz and Bruker AV 400 MHz spectrometer respectively. The copolymer samples were prepared in D_2O.

4.3.4 Flocculation test for kaolin

Kaolin (particle size 1µ) suspension in water (3.0 wt-%) was used for the flocculation test. Kaolin suspension was prepared by stirring kaolin solution using overhead stirrer at 400 rpm for 30 min. In a typical flocculation study, to a 100 ml kaolin suspension, a known volume of flocculant solution (1g L^{-1}) was added and stirred for 5 min (with 300 rpm for first 2 min and at 100 rpm for 3 min) using an overhead stirrer, Heidolph RZR 2012, Germany with cross blade impeller. After 5 min, stirring was stopped and immediately 1 ml aliquot was drawn from the central portion of the solution. The transmittance (%) was measured for this solution using Shimadzu UV-PC 1601 UV-Vis spectrophotometer, Japan in the kinetic mode at 700 nm. This value of the transmittance was taken as zero minute reading. The solution was allowed to settle and the aliquots were drawn every 3 min for ~40 min and transmittance was measured. Then transmittance vs time was plotted to find out the time required for maximum flocculation to occur. For the zeta potential measurement, the supernatant liquid was taken after 40 min flocculation with different dosages of flocculant.

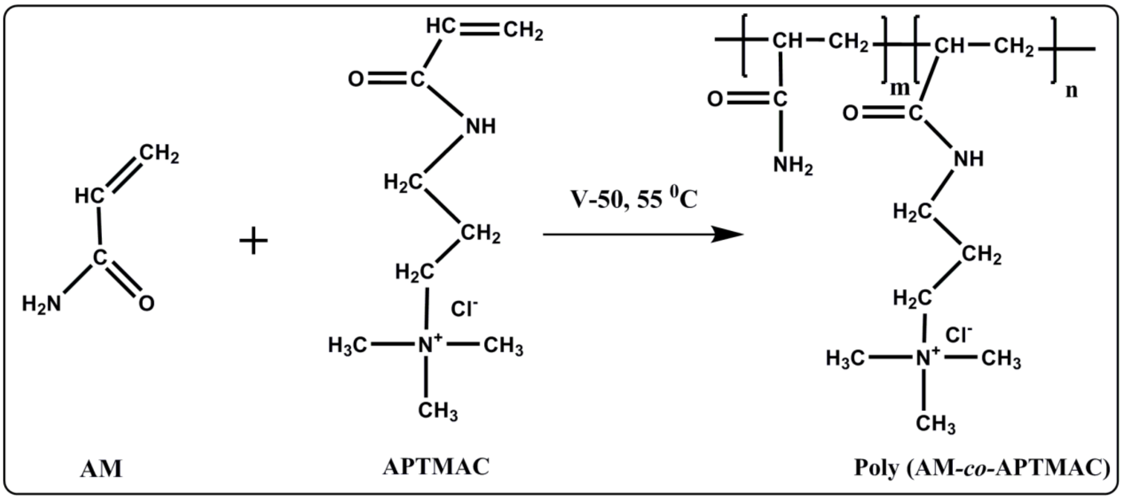
4.3.5 Floc characterization

The procedures for floc characterizations were reported earlier in chapter-3 under section 3.3.7 ***(Initial settling rate (ISR) 3.3.7.1, Filter Cake Moisture Content (FCMC) and optical microscopy studies 3.3.7.2)***

4.4 Results and Discussion

4.4.1 Synthesis and characterization of flocculants

Cationic flocculants were prepared using acrylamide and APTMAC at three different mole ratios (AM: APTMAC; 80:20, 5050 and 40:60). Amongst a few cationic monomers available, APTMAC was chosen considering its high reactivity ratio with AM. Synthesizing an efficient cationic flocculant lies in obtaining high molecular weight and high zeta potential copolymer. The acrylamide monomer with its high ratio of propagation to termination constant, gives high molecular weight to the polymer. Whereas, the cationic monomer provides an overall charge density to the copolymer. Therefore, it is very important to critically balance both the monomer contents to obtain high molecular weight and high zeta potential polymer for efficient flocculation. Accordingly, three copolymers, with varying AM and APTMAC content were prepared. The quantitative yields of the copolymers AA-8020, AA-5050 and AA-4060 were determined to be 91, 92, and 93% respectively. The copolymers were coded as AA-8020, AA-5050 and AA-4060, respectively. The reaction scheme for the synthesis of poly (AM-co-APTMAC) is shown in scheme-4.1. The structural characterization of the copolymers was carried out using ^{1}H and ^{13}C NMR spectroscopy.



Scheme-4.1: Reaction scheme for the synthesis of poly (AM-co-APTMAC)

4.4.2 Chemical structure by NMR spectroscopy

We show in figure-4.1, the ^{1}H NMR spectra of poly (AM-co-APTMAC) [AA-4060] and a homopolymer of polyacrylamide. The methyl ($-CH_3$) proton peaks of APTMAC appear at 3.4 ppm and the methylene ($-CH_2-$) protons of APTMAC attached to nitrogen atom give peaks in the range of 3.2 - 3.3 ppm. The methylene ($-CH_2-$) proton peaks of the backbone chain of AM and APTMAC appear in the range of 1.6 - 1.7 ppm. All the characteristic peaks of the copolymer assigned, agree with those reported in the literature. [11,12]

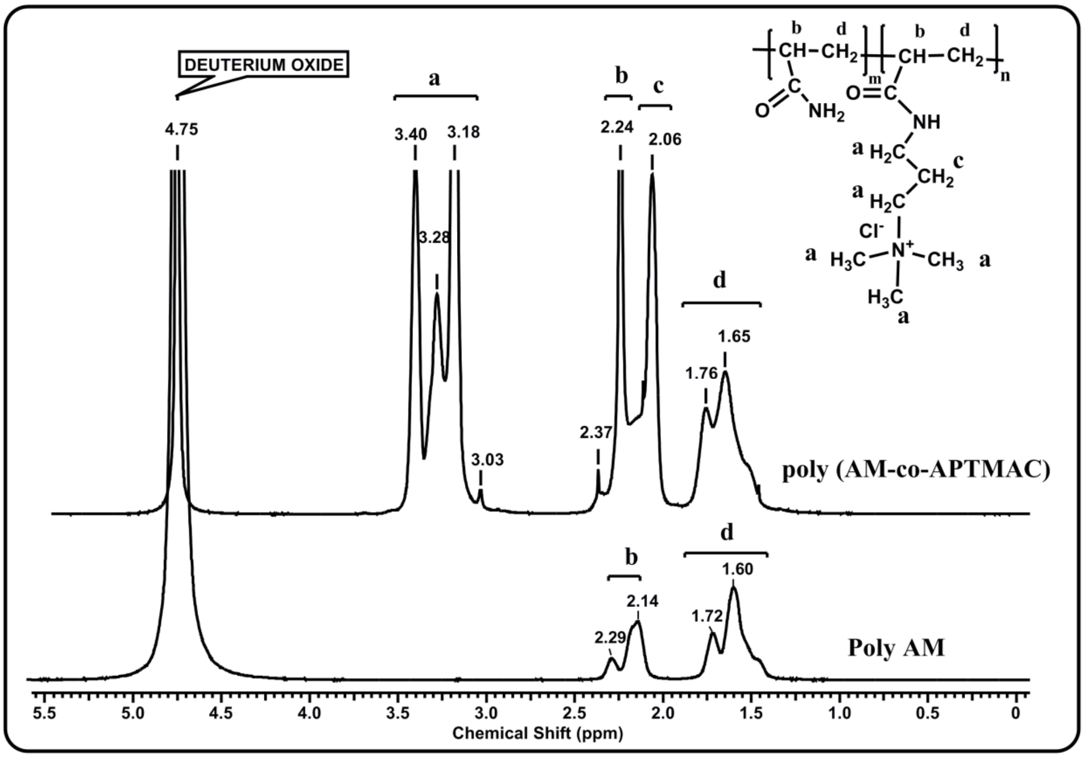


Figure-4.1: 500 MHz ^{1}H NMR spectra for Polyacrylamide and Poly (AM-co-APTMAC) [AA-4060]

We also show in Figure-4.2, the ^{13}C NMR spectrum of poly (AM-co-APTMAC) [AA-4060]. The methyl ($-CH_3$) carbon peaks of APTMAC appear at 53.17 ppm and the peaks for methylene ($-CH_2-$) carbon of APTMAC attached to amide nitrogen appear at 36.45 ppm and methylene ($-CH_2-$) carbon of backbone chain of AM and APTMAC appear at 35.01 ppm. The methylene ($-CH_2-$) carbon of APTMAC attached to nitrogen gives a peak at 64.22 ppm and the peak for methylene ($-CH_2-$) carbon next to carbon attached to nitrogen appears at 22.58 ppm. All the characteristic peaks of the copolymer assigned agree with the earlier reported values[13]. Both the ^{1}H and ^{13}C NMR spectra confirm the chemical structure of the copolymer.

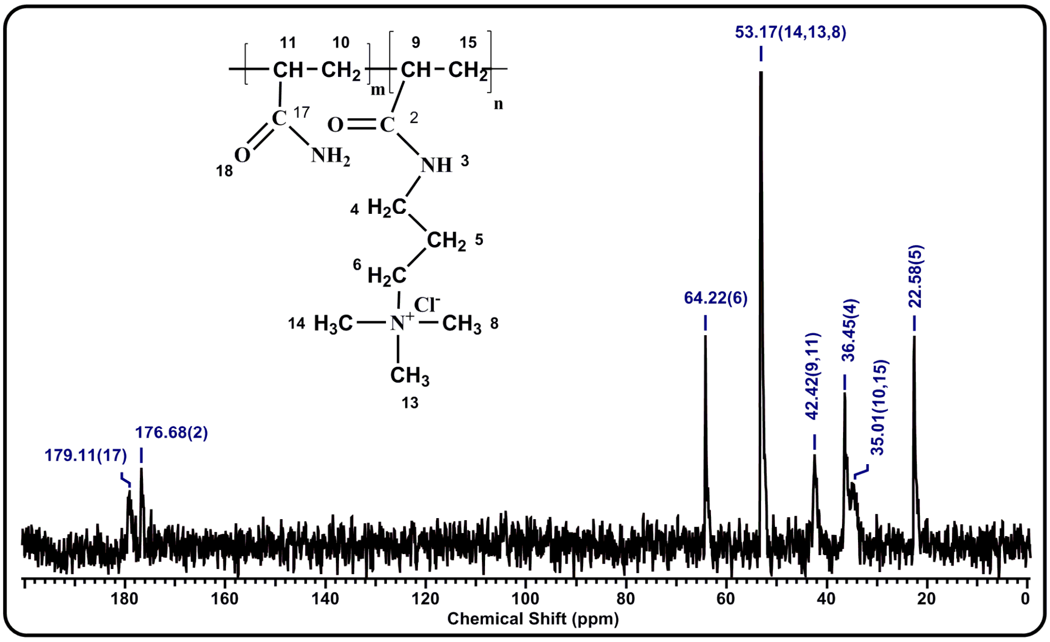


Figure-4.2: 400 MHz ^{13}C NMR spectra for Poly (AM-co-APTMAC) [AA-4060]

Figure-4.3 and 4.4 represent the ^{1}H and ^{13}C stacked NMR spectra for all the three compositions AA-8020, AA-5050 and AA-4060 respectively. It can be clearly seen that the intensity of peaks for APTMAC increases from AA-8020 to AA-4060, indicating increased incorporation of APTMAC with increasing feed ratio.

