DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

EVALUATION OF TREATMENT PERFORMANCE OF ALUMINIUM BASED COAGULANT AIDS IN WATER TREATMENT

by

Elchin JABRAYILZADA

April, 2014
İZMİR

EVALUATION OF TREATMENT PERFORMANCE OF ALUMINIUM BASED COAGULANT AIDS IN WATER TREATMENT

A Thesis Submitted to the
Graduate School of Natural and Applied Sciences of Dokuz Eylül University
In partial Fulfillment of the Requirements for the Degree of Master of Science in Environmental Engineering, Environmental Engineering Program

by

Elchin JABRAYILZADA

April, 2014
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M. Sc THESIS EXAMINATION RESULT FORM

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ACKNOWLEDGEMENTS

In particular, I would like to appreciate Prof. Dr. Deniz DÖLGEN for supervising my thesis, her openess to my ideas and for her advice, support, encouragement and feedback throughout the years.

In addition, many people have supported me in different ways. I would like to thank my family especially my dear father who did not spare me and dear Cihan GÜNEŞ and Assoc. Prof. Sevgi TOKGÖZ GÜNEŞ for their great assistance during my experiments in the laboratory and for sharing their expert knowledge with me.

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EVALUATION OF TREATMENT PERFORMANCE OF ALUMINIUM BASED COAGULANT AIDS IN WATER TREATMENT

ABSTRACT

Aluminium based coagulants are used in drinking water treatment to enhance the removal of particulate matters and colloids through coagulation/flocculation processes. Especially, polymeric aluminium compounds are reported as effective over a wider pH range even at low doses. Reduction in the dosages has prime importance especially for the alum based coagulants. Because, it has been hypothesized that higher aluminium exposure is a risk factor for the onset of Alzheimer's disease in humans. Therefore, the principal aim of the thesis was to investigate the treatment performance of aluminium sulphate (alum), poly aluminium chloride (PAC), and poly aluminium chlorosulphate (PACS). In order to optimize the coagulant type and dosage, determination of optimal pH and other operational conditions (i.e. optimization of mixing time and intensity for rapid and slow mixings), jar test that is a simple and effective method that simulates the coagulation/flocculation processes was used in the experiments. In the framework of the thesis, required chemical dosage and optimal pH was also determined theoretically by using PHREEQC interactive program before the jar test procedure. The results verified with jar test experiments.

The data obtained from the experiments shown that increased chemical doses were resulted higher treatment performance in terms of turbidity. Optimal poly aluminium chloride dose was determined as 6 ppm (1.5 milligram per liter) yielding 4.3 NTU effluent turbidity. Optimal pH was 7 and in order to adjust pH, sodium hydroxide was used. For the poly aluminium chlorosulphate, lower residual turbidity (i.e. 3.85 NTU) was obtained at 6 ppm (1.5 milligram per liter). The optimal pH was 6 thus lower sodium hydroxide addition was required for pH adjustment than poly aluminium chloride. Finally, effluent turbidity was 3.85 NTU for 3 ppm (0.75 milligram per liter) aluminium sulphate. Optimal pH was 7 for alum and acid/base addition was not required for pH adjustment. Therefore, optimal reagent was selected

as alum considering removal efficiency of turbidity, no additional acid or base addition, appearance, and sludge production, as well.

Keywords: Water treatment, chemical substance, coagulant, Alzheimer, Phreeqc, Jar – Test.

SU ARITIMINDA ALÜMİNYUM ESASLI KOAGÜLANT YARDIMCILARININ ARITMA PERFORMANSININ İNCELENMESİ

ÖZ

Alüminyum esaslı koagülantlar, içme suyu arıtımında koagülasyon/flokülasyon süreçleri vasıtasıyla, partiküler madde ve kolloid giderimini arttırmak amacıyla kullanılırlar. Özellikle, polimerik alüminyum bileşiklerinin geniş pH aralığında, düşük dozlarda dahi etkin oldukları raporlanmaktadır. Alüminyum esaslı koagülantlar için doz azaltılması önem taşır. Çünkü, yüksek alüminyum miktarlarına maruz kalınmasının Alzheimer hastalığı için risk faktörü olduğuna dair hipotezler bulunmaktadır. Bu nedenle, tezin başlıca amacı alüminyum sülfat (alum), poli alüminyum klorür (PAC) ve poli alüminyum klorosülfat (PACS) kimyasallarının arıtma performanslarının araştırılmasıdır. Koagülant türü ve dozunun optimizasyonu, optimum pH ve diğer koşulların (karışım süresi ve şiddeti) belirlenmesi için, koagülasyon/flokülasyon süreçlerini benzeştiren, basit ve etkin bir yöntem olan jar testi kullanılmıştır. Tez kapsamında, gerekli kimyasal dozu ve optimum pH değeri PHREEQC programı kullanılarak teorik olarak belirlenmiş, sonuçlar jar testi ile verifiye edilmiştir.

Deneysel çalışmalardan edinilen bulgular, kimyasal (koagülant) dozlarındaki artışın, türbidite giderim verimi artışıyla sonuçlandığını göstermiştir. Optimum poli alüminyum klorür dozu 6 ppm (1.5 miligram/litre), arıtılmış suyun türbidite değeri 4.3 NTU olarak belirlenmiştir. Optimum pH 7 olup, sodyum hidroksit eklenerek ayarlanmıştır. 6 ppm (1.5 miligram/litre) poli alüminyum klorür sülfat dozunda çıkış türbiditesi daha düşük bulunmuştur (3.85 NTU). Optimum pH 6 olarak belirlenmiş ve daha düşük miktarda sodyum hidroksit eklenmesi gerekmiştir. Son olarak, 3 ppm (0.75 miligram/litre) alum için çıkış suyunun türbiditesi 3.85 NTU olarak belirlenmiştir. Optimum pH 7 olup, ayarlamak için asit/baz kullanılmasına gerek olmamıştır. Bu yüzden, türbidite giderim verimi, asit veya baz eklenmesi, görünüm (berraklık) ve çamur oluşumu göz önüne alarak optimum koagülat olarak alum belirlenmiştir.

Anahtar kelimeler: Su arıtımı, kimyasal madde, koagülant, Alzheimer, Phreeqc, Jar – Test.

CONTENTS

Page

M. Sc THESIS EXAMINATION RESULT FORM....ii
ACKNOWLEDGEMENTS.... iii
ABSTRACT....iv
ÖZ....vi
LIST OF FIGURES....xi
LIST OF TABLES....xii

CHAPTER ONE - INTRODUCTION....1

CHAPTER TWO - CHEMICAL TREATMENT (COAGULATION/ FLOCCULATION)....4

2.1 Coagulation....5
2.2 Flocculation....6
2.3 Surface Complexation....8
2.3.1 Phreeqc Interactive....9
2.4 Effect of Coagulation and Flocculation:....11
2.4.1 Zeta Potential....12
2.4.2 Van Der Waals Force....13

CHAPTER THREE - CHEMICALS IN COAGULATION / FLOCCULATION PROCESS....15

3.1 Coagulants....16
3.1.1 Iron Salts (Iron Based Coagulants)....17
3.1.2 Aluminum Salts (Aluminum Based Coagulants)....19
3.1.3 Aluminum Polymers....20
3.1.3.1 Poly Aluminum Chloride - PAC....21
3.1.3.2 Poly Aluminum Chlorosulphate - PACS....22

3.1.3.3 Concerns Regarding toUtilization of the Aluminum Based Coagulants 23
3.1.4 Lime 23
3.1.5 Synthetic Organic Coagulants 24
3.2 Coagulant Aids 24
3.2.1 Activated Silica 24
3.2.2 Weighting Agents 25
3.2.3 Polymers 25
3.3 Alkaline Chemicals and Acids 26

CHAPTER FOUR - MATERIAL AND METHODS 28

4.1 Characteristics of the Raw Water 28
4.2 Chemicals Used in the Experiments 31
4.3 The Analytic Methods and Equipments Used in the Experiments 31
4.4 Preparation of the Solutions 33
4.5 Experimental Set – Up (Jar – Test) 33

CHAPTER FIVE - EXPERIMENTAL RESULTS 36

5.1 Determination of the Optimal Chemical Dosage and pH by PHREEQC Interactive Program 36
5.2 The Results of the Jar Test for Poly Aluminum Chloride - PAC 37
5.2.1 Determination of the Optimal Dosage of Poly Aluminum Chloride-PAC.37
5.2.2 Determination of the Optimal pH for Poly Aluminum Chloride-PAC 41
5.3 The Results of the Jar Test for Poly Aluminum Chlorosulphate - PACS 43
5.3.1 Determination of the Optimal Dosage of Poly Aluminum Chlorosulphate – PACS 43
5.3.2 Determination of the Optimal pH for Poly Aluminum Chlorosulphate - PACS 46
5.4 The Results of the Jar Test for Aluminum Sulphate - Alum 49

5.4.1 Determination of the Optimal Dosage of Aluminum Sulphate –Alum 49
5.4.2 Determination of the Optimal pH for Aluminum Sulphate - Alum 52

CHAPTER SIX – EVALUATION OF THE RESULTS 55

REFERENCES 63

APPENDICES 68

LIST OF FIGURES

Page

Figure 2.1 Microfloc and macrofloc formation 11
Figure 2.2 The ionic concentration and potencial difference from the charged surface of a particle suspended in a dispersion medium..... 13
Figure 4.1 The water treatment plant (Petkim, Aliaga) 29
Figure 4.2 The flow diagram of water treatment plant 30
Figure 4.3 Jar Testing apparatus. 34
Figure 5.1 Dosage calculation with Phreeqc interactive. 36
Figure 5.2 Calculation of NaOH dosage with Phreeqc interactive. 37
Figure 5.3 The variation of the turbidity parameter at various PAC doses. 40
Figure 5.4 The variation of the conductivity parameter at various PAC doses. 40
Figure 5.5 The optimal pH for PAC. 43
Figure 5.6 The variation of turbidity parameter at various PACS doses. 47
Figure 5.7 The variation of the conductivity parameter at various PACS doses 47
Figure 5.8 The optimal pH for PACS 48
Figure 5.9 The variation of turbidity parameter at various alum doses 51
Figure 5.10 The variation of conductivity parameter at various alum doses 52
Figure 5.11 The optimal pH for Alum 54
Figure 6.1 The variation of the turbidity with respect to dosage 57
Figure 6.2 The variation of the turbidity efficiency with respect to dosage 58
Figure 6.3 The testing of PAC 59
Figure 6.4 The testing of PACS 59
Figure 6.5 The testing of Alum 60
Figure 6.6 Comparison of Alum and PAC..... 60
Figure 6.7 Comparison of Alum and PACS 61

LIST OF TABLES

Page

Table 2.1 The relations of zeta potential with colloid stability..... 12
Table 3.1 Chemicals used in coagulation / flocculation processes as coagulant and coagulant aid..... 16
Table 3.2 Typical aluminum based coagulants used in water treatment 19
Table 3.3 The formula and specification of PAC 22
Table 3.4 The formula and specification of PAC 22
Table 4.1 Guzelhisar Dam specification. 28
Table 4.2 Characteristics of the raw water. 30
Table 4.3 Water quality analysis and the equipment used in the experiments 33
Table 5.1 The effect of 1 ppm PAC dose on treatment performance. 38
Table 5.2 The effect of 3 ppm PAC dose on treatment performance 38
Table 5.3 The effect of 6 ppm PAC dose on treatment performance. 39
Table 5.4 The effect of pH on treatment performance (conditions: 6 ppm PAC and pH 6). 41
Table 5.5 The effect of pH on treatment performance (conditions: 6 ppm PAC and pH 42
Table 5.6 The effect of pH on treatment performance (conditions: 6 ppm PAC and pH 8). 42
Table 5.7 The effect of 1 ppm PACS on treatment performance. 44
Table 5.8 The effect of 3 ppm PACS on treatment performance. 44
Table 5.9 The effect of 6 ppm PACS on treatment performance. 45
Table 5.10 The effect of pH on treatment performance (conditions: 6 ppm PACS and pH 6). 47
Table 5.11 The effect of the pH on treatment performance (conditions: 6 ppm PACS and pH 7)..... 47
Table 5.12 The effect of the pH on treatment performance (conditions: 6 ppm PACS and pH 8). 48
Table 5.13 The effect of 1 ppm alum on treatment performance 49
Table 5.14 The effect of 3 ppm alum on treatment performance 50
Table 5.15 The effect of the 6 ppm alum on treatment performance..... 50

Table 5.16 The effect of pH on treatment performance (conditions: 3 ppm alum and pH 6) 53
Table 5.17 The effect of pH on treatment performance (conditions: 3 ppm alum and pH..... 53
Table 5.18 The effect of pH on treatment performance (conditions: 3 ppm alum and pH..... 54
Table 6.1 Treatment performance of PAC 56
Table 6.2 Treatment performance of PACS 56
Table 6.3 Treatment performance of Alum 57
Table 6.4 The results of optimal dosages and ptimal pH of three chemicals 58

CHAPTER ONE
INTRODUCTION

Coagulation and flocculation are important unit processes in water treatment plants and mostly used to remove particulate matter, turbidity, and colour. Coagulation and flocculation processes involve the addition of chemicals to destabilize colloidal materials and then aggregation of destabilized particles into larger flocs. Since colloids in water are negatively charged, destabilization is achieved by adding positively charged ions that interact specifically with the negative colloids and reduce (or neutralize) their charge. Therefore, coagulation is usually accomplished by the addition of inorganic coagulants such as aluminium or iron based salts.

Aluminium based coagulants such as aluminium sulphate (known as alum) or complex forms of aluminium compounds are used in drinking water treatment to enhance the removal of particulate matters and colloids through coagulation/flocculation processes. Polymeric aluminium compounds are reported as more effective over a wider pH range and at lower temperatures than alum. Moreover, required dose of the coagulant is decreased due to the higher charge density of polymeric forms. Reduction in the dosages has prime importance especially for the alum based coagulants. Because, there is considerable concern throughout the world over the levels of aluminium found in drinking water sources (raw water) and treated water. Higher concentrations of aluminium in treated water results with the increase in turbidity and precipitation of aluminium hydroxide in the pipeline (Rahman, 1992). Residual aluminium concentration also reduces the disinfection efficiency. In addition, orally ingested aluminium is acutely toxic to humans despite the widespread occurrence of this element in foods, drinking water and many antacid preparations (Niquette et al, 2004). It has been hypothesized that aluminium exposure is a risk factor for the onset of Alzheimer's disease in humans (World Health Organization - WHO, 1998). Although, a health-based guideline for the presence of aluminium in drinking water has not been established, water treatment plants using aluminium-based coagulants should optimize their operations

to reduce residual aluminium levels in treated water as a precautionary measure. Therefore, utilization of optimal doses is important issue and in this framework since the polymeric forms of aluminium compounds reduce the doses is an important tool, as well.

In order to reduce the required reagent dosage, recent studies are focused on the pre-hydrolyzed, preformed or polymeric Al salts, also known as inorganic polymeric coagulants (IPCs). Aluminium chlorohydrate, poly aluminium chloride, poly aluminium sulphate chloride, poly aluminium silicate chloride and forms of poly aluminium chloride with organic polymers are representative products of the IPCs.

The principle aim of the thesis is to investigate the treatment performance of aluminium sulphate (alum), poly aluminium chloride (PAC), and poly aluminium chlorosulphate (PACS). In order to optimize the coagulant type and dosage, determination of optimal pH and other operational conditions (i.e. optimization of mixing time and intensity for rapid and slow mixings), jar test that is a simple and effective method that simulates the coagulation/flocculation processes was used in the experiments.

In the framework of the thesis, required chemical dosage and optimal pH was also determined theoretically by using PHREEQC interactive program before the jar test procedure. PHREEQC is a thermodynamic equilibrium program designed to model chemical speciation in aqueous solutions, determine the saturation states of solutions with minerals and gases, and predict the results of various reactions, such as dissolution of minerals and oxidation. Thus, the model, i.e. PHREEQC was used to predict the chemical reactions that will occur in response to mixing coagulant with the raw water.

During the experimental studies, raw water samples were taken from the Petkim water purification water plant. Because, the chemicals that are effective even at low doses and economical (affordable) were intended to investigate by the operators of the Petkim water treatment. In the existing systems, poly aluminium chloride (PAC)

has been used as coagulant. Researches aimed an improvement on the turbidity removal, dosage reduction and reduction in the sludge production, as well.

Experimental studies were carried out in the Dokuz Eylül University between 01.08.2013 – 01.02.2014. During the experimental studies, optimal dose and operational conditions of each chemical were investigated separately. The pH, turbidity, conductivity, and temperature were measured for both raw water and treated water samples (i.e. supernatant) using Standard Methods. The redox potential was determined using Phreeqc interactive program. Thus, optimal chemical and operational conditions were determined.

The thesis was structured at six major parts. In the first chapter the objective of the thesis is presented. Chapter 2 and 3 includes information about coagulation/flocculation processes and coagulants used in water treatment. The materials and the methods used in the experiments are summarized in Chapter 4. The results obtained from the jar test experiments and the model used in the thesis was explained in Chapter 5. The results of the measurement (optimal dosage and optimal pH of the chemicals) were presented at tables and depicted in various Figures at Chapter 5. Finally, the results were evaluated and concluded in Chapter 6.

CHAPTER TWO
CHEMICAL TREATMENT (COAGULATION / FLOCCULATION)

The large particles of suspended matter in raw water can be removed by allowing them to settle out in a pre sedimentation basin. However, there are smaller particles in almost all surface water and some groundwater that will not settle out within a reasonable time without some help to accelerate the process. The common term for this suspended matter is non – settleable solids, which usually consist of a combination of biological organisms, bacteria, viruses, protozoan, organic matter, and inorganic solids. The term applied to all suspended matter in water is turbidity (Environmental Protection Agency - EPA, 2002).

The treatment most used to remove turbidity is known as conventional treatment. This is the combination of the following steps (EPA, 2002):

1. Coagulation: adding and rapid mixing of chemical coagulants into the raw water.
2. Flocculation: slow mixing of the chemicals with the raw water to assist in building up particles of floc.
3. Sedimentation: allowing the floc to settle out of the water.
4. Filtration: removing almost all of the suspended matter that remains by passing the water through filters.