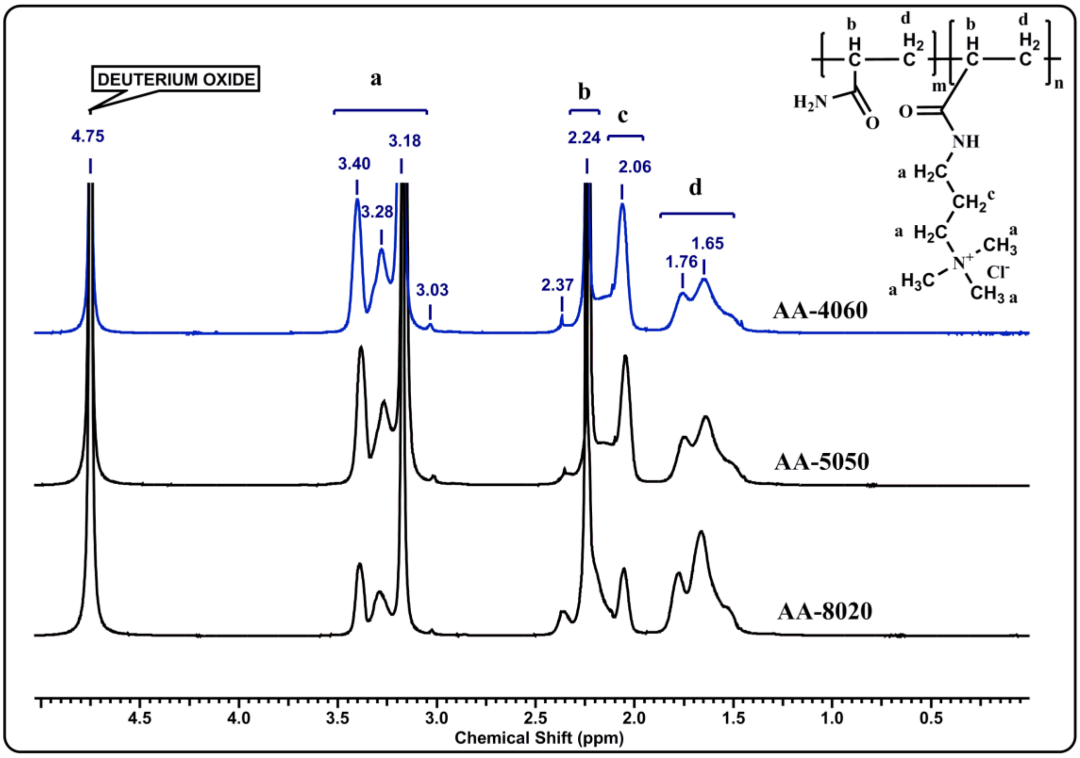


Figure-4.3: 500 MHz ^{1}H NMR spectra for AA-8020, AA-5050 and AA-4060

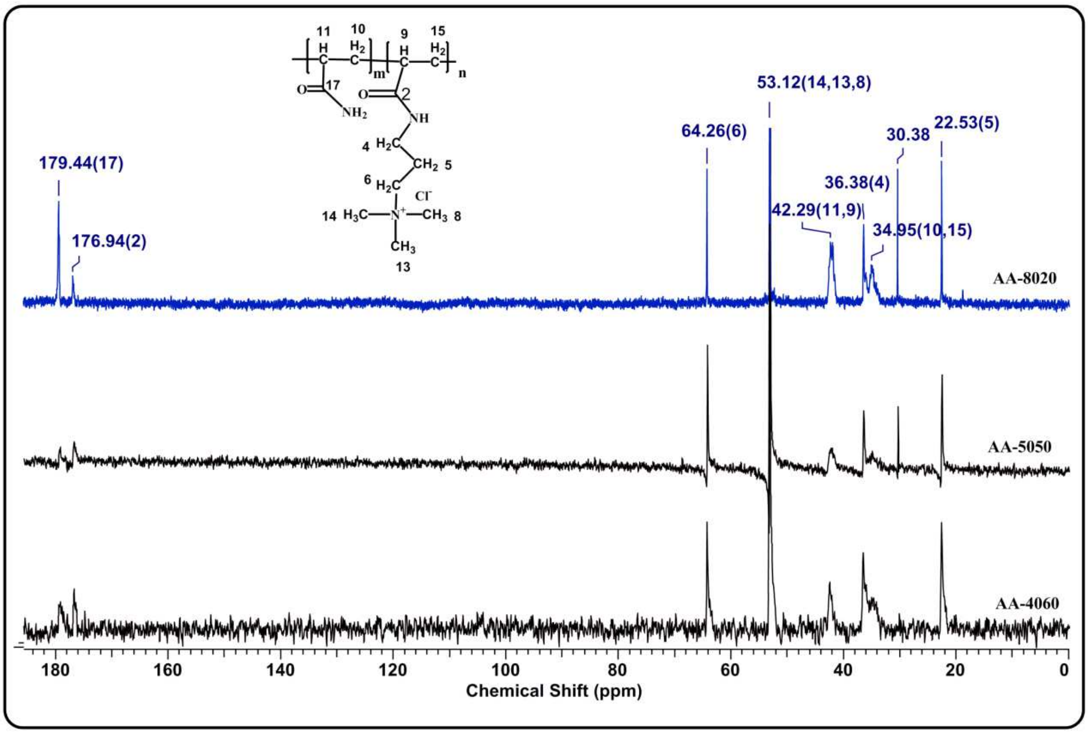


Figure-4.4: 400 MHz ^{13}C NMR spectra for AA-8020, AA-5050 and AA-4060

4.4.3 Molecular weight and zeta potential

The molecular weight and zeta potential of the copolymers were determined using GPC and particle size analyzer, respectively. We show in table-4.1 the molecular weights and zeta potential of AA-8020, AA-5050 and AA-4060 samples.

Table-4.1: Molecular weight and Zeta potential of copolymers

Samples	**M_w (Kg mol^{-1})**	**M_n (Kg mol^{-1})**	**PDI (M_w/M_n)**	**pH**	**Zeta potential (mV)**
AA-8020	275	166	1.6	6.5-7.0	(+) 52.0 - 55.0
AA-5050	207	169	1.22	6.5-7.0	(+) 62.0 - 66.0
AA-4060	185	162	1.1	6.5-7.0	(+) 90.0 - 93.0
Kaolin	-	-	-	6.5-7.0	(-) 18.0 - 20.0

It can be readily seen that when the acrylamide content in the copolymer is high, the copolymer yields high molecular weight but low zeta potential (AA-8020). Whereas, the high content of cationic comonomer, APTMAC (AA-4060) gives higher zeta potential due to the presence of high charge density on the polymer and yields low molecular weight copolymer. The copolymer with equal feed ratio shows the values in between both the AA-8020 and AA-4060. The particle size of the polymer also increases with the increase in APTMAC content. This is because the increased APTMAC content will increase the charge on the polymer. This leads to charge repulsion and open coil confirmation of polymer making it to increase in size. This open coil confirmation is favourable for effective binding to cause flocculation.

4.4.4 Flocculation of Kaolin

The flocculation efficiency of copolymers, AA-8020, AA-5050 and AA-4060 on kaolin aqueous suspension was examined by measuring the transmittance on kaolin suspension after the equilibrium flocculation (~40 min). The kaolin bears a negative charge on the surface in the pH range of 6.5 - 7.5 and exhibits the zeta potential of (-) 18 - 20.0 mV. The average size of kaolin particles was ~1.0 µm. The efficiency of flocculation of kaolin suspension (3.0 wt %) was investigated at different dosages of flocculants.

A typical set-up for the kaolin flocculation is shown in figure 3.7 of chapter-3. Figure-3.7a shows the kaolin suspension before the addition of flocculant which is stable and looks milky. Upon addition of cationic flocculant and initial stirring milky suspension turns into a clear solution after stopping the stirring (figure-3.7b). The kaolin particles begin to settle at the bottom the transmittance of the clear solution was measured. Similar experiments were carried out for different dosages of flocculants.

Figure-4.5 shows the percentage transmittance of kaolin supernatant liquid vs different dosage of flocculants, AA-8020, AA-5050 and AA-4060 taken at pH 7 and at equilibrium flocculation time of ~ 40 min.

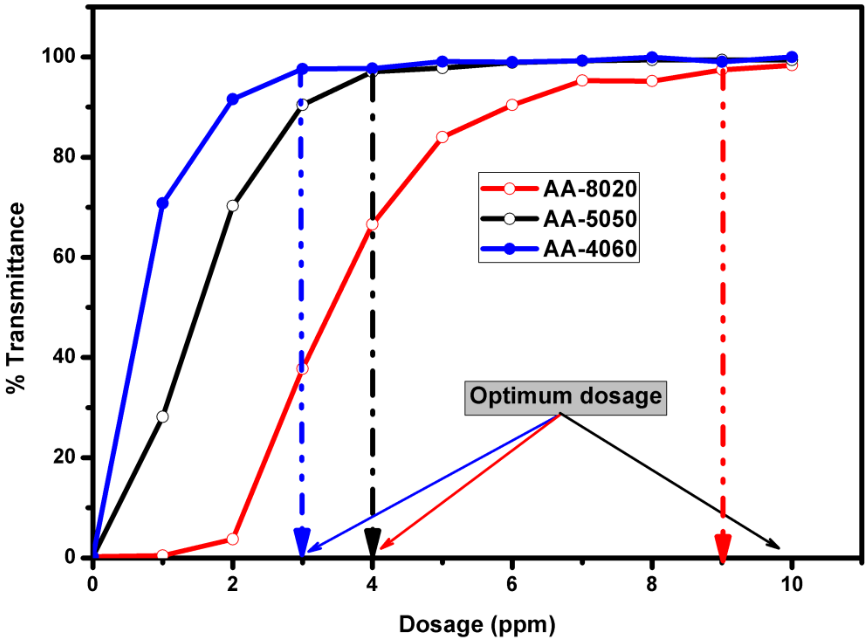


Figure-4.5: Transmittance of kaolin supernatant vs dosage of flocculants after 40 min of equilibrium flocculation

It can be revealed from the figure that, AA-4060 shows nearly 95-98 % transmittance at the dosage range of 3 - 5 ppm and remains constant till 10 ppm. The AA-5050 showed 95 -98% transmittance at the dosage range of 4 - 6 ppm. Whereas, AA-8020 flocculant showed 95-98 % transmittance at the dosage range of about 9 - 10 ppm. Therefore, the optimum dosage levels for AA-4060, AA-5050 and AA-8020 flocculants for kaolin flocculation can be considered as 3.0 ppm, 4 ppm and 9.0 ppm, respectively. These flocculants showed efficient flocculation and the optimum dosages were found to be quite low compared to the values reported earlier.[14]

The AA-4060 flocculant contains more of cationic polymer and exhibits a high degree of charge with high zeta potential (+ 93 mV). In this case, the driving force for the flocculation could be attributed to the charge neutralization followed by bridging. However, because of the high charge content of the polymer (AA-4060), the possibility of some contribution of patch mechanism for flocculation cannot be ruled out. In case of flocculant AA-5050 where, the charge is moderate with moderate zeta potential (+ 66 mV) has moderate molecular weight (207 Kg mol^{-1}). Here the driving force for flocculation is charge neutralization followed by bridging. For the flocculant AA-8020, higher dosage level (~9.0 ppm) was required to get 95-98% transmittance in the flocculation. In AA-8020 flocculant, the charge density is low (zeta potential + 55mV) but the molecular weight is high (275 Kg mol^{-1}). Because of the high molecular weight, the long polymer chain can get attached to a large number of kaolin particles and the flocculation can occur through the bridging mechanism. The requirement of more number of polymer chains for bridging leads to high optimum dosage for AA-8020. These observations clearly indicate that charge density on the polymer plays a dominant role in the flocculation of kaolin suspension studied here.

We also measured the zeta potential of kaolin supernatant solution as a function of different dosage of flocculants AA-8020, AA-5050 and AA-4060. The results are shown in figure-4.6.

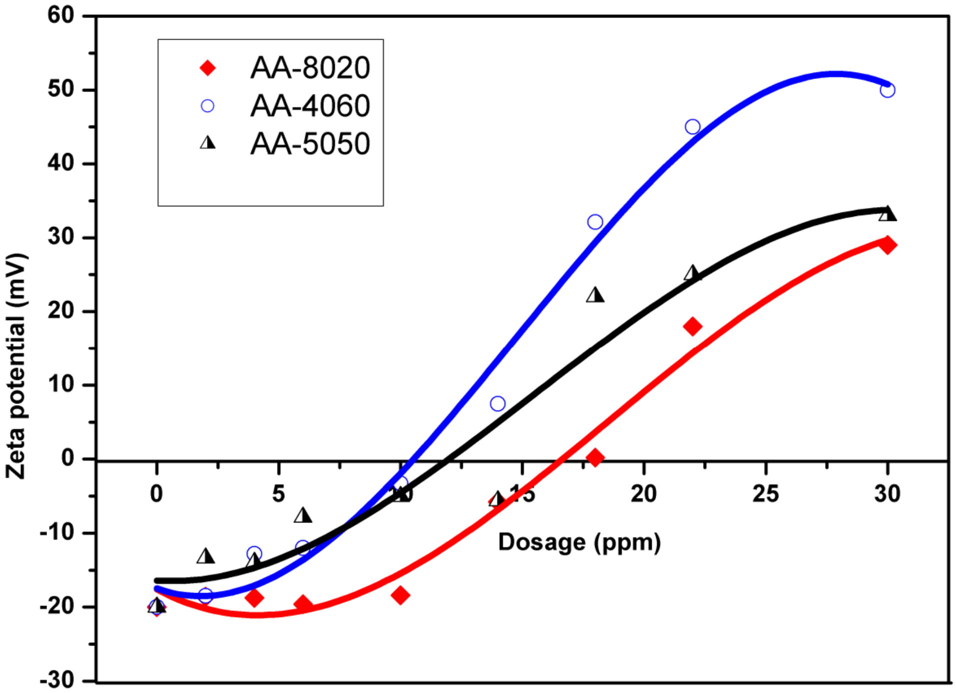


Figure-4.6: Zeta potential of kaolin suspension supernatant at different dosages after equilibrium flocculation using AA-8020, AA-5050 and AA-4060

It is observed that, the zeta potential of kaolin solution changed from (-) 20 mV to (+) 50 mV with an increase in the dosage of flocculants. This is due to the fact that the oppositely charged flocculants neutralized and diminished the surface charge of the suspended kaolin particles resulting into the formation of kaolin flocs. However, it is surprising to see from the figure-4.6 that the zeta potential of the kaolin supernatant did not reach zero value at 95% transmittance for the optimum dosage of AA-8020, AA-5050 and AA-4060 flocculants. The zeta potential values remained at (-) 10 to (-) 20 mV. This could be due to the presence of still some very fine particles of unneutralized kaolin present in the supernatant liquid. Further, the kaolin fine particles are partially or heterogeneously bound by flocculants to form micro flocs that cannot settle down and hence they float and show reduced zeta potential value.

At higher dosage content, the zeta potential values crossed the zero value and attained positive zeta potentials. These observations clearly indicate that there seems to be a broad flocculation regime and the possibility of both charge neutralization and bridging mechanism followed for the flocculation.

It is also observed form the figure, that the dosages at which the zeta potential is zero for AA-8020, AA-5050 and AA-4060 were 16, 12 and 10 ppm respectively. These dosages are more than 3-4 times higher than the optimum dosage. At optimum dosage more than 95 % clarity or kaolin was flocculated and that supernatant water can be reused to suspend kaolin for the next cycle of kaolin mining. This will enormously improve the economy and efficiency of the recovery process.

4.4.5 Kinetics of flocculation

In order to understand the kinetics of flocculation, we measured the percentage transmittance of kaolin suspension as a function of time for flocculants, AA-8020, AA-5050 and AA-4060 at their optimum dosage and at different dosages. Figure-4.7 shows the results of % transmittance vs time for three flocculants at their optimum dosage. The figures 4.8 to 4.10 shows the results of % transmittance vs time for three flocculants at different dosages.

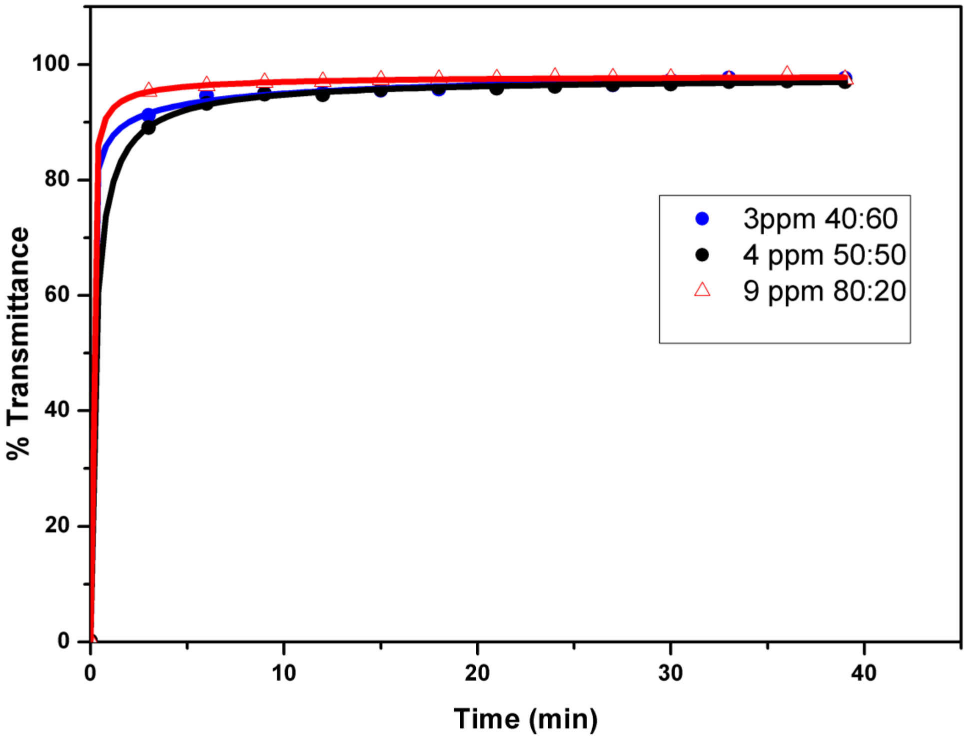


Figure-4.7: Kinetics of flocculation at optimum dosage

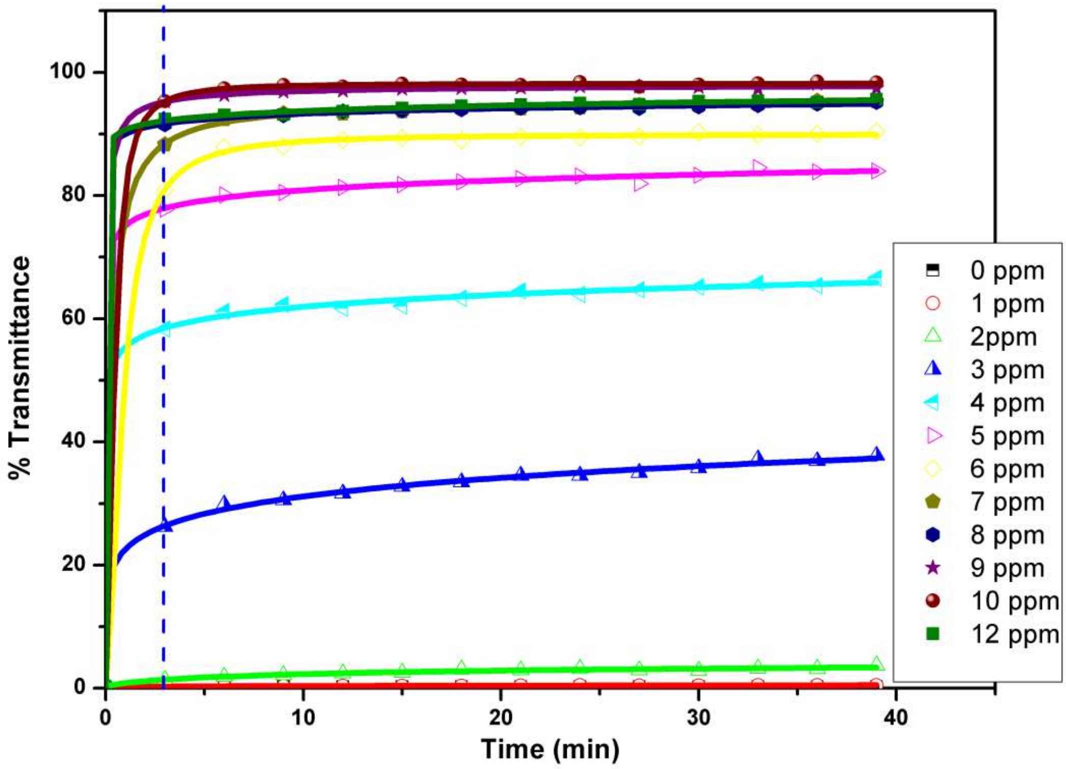


Figure-4.8: Kinetics of flocculation at different dosages of AA-8020

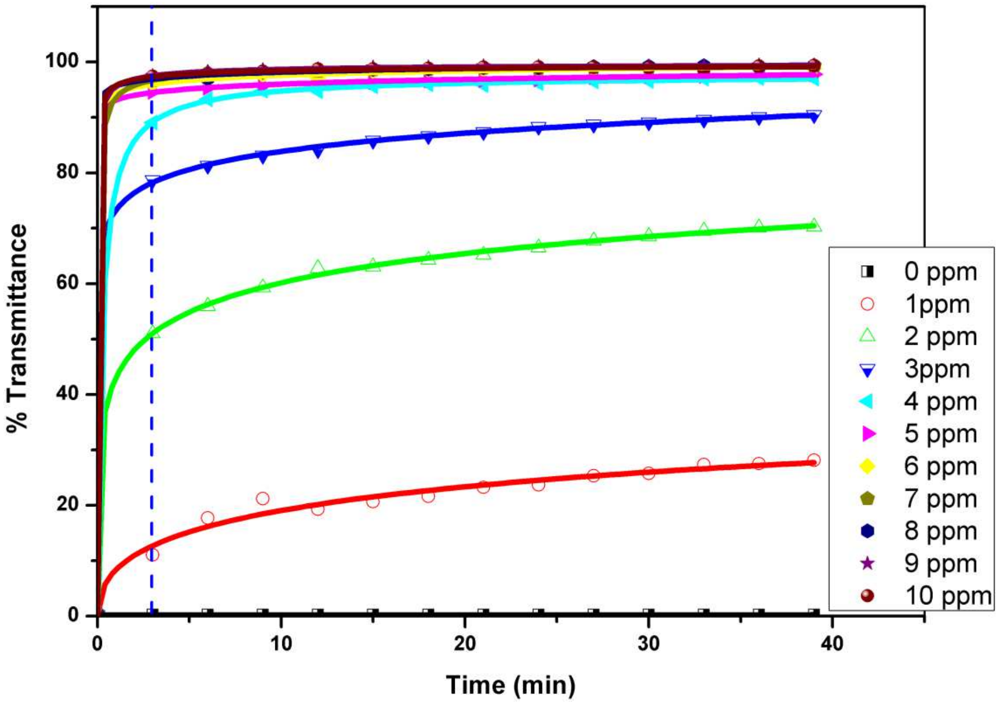


Figure-4.9: Kinetics of flocculation at different dosages of AA-5050

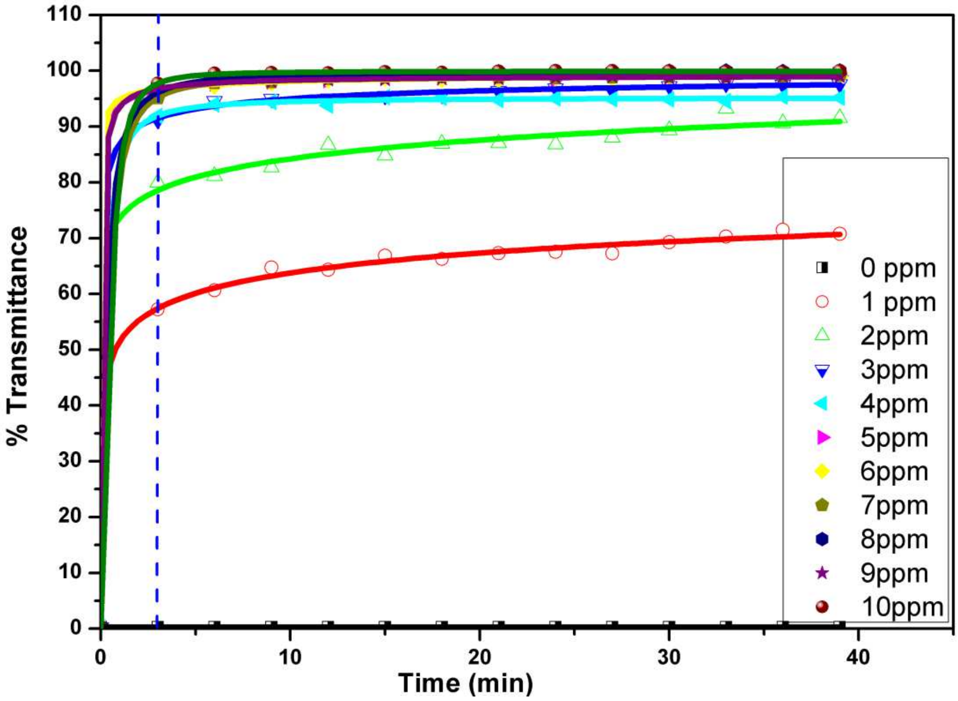


Figure-4.10: Kinetics of flocculation at different dosages of AA-4060

It is clearly seen that 95 - 98% transmittance could be achieved within 3 min of flocculant addition to the kaolin suspension at their respective optimum dosages of flocculants. The AA-4060 flocculant gave maximum % transmittance at an optimum dosage of 3 ppm. These studies indicate that the charge on the flocculant (zeta potential) plays a dominant role compared to molecular weight for the efficient flocculation of Kaolin suspension.

From figure-4.8 to 4.10, it can be seen that the dosages prior to the optimum dosage also shows reasonably good % transmittance, which indicates that the flocculants have a broader flocculation range.

4.4.6 Floc characterization

4.4.6.1 Initial settling rate (ISR)

Figure 4.11 shows the interface height vs time for flocculants AA-4060, AA-5050 and AA-8020 at their optimum dosage levels of 3, 4 and 9 ppm respectively. It can be readily seen that, the interface height decreases rapidly within the first 100 seconds and remains almost constant after 250 seconds for all the flocculants. This predicts the initial settling rate of ~0.1cm s^{-1} for the flocculants. These observations clearly reveal that AA-4060, AA-5050 and AA-8020 flocculate kaolin suspension very rapidly.

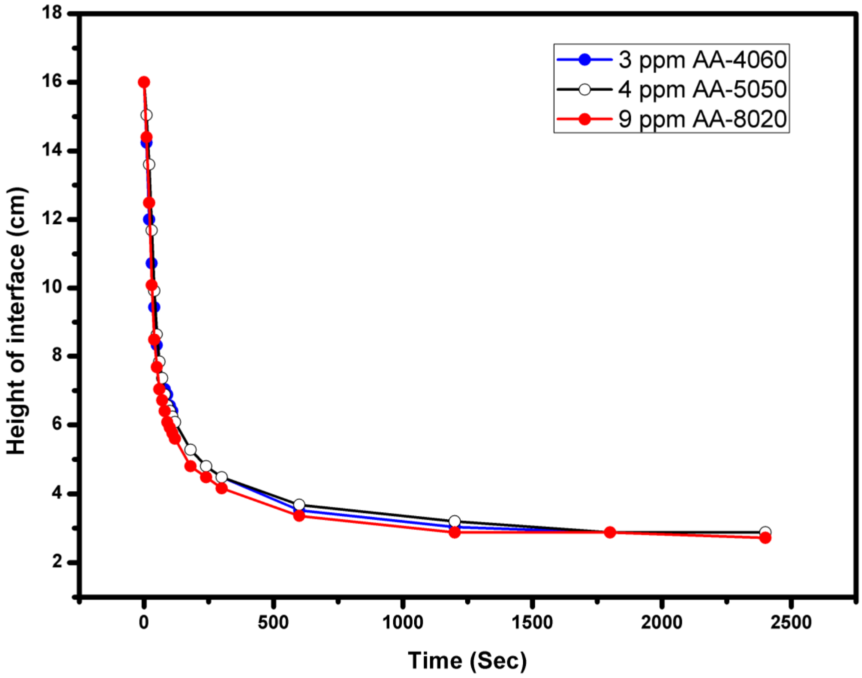


Figure-4.11: Initial settling rate of AA-4060, AA-5050 and AA-8020

4.4.6.2 Filter Cake Moisture Content (FCMC)

Figure-4.12 shows the results of FCMC for AA-4060, AA-5050 and AA-8020 at different dosages. The FCMC of AA-4060, AA-5050 and AA-8020 remained independent with respect to dosage in the range of 2 to 10 ppm used in this work. However, the earlier reports indicate a decrease in FCMC with an increase in dosage levels when the dosage levels are quite high (~40 to 50 ppm). We observed a very small change in FCMC with these low dosage levels. Nevertheless, these small dosages (2-10 ppm) were found to be efficient in flocculation and gave more than 95 % transmittance in the flocculation process. The FCMC of AA-4060 showed slightly higher FCMC to AA-8020 and AA-5050, which could be attributed to the high charge in the polymer which results into increased hydrophilicity of flocculant and absorbs more moisture. The AA-5050 showed less FCMC value than both AA-8020 and AA-4060; this may be because AA-5050 has lesser molecular weight than AA-8020 and lesser charge than AA-4060 hence the water retention is less.

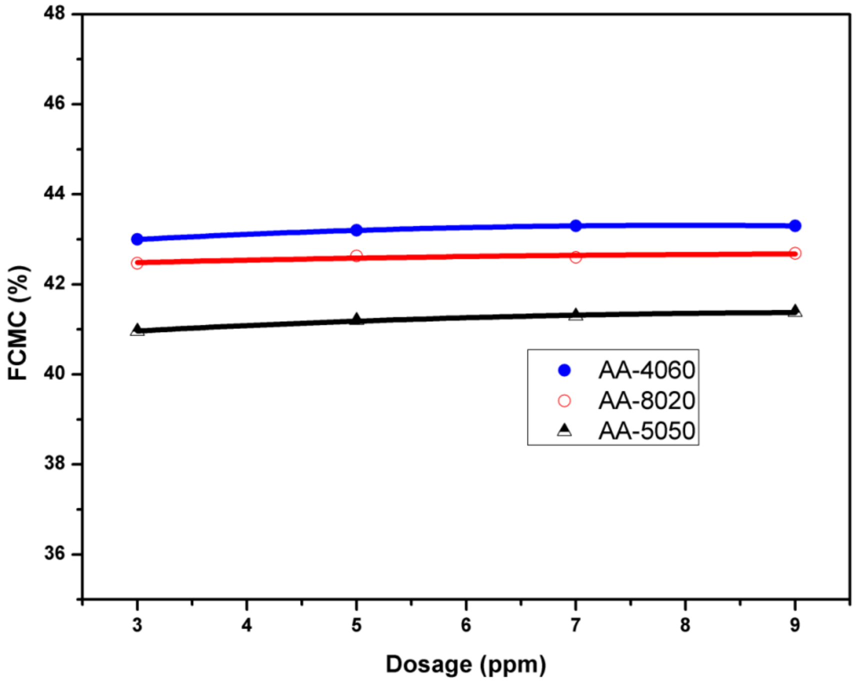


Figure-4.12: Filter cake moisture content study of AA-4060, AA-5050 and AA-8020 at different dosages

The visual observation of the filter cakes after the flocculation using AA-4060, AA-5050 and AA-8020 at different dosages was made and photographs are shown in figure-4.13.