In the production of drinking water, coagulation and flocculation are almost universally used before filtration, except where water is treated by slow sand filtration. Failure or inadequacy in any of the stages will have adverse effects on the subsequent stages may result in the production of water with excessive turbidity and other undesirable qualities. Thus, chemical dosing which is not optimal means that the conditions for coagulation are not the optimum; the floc formed may be unsuitable for the method of clarification in use, is not removed efficiently and passes on the filters where it may break through to appear as turbidity in the final water or seriously reduce the length of filter run.

In the coagulation and flocculation processes, non – settable solids are converted into large and heavier settleable solids by chemical – physical changes brought about by the adding and mixing coagulant chemicals into the raw water. The settleable solids can then be removed by the sedimentation and filtration processes. The objective of flocculation and coagulation is to condition impurities, mainly non - settleable solids and colour, for removal from the water being treated. Coagulating chemicals cause non - settleable particles to pile together to form floc. In the coagulation process, chemicals are added which will initially cause colloidal particles to become destabilised and pile together. The particles collect together to form larger particles in the flocculation process. When parts of floc clump together, they may form larger, heavier flocs which settle out and are removed as sludge. In other cases flocs are removed from the water by flotation.

2.1 Coagulation

The term coagulation describes the effect produced when certain chemicals are added to raw water containing slowly settling or non - settleable particles. The chemicals hydrolyse colloidal particles, which begin to form agglomerations termed floc which will be removed by clarification and filtration. Four methods are used to bring about coagulation process: double – layer compression, charge neutralization, entrapment in a precipitate, and intra particle bridging.

When the concentration of counter ions in the dispersion medium is smaller, the thickness of the electric double layer is larger. Two approaching colloid particles cannot come close to each other because of the thicker electric double layer, therefore, the colloid is stable. Now, visualize adding more counter ions. When the concentration is increased, the attracting force between the primary charges and the added counter ions increase causing the double layer to shrink. The layer is then said to be compressed. As the layer is compressed sufficiently by the continued addition of more counter ions, a time will come when the Van Der Waals force exceeds the force of repulsion and coagulation results.

The charge of a colloid can also be directly neutralized by the addition of ions of opposite charges that have the ability to directly adsorb to the colloid surface. For example, the positively charged dodecylammonium tends to be hydrophobic and such as, penetrates directly to the colloid surface and neutralize it. This is said to be direct charge neutralization, since the counter ion has penetrated directly into the primary charges. Another direct charge neutralization method would be the use of a colloid of opposite charge. Direct charge neutralization and the compression of the double layer may complement each other.

A characteristic of some cations of metal salts such as Al (III) and Fe (III) is that of forming a precipitate when added to water. For this precipitation to occur, a colloidal particle may provide as the seed for a nucleation site, thus, entrapping the colloid as the precipitate forms. Moreover, if several of these particles are entrapped and are close to each other, coagulation can result by direct binding because of the proximity.

The last method of coagulation is intra particle bridging. A bridging molecule may attach a colloid particle to one active site and a second colloid particle to another site. An active site is a point in the molecule where particles may attach either by chemical bonding or by mere physical attachment. If the two sites are close to each other, coagulation of the colloids may occur or the kinetic movement may loop the bridge assembly around causing the attached colloids to bind because for now they are hitting each other, thus bringing out coagulation.

2.2 Flocculation

Flocculation is a process of water movement that promotes the collecting together of the small floc particles (microflocs) produced by coagulation into larger masses better suited for removal by clarification processes.

The flocculation process describes conditions for contact between particles to promote their collecting together into flocs for ease of removal, especially by

clarification and by filtration. These collisions between particles result from gentle stirring created by a mechanical or other means of mixing, at a rate much slower than the mixing rate in coagulation, sometimes in dedicated flocculation basins. In these basins which utilize the sludge blanket effect these collisions between particles result from hydraulic mixing.

The mechanism of flocculation can be studied in two stages:

1. Adsorption of polymer onto the particles
2. The formation of aggregates

Adsorption is possible when the polymer and the surface are of opposite charge, resulting in nonspecific electrostatic interaction. In theory, any positively charged mineral should adsorb any anionic polymer and vice versa. With large amounts of adsorbed polymer, recharging of the particles and stabilization should occur. Since the particle will then be of opposite charge to the initial charge, further adsorption of flocculants will cease (EPA, 2002).

In aqueous suspensions, the particle surface has an electrical (usually negative) charge, which, for example, in mineral solids originates from the dissociation of protons from surface hydroxyl groups belonging to silicate groups. If counter ions (e.g., Ca^{2+} or Mg^{2+}) are present in the surrounding water, they accumulate on the surface of the suspended particles, forming an ionic double layer. The excess negative charge at the shear surface of the double layer (the zeta potential) can be measured with a zeta meter. As the zeta potential increases, the columbic repulsion between the particles becomes stronger and the suspension is more stable.

Many authors distinguish between coagulation and flocculation. Flocculation is usually taken to mean the process in which particles are interlinked by molecular chains with no change in the zeta potential (anionic and non – ionic organic flocculants). Coagulation, however, is taken to mean the electrical neutralization of suspended particles, as brought about by iron and aluminium hydroxide.

2.3 Surface Complexation

Sorption is combining in two types: matrix sorption and surface sorption and they differ from each other. Matrix sorption can be defined as absorption, but surface sorption is adsorption. In this part surface sorption will be described generally.

Surface sorption may occur by physical bonding forces (Van Der Waals, it is also called physisorption), by chemical bonding (Coulomb forces) and by Hydrogen bonding (Chemisorptions). Physisorption is reversible in most cases, but remobilization of components bounding by chemisorptions is difficult. Differently charged of molecules influence the ion exchange and especially ion exchange is based on it. There are interactions between liquid and solid phases and numerous equations describe them. These equations change from simple equations to complicated mechanistic models and it is based on surface complexation.

In order to describe the phenomenon of sorption is using surface complexation surface theory. At the surface of iron, aluminium, hydroxides as humic substances, there are cations that are not completely surrounded by oxygen ions on the contrary the cations in the interior of the crystal lattice. Their valence electrons, so they may bind water molecules. After sorption, the protons of these water molecules rearrange such that every surface oxygen atom binds only one proton. The second proton binds to oxygen atoms in the crystal lattice. Thus, a layer of functional groups is formed containing O, S, or N on the surface of the mineral (Brodjer, 2008).

After Stumm and Morgan (1996) the reaction can be described as follows:

$$\{GH\}+Mez^{+} \leftrightarrow \{GMez^{-1}\} + H^{+} \qquad (2.1)$$

Here, GH is a functional group as $(R\text{-}COOH)_n$ or $(=AlOH)_n$. The capability of functional groups to form complexes strongly depends on the acid – base behaviour and, hence, on pH changes in an aquatic system.

Similar to complexes in solution, surface complexes can be distinguished in inner-spherical complexes, where the ion is directly bound to the surface, and outer-spherical complexes where the ion is covered by a hydration sleeve with electrostatic binding. The inner-sphere complex is much stronger and independent of electrostatic forces, i.e. a cation can also be sorbed on a positively charged surface (Drever, 1997).

2.3.1 Phreeqc Interactive

Phreeqc can be used as a speciation program to calculate saturation indices and the distribution of aqueous species. Analytical data for mole balances can be defined for any valence state or combination of valence states for an element. Distribution of redox elements among their valence states can be based on a specified pe or any redox couple for which data are available. Phreeqc allows the concentration of an element to be adjusted to obtain equilibrium (or a specified saturation index or gas partial pressure) with a specified phase. Solution compositions can be specified with a variety of concentration units. In batch – reaction calculations, Phreeqc is oriented toward system equilibrium rather than just aqueous equilibrium. For a purely equilibrium calculation, all of the moles of each element in the system are distributed among the aqueous phase, pure phases, solid solutions, gas phase, exchange sites, and surface sites to attain system equilibrium. Non – equilibrium reactions can also be modelled, including aqueous – phase mixing, user – specified changes in the elemental totals of the system, kinetically controlled solid-liquid heterogeneous reactions, and to a limited extent kinetically controlled aqueous homogeneous reactions. Mole balances on hydrogen and oxygen allow the calculation of pe and the mass of water in the aqueous phase, which allows water – producing or consuming reactions to be modelled correctly.

The program Phreeqe dates back to 1980 (Parkhurst, 1980), at that time written Fortran and named Phreeqc. The option of the program comprised (Broder & Britta, 2008):

- Mixing of waters
- Modelling equilibrium between solid and aqueous phase by dissolution – precipitation modelling
- Modelling effects of changes in temperature
- Calculation of element concentrations, molalities, activates of aquatic species, pH, PE, saturation index, mole transfer as function of reversible / irreversible reactions

In 1988, a version of Phreeqc was written including Pitzer equations for ionic strengths greater 1 mol/L thus applicable for brines or highly concentrated electrolytic solutions (Plummer et al., 1988). Phreeqc (Appelo & Postma, 1994) included all options of Phreeqc and additionally a one dimensional transport module taking into account dispersion and diffusion. Phrkin was an add-on module to Phreeqe to model kinetically controlled reactions.

In 1995 Phreeqc (Parkhurst, 1995) was completely rewritten using the C programming language. This version removed nearly all limits regarding number of elements, aquatic species, solutions, phases, exchangers and surface complexes by abandoning FORTRAN formats in the input files. Additionally, the equation solver was revised (more robust now) and several other options were added. With the 1995 version to the present, many options have been possible. The most recent version, Phreeqc in the version 2 (Parkhurst & Appelo, 1999), additionally allows for the following simulations:

- The formation of ideal and non-ideal solid solution minerals
- Kinetic reactions with user-defined conversion rate
- Change the number of exchanger places with dissolution or precipitation of reactants
- Inclusion of isotope balances in inverse modelling

2.4 Effect of Coagulation and Flocculation

The coagulation – flocculation processes neutralize or reduce the zeta potential of non - settleable solids allowing the Van Der Waals force (Zeta Potential and Van Der Waals force are described in the following) of attraction to begin pulling particles together. These particles are then able to gather into small groups of microfloc, as shown in figure 2.1 (American Waste Water Association - AWWA, 1979). Although these particles are larger than the original colloids, they are held together rather weekly. Individual particles are invisible to the naked eye and are still non - settleable. However, the gentle stirring action created by the flocculation process brings the microfloc particles together to form large and relatively heavy floc particles (macrofloc), which can settle or be filtered.

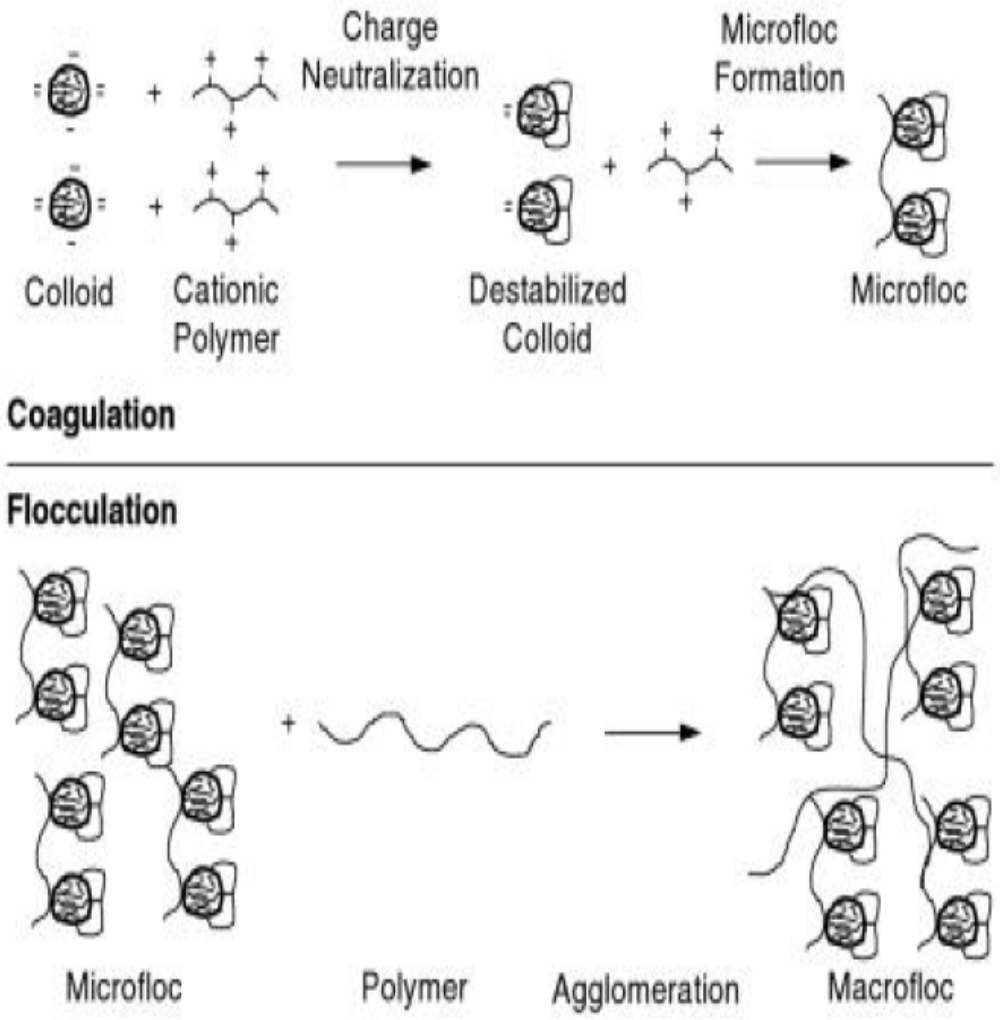

Figure 2.1 Microfloc and macrofloc formation (AWWA, 1979).

2.4.1 Zeta Potential

Zeta potential is a scientific term for electro kinetic potential in colloidal systems. In the colloidal chemistry literature, it is usually denoted using the Greek letter zeta (ζ), hence ζ-potential. From a theoretical viewpoint, the zeta potential is the electric potential in the interfacial double layer (DL) at the location of the slipping plane versus a point in the bulk fluid away from the interface. In other words, zeta potential is the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle (Mcknaught & Wilkinson, 1997).

The significance of zeta potential is that its value can be related to the stability of colloidal dispersion. The zeta potential indicates the degree of repulsion between adjacent, similarly charged particles in dispersion. For molecules and particles that are small enough, a high zeta potential will confer stability, the solution or dispersion will resist aggregation. When the potential is low, attraction exceeds repulsion and the dispersion will break and flocculate. Therefore, colloids with high zeta potential (negative or positive) are electrically stabilized while colloids with low zeta potentials tend to coagulate or flocculate as outlined in the table 2.1.

Table 2.1 The relations of zeta potential with colloid stability (Mcknaught & Wilkinson, 1997)

Zeta Potential (mV)	Stability behaviour of the colloid
From 0 to $\pm$ 5	Rapid coagulation or flocculation
From 10 to $\pm$ 30	Incipient stability
From 30 to $\pm$ 40	Moderate stability
From 40 to $\pm$60	Good stability
More than $\pm$61	Excellent stability

We can see from the related table that when the zeta potential is low, coagulation and flocculation occur rapidly and as can be defined when the zeta potential's cost is

more than ±61, then stability of colloid is excellent stability and almost coagulation or flocculation does not occur. In the below diagram showing the ionic concentration and potential difference as a function of distance from the charged surface of a particle suspended in a dispersion medium.

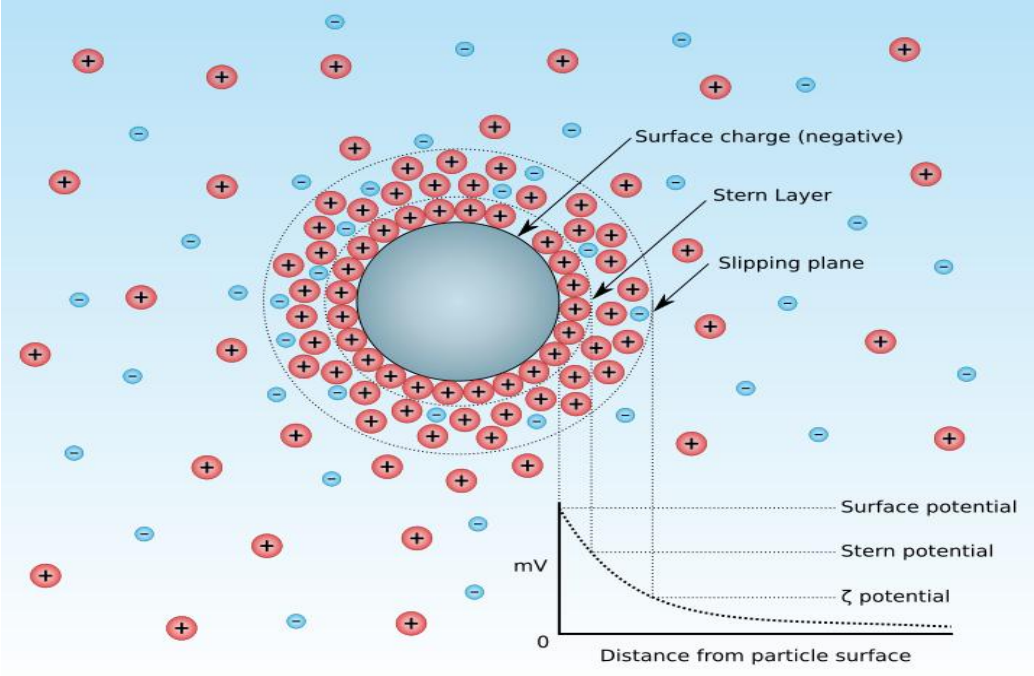

Figure 2.2 The ionic concentration and potential difference from the charged surface of a particle suspended in a dispersion medium (McNaught & Wilkinson, 1997).

McNaught & Wilkinson (1997) say that zeta potential is widely used for quantification of the magnitude of the electrical charge at the double layer. However, zeta potential is not equal to the Stern potential or electric surface potential in the double layer. Such assumptions of equality should be applied with caution. Nevertheless, zeta potential is often the only available path for characterization of double – layer properties. Zeta potential should not be confused with electrode potential or electrochemical potential.