Figure-4.13: Photographs of filter cakes after flocculation and drying for AA-4060 (a-d) AA-5050 (e - h) and AA-8020 (i-l)

It is observed that, as the dosage increase, the surface of the filter cake becomes smoother and softer. This could be due to the formation of dense flocs at higher dosages of flocculant.

4.4.6.3 Optical microscopic studies

The optical microscopy was performed on kaolin flocs obtained under different dosages of AA-4060, AA-5050 and AA-8020 flocculants. The optical micrographs are shown in figure-4.14. Kaolin suspension without any flocculant does not show the flocs and one can see a uniform suspension [figure-4.14 (a)]

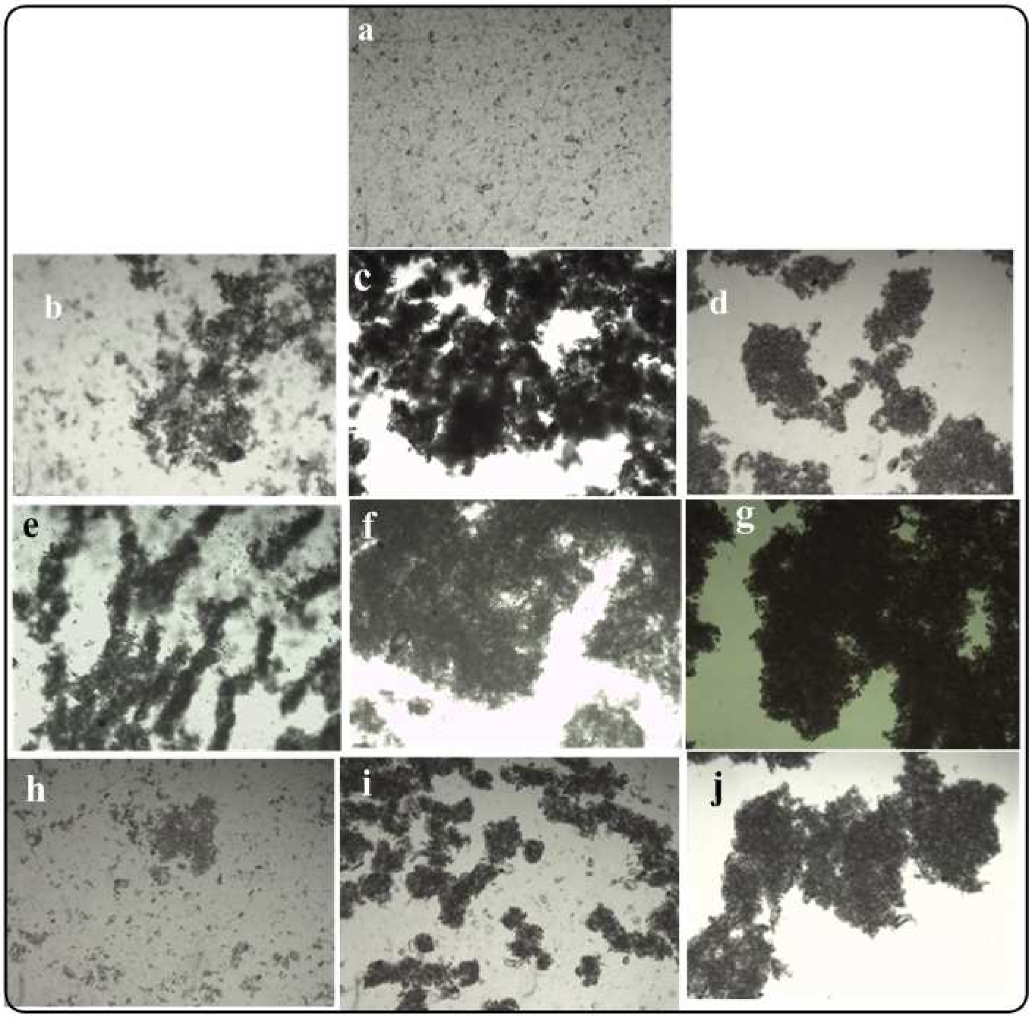


Figure-4.14: Optical micrographs of kaolin flocculation at different dosages Kaolin (a), AA-4060 (b-d), AA-5050 (e-g) and AA-8020 (h-j)

However, upon flocculation, kaolin flocs are observed very clearly and the floc size increases with the dosage of flocculant. The observed optimum dosages of 3, 4 and 9 ppm for flocculants AA-4060, AA-5050 and AA-8020 respectively show more than 95 % transmittance in the supernatant liquid after the floc formation. This is visible in the micrographs of figure-4.14 (b), (e) and (j).

4.5 Conclusions

In conclusion, we have shown that the cationic flocculants based on the copolymer of acrylamide (AM) and 3-acrylamidopropyltrimethylammonium chloride (APTMAC) efficiently flocculates kaolin from aqueous solution. Depending on the ratio of monomers, the copolymers could be obtained with different molecular weight and zeta potentials which are very important properties required for good flocculation. The optimum dosages for maximum flocculation were found to be 3.0, 4.0 and 9.0 ppm for AA-4060, AA-5050 and AA-8020 copolymers, respectively. The minimum time required for maximum flocculation was determined to be 3-4 minutes in the laboratory scale. The copolymer (AA-4060) with high zeta potential gave the best flocculation efficiency. The floc characterization was performed interms of floc size and FCMC. Based on the results it was proposed that the charge neutralization and bridging are the main mechanisms for driving the flocculation. These copolymers show great promise in the flocculation of kaolin from aqueous streams in industries.

4.6 References

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SYNTHESIS OF CHITOSAN GRAFT COPOLYMER FLOCCULANTS

CHAPTER-5

In this chapter we report on the graft polymerization of chitosan with APTMAC. The feed weight ratio of APTMAC was varied to get different graft copolymers. The characterization of graft copolymer was done using NMR, GPC and zeta potential measurements. The flocculation efficiency was studied using kaolin suspensions. The flocs were characterized by FCMC, ISR and optical microscopic analysis. The flocculation efficiency was correlated to charge and molecular weight of the polymer.

5.1 Introduction

The use of biopolymers for flocculation applications has been practiced since many decades. The bio polymer based flocculants mostly use polymers such as starch[1–5], cellulose[6–9], chitosan[10–15], Pullulan[16,17], guar gum[18–21], natural gums[22–24] etc. The advantage of using chitosan over other biopolymers is that it is not a feedstock for humans and animals and hence will not deplete the food source. The other advantages of using chitosan are, it is biodegradable, non-toxic and environmental friendly[25–30]. Chitosan is the second largest available carbohydrate polymer on earth next only to cellulose and is available in plenty at lesser cost. The use of chitosan alone as flocculant is not very effective for flocculating kaolin because of working pH limitations and also due to low molecular weight[12,31]. One of the major drawbacks of using chitosan is its solubility, because of inter and intra molecular hydrogen bonding, chitosan dissolves only in acidic solution of pH less than 5. At this acidic pH, there is a possibility of increased degradation of chitosan which results in reduction of its molecular weight and hence the flocculation efficiency[12]. The flocculant based on chitosan graft polymer which is also soluble in pH 6 and above is preferred to avoid its degradation and loss of flocculation efficiency. Chemical modification of chitosan by grafting, using vinyl monomers and monomers with cationic charge has been reported[10,14,27,32–35]. The grafting improves the solubility of chitosan by interrupting the inter and intra molecular hydrogen bonds. This addresses the issue of solubility and charge on chitosan for efficient flocculation. The graft polymers are partially biodegradable because of the polysaccharide backbone and are stable for shearing since the presence of flexible synthetic polymer chain is grafted onto a rigid or semi-rigid polysaccharide backbone. This flexible grafted chain helps in adsorption to the colloidal particles, improving the flocculation efficiency. There are many methods to graft chitosan but potassium persulfate induced free radical polymerization yields better grafted chitosan flocculants which are easily soluble in water. The other methods such as gamma radiation induced grafting results in graft polymers having lesser solubility in water[12]. There are many cationic monomers grafted onto chitosan. The use of (2-methacryloyloxyethyl)trimethylammonium chloride (MOETMAC) has been reported by Jian-Ping Wang et al[13,36]. The chitosan grafted MOETMAC shows broader pH flocculation range but has a limited solubility in water. The grafting of both acrylamide and MOETMAC was also reported[31] wherein, the acrylamide monomer contributes to increase the molecular weight and the MOETMAC enhances the charge density. The use of 3-acrylamidopropanetrimethylammonium chloride (APTMAC) for grafting onto chitosan and its application for kaolin recovery is not reported to the best of our knowledge.

In this work, we have synthesized cationic chitosan flocculants based on the graft copolymerization of chitosan (Chi) with cationic monomer (3-Acrylamidopropyl) trimethylammonium chloride (APTMAC) for flocculation of kaolin suspension and demonstrated an efficient flocculation in very small dosages (2-4 ppm) of flocculants. The chemical structure of the graft copolymer was determined using ^{1}H and ^{13}C NMR spectroscopy. The flocculation efficiency was correlated to the zeta potential and molecular weight of the copolymer. The characterizations of flocculants in terms of filter cake moisture content (FCMC), initial settling rate (ISR) and optical micrographs of kaolin suspension were studied and correlated to the flocculation of kaolin suspensions.

5.2 Experimental

5.2.1 Materials and Methods

Chitosan (Chi), 3-Acrylamidopropyltrimethylammonium chloride (APTMAC) (75 wt-% aqueous solution), potassium persulfate were procured from Aldrich, USA and were used as received. Deionized water (conductivity 0.055 µS cm^{-1} at 25° C) (TKA instruments, GmbH Stockland) was used for all the reactions. Laboratory grade acetone was purchased from Rankem, Mumbai, India. Kaolin was procured from Thomas Baker Chemicals, Mumbai, India. Chromatography grade acetic acid was obtained from Sisco Research Laboratory, Mumbai, India. Analytical grade sodium acetate was procured from Sd-fine chemicals, Mumbai, India and was used as received.

5.2.2 Synthesis of cationic flocculant: chitosan grafted with APTMAC

Cationic flocculants were prepared by grafting APTMAC onto chitosan using Potassium persulfate as an initiator. The free radical was generated on the chitosan backbone, which eventually polymerizes the APTMAC monomer into a graft chain. In a typical reaction, 3 g accurately weighed chitosan was transferred to a 500 ml capacity flanged double jacketed reactor, equipped with an overhead stirrer and a temperature controlled circulating water bath. To this 300 ml of 1% acetic acid aqueous solution was added (to obtain 1 Wt% chitosan solution). The solution was stirred till chitosan was completely dissolved. The argon gas was purged into the solution for 30 min to remove any dissolved oxygen. Then the temperature was increased to 56º C and 120 mg of $K_2S_2O_8$ was added with continuous stirring with continuous purging of argon gas. After 5 minutes of the addition of $K_2S_2O_8$, required amount of APTMAC monomer solution was added drop wise[37]. This delayed addition was performed to avoid possible homo polymerization of APTMAC. The reaction continued for 3 hours. The copolymer was recovered by precipitation in acetone and dried in a vacuum oven at 40° C. Three graft copolymers with different feed ratios (wt %) of APTMAC and chitosan (Chi: APTMAC; 1:3, 1:5 and 1:8) were prepared and denoted as CA-1:3, CA-1:5 and CA-1:8, respectively. The chemical structure of the copolymers was characterized using ^{1}H and ^{13}C NMR spectroscopy. The molecular weights of the copolymers were determined using gel permeation chromatography (GPC).

5.3 Characterizations

5.3.1 Gel permeation chromatography (GPC)

The molecular weight (MW) of copolymers was determined using Agilent 1200 GPC with Shodex OH pak SB-800 series columns. The mobile phase used was 0.3 N CH_3COOH and 0.2 N CH_3COONa with a flow rate of 0.8 ml/min. 100 µl was the sample injection volume. The GPC column temperature was maintained at 40° C, and Pullulan standards were used for calibration.

5.3.2 Zeta potential and Particle size measurements

Zeta potential and Particle size measurements were carried out at 25° C using Brookhaven 90 plus particle size analyzer, USA. The polymer concentration used was 0.1 g dL^{-1}.

5.3.3 NMR studies

The ^{1}H and ^{13}C NMR spectra of copolymers were recorded on Bruker AV 400 MHz spectrometer. The samples were prepared in D_2O.

5.3.4 Flocculation test for kaolin

Kaolin (particle size 1μ) suspension in water (3.0 wt-%) was used for the flocculation test. Kaolin suspension was prepared by stirring kaolin solution using overhead stirrer at 400 rpm for 30 min. In a typical flocculation study, to a 100 ml kaolin suspension, a known volume of flocculant solution (1g L^{-1}) was added and stirred for 5 min (with 300 rpm for first 2 min and at 100 rpm for 3 min) using an overhead stirrer, Heidolph RZR 2012, Germany with cross blade impeller. After 5 min, stirring was stopped and immediately, 1 ml aliquot was drawn from the central portion of the solution. The transmittance (%) was measured for this solution using Shimadzu UV-PC 1601 UV-Vis spectrophotometer, Japan, in the kinetic mode at 700 nm. This value of the transmittance was taken as zero minute reading. The solution was allowed to settle and the aliquots were drawn at a predetermined time till 40 min and transmittance was measured. Then transmittance vs time was plotted to find out the time required for maximum transmission to occur. For the zeta potential measurement, the supernatant liquid was taken after 40 min of flocculation. Solutions with different dosages of flocculant were examined.

5.3.5 Floc characterization

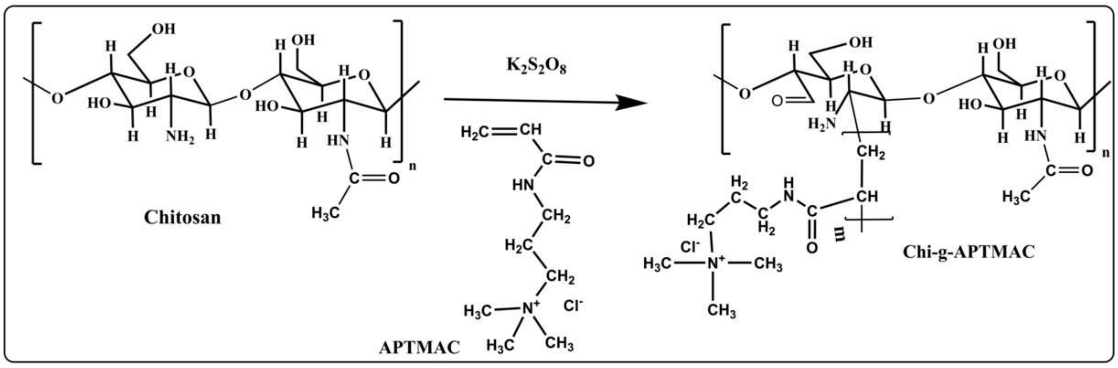
The procedures for floc characterizations were reported earlier in chapter-3 under section 3.3.7 (***Initial settling rate (ISR) 3.3.7.1, Filter Cake Moisture Content (FCMC)*** *and* ***optical microscopy studies 3.3.7.2)***

5.4 Results and Discussion

5.4.1 Synthesis and characterization of flocculants

Chitosan is structurally similar to cellulose, but it has amino (-NH_2) groups and acetamido (-$NHCOCH_3$) groups at the C_2 position of the anhydroglucose unit (AGU). These functional groups help in the chemical modification of chitosan to improve its solubility and widen its applications. Among various methods, graft copolymerization is the most attractive and a large number of vinyl monomers have been graft copolymerized onto chitosan using free radical initiation or γ-irradiation techniques. In the chitosan grafted copolymers, the rigid nature of chitosan can give a more extended conformation in solution along with a high charge density. On the other hand, the grafted polymer chain gives flexibility to the overall polymer. Chitosan is a unique polysaccharide with a positive charge in its structure in the acidic medium and helps in synthesizing cationic flocculants.

Grafting of cationic monomers onto chitosan can enhance the charge density of the copolymer which is generally a desired parameter for an efficient flocculant. In this work, a cationic monomer namely 3-acrylamidopropanetrimethylammonium chloride (APTMAC) was chosen to graft copolymerize onto chitosan due to its high reactivity ratio[38,39]. Copolymers with different contents of APTMAC (Chitosan: APTMAC Wt% 1:3; 1:5 and 1:8) were synthesized and denoted as CA-1:3, CA-1:5 and CA-1:8 respectively. The reaction pathway for the synthesis of chitosan-g-APTMAC is shown in scheme-5.1. The quantitative yields of the graft copolymers CA-1:3, CA-1:5 and CA-1: 8 were 42, 43, and 56% respectively.



Scheme-5.1: Reaction scheme for the synthesis of chitosan-g-APTMAC copolymers

5.4.2 Chemical structure by NMR spectroscopy

We show in figure-5.1, the ^{1}H NMR spectrum of representative CA-1:8 and chitosan. The methyl (-CH_3) proton peaks of APTMAC appear at 3.3 ppm and the methylene (-CH_2-) protons of APTMAC attached to nitrogen atom give peaks in the range of 3.2–3.3 ppm. The methyl (-CH_3) proton peak of the acetyl group of N-acetyl glucosamine appears at 2 ppm, the proton peak for H_2 of chitosan appear at 3.0 ppm and the proton peaks for ring H_3 to H_6 of chitosan appear at 3.5 - 3.8 ppm. All the characteristic peaks of the graft copolymer assigned match with those reported in the literature[16,40,41].

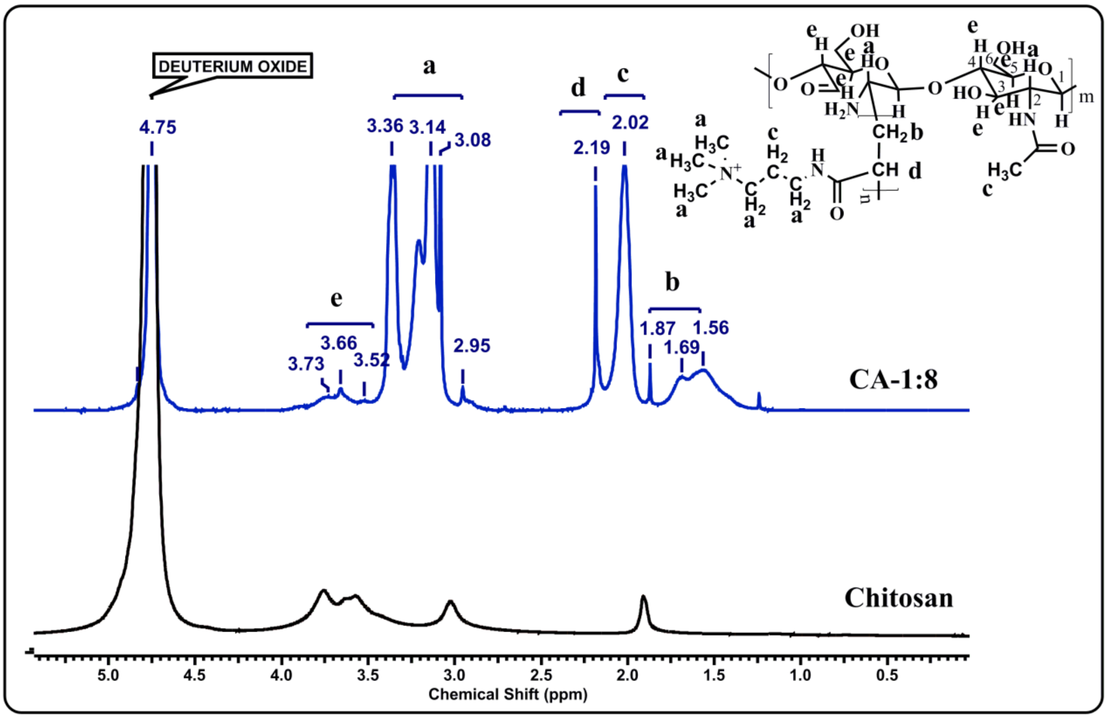


Figure-5.1: 400 MHz ^{1}H NMR spectrum for chitosan and CA-1:8

Figure-5.2 shows the representative ^{13}C NMR spectrum of CA-1:5 and chitosan. The methyl (-CH_3) carbons of APTMAC appear at 53.1 ppm and the peaks for methylene (-CH2-) carbons of APTMAC attached to amide nitrogen appear at 36.5 ppm and methylene (-CH_2-) carbon of backbone chain of APTMAC appears at 36.0 ppm. The methylene (-CH_2-) carbon of APTMAC attached to nitrogen gives a peak at 64.1 ppm and peak for methylene (-CH_2-) carbon next to carbon attached to nitrogen, appear at 22.5 ppm. The carbons of the chitosan ring C5, C8 and C9 appear at 56.1, 71.7 and at 74.8 ppm respectively. The C6 carbon appears at 60.1 ppm. Both the ^{1}H and ^{13}C NMR spectra confirm the chemical structure of the graft copolymer in comparison with chitosan.

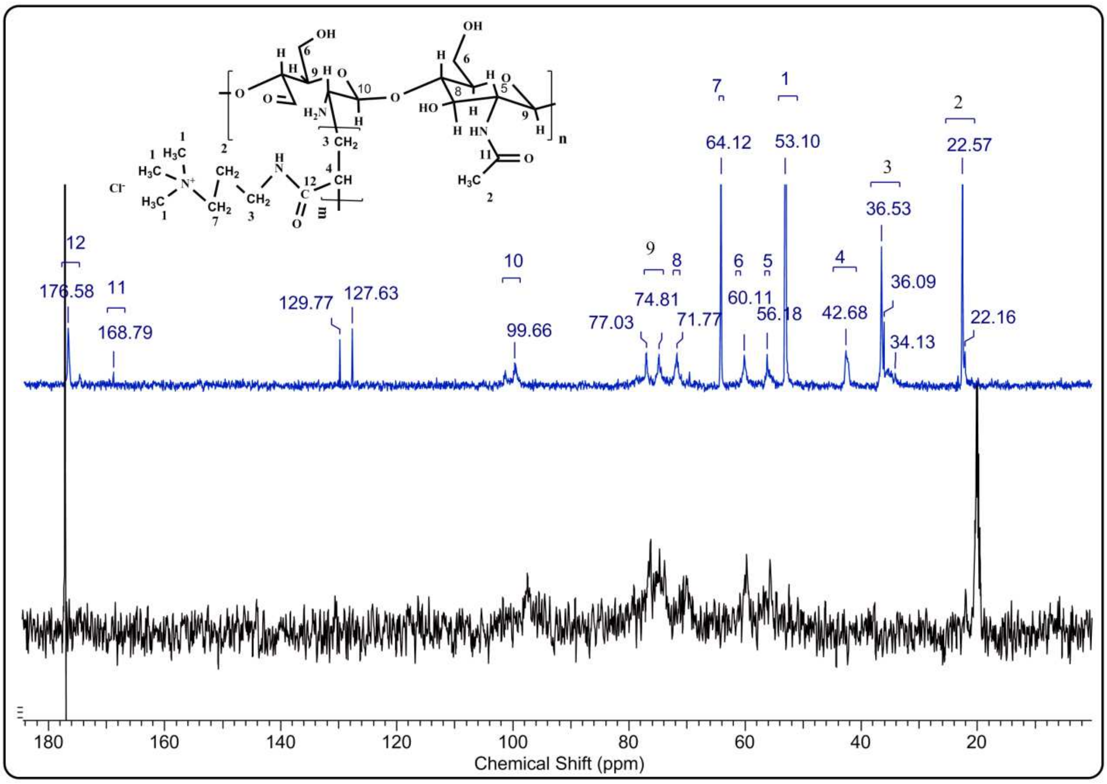


Figure-5.2: 400 MHz ^{13}C NMR spectrum of chitosan and CA-1:5

Figures 5.3 and 5.4 show the ^{1}H and ^{13}C stacked NMR spectra of all the three compositions respectively (CA-1:3, CA-1:5 and CA-1:8). The combined stack plots of the NMR spectra clearly indicate the successive increase in the intensities of the peaks for APTMAC with increase in its feed weight %.