2.4.2 Van Der Waals Force

Van Der Waals forces include attractions and repulsions between atoms, molecules, and surfaces, as well as other intermolecular forces. They differ from covalent and ionic bonding in that they are caused by correlations in the fluctuating

polarizations of nearby particles. Intermolecular forces have four major contributions:

1. A repulsive component resulting from the Pauli exclusion principle that prevents the collapse of molecules.

2. Attractive or repulsive electrostatic interactions between permanent charges (in the case of molecular ions), dipoles (in the case of molecules without inversion center), quadro poles (all molecules with symmetry lower than cubic), and in general between permanent multi poles. The electrostatic interaction is sometimes called the Keesom interaction or Keesom force after Willem Hendrik Keesom.

3. Induction (also known as polarization), which is the attractive interaction between a permanent multi pole on one molecule with an induced multi pole on another. This interaction is sometimes called Debye force after Peter J.W. Debye.

4. Dispersion (usually named after Fritz London), which is the attractive interaction between any pair of molecules, including non-polar atoms, arising from the interactions of instantaneous multi poles.

In physical chemistry, the Van Der Waals force (or Van Der Waals interaction), named after Dutch scientist Johannes Diderik Van Der Waals, is the sum of the attractive or repulsive forces between molecules (or between parts of the same molecule) other than those due to covalent bonds, the hydrogen bonds, or the electrostatic interaction of ions with one another or with neutral molecules or charged molecules (International Union of Pure and Applied Chemistry – IUPAC, 1997).

CHAPTER THREE
CHEMICALS IN COAGULATION / FLOCCULATION PROCESS

Coagulation is carried out by the addition of a chemical called as “coagulant” and results with the charge neutralization destabilization of colloids. Following surface charge neutralization, particles connect to each other and then flocs are formed. Since colloids in water are negatively charged, destabilization is achieved by adding positively charged ions that interact specifically with the negative colloids and reduce (or neutralize) their charge. Therefore, coagulation is usually accomplished by the addition of inorganic coagulants such as aluminium or iron based salts.

Coagulant aids (or flocculants) are preferably used (i) to increase the agglomeration ability of the particulate matters (produce denser and stronger flocs), (ii) to reduce the flocculation time, (iii) to maintain optimal conditions for coagulation/flocculation, (iv) to expand the pH range, and finally (v) to improve the treatment efficiency. For this purpose, polymeric compounds, sodium aluminates, bentonite, kaolin, etc. are used during the flocculation stage as coagulant aids. Coagulants and coagulant aids commonly used in water treatment are summarized in the following Table 3.1:

Table 3.1 Chemicals used in coagulation/flocculation processes as coagulant and coagulant aid (Benefield & Weand, 1982)

Chemical Name	**Chemical Formula**	**Coagulant**	**Coagulant Aids**
Aluminium Sulphate	$Al_2(SO_4)_3$	√	
PAC	% 10 Al_2O_3	√	
PACS	% 18 Al_2O_3	√	
Ferric Chloride	$FeCl_3 . 6 H_2O$	√	
Ferric Sulphate	$Fe_2(SO_4)_3 \cdot 9 H_2O$	√	
Ferrous Sulphate	$FeSO_4 \cdot 7 H_2O$	√	
Calcium Hydroxide	$Ca(OH)_2$	√	√
Calcium Oxide	CaO	√	√
Sodium Aluminates	$Na_2Al_2O_4$	√	√
Activated Silica			√
Bentonite			√
Calcium Carbonate	$CaCO_3$		√
Sodium Silicate	Na_2SiO_3		√
Anionic Polymer	Various		√
Nonionic Polymer	Various		√
Cationic Polymer	Various	√	√

3.1 Coagulants

Coagulants used in colloid destabilization are generally inorganic nature. Aluminium or iron salts, and lime are favoured inorganic coagulants in water treatment. Ferric coagulants may have some advantages when coagulating certain types of water. The advantages of ferric coagulants are (i) effective coagulation over a wider pH range, usually from pH 4 to 9; (ii) production of the strong and heavy flocs which can settle rapidly and (iii) effective in colour, taste, and odour-producing matter removals. On the other hand, aluminium based coagulants such as aluminium sulphate (known as alum) or complex forms of aluminium compounds are used in drinking water treatment to enhance the removal of particulate matters and colloids through coagulation/flocculation processes. Polymeric aluminium compounds are

more effective over a wider pH range and at lower temperatures than alum. Moreover, required dose of the coagulant is decreased due to the higher charge density of polymeric forms. Lime is also preferably used chemical because of its lower cost. However, higher doses of lime results with higher pH and sludge quantity, as well.

A new class of coagulants – pre-hydrolyzed, preformed or polymeric Al and Fe salts, also known as inorganic polymeric coagulants (IPCs) – has been launched on the market in the 80's, and considerable developments have been realized for pre-hydrolyzed aluminium and iron based coagulants. Aluminium chlorohydrate, poly aluminium chloride, poly aluminium sulphate chloride, poly aluminium silicate chloride and forms of poly aluminium chloride with organic polymers are representative products of the IPCs. Iron forms comprise of poly ferric sulphate and ferric salts with polymers. In addition, polymerized aluminium – iron blends are also available. The principal advantages of pre – polymerized inorganic coagulants are higher efficiency over wide ranges of pH and raw water temperatures. They are less sensitive to low water temperatures; lower dosages are required to achieve water treatment goals; less chemical residuals are produced; and lower chloride or sulphate residuals are produced, resulting in lower final water TDS (Bucişcanu, 2008). They also produce lower metal residuals.

3.1.1 Iron Salts (Iron Based Coagulants)

The iron salts used in treatment consist of ferric sulphate, ferrous sulphate, ferric chloride and ferric chloride sulphate. The ferric chloride and ferric sulphate are widespread iron salts used in water treatment plants. Ferric sulphate ($Fe_2 (SO_4)_3 \cdot 9H_2O$) is supplied as a red-brown powder or as granules. It is difficult to dissolve and the solution is corrosive to aluminium, concrete and most steels. In a manner corresponding to the reaction of aluminium sulphate, the formation of a ferric hydroxide floc is the result of the reaction between the acidic coagulant and the natural alkalinity of the water, which usually consists of calcium bicarbonate, as expressed by the equation below, with the insoluble products (precipitates).

$$Fe_2(SO_4)_3 + 3Ca(HCO_3)_2 \rightarrow 2Fe(OH)_3\downarrow + 3CaSO_4 + 6CO_2 \quad (3.1)$$

Ferric chloride is supplied in the anhydrous form as a green-black powder, chemical formula $FeCl_3$, and also as a dark-brown syrupy liquid or as crystal ferric chloride $FeCl_3 \cdot 6H_2O$. The solution is very corrosive and attacks almost all metals and concrete. In coagulation, the reaction is defined by the following equation, with the insoluble products (precipitates).

$$2FeCl_3 + 3Ca(HCO_3)_2 \rightarrow 2Fe(OH)_3\downarrow + 3CaCl_2 + 6CO_2 \quad (3.2)$$

The production of calcium chloride ions in the above reaction may increase the corrosives of the water and ferric sulphate, despite its higher price, is usually preferred to ferric chloride.

Water treatment with iron coagulants requires intensive control due to excessive concentrations of residual iron. Higher iron concentration in water, results with the discoloration on the clothes during the washing operation, and consumer objections, as well.

The production of iron – based coagulants often depends on the availability of iron powders. Iron residues may be used as inexpensive sources. Liquid residues from metallurgical industries, containing ferrous iron in acid solution, may also be used to make iron salt solutions. Both of these iron sources are subject to contain more impurities than the use of purified iron powders. Iron salts are produced from the reaction of iron powders with acid or an oxidant. The complex iron – based coagulants are made using basic iron salts; therefore their prices are higher than those of iron salts (Niquette et al., 2004).

Although, complex forms of iron coagulant are available in the market (e.g. poly ferric chloride, etc.), their applications in water treatment practices are limited (Eagle, 2002 & Wang, 1987). Poly ferric sulphate (PFS) can be produced from Fe (II)-containing minerals (such as pyrite – FeS_2, copperas – $FeSO_4 \cdot 7H_2O$ or

magnetite –Fe_2O_3). PFS synthesis can be performed in two ways: (1) A two-step procedure, in which oxidation of Fe^{2+} to Fe^{3+} and basification occur consecutively. Protected oxidizing reaction takes place in the presence of sulphuric acid in excess; basification agents are weak bases such as Na_2CO_3 and $NaHCO_3$. During a subsequent ageing step, polymeric species arise. (2) A one-step procedure, in which PFS synthesis can take place by simultaneous oxidation and basification selecting appropriate oxidizer and reaction condition. Common oxidizing agents are nitric acid, peroxides, alkaline chlorates and per chlorates, ozone, per sulphates, with or without a catalyst.

Poly ferric sulphate (PFS) is a relatively new pre - polymerized Fe (III) coagulant. PFS consists of hydrolysis and polymeric iron species. PFS are promising alternative to the conventional coagulants, because it is more effective especially at lower temperatures and in broader pH range. In addition, lower coagulant dosages result with similar efficiency and reduced residual metal ions. Besides, PFS is less corrosive than other iron based coagulants (Shi et al. 2004).

3.1.2 Aluminium Salts (Alum Based Coagulants)

Aluminium based coagulant such as alum or polymeric aluminium compounds are widely used conventional coagulants in water treatment. Typical aluminium based coagulants used in water treatment are presented in Table 3.2.

Table 3.2 Typical aluminium based coagulants used in water treatment

Chemical	**Symbol**	**Composition**
Aluminium Sulphate	ALUM	$Al_2(SO_4)_3 \cdot 18H_2O$
Aluminium Chlorohydrate	ACH	$Al_2(OH)_3Cl_3$
Poly Aluminium Chloride	PAC	$Al_2(OH)_5Cl$
Poly Aluminium Chlorosulphate	PACS	$Al_3(OH)_{4.95}Cl_3 \cdot 55(SO_4)_{0.25}$
Poly Aluminium Sulphate	PAS	$Al(OH)_3SO_4$
Sodium Aluminates	-	$NaAlO_2$

When aluminium coagulants (aluminium sulphate, aluminium chloride, aluminium sulphate + sodium carbonate, sodium aluminates) are added to the water, aluminium ions are hydrolyzed rapidly and hydroxides of the metal are produced entrapping the neutralized charged particles (colloids). These consecutive processes, i.e. dissolution and hydrolyses, may be represented with the following simplified equation. During the metal hydroxide precipitation for alum, sulphuric acid is also formed as a by-product. The sulphuric acid reacts with alkalinity in the raw water to produce carbon dioxide, thus depressing the pH.

$$Al_2(SO_4)_3 + 6H_2O \rightarrow 2Al(OH)_3 \downarrow + 3H_2SO_4 \qquad (3.3)$$

Sodium aluminate which is either in liquid or dry form has been used to a limited extent as a coagulant and for water softening. The previous efforts to apply the material as a substitute for alum were not successful in many cases. The relatively high cost of the product over alum precluded also its use. The application of the product only as an accelerating matter has been much more successful.

3.1.3 Aluminium Polymers

Recently, a number of alternative aluminium – based coagulants have been developed for water treatment applications. Aluminium polymers are used both for neutralization and connecting the colloids so that coagulation may take place more efficiently (Degremont, 1991). Moreover, polymers promote the agglomeration of crystallized forms of aluminium hydroxide which ultimately precipitates.

The overall formula for these compounds is $(Al_n(OH)_p(Cl)_q(SO_4)_r)$. The length of the polymerized chain, molecular weight and number of ionic charges is determined by the degree of polymerization.

The poly aluminium coagulants are effective over a broader pH range and in general consume considerably less alkalinity than alum. Other advantages of poly aluminium coagulants to the alum based ones include the followings:

- lower residual aluminium concentrations in the treated water (typically 0.01-0.05 mg/L)
- advanced settling properties at low raw water temperatures
- reduced sludge production at an equivalent doses of alum
- lower dosage requirement

The complex forms of aluminium coagulants usually cost twice as much as alum because they are derived from these salts. In order to reduce the costs and to obtain constantly good quality water, producers often use alum in cases when raw water is easily treatable and they use complex forms, like PASS, when raw water is difficult to treat. Complex forms are preferably utilized in winter when raw water is cold and the chemical reactions are slower. PASS is preferred to alum in cold conditions because it instantly forms hydroxide aluminium flocs that adsorb contaminants on their surfaces. The optimized use of PAC, PASS and other complex forms normally produce lower soluble alumina residuals in the treated water than alum does. The other complex forms, PAS, poly – aluminium chloride and pre – hydrolyzed alum, are also more effective than alum in cold water conditions and their selection is dependent on the raw water characteristics (pH, alkalinity, organic content, inorganic impurities) and the clarification process being used. Their use could also decrease or eliminate the need for polymer.

Among the various aluminium based coagulants, PAC and PACS are specially emphasized in this section since they have been experienced in the thesis.

3.1.3.1 Poly Aluminium Chloride (PAC)

Poly aluminium chloride (PAC) has been developed as an alternative coagulant to alum by an Indian manufacturer. PAC hydrolyses easily, emitting poly hydroxides with long molecular chains and greater electrical charge in the solution, thus contributing to maximise the physical action of the flocculation. Better coagulation is obtained with PAC at medium and high turbidity waters. Floc formation with PAC is quite rapid. The sludge produced by PAC is more compact than that produced by

alum. It can cause rapid coagulation of water at different turbidity, produces less sludge and leaves less amount of residual aluminium. The formula and specification of the product is presented in Table 3.3.

Table 3.3 The formula and specification of PAC (Al – Dawery & Al – Jouburi, 2002).

PAC	$Al_2(OH)_5Cl$
Appearance	Clear
Al_2O_3	10%
Density (25 °C)	1,14±0,5
pH (in % 5 solution)	5
Basicity	68%

3.1.3.2 Poly Aluminium Chlorosulphate (PACS)

In order to further improve the coagulating effect of polymerized Al (III) chemicals, larger size and higher cationic charge poly aluminium salts are developed. It has been found that poly aluminium chlorosulphate (PACS) has larger species than PAC therefore; PACS should be more effective than PAC in water and wastewater treatment. Experimental evidence that PACS gives better coagulation performance than PAC, however, has not previously been shown. The formula and specification of the product is presented in Table 3.4.

Table 3.4 The formula and specification of PACS (David & James, 2003) .

PACS	$Al_3(OH)_{4.95}Cl_3{\cdot}55(SO_4)_{0.25}$
Appearance	Clear
Al_2O_3	18%
Density (25 °C)	1,275±0,5
pH (in % 5 solution)	4.5
Basicity	84%

3.1.3.3 Concerns Regarding to Utilization of the Aluminium Based Coagulants

Typically, a portion of the alum added to the raw water is not removed during treatment and remains as residual in treated water. The occurrence of aluminium in treated water has been considered for many years to be an undesirable aspect of treatment practice (Driscoll & Letterman, 1988; Benschoten & Edzwald, 1990). There is considerable concern throughout the world over the levels of aluminium found in drinking water sources (raw water) and treated drinking water. A high (3.6 to 6 mg/l) concentration of aluminium in treated water gives rise to turbidity, reduces disinfection efficiency, and may precipitate as $Al(OH)_3$ during the course of distribution (Rahman, 1992). Moreover, the possibility of an association between aluminum and neuropathological diseases including presenile dementia and Alzheimer's disease is frequently hypothesised (Schecher & Driscoll, 1988; Crapper & Boni, 1980; Davidson et al., 1982; Martyn et al., 1989; Gardner & Gunn, 1991; Jekel, 1991). Therefore, utilization of optimal doses is important issue and in this framework since the polymeric forms of aluminium compounds reduce the doses is an important tool, as well.

3.1.4 Lime

Lime may be used as a coagulant without additional chemicals for waters having a high content of magnesium compounds. A large proportion of the magnesium is thus changed to a bulky flocculent mass. However, when waters containing magnesium are coagulated with lime, they have a high alkalinity.

Lime may be purchased in the form of either quicklime, CaO, or hydrated lime, $Ca(OH)_2$. Quicklime contains from 75 to 99 percent of pure calcium oxide, but it must be slaked with water before it is used. Hydrated lime, on the other hand, is slaked lime that is ready for use, and it contains between 80 and 99 percent of calcium hydroxide. Quicklime is cheaper than hydrated lime, and therefore it is used almost entirely in large plants. However, hydrated lime is usually preferred for small plants, because the saving in the cost of chemical by using quicklime is not enough

to compensate for the costs of the labour and equipment that are required for slaking the quicklime (Dezhuane, 1990).

3.1.5 Synthetic Organic Coagulants

Synthetic organic coagulants are synthetic organic molecules, cationic in nature, and are only available in liquid form. These coagulants may be used directly and totally or partially serve as a replacement for an inorganic coagulant. The use of organic coagulants leads to a substantial reduction in the amount of sludge produced. The sludge that is extracted is denser and also stickier. Thus, the organic coagulants are not suitable for every type of separation processes (Degremont, 1991).

3.2 Coagulant Aids

Coagulant aids are used to improve the settling characteristics of floc produced by aluminium or iron coagulants. Coagulant aids are added (i) to improve coagulation, (ii) to obtain stronger and settleable floc, (iii) to overcome the effect of temprature decreases, (iv) to reduce the coagulant dose, and (v) to decrease sludge production. In practice, there are three types of coagulant aids, these are activated silica, weighting agents (clay, bentonite, etc.), and polymers.

3.2.1 Activated Silica

Activated silica has been used as a coagulant aid with alum since the late 1930s and remains in use today. Activated silica increases the rate of coagulation, reduces the coagulant dosage. It gives good results especially when used together with alum in cold water. It is added after the coagulant and prepared immediately before use by partially neutralizing the alkalinity of a solution of sodium silicate, Na_2SiO_3.

The chief advantage of using activated silica is that strengthens the floc, making it less likely to break apart during sedimentation or filtration. In addition, the resulting floc is larger and denser and settles more quickly. Improved colour removal and

better floc formation at flow temperatures can also result. Activated silica is usually added after the coagulant, but adding it before can also be successful, especially with low – turbidity water. It should never be added directly with the alum because they react with each other.