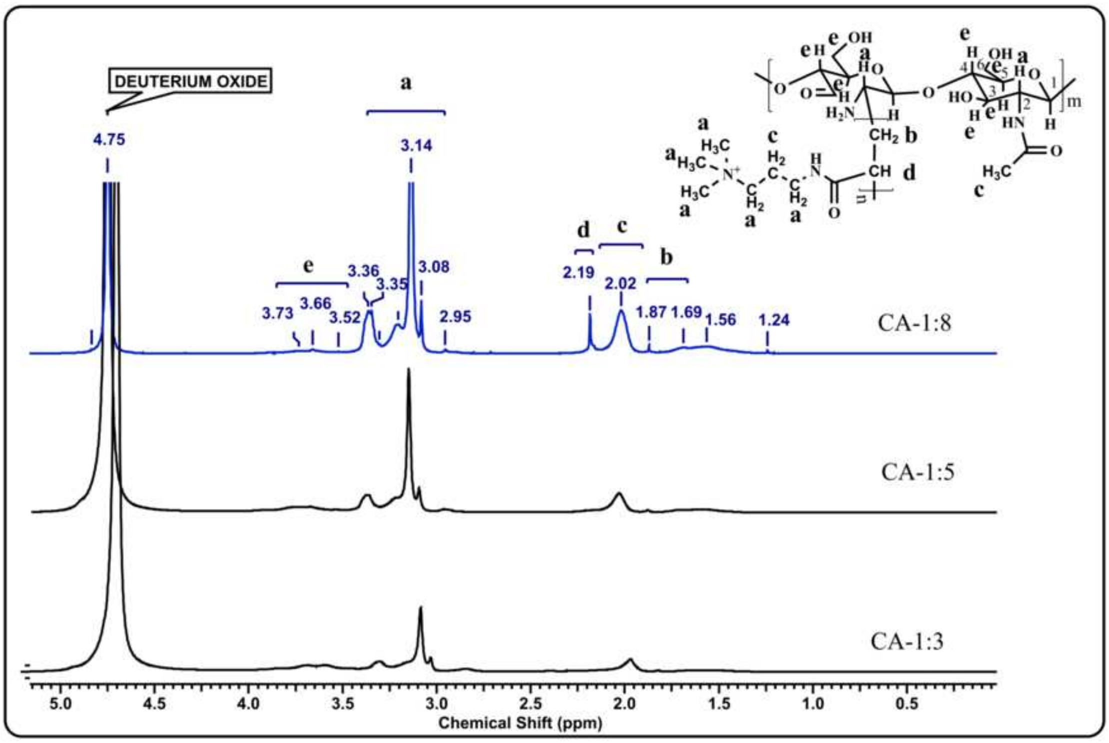


Figure-5.3: 400 MHz ^{1}H NMR spectra of CA-1:3, 1:5 and 1:8

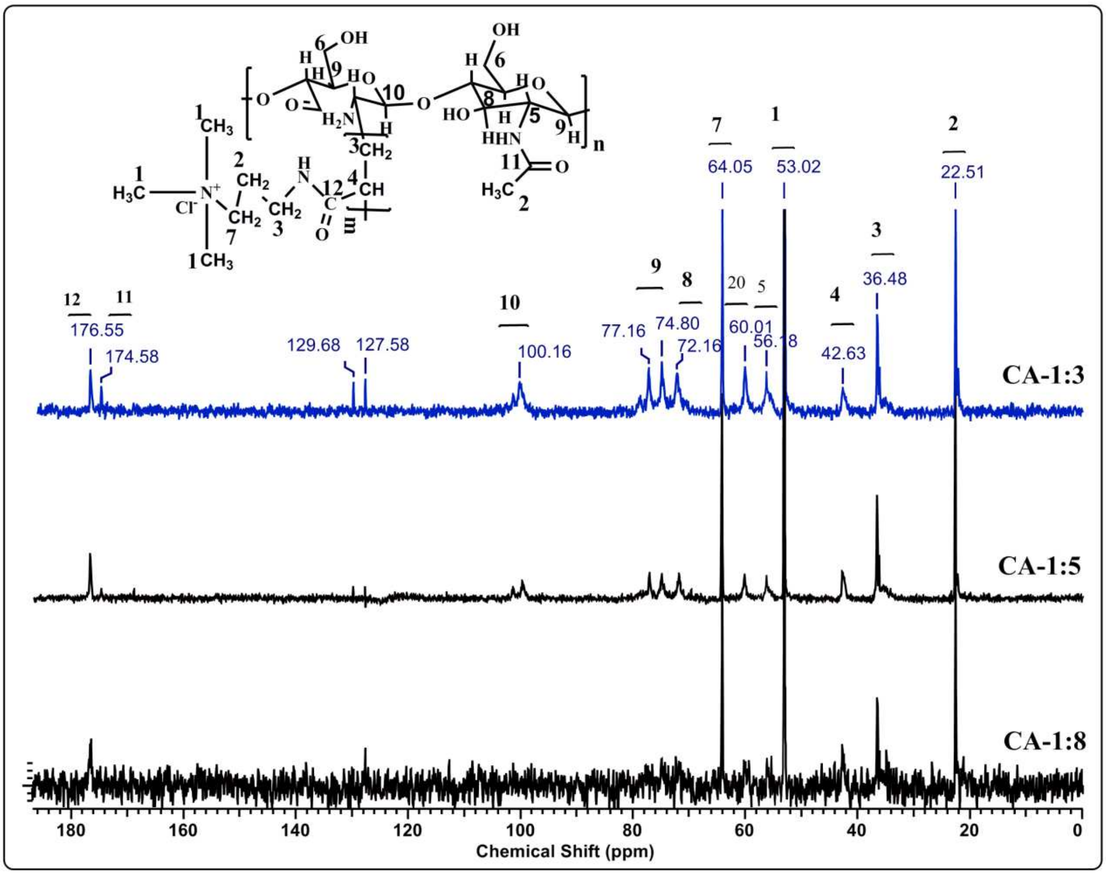


Figure-5.4: 400 MHz ^{13}C NMR spectrum of CA-1:3, 1:5 and 1:8

5.4.3 Molecular weight and zeta potential

The molecular weight and zeta potential of the graft copolymers were determined using GPC and particle size analyzer, respectively. Table-5.1 shows the molecular weights and zeta potential of CA-1:3, CA-1:5 and CA-1:8 samples.

Table-5.1: Molecular weight and Zeta potential of copolymers

Samples	**M_w** **(Kg mol^{-1})**	**M_n** **(Kg mol^{-1})**	**PDI** **(M_w/M_n)**	**pH**	**Zeta potential** **(mV)**
CA-1:3	408	285	1.4	6.0-7.0	(+) 32.0 - 35.0
CA-1:5	790	229	3.4	6.0-7.0	(+) 50.0 - 53.0
CA-1:8	826	316	2.6	6.0-7.0	(+) 55.0 - 58.0
Kaolin	-	-	-	6.0-7.0	(-) 18.0 - 20.0
Chitosan	375	-	-	-	-

It can be seen from table-5.1 that when the APTMAC content in the graft copolymer increases, the molecular weight and zeta potential increases from CA-1:3 to CA-1:8. The higher content of APTMAC in graft copolymer (CA-1:8) shows higher zeta potential value. The particle size of the polymer also increased with the increase in APTMAC content. This can be attributed to the extended coil conformation as a result of the repulsion in the like charges of the polymer arrangement by the presence of APTMAC. This extended coil confirmation is favourable for effective binding to cause efficient flocculation.

5.4.4 Flocculation of Kaolin

The flocculation efficiency of graft copolymers, CA-1:3, CA-1:5 and CA-1:8 on kaolin aqueous suspension was examined by measuring the transmittance on kaolin suspension after the equilibrium flocculation (~40 min). The kaolin bears a negative charge on the surface in the pH range of 6.5 - 7.5 and exhibits the zeta potential of (-) 18 - 20.0 mV. The average size of kaolin particles was ~1.0 µm. The efficiency of flocculation of kaolin suspension (3.0 wt %) was investigated at different dosages of flocculants.

A typical set-up for the kaolin flocculation is shown in figure 3.7 of chapter-3. Figure-3.7a shows the kaolin suspension before the addition of flocculant, which is stable and looks milky. Upon addition of cationic flocculant and initial stirring, milky suspension turns into a clear solution after stopping the stirring (figure-3.7b). The kaolin particles begin to settle at the bottom. The transmittance of the clear solution was measured. Similar experiments were carried out for different dosages of flocculants.

Figure-5.5 shows the percentage transmittance of kaolin supernatant liquid vs different dosages of flocculants, CA-1:3, CA-1:5 and CA-1:8 taken at pH 7 and at equilibrium flocculation time of ~ 40 min.

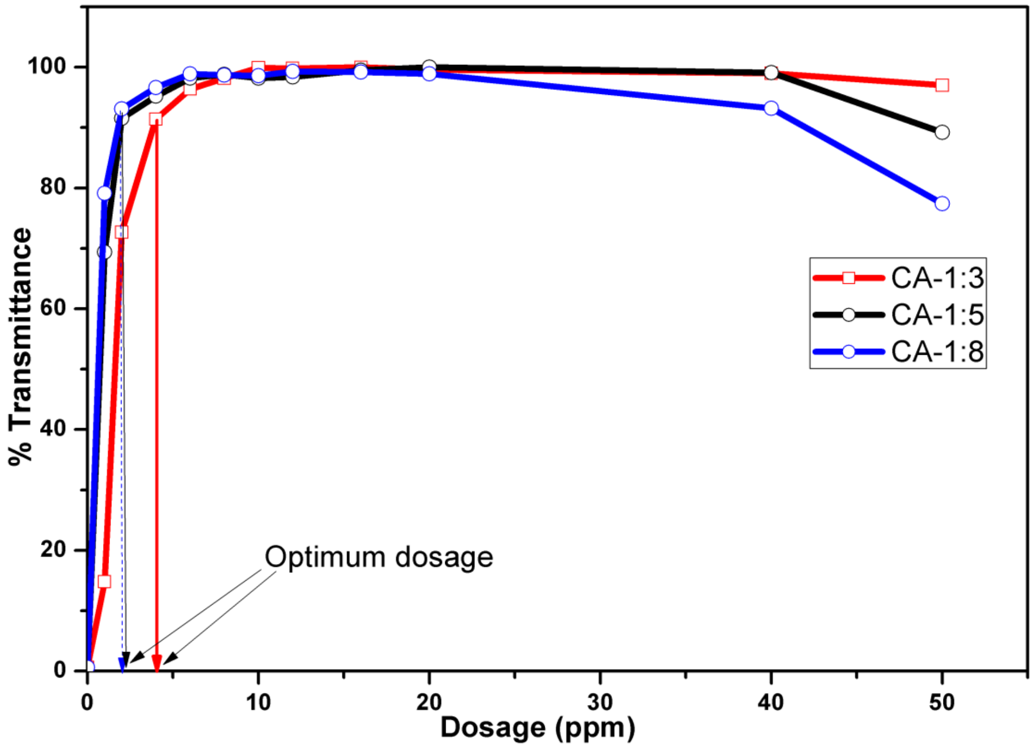


Figure-5.5: Transmittance of kaolin supernatant vs. dosage of flocculants after 40 min of equilibrium flocculation

It can be clearly observed from the figure that, CA-1:8 shows more than 90 % transmittance at the dosage range of 2 - 6 ppm and remains constant till 20 ppm. After 20 ppm, the % transmittance reduced with the further increase in flocculant dosage. This is due to the colloidal restabilization. CA-1:5 also shows more than 90% transmittance at the dosage range of 2 - 6 ppm and remains constant till 40 ppm.

The % transmittance decreases after 40 ppm which is due to colloidal restabilization. Whereas, CA-1:3 flocculant showed more than 90 % transmittance in the dosage range of about 4 - 10 ppm and remains constant till 50 ppm and showed no colloidal restabilization. This could be attributed to lesser charge on the CA-1:3. These observations clearly show that the charge on the polymer is directly proportional to the feed weight ratio of APTMAC, which is further evidenced by NMR studies. The optimum dosage levels for CA-1:3, CA-1:5 and CA-1:8 flocculants for kaolin flocculation could be considered as 2.0 ppm, 2.0 ppm and 4.0 ppm, respectively. These flocculants showed efficient flocculation and the optimum dosages were found to be significantly lower compared to the values reported earlier[13,36].

The CA-1:8 and CA-1:5 flocculants contain more of APTMAC polymer and exhibit a high degree of charge with high zeta potential (+ 50 to 60 mV). In this case, the driving force for the flocculation could be attributed to the charge neutralization followed by bridging. However, the possibility of electrostatic patch mechanism in flocculation cannot be ruled out as there is a colloidal restabilization at higher dosage. For the flocculant CA-1:3, higher dosage level (∼4.0- 8.0 ppm) was required to get 95-98% transmittance in the flocculation. In CA-1:3 flocculant, the charge density is low (zeta potential + 32 mV) and also the molecular weight is low (408 Kg mol^{-1}). Because of the lower charge density and low molecular weight more flocculant is needed to cause flocculation. These observations clearly indicate that charge density on the polymer plays a dominant role in the kaolin flocculation.

We also measured the zeta potential of kaolin supernatant solution as a function of different dosage of flocculants CA-1:3, CA-1:5 and CA-1:8. The results are shown in figure-5.6.

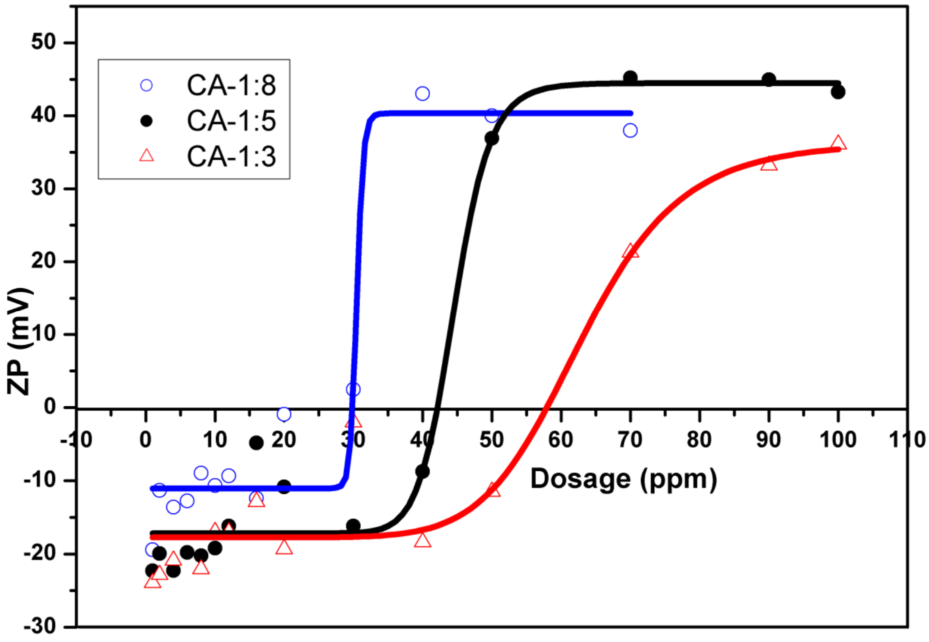


Figure-5.6: Zeta potential of kaolin suspension supernatant at different dosages after equilibrium flocculation using CA-1:8, CA-1:5 and CA-1:3

It is observed that the zeta potential of kaolin solution changed from (-) 20 mV to (+) 50 mV with an increase in the dosage of flocculants. This is due to the fact that the oppositely charged flocculants neutralize and diminish the surface charge of the suspended kaolin particles resulting into the formation of kaolin flocs. However, it is interesting to note from the figure-5.8 that the zeta potential of the kaolin supernatant did not reach zero value at 95% transmittance for the optimum dosage of CA-1:8, CA-1:5 and CA-1:3 flocculants. The zeta potential values remained at (-) 10 to (-) 20 mV. This could be attributed to the presence of small quantities of very fine particles of unneutralized kaolin present in the supernatant liquid. Further, the kaolin fine particles are partially or heterogeneously bound by flocculants to form micro flocs that cannot settle down and hence float and show reduced zeta potential value.

At higher dosage content, the zeta potential values crossed the zero value and attained positive values of zeta potential. These observations clearly indicate that there seems to be a broad flocculation regime and the possibility of both charge neutralization and bridging mechanism for driving the flocculation.

It is also observed form the figure that the dosages at which the zeta potential is zero for CA-1:8, CA-1:5 and CA-1:3 were 30, 40 and 58 ppm respectively. These dosages are more than 10 times higher than the optimum dosage. At optimum dosage, more than 95 % clarity or kaolin was flocculated and that supernatant water can be reused to suspend kaolin for next cycle of kaolin mining. This can enormously improve the economy and efficiency of the recovery process.

5.4.5 Kinetics of flocculation

In order to understand the kinetics of flocculation, the percentage transmittance of kaolin suspension as a function of time were measured for flocculants, CA-1:8, CA-1:5 and CA-1:3 at different doses and also at their optimum dosage. Figure-5.7 shows the results of % transmittance vs time for three flocculants at their optimum dosage and figure-5.8 to 5.10 shows the % transmittance vs time for three flocculants at different dosages.