A major disadvantage of using activated silica is the precise control required during the activation step to produce a solution that will not get. Too much silica will actually slow the formation of floc and cause filter clogging.

3.2.2 Weighting Agents

When some natural materials are added to water, they form additional particles that enhance floc formation. Weighting agents are principally used to treat water high in colour, low in turbidity, and low in mineral content. This type of water would otherwise produce small, slowly settling floc.

Clays can act much like activated silica in that they have a slight negative charge and can increase the density of the flocs, thus increasing the settling of flocs. Bentonite clay is a common weighting agent. Dosages in the range of 10 to 50 mg/L usually produce rapidly settling floc. In water with low turbidity, the clay increases turbidity, which speeds formation of floc by increasing the number of chance collisions between particles. Powdered limestone and powdered silica can also be used as weighting agents.

3.2.3 Polymers

Polymers are long chain carbon compounds of high molecular weight that have many active sites. The most effective polymers used in water treatment as coagulant aids are the anionic and non - ionic polymers.

Natural organic poly electrolytes such as sodium alginates and some soluble starch products have long been used in water treatment. Newer synthetic poly

electrolytes are now widely available. Proprietary coagulants consisting of solutions of synthetic poly electrolytes and metal salts are also on the market.

Polymers (also called poly electrolytes) can be classified as cationic, anionic, and non - ionic (or neutral). Cationic poly electrolytes produce positively charged ions when dissolved in water. Since the colloids commonly found in raw water are usually negatively charged, they have been widely used in treatment plants. They can be used as a coagulant or as an aid together with alum or ferric sulphate. Utilization of cationic poly electrolytes is resulted with reduced coagulant doses, better floc formation and settles ability, less sensitivity to pH and the flocculation of living organisms, such as bacteria, and algae.

Anionic poly electrolytes produce negatively charged ions when dissolved in water and have been used to remove positively charged solids. Anionic poly electrolytes are also used primarily with aluminium and iron coagulants. Advantages are increased floc size, improved settling properties, and generally stronger floc.

Non - ionic polyelectrolyte's has balanced, or neutral charge ion and released both positively and negatively charged ions when dissolving in water.

3.3 Alkaline Chemicals and Acids

The pH is a prominent factor in the removal of colloids. The optimum pH is important both for coagulation and flocculation stages. The pH necessary for chemical reactions should be adjusted by the addition of acids or a base.

The alkalinity serves to neutralize the sulphuric acid which forms, together with hydroxide, when sulphates hydrolyse. If left in the water the acid would recombine with the hydroxide and revert to sulphate. Hydroxide is the desired end product as it is insoluble, floc – forming and heavier than water, and it carries the negative electric charge necessary to neutralize the positive charges of the colloidal particles. Therefore, when the natural alkalinity is insufficient to react with the coagulants,

alkalinity must to be added either as lime or soda – ash. Alkaline chemicals are also added, if required, to provide the optimum pH value for coagulation to take place.

In very alkaline water, the addition of the optimum dose, for colour and turbidity removal, of a metallic salt such as alum or ferric sulphate, may not depress the pH to the optimum level for coagulation. Increasing the dose of metallic salt will further depress the pH, but will result in a very undesirable increase in the soluble metallic content of the water, which will carry through the filters to supply. Dosing with a strong mineral acid, such as sulphuric acid, will depress the pH without the unwelcome increase in the soluble metallic content of the water.

CHAPTER FOUR
MATERIAL AND METHODS

In this section, sampling of the raw water, preparation of the samples, experimental studies (i.e. jar test experiments), chemical preparation and the measurements including the equipment used in the measurements are explained.

The raw water used in the experiments was obtained from Petkim. The Guzelhisar Dam is the main water source for Petkim and other industrial plants in the region. Dam was constructed by Petkim at 1982 and has been operated for compensating neighbour industrial plants, like Tüpraş, Petrol Ofisi, Enka and İzsu (Aliağa Municipality) water requirements and processed by State Hydraulic Works of Turkey. The specification of Guzelhisar Dam is presented on the Table 4.1.

Table 4.1 Guzelhisar Dam specification.

Area of raining	450 km^2
Minimum Water Level	63 m
Normal Water Level	104 m
Maximum Water Level	107 m
Dead Volume	12 x 10^6 m^3
Active Volume	143 x 10^6 m^3
Total Storage Volume	155 x 10^6 m^3

4.1 Characteristics of the Raw Water

Raw water samples were taken from Petkim water treatment plant. Petkim water treatment plant consists of two lines. Line 1 capacity is 4800 m^3 / h and constructed by Lurgi (Germany) in 1983, but Line 2 capacity is 3000 m^3 / h and constructed by OTV (France) in 2005. The total capacity of plant is 7800 m^3 / h. The plant is presented in Figure 4.1:



Figure 4.1 The water treatment plant (Petkim, Aliaga)

Treatment plant comprises of coagulation/flocculation and sedimentation units. Poly aluminium chloride and anionic polyelectrolyte are used for coagulation and flocculation purposes. Following to coagulation and flocculation, flocs are settled in the sedimentation tank. Following to sedimentation unit, in order to reduce the turbidity, water are filtered by using gravity filters. Filtration is performed by anthracite and biodagene. After filtration, demineralization unit is used to obtain drinking water (potable water). Drinking water is transferred to the central distribution tank for supplying the water for all complexes. Sludge which is produced from sedimentation tank is removed by dewatering system as sludge cake. The flow diagram of water treatment plant is presented in the Figure 4.2:

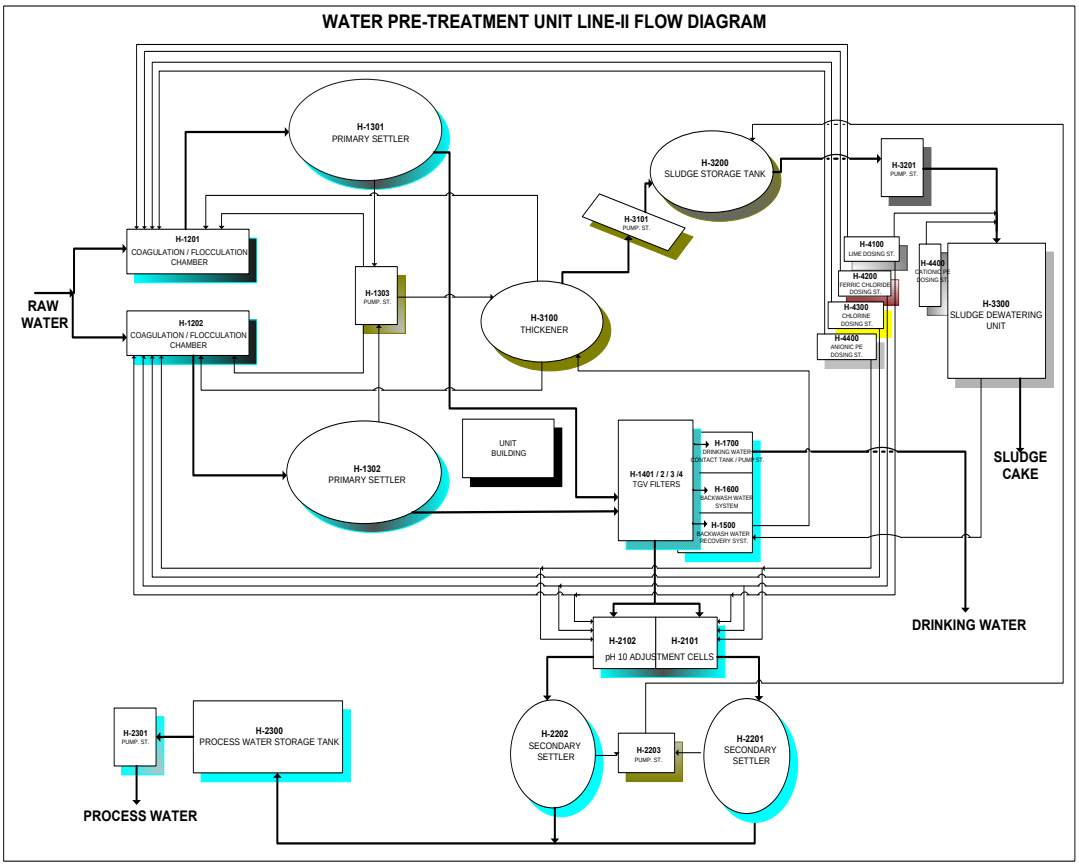

Figure 4.2 The flow diagram of water treatment plant.

All collected samples were stored in a cool (°C) and dark place. Their specific characteristics are presented in Table 4.2.

Table 4.2 Characteristics of the raw water

Parameter	**Unit**	**Measured Value**
pH	-	6.5 - 7.2
Turbidity	NTU	17.75 - 17.92
Conductivity	µS / cm	185 – 188
Temperature	°C	27 – 29
Redox Potential / EH	mV	508 – 512

4.2 Chemicals Used in the Experiments

In order to decrease the chemical dosage and improve the treatment performance, coagulant and coagulant aids were used. The commercially available coagulants examined in the study were aluminium sulphate (alum), poly aluminium chloride (PAC), poly aluminium chlorosulphate (PACS) and anionic poly electrolyte.

Alum ($Al_2(SO_4)_3$) contains 16% (w/w) Al_2O_3 and having density of 1.15 g/cm^3. The pH of the alum in 5% solution is reported as 3. The poly aluminium chlorosulphate - PACS ($Al_3(OH)_{4.95}Cl_3{\cdot}55(SO_4)_{0.25}$) contains 18% (w/w) Al_2O_3, and having a density of 1.275 g/cm^3. The pH of the PACS in 5% solution is reported as 4.5. The poly aluminium chloride - PAC ($Al_2(OH)_5Cl$) containing 10% (w/w) Al_2O_3, and having a density of 1.14 g/cm^3. The pH of the PACS in 5% solution is reported as 5.

Before the jar test experiments, required chemical dosage and optimal pH is also determined theoretically by using PHREEQC interactive program.

4.3 The Analytic Methods and Equipment Used in the Experiments

In the experiments pH, turbidity, conductivity, and temperature were measured for both raw water and treated water samples. The methods and equipment used in the experiments are described here in detail.

pH: The pH defines the acidic or basic nature of the water. The pH is one of the most important parameter in water treatment, especially for effective coagulation performance. Each coagulant has own optimum operating pH range. Therefore in the experiments pH measurement was done to define the raw water pH value as first and then to determine the pH of the solution after the chemical addition. The pH of the samples was determined electrometrically using a glass electrode. In the experiments, portable equipment, i.e. WTW Multi 3430 Multi parameter Meter, was

used. The pH meter was calibrated before the experiments using a series of standard solutions of known pH.

Turbidity: The presence of suspended solids and colloidal particles in the water gives the liquid a cloudy appearance called as turbidity and is important parameter in water treatment. It is measured either in Nephelometric Turbidity Unit (NTU) or Formazin Turbidity Unit (FTU) by turbidity meter. The method used in the experiments is based upon a comparison of the intensity of light scattered by the sample under defined conditions with the intensity of light scattered by a standard reference suspension. The higher the intensity of scattered light results the higher the turbidity.

In the experiments turbidity was measured according to the Nephelometric method, i.e. Standard Method 2130B (APHA, et al., 1998) by using a Portable Hach 2100P turbid meter.

Conductivity: Conductivity is a measure of the ability of water to pass an electrical current. It is an indirect measure of the presence of inorganic dissolved solids such as chloride, nitrate, sulphate, phosphate, sodium, magnesium, calcium, iron and aluminium. The presence of these substances increases the conductivity of the water. Organic substances like oil, alcohol, and sugar do not conduct electricity very well, and thus have a low conductivity in water. The basic unit of measurement of conductivity is the mho or siemens. Conductivity is measured in microchips per centimetre (μmhos/cm) or microsiemens per centimetre (μs/cm).

A Potentiometric method based on induction and eliminates the effects of polarization was used in the experiments. WTW Multi 3430 Multiparameter Meter was used for measurements.

Temperature: Water temperature is a controlling factor for aquatic life: it controls the rate of metabolic activities, reproductive activities and therefore, life cycles. If stream temperatures increase, decrease or fluctuate too widely, metabolic

activities may speed up, slow down, malfunction, or stop altogether. In the experiments, digital stem thermometer with stainless steel probe was used to measure the temperature of the samples.

Table 4.3 Water quality analysis and the equipment used in the experiments

Parameter	Instrument	Method
pH	WTW Multi 3430 Multi parameter Meter	Electrometric method
Turbidity	Portable Hach 2100P Turbid meter	Nephelometric method
Conductivity	WTW Multi 3430 Multi parameter Meter	Potentiometric method
Temperature	Digital Stem Thermometer with stainless steel probe	-
EH	WTW Multi 3430 Multi parameter Meter	Standard hydrogen electrode method

4.4 Preparation of the Solutions

Before the jar test stock solution of chemicals was prepared by using chemicals and distilled water. Stock solution was diluted to obtain 1, 3, 6 ppm PAC, PACS, Alum as coagulant, and 1 ppm for anionic poly electrolyte.

4.5 Experimental Set – Up (Jar – Test)

In the experiments, jar test that is a simple and effective method that simulates the coagulation/flocculation processes was used. The main purpose of the jar test experiment is to optimize the coagulant type and dosage, determination of optimal pH and other operational conditions (i.e. optimization of mixing time and intensity for rapid and slow mixings).

In this study, Stuart Model SW – 1 Flocculator was used for jar test experiments. The SW1 accommodates up to six samples and is specially designed with mixer that

can be operated at various speeds. A digital display clearly indicates the speed of the rotational stainless steel paddles, which can be varied from 25 to 250 rpm. Two pre-set programs allow routine speed and time parameters to be input and then selected by simply pressing one button.

Jar testing process applied in the experiments is summarized below:

- Filling of the raw water samples to the beakers
- Addition of the chemicals to each beaker
- Rapid mixing (stirring) at 100 rpm for 2 minutes
- Slow mixing at 40 rpm for 20 minutes
- Settling through 30 minutes
- Sampling form the supernatant of each beaker

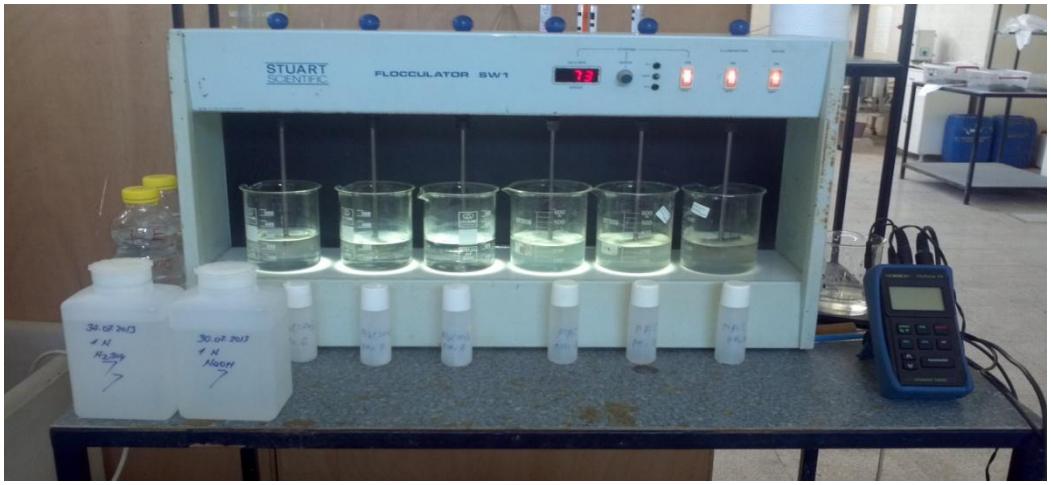

Figure 4.3 Jar Testing apparatus (Flocculator - Stuart Model SW1)

During the experimental studies, optimal dose and conditions of each chemical were investigated separately. Samples taken from the supernatant at the end of the coagulation/flocculation/sedimentation process were analyzed. The pH, conductivity, turbidity, and EH measurements were done for each sample.

The list of the materials and equipment used in the experiments are presented below:

- ► Beakers (600 mL)
- ► Analytical balance
- ► Magnetic stirrer
- ► Pipettes (10 mL)
- ► NaOH and H_2SO_4
- ► Chemicals (PAC, PACS and Alum)
- ► Coagulant aid (Anionic polyelectrolyte)
- ► Raw water
- ► pH and conductivity meters
- ► Turbidimeter

CHAPTER FIVE
EXPERIMENTAL RESULTS

Results of the experimental studies are presented in this section. As it stated previous chapters, optimal chemical dosage and pH was determined theoretically by using PHREEQC interactive program as first, and the results were verified with jar test study.

5.1 Determination of the Optimal Chemical Dosage and pH by PHREEQC Interactive Program

In order to determine the dosages of chemicals PHREEQC were carried out using coagulant chemical and sodium hydroxide. The optimal chemical dosage and NaOH doses on the changing of pH are depicted in Figures 5.1 and 5.2 respectively.

Varied pH values were applied in order to determine the optimal pH value. The Figure 5.2 shows that Sodium hydroxide (NaOH) was used in 10 steps to adjust the pH. Optimal dose of chemical determined theoretically at previous based on the Figure 5.1.

AlCl3 (mg	pH	pe	Al(OH)3(a)	d_Al(OH)3(a)	AlumK	d_AlumK	Alunite	d_Alunite	Basaluminite	d_Basaluminite
0	8.28	4	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
8	7.24346	11.6308	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.00E+01	1.37E-05
16	6.88927	12.0559	0.00E+00							
24	6.64055	12.3543	0.00E+00							
32	6.4325	12.604	0.00E+00							
40	6.23613	12.8397	0.00E+00							
48	6.04173	13.073	0.00E+00							
56	5.84053	13.3144	0.00E+00							
64	5.57344	13.6349	0.00E+00							
72	5.13874	14.1566	0.00E+00							
80	4.71744	14.662	0.00E+00							
NaOH (m	pH	pe	Al(OH)3(a)	d						
20	7.82181	11.2251	0.00E+00							
40	8.19778	10.8492	0.00E+00							
60	8.26849	10.7784	0.00E+00							
80	8.34033	10.7066	0.00E+00							
100	8.42135	10.6256	0.00E+00							
120	8.50609	10.5409	0.00E+00							
140	8.58767	10.4593	0.00E+00							
160	8.66173	10.3852	0.00E+00							
180	8.72712	10.3198	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
200	8.78445	10.2625	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00

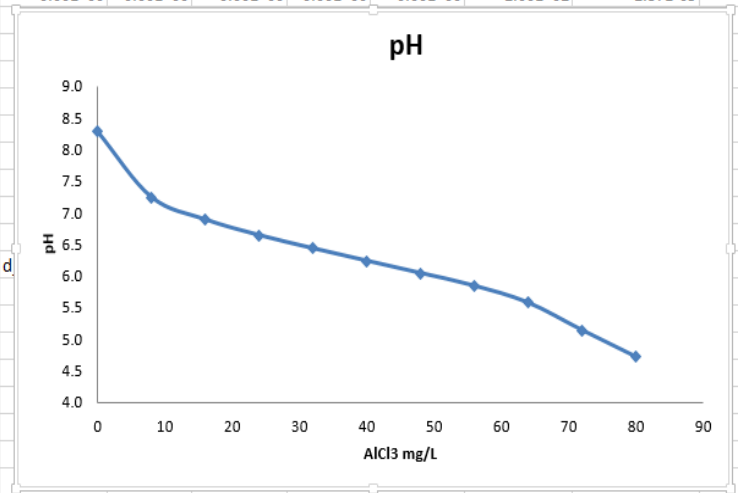

Figure 5.1 Dosage calculations with Phreeqc Interactive.

step	NaOH mg	pH	pe	Al(OH)3(a)	d_Al(OH)3(a)	AlumK	d_AlumK	Alunite	d_Alunite	Basaluminite	d_Basaluminite
1	2	5.59	1.35E+01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	8.00E-06	8.00E-06
2	4	6.43	1.26E+01	4.01E-06	4.01E-06	0.00E+00	0.00E+00	0.00E+00	0.00E+00	7.98E-06	7.98E-06
3	6	6.96	1.21E+01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	7.43E-06	7.43E-06
4	8	7.21	1.18E+01	0.00E+00	0.00E+00						
5	10	7.36	1.17E+01	0.00E+00	0.00E+00						
6	12	7.48	1.16E+01	0.00E+00	0.00E+00						
7	14	7.58	1.15E+01	0.00E+00	0.00E+00						
8	16	7.68	1.14E+01	0.00E+00	0.00E+00						
9	18	7.76	1.13E+01	0.00E+00	0.00E+00						
10	20	7.82	1.12E+01	0.00E+00	0.00E+00						

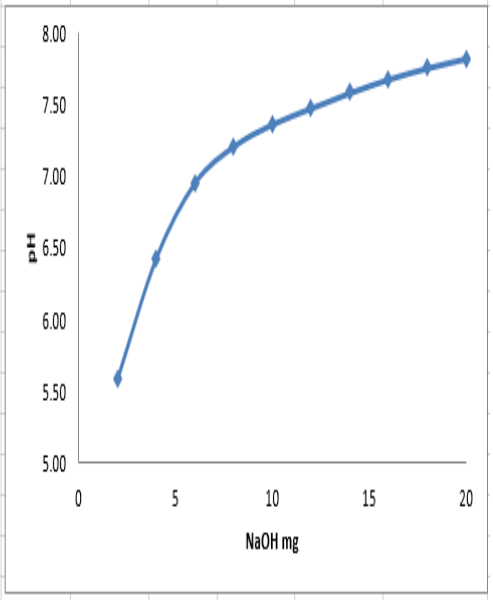

Figure 5.2 Calculation of NaOH dosages with Phreeqc Interactive.

5.2 The Results of the Jar Tests for Poly Aluminium Chloride - PAC

5.2.1 Determination of the Optimal Dose of Poly Aluminium Chloride - PAC

In order to determine the optimal PAC dose [$Al_2(OH)_5Cl$], experiments were carried out using solutions 1 ppm, 3 ppm, and 6 ppm PAC at 28.1 $^{\circ}$C, 28 $^{\circ}$C and 28.2 $^{\circ}$C temperatures relatively. The pH was adjusted in the range of 6.5-7.5. A coagulant aid, i.e. anionic polyelectrolyte was also introduced during the coagulation. Beakers were stirred at 100 rpm for 2 minutes in coagulation, and then stirred at 40 rpm for 20 minutes in flocculation. Following to coagulation/flocculation processes, beakers settled down through 30 minutes. Samples taken from the supernatant were analyzed and the results are presented in Tables 5.1 - 5.3, for each dose separately. The effect of the coagulant dose on the removals of turbidity and conductivity are depicted in Figures 5.3 and 5.4 respectively.

Table 5.1 The effect of 1 ppm PAC dose on treatment performance.

PAC	**1 ppm (0.25 mg/l)**
Anionic PE	**1 ppm**
NaOH	**0.4 ml**
pH	4.65 / 6.85
Conductivity	320 µS / cm
Turbidity	10.1 NTU
Temperature	28.1 ˚C
EH	512 mV

Table 5.2 The effect of 3 ppm PAC dose on treatment performance.

PAC	**3 ppm (0.75 mg/l)**
Anionic PE	**1 ppm**
NaOH	**0.65 ml**
pH	4.52 / 7.06
Conductivity	344 µS / cm
Turbidity	7.4 NTU
Temperature	28 ˚C
EH	512 mV

Table 5.3 The effect of 6 ppm PAC dose on treatment performance.

PAC	**6 ppm (1.5 mg/l)**
Anionic PE	**1 ppm**
NaOH	**1.00 ml**
pH	4.46 / 7.25
Conductivity	365 µS / cm
Turbidity	3.25 NTU
Temperature	28.2 ˚C
EH	512 mV

The variation of the turbidity parameter at various PAC doses is shown in Figure 5.3. For 1 ppm PAC addition, turbidity was decreased from 17.75 NTU to 10.1 NTU yielding approximately 43% efficiency. Increased PAC doses resulted with lower turbidity effluents. For the highest PAC dose, i.e. 6 ppm, effluent turbidity was measured as 3.25 NTU performing 82% of turbidity removal.

The variation of the conductivity for various PAC doses is also presented in Figure 5.4. Conductivity of the water was increased with the chemical addition, in general. It was increased from 185 µS / cm to 320 µS / cm for 1 ppm PAC dose. However, increased doses were not resulted significant increase in conductivity measurements. For the highest dosage, i.e. 6 ppm PAC, conductivity was measured as 365 µS / cm.

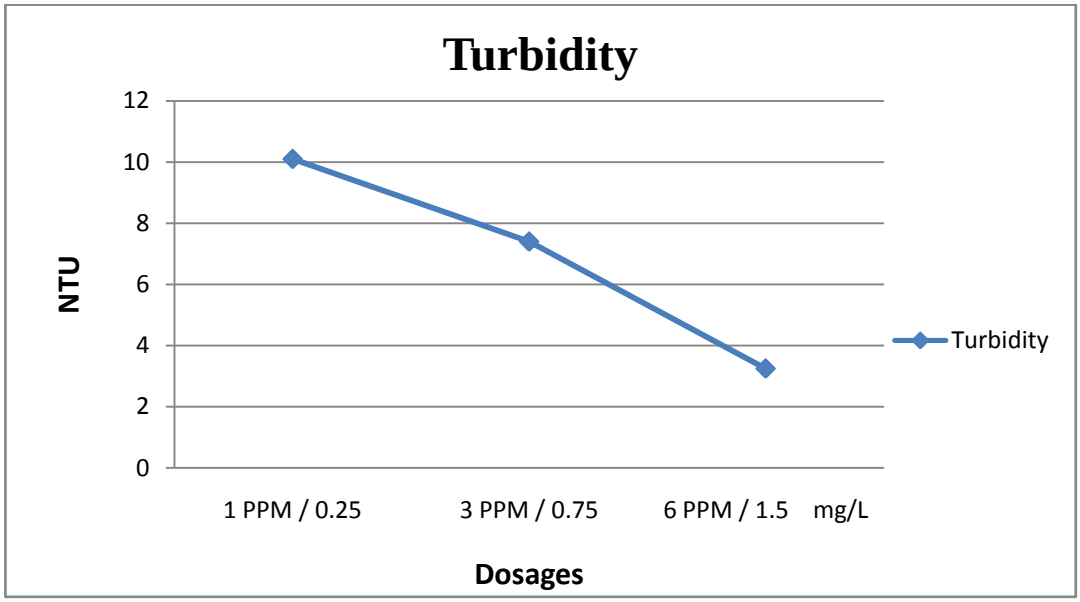

Figure 5.3 The variation of the turbidity parameter at various PAC doses.

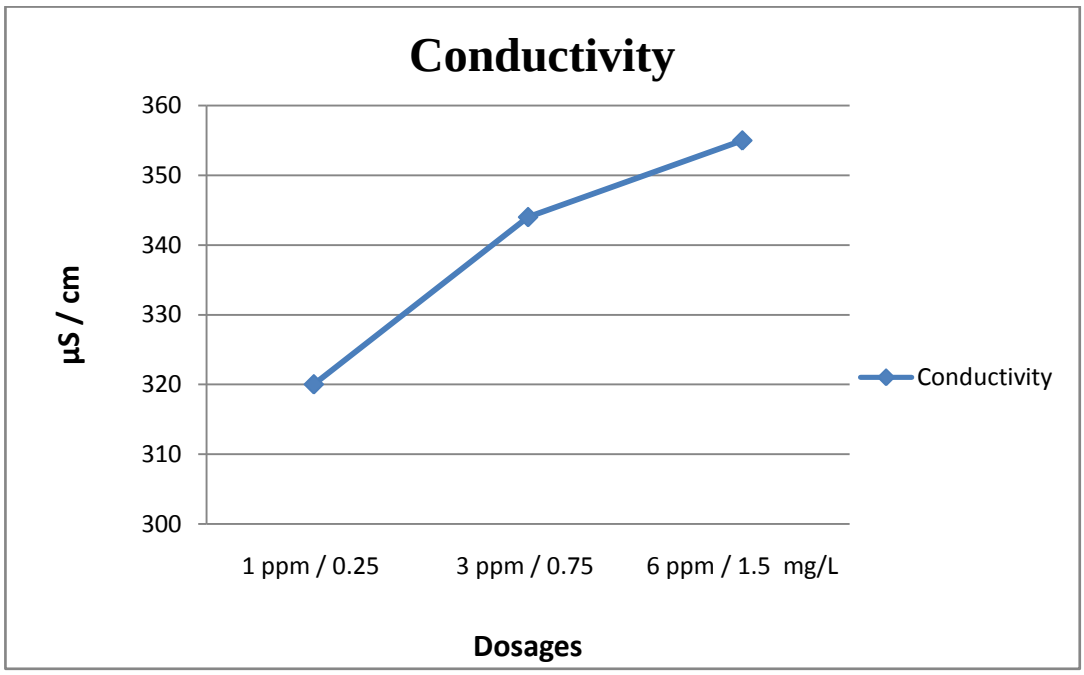

Figure 5.4 The variation of the conductivity parameter at various PAC doses.

5.2.2 Determination of the optimal pH for Poly Aluminium Chloride

Varied pH values were applied in order to determine the optimal pH value. Sodium hydroxide (NaOH) was used to adjust the pH in range of 6 to 8 at 28 ˚C of temperature. Optimal PAC dose determined at previous step was used in the pH experiments. Rapid mixing at 100 rpm for 2 minutes and slow mixing at 40 rpm for 20 minutes were applied in the jar test. After that, samples were settled down through 30 minutes. And, removal efficiencies at various pH conditions were determined and the results are presented in Tables 5.4 – 5.6. The effect of the pH and temperatures on treatment performance in terms of turbidity parameter is given in the Figure 5.5 and Tables 5.4 – 5.6. As can be seen from Tables 5.8 to 5.10, the lowest turbidity was performed at pH 7 as 4.3 NTU. For pH values of 6 and 8, turbidity measurements were higher than pH 7. Therefore, optimal pH for optimal PAC dose was decided as 7.

Table 5.4 The effect of pH on treatment performance (conditions: 6 ppm PAC and pH 6).

PAC	**6 ppm (1.5 mg / L)**
Anionic PE	**1 ppm**
NaOH	**0.5 ml**
pH	4.46 / 6
Conductivity	370 μS / cm
Turbidity	5.75 NTU
Temperature	28 ˚C
EH	512 mV

Table 5.5 The effect of pH on treatment performance (conditions: 6 ppm PAC and pH 7).

PAC	**6 ppm (1.5 mg / L)**
Anionic PE	**1 ppm**
NaOH	**1.2 ml**
pH	4.46 / 7
Conductivity	435 µS / cm
Turbidity	4.3 NTU
Temperature	28 ˚C
EH	512 mV

Table 5.6 The effect of pH on treatment performance (conditions: 6 ppm PAC and pH 8).

PAC	**6 ppm (1.5 mg / L)**
Anionic PE	**1 ppm**
NaOH	**1.9 ml**
pH	4.46 / 8
Conductivity	620 µS / cm
Turbidity	6.5 NTU
Temperature	28 ˚C
EH	510

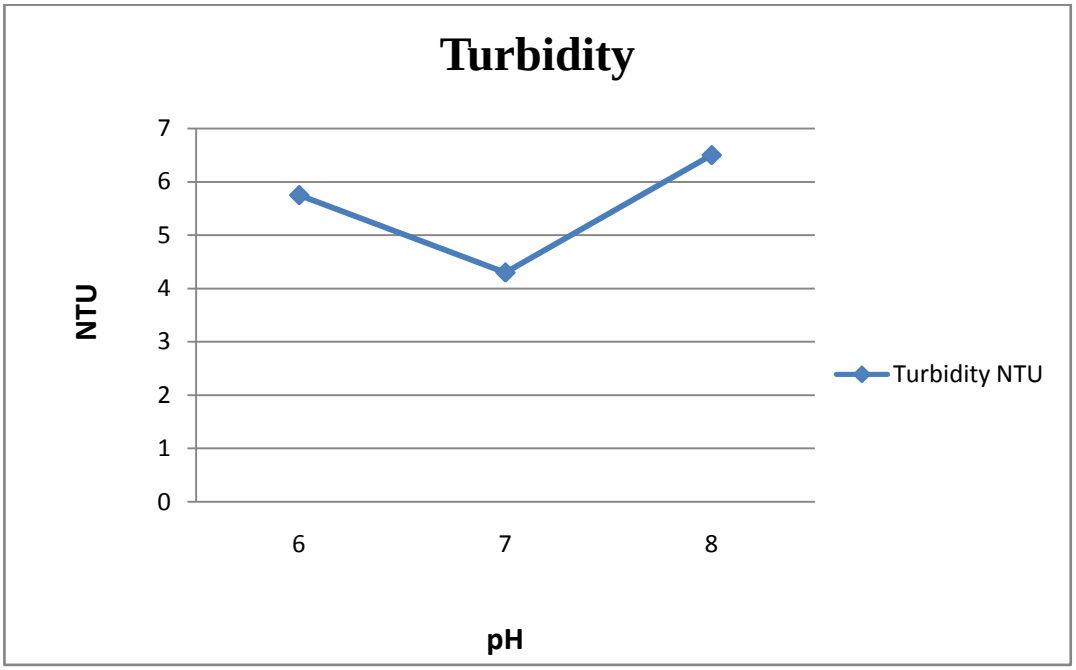

Figure 5.5 The optimal pH for PAC.

5.3 The Results of the Jar Tests for Poly Aluminium Chlosulphate - PACS

5.3.1 Determination of the Optimal Dose of Poly Aluminium Chlosulphate - PACS

In order to determine the optimal PACS dose [$Al_3(OH)_{4.95}Cl_3{\cdot}55(SO_4)_{0.25}$], experiments were carried out using solutions 1 ppm, 3 ppm, and 6 ppm PACS at 27 $^{\circ}$C, 28 $^{\circ}$C and 27 $^{\circ}$C of temperatures relatively. The pH was adjusted in the range of 6.5 - 7.5. A coagulant aid, i.e. anionic polyelectrolyte was also introduced during the coagulation. Beakers were stirred at 100 rpm for 2 minutes in coagulation, and then stirred at 40 rpm for 20 minutes in flocculation. Following to coagulation/flocculation processes, beakers settled down through 30 minutes. Samples taken from the supernatant were analyzed and the results are presented in Tables 5.7 - 5.9, for each dose separately. The effect of the coagulant dose on the removals of turbidity and conductivity are depicted in Figures 5.6 and 5.7 respectively.

Table 5.7 The effect of 1 ppm PACS on treatment performance.

PACS	**1 ppm (0.25 mg/L)**
Anionic PE	**1 ppm**
NaOH	**0.35 ml**
pH	5.8 / 6.95
Conductivity	198 μs / cm
Turbidity	9.2 NTU
Temperature	27 ˚C
EH	510 mV

Table 5.8 The effect of 3 ppm PACS on treatment performance.

PACS	**3 ppm (0.75 mg/L)**
Anionic PE	**1 ppm**
NaOH	**0.70 ml**
pH	5.1 / 7.4
Conductivity	207 μS / cm
Turbidity	6.1 NTU
Temperature	28 ˚C
EH	510 mV

Table 5.9 The effect of 6 ppm PACS on treatment performance.

PACS	**6 ppm (1.5 mg/L)**
Anionic PE	**1 ppm**
NaOH	**1.00 ml**
pH	4.85 / 7.1
Conductivity	240 µS / cm
Turbidity	3.15 NTU
Temperature	27 ˚C
EH	510mV

The variation of the turbidity parameter at various PACS doses is shown in Figure 5.6. For 1 ppm PACS addition, turbidity was decreased from 17.88 NTU to 9.2 NTU yielding approximately 48% efficiency. Increased PACS doses resulted with lower effluent turbidity. For the highest coagulant dose, i.e. 6 ppm PACS, effluent turbidity was measured as 3.15 NTU performing 82% of turbidity removal.