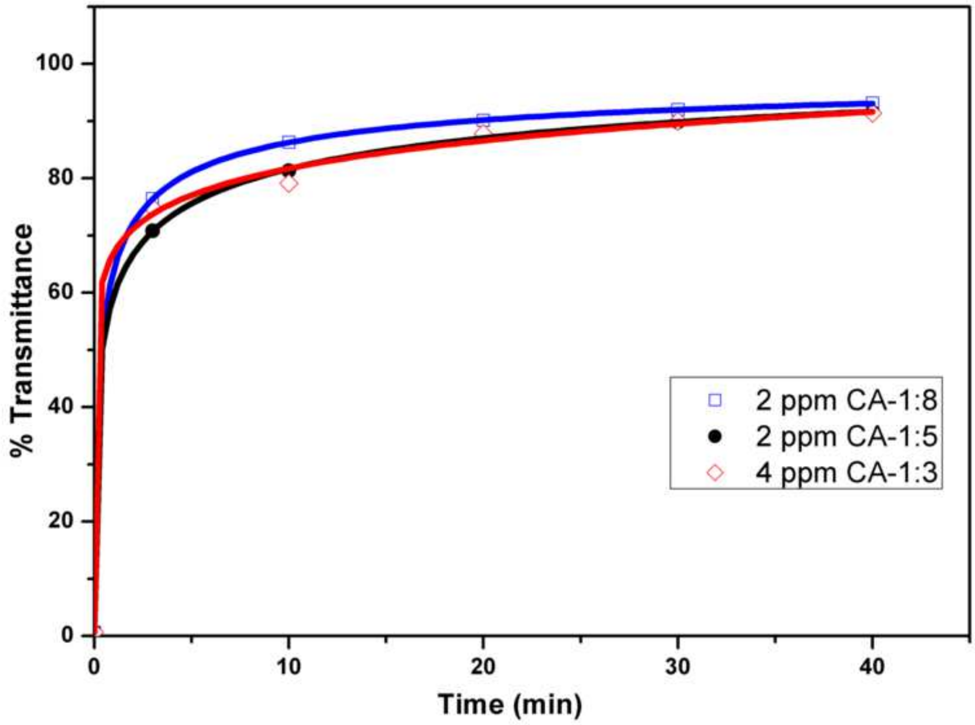


Figure-5.7: Kinetics of flocculation of CA-1:8, CA-1:5 and CA-1:3 at optimum dosage

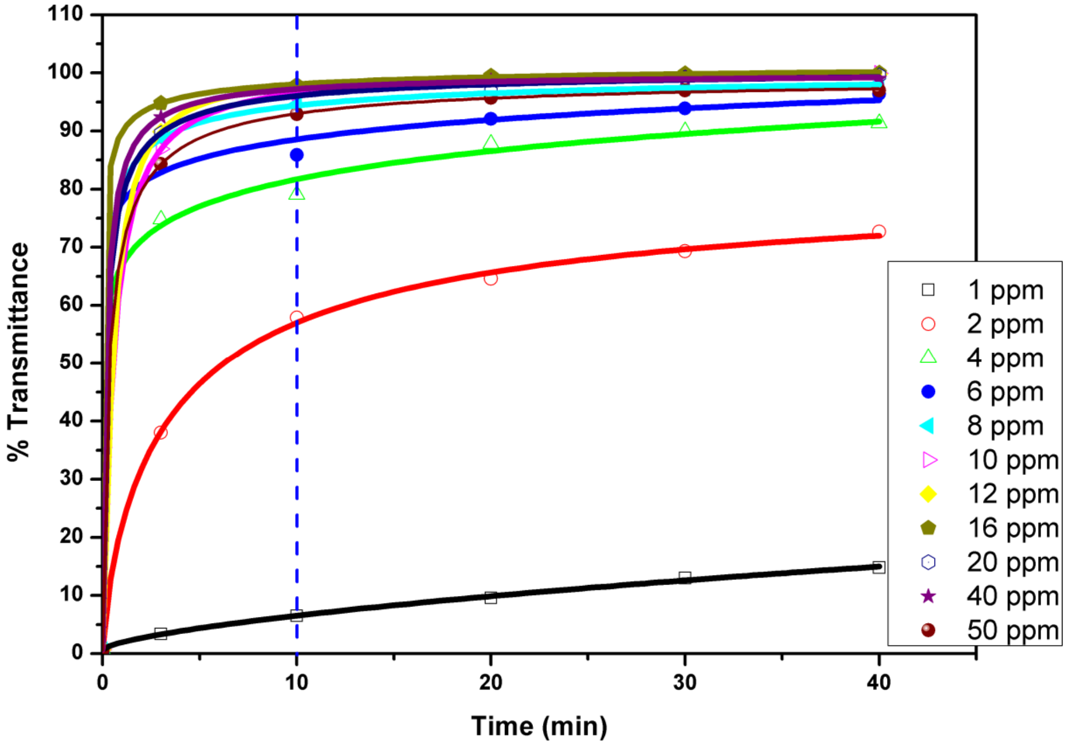


Figure-5.8: Transmittance of kaolin supernatant vs. time of CA-1:3

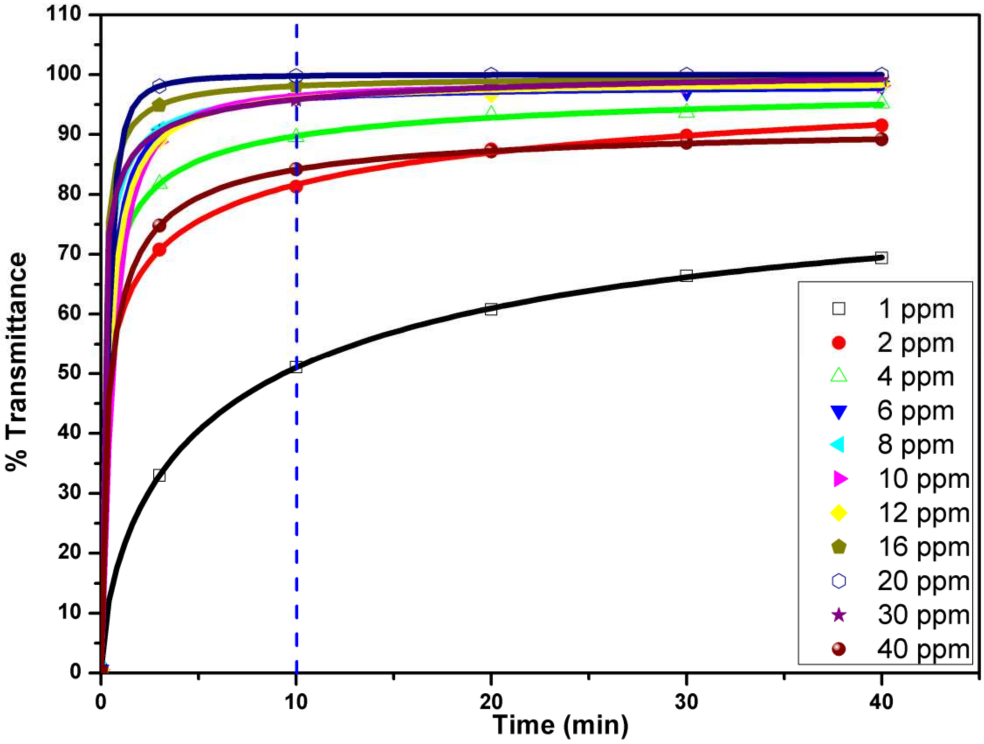


Figure-5.9: Transmittance of kaolin supernatant vs. time of CA-1:5

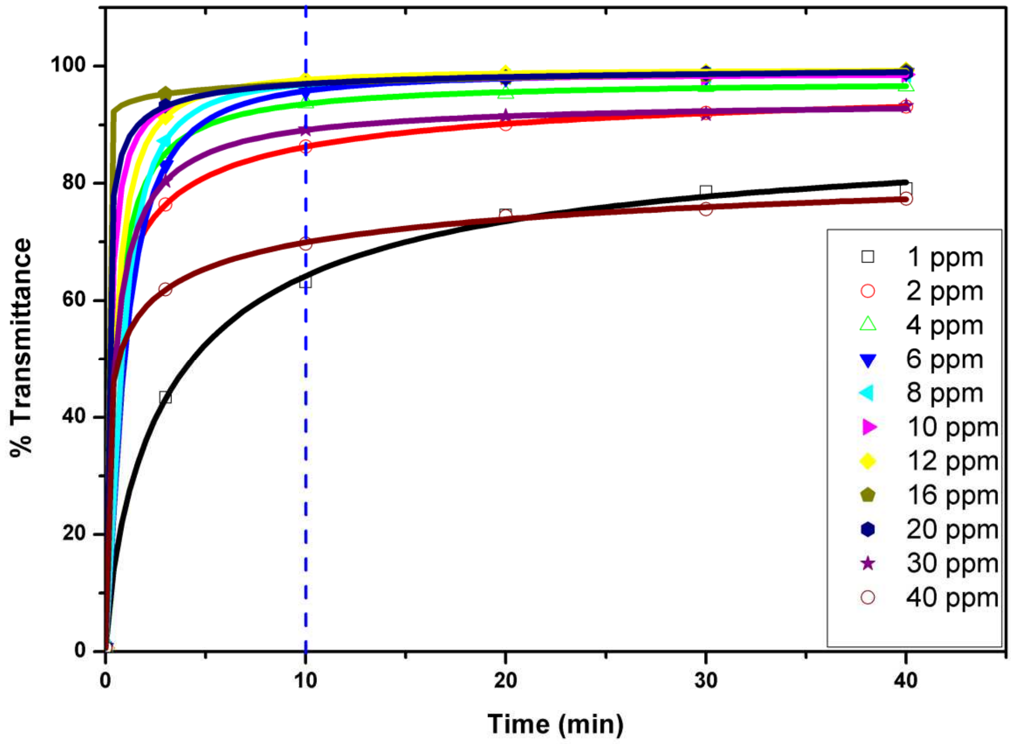


Figure-5.10: Transmittance of kaolin supernatant vs. time of CA-1:8

It is clearly seen that, 80 - 85% transmittance could be achieved within 10 min of flocculant addition to the kaolin suspension at their respective optimum dosages of flocculants. At the end of 40 min, the % transmittance reached to 90%, which indicated a bridging mechanism for the flocculation. The initial phase of time during flocculation is involved in charge neutralization and later the bridging occurs for the effective flocculation. The % transmittance increases with time indicating that bridging occurs with time. Further the high molecular weight of the polymer also contributes to the bridging. Both CA-1:8 and CA-1:5 gave maximum % transmittance of more than 90% at an optimum dosage of 2 ppm. This is because the charge required to neutralize the kaolin particles is just sufficient in CA-1:5 and the bridging mechanism causes the increase in % transmittance. The increased charge density in CA-1:8 resulted in 90 % transmittance in a short time. These studies indicate that both charge and molecular weight play important role in the efficient flocculation.

5.4.6 Floc characterization

5.4.6.1 Initial settling rate (ISR)

Figure-5.11 shows the interface height vs. time for flocculants CA-1:8, CA-1:5 and CA-1:3 at their optimum dosage levels of 2, 2 and 4 ppm respectively. It can be readily seen that the interface height decreases rapidly within the first 100 seconds and remains almost constant after 250 seconds for all the flocculants. This predicts the initial settling rate of ~0.1cm s^{-1} for the flocculants. These observations clearly reveal that CA-1:8, CA-1:5 and CA-1:3 flocculate kaolin suspension very rapidly.

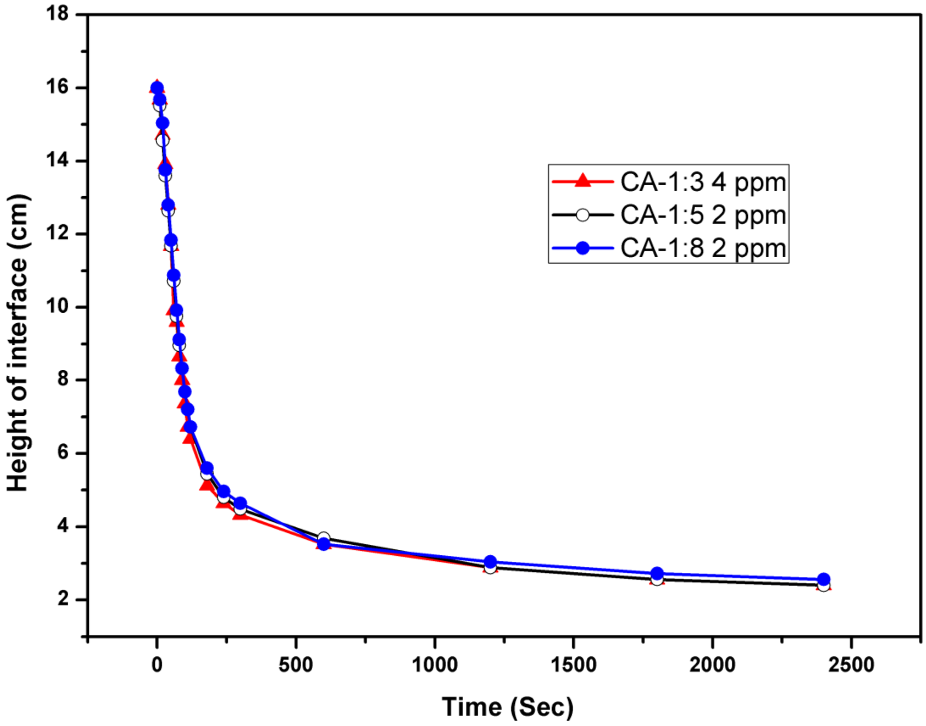


Figure-5.11: Initial settling rate of CA-1:8, CA-1:5 and CA-1:3

5.4.6.2 Filter Cake Moisture Content (FCMC)

Figure-5.12 shows the results of FCMC for CA-1:8, CA-1:5 and CA-1:3 at different dosages. The FCMC of CA-1:8, CA-1:5 and CA-1:3 remained independent of dosages in the range of 2 to 10 ppm. However, the earlier reports indicate a decrease in FCMC with an increase in dosage levels when the dosage levels are quite high (~40 to 50 ppm). We observed a very small change in FCMC with these low dosage levels. Nevertheless, these small dosages (2-10 ppm) were found to be efficient in flocculation and gave more than 95 % transmittance in the flocculation process. The FCMC of CA-1:8 showed slightly higher FCMC to CA-1:5 and CA-1:3 which could be attributed to the high charge and molecular weight in the polymer which results into increased hydrophilicity of flocculant and absorbs more moisture. Further, the FCMC is in the decreasing order with decreasing APTMAC content. This clearly shows that charge on the polymer and molecular weight influences the FCMC.