The variation of the conductivity for various PACS doses is presented in Figure 5.7. Conductivity of the water was increased with the chemical addition. It was increased from 186 µS / cm to 198 µS / cm for 1 ppm PACS dosage. For the highest dosage, i.e. 6 ppm PACS, conductivity was measured as 240 µS / cm.

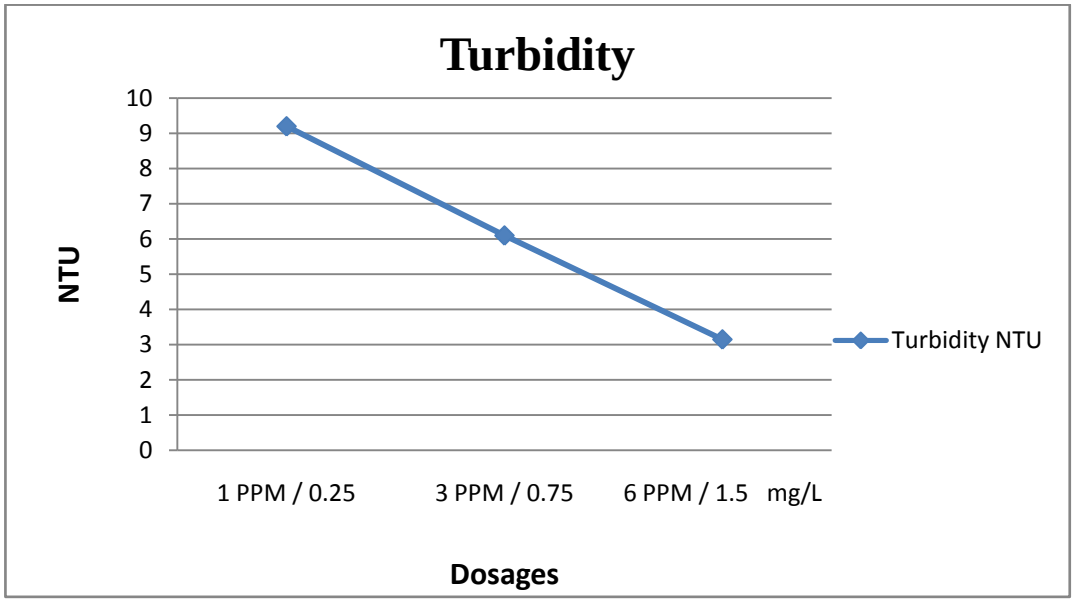

Figure 5.6 The variation of turbidity parameter at various PACS doses.

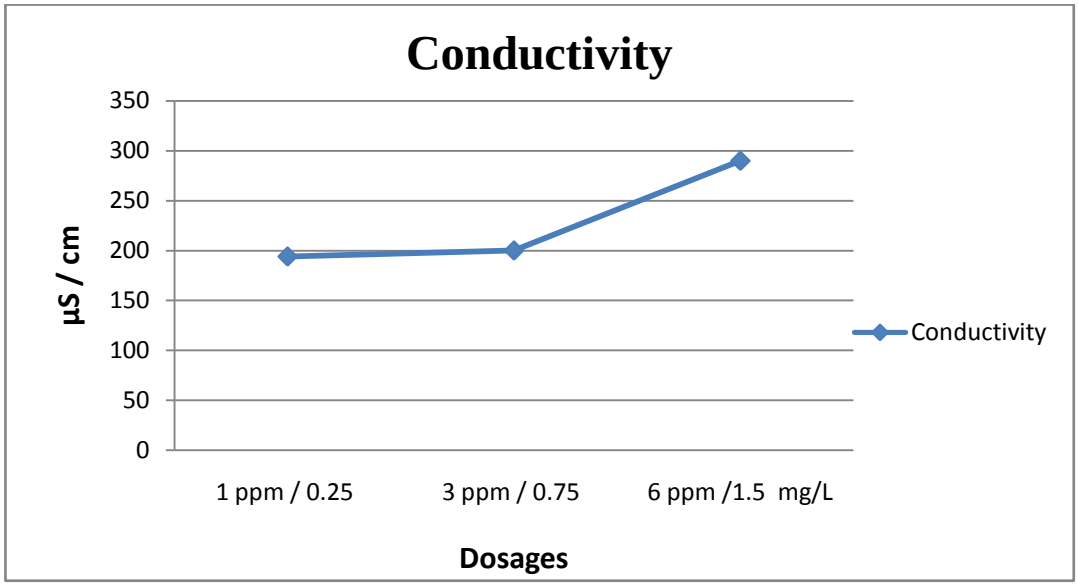

Figure 5.7 The variation of the conductivity parameter at various PACS doses.

5.3.2 Determination of the Optimal pH for Poly Aluminum Chlorosulphate

Varied pH values were applied in order to determine the optimal pH of PACS. Sodium hydroxide (NaOH) was used to adjust the pH in range of 6 to 8 at 27 ˚C, 25 ˚C and 26 ˚C of temperatures relatively. Optimal PACS dose determined at previous step was used in the experiments. Rapid mixing at 100 rpm for 2 minutes and slow mixing at 40 rpm for 20 minutes were applied in the jar test. After that, samples were

settled down through 30 minutes. And, removal efficiencies at various pH conditions and temperatures were determined and the results are presented in Tables 5.10 – 5.12. The effect of pH and temperatures on treatment performance in terms of turbidity parameter is given in the Figure 5.8 and Tables 5.10 – 5.12.

Table 5.10 The effect of pH on treatment performance (conditions: 6 ppm PACS and pH 6).

PACS	**6 ppm (1.5 mg/L)**
Anionic PE	**1 ppm**
NaOH	**0.35 ml**
pH	4.85 / 6
Conductivity	270 µS / cm
Turbidity	3.85 NTU
Temperature	27 ˚C
EH	510 mV

Table 5.11 The effect of the pH on treatment performance (conditions: 6 ppm PACS and pH 7).

PACS	**6 ppm / 1.5 mg/L**
Anionic PE	**1 ppm**
NaOH	**0.75 ml**
pH	4.85 / 7
Conductivity	290 µS / Cm
Turbidity	4.15 NTU
Temperature	25 ˚C
EH	510 mV

Table 5.12 The effect of the pH on treatment performance (conditions: 6 ppm PACS and pH 8).

PACS	**6 ppm (1.5 mg/L)**
Anionic PE	**1 ppm**
NaOH	**1.2 ml**
pH	4.85 / 8
Conductivity	340 µS / cm
Turbidity	5.2 NTU
Temperature	26 ˚C
EH	511 mV

As can be seen from Tables 5.10 to 5.12, the lowest turbidity was performed at pH 6 as 3.85 NTU. For pH 6 and 8 turbidity measurements were higher than pH 6. Therefore, optimal pH for optimal PACS dose was decided as 6.

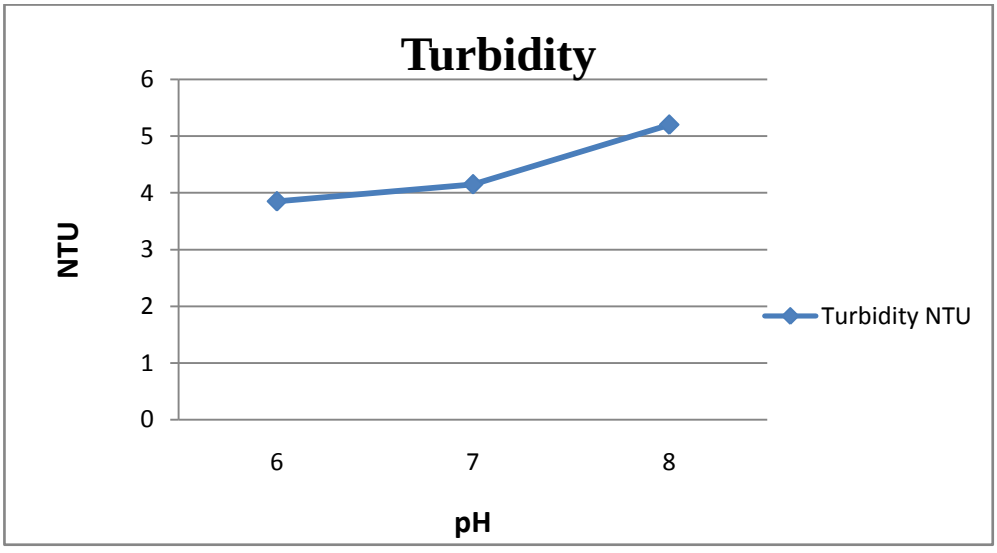

Figure 5.8 The optimal pH for PACS.

5.4 The Results of the Jar Tests for Aluminium Sulphate (Alum)

5.4.1 Determination of the Optimal Dose of Aluminium Sulphate (Alum)

In order to determine the optimal alum dose [$Al_2(SO4)_3$], experiments were carried out using solutions 1 ppm, 3 ppm, and 6 ppm alum at 29 °C of temperature. The pH was adjusted in the range of 6.5-7.5. A coagulant aid, i.e. anionic polyelectrolyte was also introduced during the coagulation. Beakers were stirred at 100 rpm for 2 minutes in coagulation, and then stirred at 40 rpm for 20 minutes in flocculation. Following to coagulation/flocculation processes, beakers settled down through 30 minutes. Samples taken from the supernatant were analyzed and the results are presented in Tables 5.13 - 5.15, for each dose separately. The effect of the coagulant dose on removals of turbidity and conductivity are depicted in Figures 5.9 and 5.10 respectively.

Table 5.13 The effect of 1 ppm alum on treatment performance.

$Al_2(SO_4)_3$	**1 ppm (0.25 mg/L)**
Anionic PE	**1 ppm**
NaOH	**0.1 ml**
pH	7.13 / 7
Conductivity	194 µS / cm
Turbidity	11.2 NTU
Temperature	29 °C
EH	508 mV

Table 5.14 The effect of 3 ppm alum on treatment performance.

$Al_2(SO_4)_3$	**3 ppm (0.75 mg/L)**
Anionic PE	**1 ppm**
NaOH	**-**
pH	7.00
Conductivity	200 μS / cm
Turbidity	4.64 NTU
Temperature	29 ˚C
EH	508 mV

Table 5.15 The effect of the 6 ppm alum on treatment performance.

$Al_2(SO_4)_3$	**6 ppm (1.5 mg/L)**
Anionic PE	**1 ppm**
NaOH	**0.4 ml**
pH	6.6 / 7.00
Conductivity	290 μS / cm
Turbidity	3.16 NTU
Temperature	29 ˚C
EH	508 mV

The variation of the turbidity parameter at various alum doses is shown in Figure 5.9. For 1 ppm alum addition, turbidity was decreased from 17.92 NTU to 11.2 NTU yielding approximately 37% efficiency. Increased alum doses resulted with lower

turbidity effluent. For the highest coagulant dose, i.e. 6 ppm alum, effluent turbidity was measured as 3.16 NTU performing 82% of turbidity removal.

The variation of the conductivity for various alum doses is presented in Figure 5.10. Conductivity of the water was increased with the chemical addition. It was increased from 188 µS / cm to 194 µS / cm for 1 ppm PAC dosage. For the highest dosage, i.e. 6 ppm PAC, conductivity was measured as 290 µS / cm.

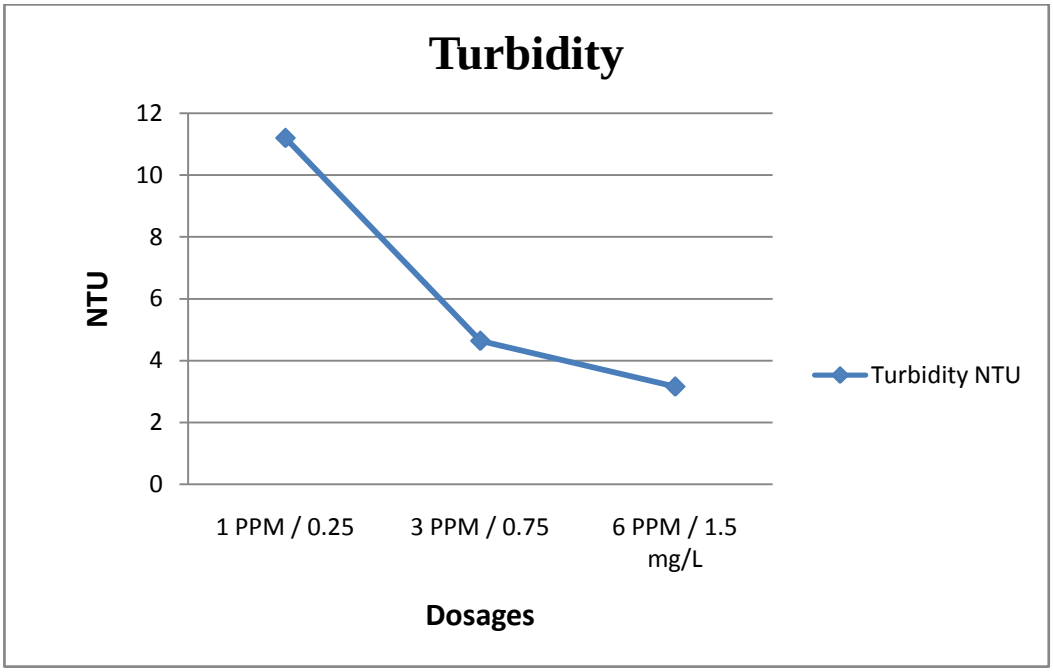

Figure 5.9 The variation of turbidity parameter at various alum doses.

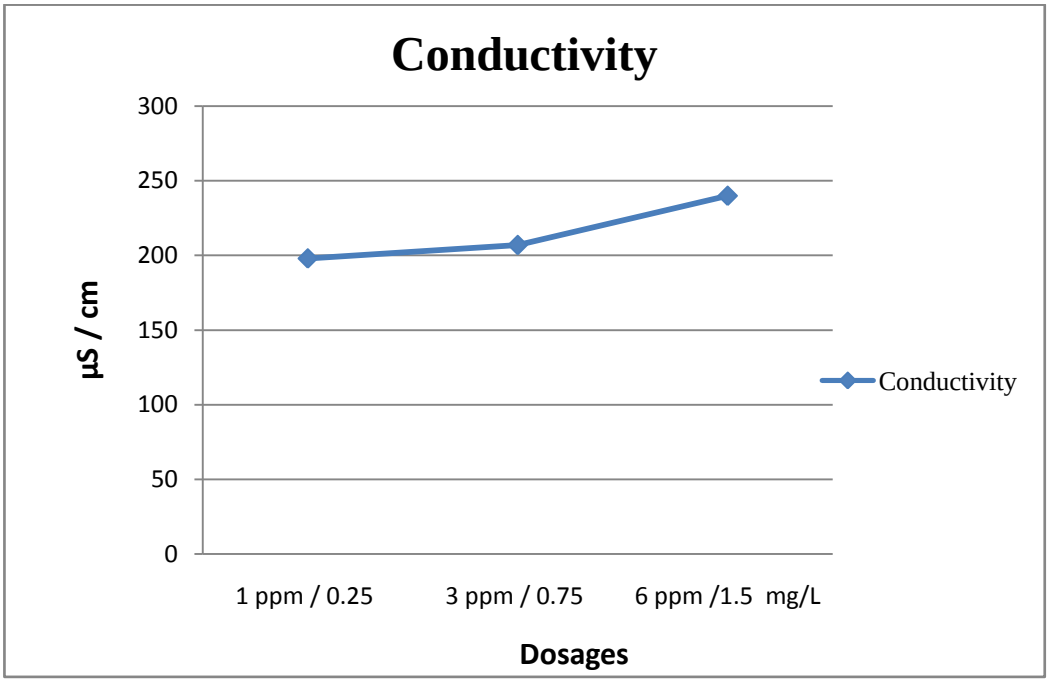

Figure 5.10 The variation of conductivity parameter at various alum doses.

5.4.2 Determination of the Optimal pH for Aluminium Sulphate (Alum)

Varied pH values were applied in order to determine the optimal pH of alum. Sodium hydroxide (NaOH) was used to adjust the pH in range of 6 to 8 at 25 ˚C of temperature. Optimal alum dose determined at previous step was used in the experiments. Rapid mixing at 100 rpm for 2 minutes and slow mixing at 40 rpm for 20 minutes were applied in the jar test. After that, samples were settled down through 30 minutes. And, removal efficiencies at various pH conditions were determined and the results are presented in Tables 5.16 – 5.18. The effect of pH on treatment performance in terms of turbidity parameter is given in the Figure 5.11.

Table 5.16 The effect of pH on treatment performance (conditions: 3 ppm alum and pH 6).

$Al_2(SO_4)_3$	**3 ppm (0.75 mg/L)**
Anionic PE	**1 ppm**
H_2SO_4	**0.5 ml**
pH	7 / 6.0
Conductivity	250 µS / cm
Turbidity	5.20 NTU
Temperature	25 ˚C
EH	508 mV

Table 5.17 The effect of pH on treatment performance (conditions: 3 ppm alum and pH 7).

$Al_2(SO_4)_3$	**3 ppm (0.75 mg/L)**
Anionic PE	**1 ppm**
NaOH	**-**
pH	7 / 7,0
Conductivity	200 µS / cm
Turbidity	4.64 NTU
Temperature	25 ˚C
EH	508 mV

Table 5.18 The effect of pH on treatment performance (conditions: 3 ppm alum and pH 8).

$Al_2(SO_4)_3$	**3 ppm (0.75 mg/L)**
Anionic PE	**1 ppm**
NaOH	**0.7 ml**
pH	7 / 8.0
Conductivity	290 µS / cm
Turbidity	6.4 NTU
Temperature	25 ˚C
EH	508 mV

As can be seen from Tables 5.16 to 5.18, the lowest turbidity was performed at pH 7 as 4.64 NTU. For pH 6 and 8 turbidity measurements were higher than pH 6. Therefore, optimal pH for optimal PAC dose was decided as 7.