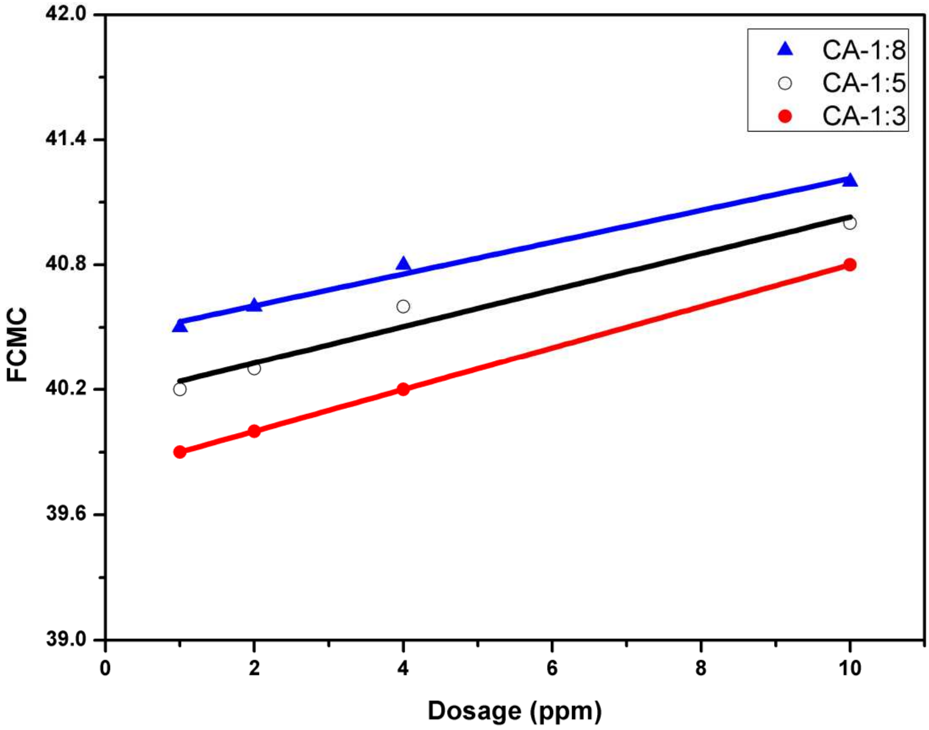


Figure-5.12: Filter cake moisture content study of CA-1:8, CA-1:5 and CA-1:3 at different dosages

The visual observation of the filter cakes after the flocculation using CA-1:8, CA-1:5 and CA-1:3 at different dosages was made and photographs are shown in figure-5.13

Figure-5.13: Photographs of filter cakes after flocculation and drying for CA-1:3 (a-d) CA-1:5 (f - i) and CA-1:8 (j-m)

It is observed that, as the dosage increase, the surface of the filter cake becomes smoother and softer. This could be due to the formation of dense flocs at higher dosages of flocculant.

5.4.6.3 Optical microscopic studies

The optical microscopy was performed on kaolin flocs obtained under different dosages of CA-1:8, CA-1:5 and CA-1:3 flocculants. The optical micrographs are shown in figure-5.14. Kaolin suspension without any flocculant does not show the flocs and one can see a uniform suspension [figure-5.14 (a)]

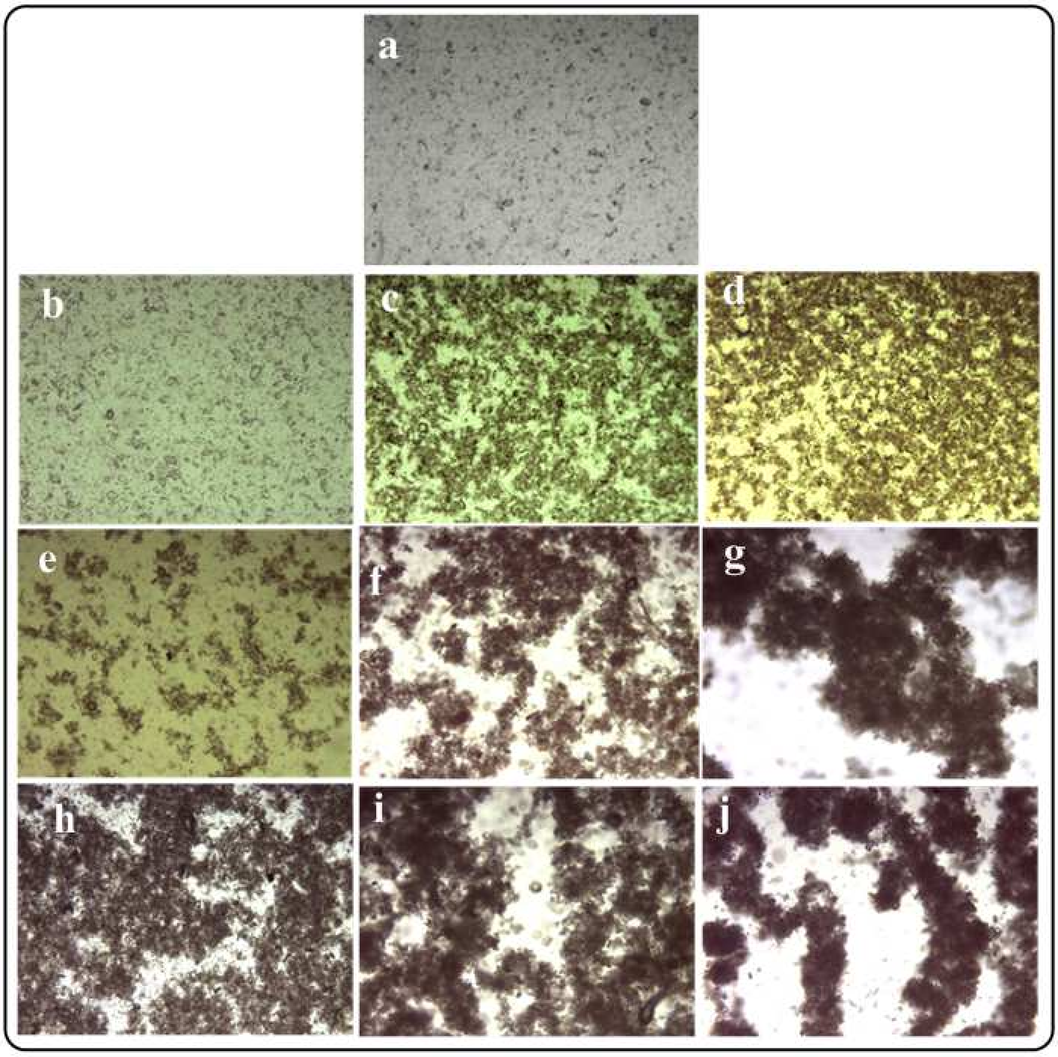


Figure-5.14: Optical micrographs of kaolin flocculation at different dosages Kaolin (a), CA-1:3 (b-d), CA-1:5 (e-g) and CA-1:8 (h-j)

However, upon flocculation, kaolin flocs are observed very clearly and the floc size increases with the dosage of flocculant. The observed optimum dosages of 2, 2 and 4 ppm for flocculants CA-1:8, CA-1:5 and CA-1:3 respectively show more than 95 % transmittance in the supernatant liquid after the floc formation. This is visible in the micrographs of figure-5.16 (c), (f) and (i).

5.5 Conclusions

In conclusion, we have shown that the cationic flocculants based on the graft copolymer of chitosan and 3-acrylamidopropyltrimethylammonium chloride (APTMAC) efficiently flocculates kaolin from aqueous solution. Depending on the ratio of monomers, the graft copolymers could be obtained with different molecular weight and zeta potentials, which are very important properties required for efficient flocculation. The optimum dosages for maximum flocculation were found to be 2.0, 2.0 and 4.0 ppm for CA-18, CA-1:5 and CA-1:3 graft copolymers, respectively. The minimum time required for maximum flocculation was determined to be 4-10 minutes in the laboratory scale. Both the copolymers CA-1:8 and CA-1:5 gave the best flocculation efficiency. The floc characterization was performed in terms of floc size and FCMC. Based on the results it was proposed that the charge neutralization and bridging are the main mechanisms for driving the flocculation. These graft copolymers show great promise in the flocculation of kaolin from aqueous streams in industries and are biodegradable and environmental friendly.

5.6 References

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SUMMARY AND CONCLUSIONS

CHAPTER-6

In this chapter summary and conclusions of the thesis work are discussed.

The main objective of this thesis work was to synthesize and characterize efficient flocculants for kaolin flocculation. Accordingly, flocculants based on copolymers of acrylamide and cationic functional monomers such as DADMAC and APTMAC and graft copolymers of chitosan and APTMAC were synthesized and evaluated for kaolin flocculation. Acrylamide monomer was selected because of its inherent property of yielding high molecular weight and the cationic monomers impart cationic charge to the flocculant, which are the most essential parameters for an efficient flocculant. Chitosan, a biopolymer grafted with APTMAC yielded partially biodegradable flocculant. These flocculants were tested for their molecular weights and charge density and examined for flocculation of kaolin suspensions. Kaolin is an important industrial mineral which has wide applications in industry. This was the motivation behind synthesizing efficient flocculants for kaolin separation.

In the first chapter a detailed literature survey on flocculants, importance of flocculants in industrial separations is presented. Various mechanisms which drives the flocculation and factors which influence the flocculation were explained. Classification of flocculants based on their structure and source was given. Major focus was given on flocculants used for kaolin separation. In view of the environmental issues, the importance and use of biopolymer based flocculants were discussed. Particular emphasis was given on chitosan based flocculants. Different methods used to study flocculation such as jar test and settling test was explained, and also the floc characterization methods such as FCMC and ISR were elaborated.

In the second chapter, the scope and objectives of the work in terms of design and synthesis of new and efficient flocculants for kaolin flocculation were given.

The third chapter dealt with synthesis of copolymers of acrylamide and DADMAC at different molar composition. The characterizations in terms of chemical structure and composition was performed using ^{1}H and ^{13}C NMR spectroscopy. The molecular weights and zeta potentials were determined using GPC and Zeta sizer. The flocculation efficiency was tested on kaolin suspension and the optimum dosages were evaluated. The optimum dosages of flocculants AD-4060, AD-5050 and AD-8020 were found to be 8 , 10 and 14 ppm, respectively. The flocs were characterized in terms of FCMC and optical microscopy. The flocculation efficiency was correlated to the molecular weight and charge on the flocculant.

In the fourth chapter, the copolymerization of acrylamide and APTMAC was discussed and copolymers with three different monomer compositions were synthesized. The chemical structure of the copolymers was confirmed by ^{1}H and ^{13}C NMR spectroscopy. The molecular weight and zeta potential were determined by GPC and zetasizer. The flocculation efficiency was tested on kaolin suspension and the optimum dosages were determined. The optimum dosages for flocculants, AA-4060, AA-5050 and AA-8020 were found to be 3 , 4 and 9 ppm respectively. The flocs were characterized in terms of FCMC and optical microscopy. The flocculation efficiency was correlated to the molecular weight and charge on the flocculant, the mechanism of flocculation was discussed in terms of charge neutralization and bridging. To the best of our knowledge this copolymer system was used for the first time for the kaolin flocculation and found to be efficient.

The fifth chapter dealt with the synthesis of biopolymer chitosan grafted APTMAC copolymers. The composition of APTMAC was varied and three graft copolymers with different APTMAC content were synthesized. The chemical structure of the graft copolymers was characterized by ^{1}H and ^{13}C NMR spectroscopy. The molecular weight and zeta potential values were determined. The flocculation efficiency was tested on kaolin suspension and the optimum dosages were determined. The optimum dosage of flocculants CA-1:8, CA-1:5 and CA-1:3 were found to be 2 , 2 and 4 ppm respectively. The flocs were characterized in terms of FCMC and optical microscopy. The flocculation efficiency was correlated to the molecular weight and charge on the flocculant.

We have successfully synthesized and characterized flocculants based on acrylamide copolymers and chitosan graft copolymers and demonstrated their applications in kaolin separation. Besides kaolin these flocculants also have a great potential in other industrial solid liquid separations by flocculation.

List of publications

1. ***Suresha P. Ranganath*** *and Manohar V. Badiger*, Flocculation of kaolin from aqueous suspension using low dosage of acrylamide based cationic flocculants, Journal of Applied Polymer Science. 47286 (2018*). Doi:10.1002/app.47286*
2. ***Suresha P. R****, Manohar V. Badiger And Bernhard Wolf*, Polyelectrolytes in dilute solution: viscometric access to coil dimensions and salt effects, RSC Advances., 5 (35), 27674 - 27681 (2015), DOI:10.1039/c5ra01376c.
3. **Suresha P. R.** and Manohar V. Badiger; Synthesis and characterization of biodegradable chitosan graft copolymers for kaolin separation. Manuscript under preparation.
4. **Suresha P. R.** and Manohar V. Badiger, polyelectrolytes based on chitosan for wound healing applications. Manuscript under preparation.
5. *Venkatakrishnan Balasubramanian, Brindha Velappan, Sandhya Kurvilla Vijayan, Hepzibah Jabamani, Vedaraman Nagarajan, John Sundar Victor,* **Suresha P. Ranganath***, Manohar V Badiger, Velappan Kandukalpatti Chinnaraj And Muralidharan Chellappa,* Studies on the use of sodium polyacrylate (SPA) for low-salt animal skin preservation, Environmental Science and Pollution Research., 2019.
6. *Rupali Shaligram Mehare,* **Suresha P. Ranganath***, Vikash Chaturvedi, Manohar V. Badiger and Manjusha V. Shelke, In Situ* Synthesis of Nitrogen and Sulfur enriched Hierarchical Porous Carbon for high-Performance Supercapacitor, Energy and Fuels., 32, 908 - 915 (2017), DOI:10.1021/acs.energyfuels.7b02305.

Conferences

1. *Participated in* ***Asian Polymer Association international Conference*** *on polymers on the frontiers of science and technology held during February 2013 at Punjab university, Chandigarh and presented a poster titled "****Synthesis and characterization of cationic polyelectrolytes for flocculation****" and received* ***best poster award.***

2. *Received* ***best poster award*** *for the poster titled "* ***Synthesis and Characterization of polymeric flocculants for protein separation****" at APA International conference on Polymers : Vision and innovations, February 2014, held at India Habitat Centre, New Delhi, India.*

3. *Represented CSIR-NCL, Pune and RGSTC, Mumbai at* ***India International Science Festival(IISF)*** *held at NPL, New Delhi, Dec 2016. Polymers for industrial application exhibition pavilion for separation of fish proteins from waste waters of marine fish industries using flocculants.*

4. *Presented poster titled "Flocculants for industrial separations" at* ***Plastivision*** *a polymer exhibition and trade show held at exhibition ground, Mumbai. This poster was presented in innovation pavilion of the exhibition.*

5. *Participated and presented a poster titled "****Design and synthesis of efficient polymeric flocculants for industrial separations****" at conference on advancements in polymer science and technology* ***APA-2015*** *held at Saurashtra university, Rajkot, Gujarat, India.*