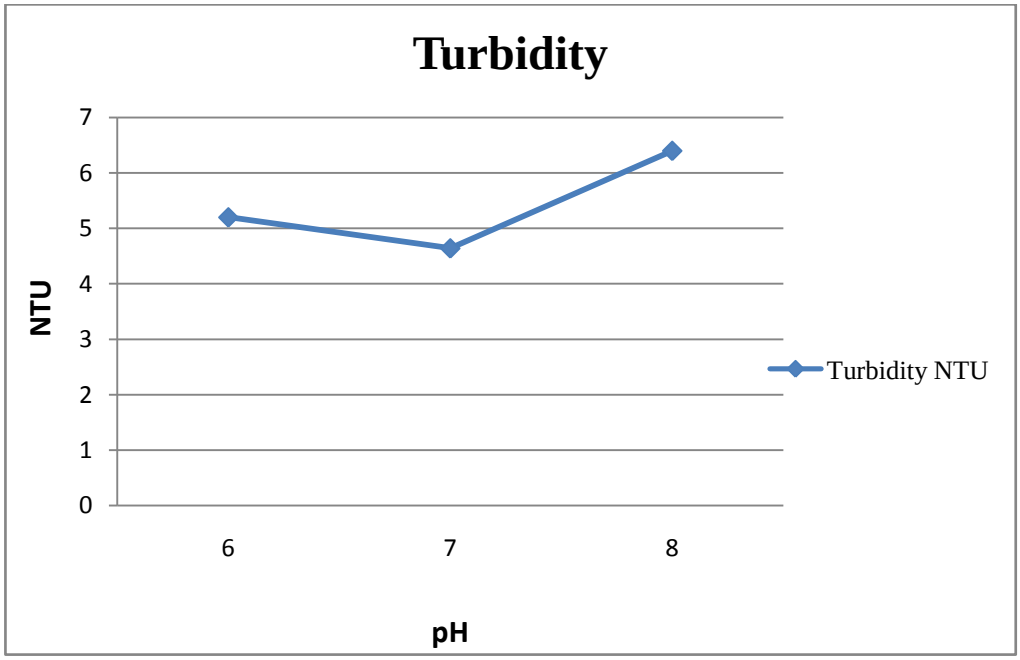

Figure 5.11 The optimal pH for Alum.

CHAPTER SIX
EVALUATION OF THE RESULTS

As it stated previous chapters, optimal chemical dosage and pH was determined theoretically by using PHREEQC interactive program as first, and the results were verified with jar test.

The dosages of chemicals determined using PHREEQC were between 0 – 80 mg of $AlCl_3$. The pH was adjusted in the range of 4.7 - 8.2. The optimal chemical dosages were in range of 8 – 16 mg (see Figure 5.1 at previous chapter).

Varied pH values were applied in order to determine the optimal pH value. The sodium hydroxide (NaOH) was used in 10 steps to adjust the pH in range of 5.59 to 7.82. Optimal dose of chemical determined as theoretically was 0 – 80 g of $AlCl_3$. As can be seen from the Figure 5.2 at previous chapter, the optimal pH was in range of 6.43 – 7.21 and the 4 – 8 mg of sodium hydroxide (NaOH) was used to adjust the optimal pH.

The results obtained for various doses of chemicals are summarized in Tables 6.1-6.3. In general, increased chemical doses were resulted higher treatment performance in terms of turbidity. For 1 ppm PAC addition, turbidity of the raw water was reduced from 17.75 to 10.1 NTU which yields 43% removal efficiency. When PAC dose increased to 3 ppm, effluent turbidity was decreased to 7.4 NTU yielding 58% efficiency. Finally for the 6ppm PAC, lowest effluent turbidity was obtained as 3.25 NTU corresponding 82% turbidity removals (see Figures 6.1 and 6.2). When PAC used as coagulant, pH adjustment was required using sodium hydroxide. Besides, PAC addition resulted with the increased conductivity due to the aluminium addition. Increased PAC doses caused increase in conductivity of the water.

Table 6.1 Treatment performance of PAC.

Parameter	**Unit**	**Raw Water**	**1ppm PAC**	**3ppm PAC**	**6ppm PAC**
pH	-	6.75	4.65/6.85	4.52/7.06	4.46/7.25
Conductivity	µS / cm	185	320	344	365
Turbidity	NTU	17.75	10.1	7.4	3.25
Temperature	˚C	29	28.1	28	28.2
EH	mV	512	512	512	512

For 1 ppm PACS addition, turbidity of the raw water was reduced from 17.92 to 9.2 NTU which yields 48% removal efficiency. When PACS dose increased to 3ppm, effluent turbidity was decreased to 6.1 NTU yielding 66% efficiency. Finally for the 6 ppm PACS, lowest effluent turbidity was obtained as 3.15 NTU corresponding 82% turbidity removal (see Figures 6.1 and 6.2). When PACS used as coagulant, pH adjustment was required using sodium hydroxide. Besides, PACS addition resulted with the increased conductivity due to the aluminium addition. Increased PACS doses caused increase in conductivity of the water.

Table 6.2 Treatment performance of PACS.

Parameter	**Unit**	**Raw Water**	**1ppm PACS**	**3ppm PACS**	**6ppm PACS**
pH	-	6.5	5.8 / 6.95	5.1 / 7.4	4.85 / 7.1
Conductivity	µS / cm	186	198	207	240
Turbidity	NTU	17.88	9.2	6.1	3.15
Temperature	˚C	27	27	28	27
EH	mV	510	510	510	510

For 1 ppm alum addition, turbidity of the raw water was reduced from 17.92 to 11.2 NTU which yields 37% removal efficiency. When alum dose increased to 3

ppm, effluent turbidity was decreased to 4.64 NTU yielding 74% efficiency. Finally for the 6 ppm alum, lowest effluent turbidity was obtained as 3.16 NTU corresponding 82% turbidity removals (see Figures 6.1 and 6.2). When PACS used as coagulant, pH adjustment was required using sodium hydroxide. Besides, PAC addition resulted with the increased conductivity due to the aluminium addition. Increased alum doses caused increase in conductivity of the water.

Table 6.3 Treatment performance of alum.

Parameter	**Unit**	**Raw Water**	**1ppm alum**	**3ppm alum**	**6ppm alum**
pH	-	7.2	7.13 / 7	7.00	6.6 / 7.00
Conductivity	µS / cm	188	194	200	290
Turbidity	NTU	17.92	11.2	4.64	3.16
Temperature	˚C	28	29	29	29
EH	mV	508	508	508	508

The variation of the turbidity with respect to dosage is depicted in Figures 6.1 and 6.2 for each chemical, i.e. PAC, PACS, and alum.

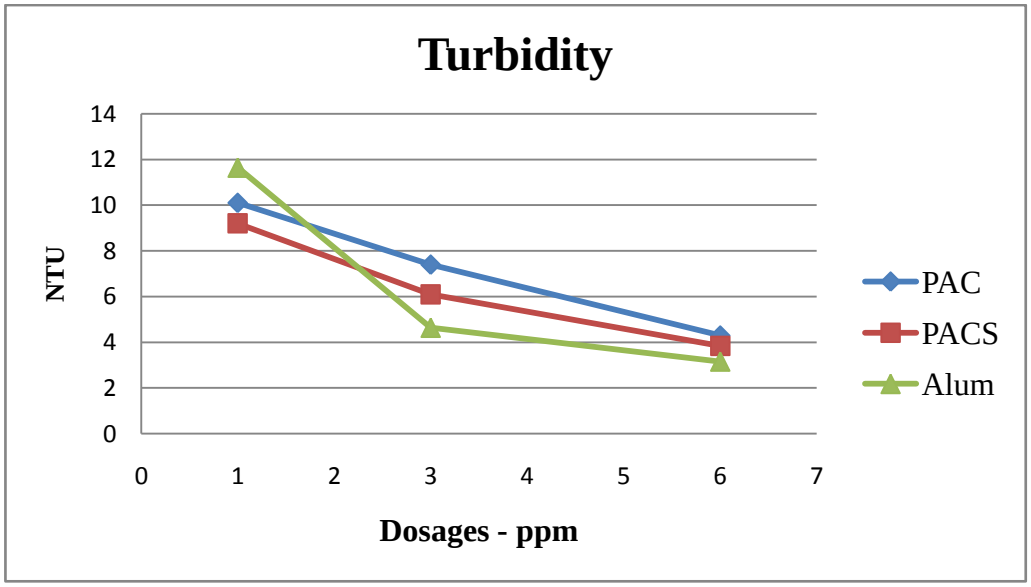

Figure 6.1 The variation of the turbidity with respect to dosage.

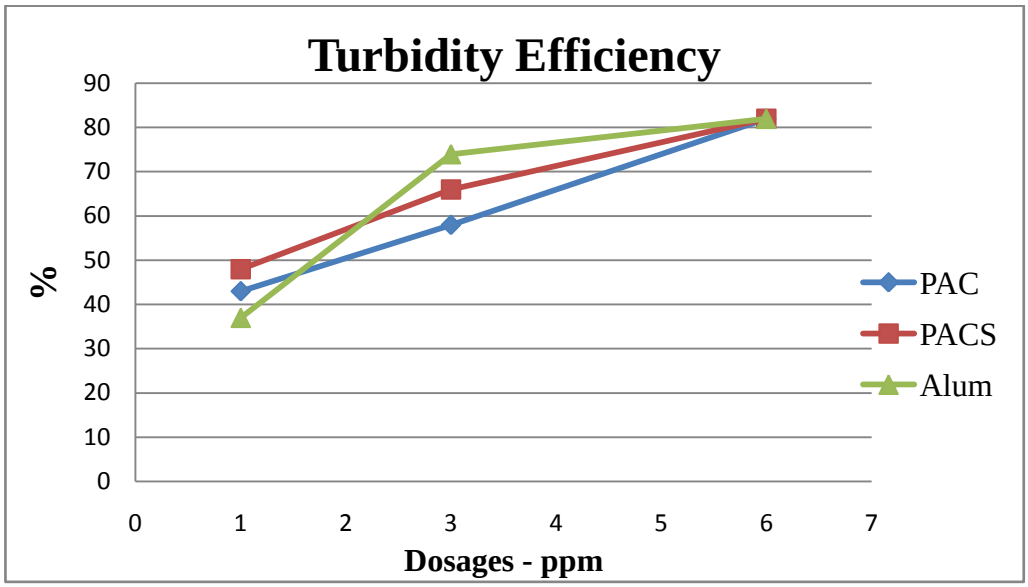

Figure 6.2 The variation of the turbidity efficiency with respect to dosage.

According to the results, the highest efficient reagent was obtained as alum. Alum was yielded lower residual turbidity than PAC and PACS. Experimental results showed that the dosage of alum required for water treatment was half of the PAC and PACS, i.e. 3 ppm (see Table 6.4). In addition, no chemical requirement for pH adjustment was performed. However, for PAC or PACS addition, certain amounts of sodium hydroxide were introduced to the water to adjust the pH. Moreover, as can be seen from Figures 6.1- 6.5, appearance of the treated water for alum case was much better than the other.

Table 6.4 The results of optimal dosages and ptimal pH of three chemicals.

	Optimal Dosage	**Optimal pH**	**Turbidity**	**Conductivity**	**NaOH**
PAC	6 PPM or 1.5 mg/L	7	4.3 NTU	435 □S / cm	1.2 ml
PACS	6 PPM or 1.5 mg/L	6	3.85 NTU	270 □S / cm	0.35 ml
Alum	**3 PPM or 0.75 mg/L**	**7**	**4.64 NTU**	**200 □S / cm**	**0 ml**

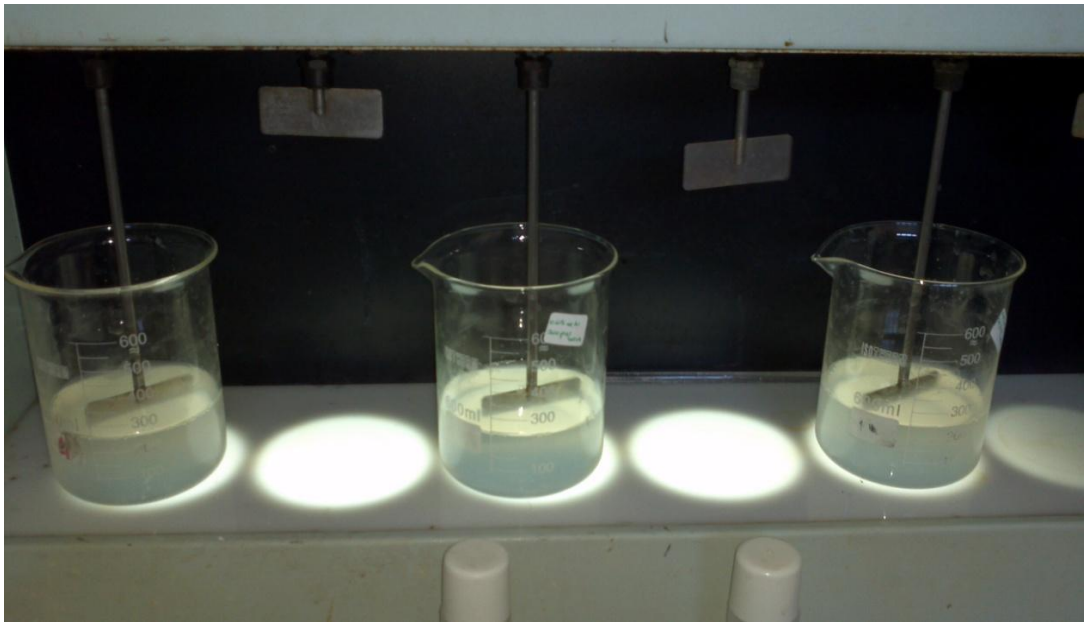

Figure 6.3 The testing of PAC.

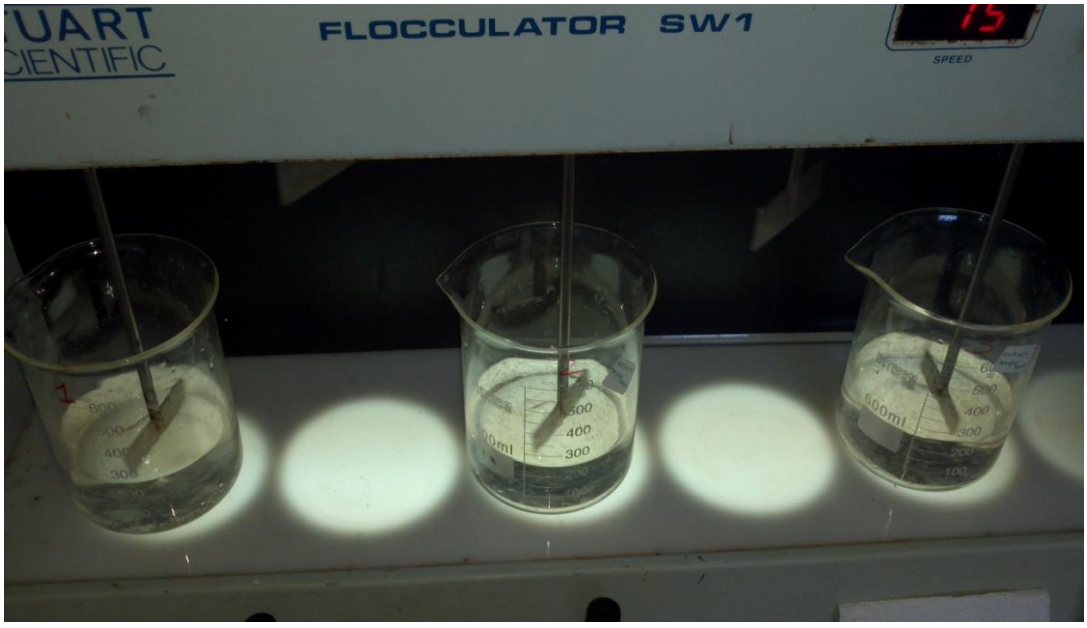

Figure 6.4 The testing of PACS.

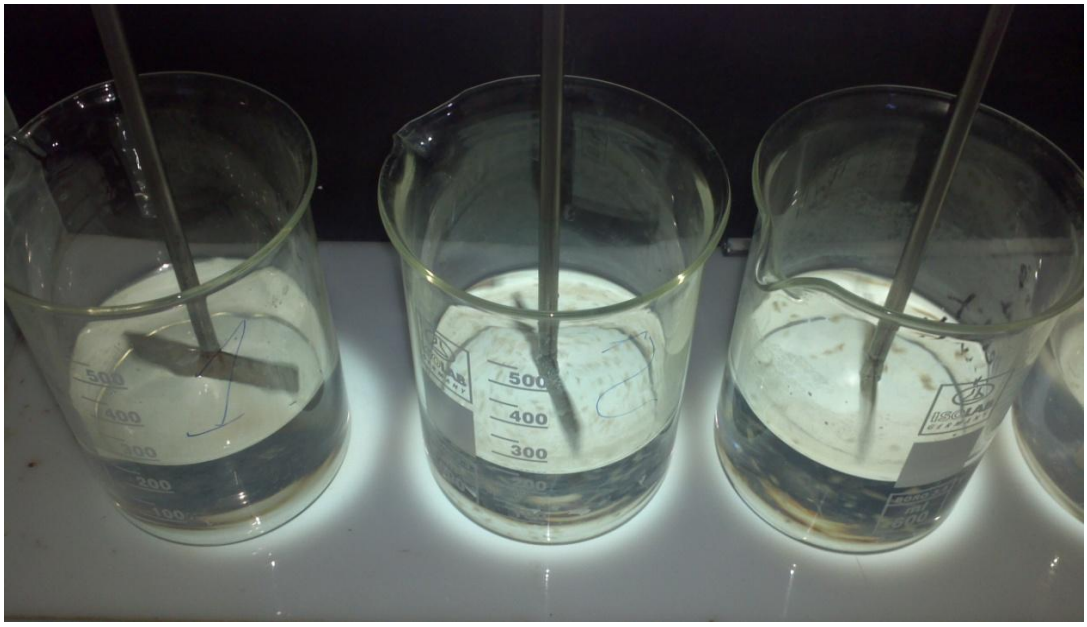

Figure 6.5 The testing of Alum.

The last three figures present the comparison of Alum with PAC and PACS:

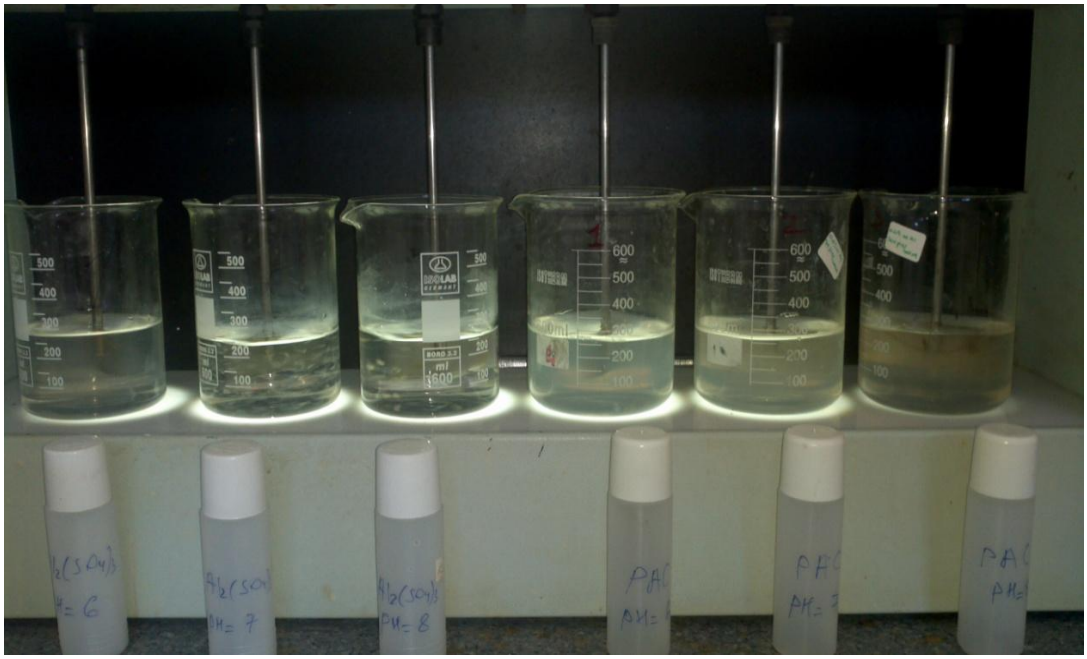

Figure 6.6 Comparisons of Alum and PAC.

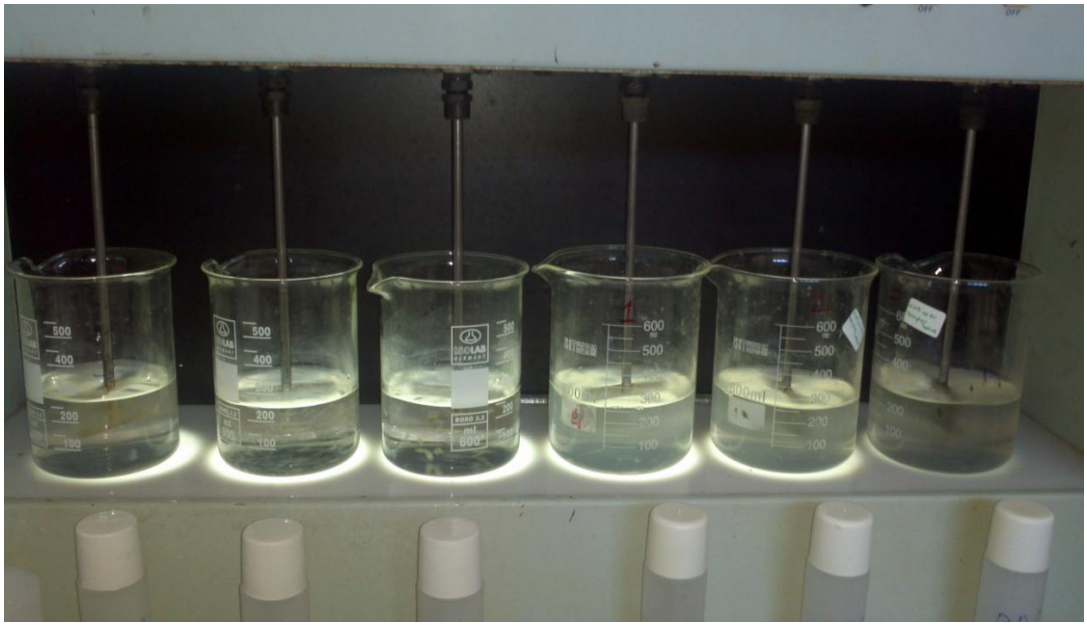

Figure 6.7 Comparisons of Alum and PACS.

As a result of the study, the following conclusions were achieved:

1. The type and dose of coagulant has a significant impact on coagulation and flocculation in water treatment.
2. Alum performed sufficient performance in water treatment when compared to PAC and PACS, the applications yielded lower residual turbidity in effluent.
3. Optimal dosage of Alum is two times less than other chemicals optimal dosages.
4. Operation treatment using Alum gave excellent results as measured by rapid formation of flocs.
5. The use of anionic polyelectrolyte as a coagulant aid was more effective in order to increase coagulation time and increased the floc formation.
6. Alum was not required pH adjustment.

Poly Aluminium Chloride is used as a coagulant in the existing Plant. Using Aluminium Sulphate (Alum) instead of Poly Aluminium Chloride (PAC), will be used two times less chemical dosages, will provide improvements in the turbidity values for effluent, reduction on the amount of aluminium in water (Al^{+3}), reduction on conductivity of process water and reduction in chemical sludge at the 30% minimum rate. The summary of performance improvements as follows:

In the plant, the annual PAC consumption was 12 tons (1 tons/month) and the annual sodium hydroxide consumption was 10 tons. Experimental studies stated that the optimal chemical was alum and the dosage was 0.75 mg/L. Therefore, when the alum is used instead of PAC, annual chemical (alum) consumption would be decreased to 6 tons without using any extra chemicals for pH adjustment.

The price of PAC (per ton) is 350 $ (i.e. annual PAC cost is 4.200$), and alum is 150 $/tons (i.e. annual alum cost is 900$). Besides, sodium hydroxide is used for pH adjustment together with PAC, and annual cost of the sodium hydroxide is 450$. As a result, total cost when PAC used is 4650 $.

- PAC costs (annual) 4.200$
- Sodium hydroxide (annual) 450$
- Total cost for PAC utilization is 4.650$

However, if alum is used instead of the PAC, annual cost is 900$. Therefore, total saving can be calculated as 3.750$ (7.875TL).

The amount of sludge will be reduced minimum rate at 30%. With PAC system, it approximately 5.5 tons per day. This is about 2.5 tons per day and an annual of 1000 tons sludge and filter press will handle less sludge, those will cause energy savings:

11 tons of sludge cake + transportation cost = 280 TL
Annual Saving = (1000 / 11) * 280 = 25.454 TL

Energy supply for 11 tons sludge cake = 145 kWh (GV-3301/2/3/4-GV-3201)
Annual Income = (1000 / 11) * 145 = 13181 kWh = 2.372 TL

Plus, savings due to transportation costs of sludge cake for disposal and lowered energy utilization due to reduced quantities of sludge production results with 27.826 TL savings in cost. As a result, totally 27.826 + 7.875 = 35.701 TL can be saved as annual.

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APPENDICES

EXPERIMENTS

Experiment #1 – The determination of optimal dosage of Poly Aluminium Chloride (PAC).

PAC	**1 ppm (0.25 mg/l)**
Anionic PE	**1 ppm**
NaOH	**0.5 ml**
pH	4.60 / 6.90
Conductivity	330 μS / cm
Turbidity	10.6 NTU
Temperature	28 ˚C
EH	511 mV

PAC	**3 ppm (0.75 mg/l)**
Anionic PE	**1 ppm**
NaOH	**0.7 ml**
pH	4.48 / 7.06
Conductivity	350 μS / cm
Turbidity	7.8 NTU
Temperature	27.8 ˚C
EH	511 mV

PAC	**6 ppm (1.5 mg/l)**
Anionic PE	**1 ppm**
NaOH	**1.1 ml**
pH	**4.4 / 7.25**
Conductivity	**375 µS / cm**
Turbidity	**3.65 NTU**
Temperature	**28.1 ˚C**
EH	**511 mV**

Experiment #1.1 – The determination of optimal pH of Poly Aluminium Chloride (PAC).

PAC	**6 ppm (1.5 mg / L)**
Anionic PE	**1 ppm**
NaOH	**0.6 ml**
pH	4.6 / 6
Conductivity	360 µS / cm
Turbidity	5.85 NTU
Temperature	28 ˚C
EH	511 mV

PAC	**6 ppm (1.5 mg / L)**
Anionic PE	**1 ppm**
NaOH	**1.4 ml**
pH	4.62 / 7
Conductivity	440 µS / cm
Turbidity	4.9 NTU
Temperature	27.9 ˚C
EH	511 mV

PAC	**6 ppm (1.5 mg / L)**
Anionic PE	**1 ppm**
NaOH	**2 ml**
pH	4.46 / 8
Conductivity	610 µS / cm
Turbidity	6.8 NTU
Temperature	28 ˚C
EH	511 mV

Experiment #2 – The determination of optimal dosage of Poly Aluminium Chlorosulphate (PACS).

PACS	**1 ppm (0.25 mg/l)**
Anionic PE	**1 ppm**
NaOH	**0.6 ml**
pH	6 / 6.90
Conductivity	200 µS / cm
Turbidity	9.8 NTU
Temperature	28 °C
EH	506 mV

PACS	**3 ppm (0.75 mg/l)**
Anionic PE	**1 ppm**
NaOH	**0.75 ml**
pH	5.2 / 7.06
Conductivity	210 µS / cm
Turbidity	6.3 NTU
Temperature	27.8 °C
EH	506 mV

PACS	**6 ppm (1.5 mg/l)**
Anionic PE	**1 ppm**
NaOH	**1.2 ml**
pH	4.9 / 7.25
Conductivity	245 µS / cm
Turbidity	4.15 NTU
Temperature	28.1 ˚C
EH	506 mV

Experiment #2.1 – The determination of optimal pH of Poly Aluminium Chlorosulphate (PACS).

PACS	**6 ppm (1.5 mg / L)**
Anionic PE	**1 ppm**
NaOH	**0.7 ml**
pH	4.7 / 6
Conductivity	366 µS / cm
Turbidity	5.95 NTU
Temperature	28 ˚C
EH	506 mV

PACS	**6 ppm (1.5 mg / L)**
Anionic PE	**1 ppm**
NaOH	**0.8 ml**
pH	4.8 / 7
Conductivity	295 µS / cm
Turbidity	4.35 NTU
Temperature	27.9 ˚C
EH	506 mV

PACS	**6 ppm (1.5 mg / L)**
Anionic PE	**1 ppm**
NaOH	**1.3 ml**
pH	4.9 / 8
Conductivity	360 µS / cm
Turbidity	5.6 NTU
Temperature	28 ˚C
EH	506 mV

Experiment #3 – The determination of optimal dosage of Aluminium Sulphate (Alum).

$Al_2(SO4)_3$	**1 ppm (0.25 mg/l)**
Anionic PE	**1 ppm**
NaOH	**0.2 ml**
pH	6.98. / 7.09
Conductivity	200 µS / cm
Turbidity	11.6 NTU
Temperature	26 ˚C
EH	509 mV

$Al_2(SO4)_3$	**3 ppm (0.75 mg/l)**
Anionic PE	**1 ppm**
NaOH	**0 ml**
pH	7.01 / 7.06
Conductivity	198 µS / cm
Turbidity	4.7 NTU
Temperature	26.8 ˚C
EH	509 mV

$Al_2(SO4)_3$	**6 ppm (1.5 mg/l)**
Anionic PE	**1 ppm**
NaOH	**0.5 ml**
pH	6.7 / 7.02
Conductivity	300 µS / cm
Turbidity	3.25 NTU
Temperature	27 ˚C
EH	509 mV

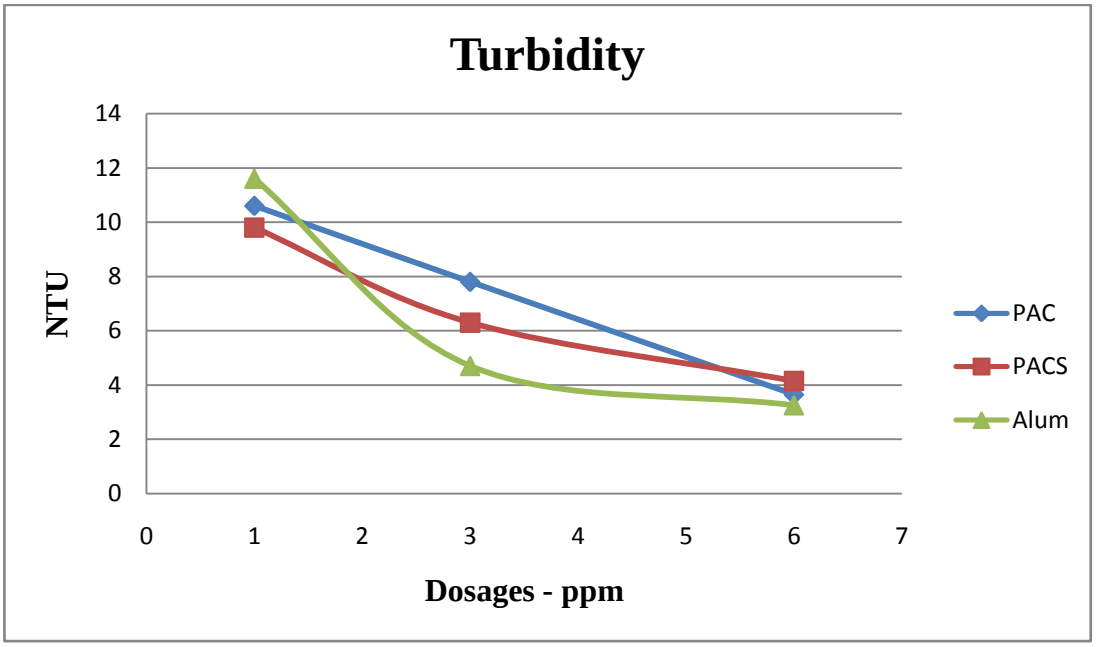
Experiment #3.1 – The determination of optimal pH of Aluminium Sulphate (Alum).

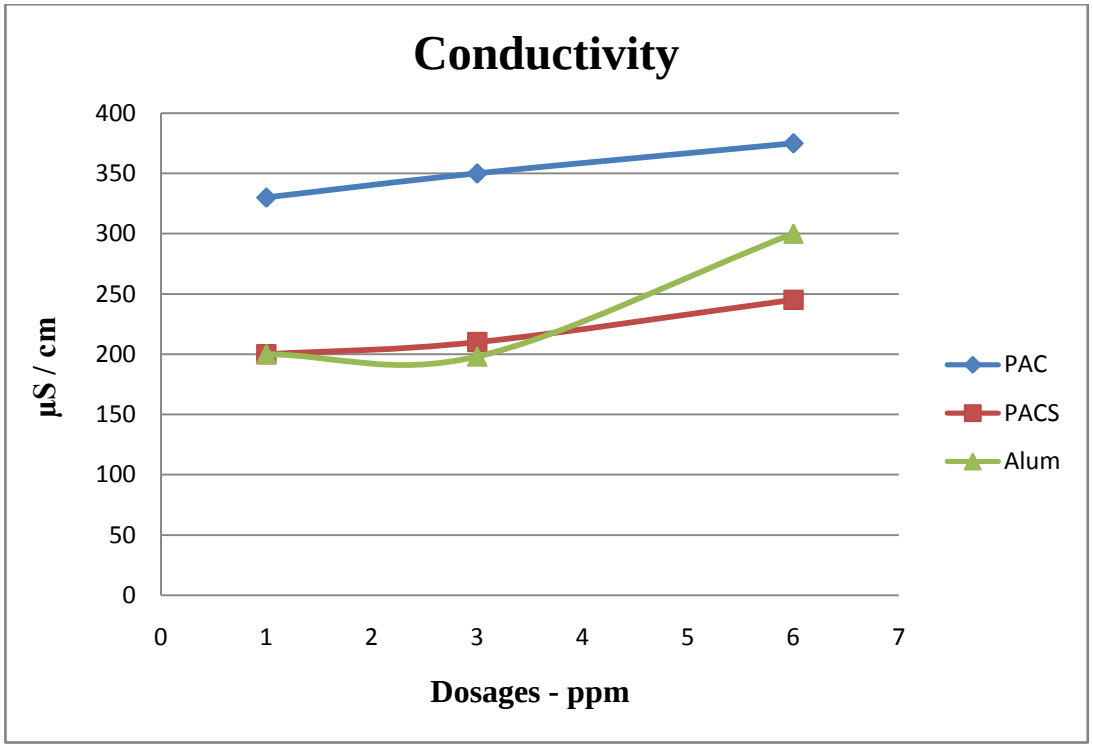
$Al_2(SO4)_3$	**3 ppm (1.5 mg / L)**
Anionic PE	**1 ppm**
H_2SO_4	**0.5 ml**
pH	6.92 / 6
Conductivity	260 µS / cm
Turbidity	5.22 NTU
Temperature	27.4 ˚C
EH	509 mV

$Al_2(SO4)_3$	**3 ppm (1.5 mg / L)**
Anionic PE	**1 ppm**
NaOH	**0 ml**
pH	7.05 / 7
Conductivity	202 µS / cm
Turbidity	4.6 NTU
Temperature	27.2 ˚C
EH	509 mV

$Al_2(SO4)_3$	**3 ppm (1.5 mg / L)**
Anionic PE	**1 ppm**
NaOH	**0.8 ml**
pH	7.1 / 8
Conductivity	305 µS / cm
Turbidity	6.6 NTU
Temperature	27.5 ˚C
EH	509 mV

The optimal dosages of three chemicals can be showed in the below Figures:





The optimal pH of the three chemicals can be showed in the below Figures:

