A COMPARISON OF EMERGING COAGULANT WITH TRADITIONAL CHEMICAL COAGULANTS FOR WASTEWATER TREATMENT

By

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Certified that the contents and forms of the thesis entitled

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List of Abbreviations

Abbreviation	**Description**
Al	Aluminum
BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
DOC	Dissolved organic carbon
Fe	Ferric
IESE	Institute of Environmental Sciences and Engineering
NEQS	National Environmental Quality Standards
NTU	Naphthalometric turbidity unit
NUST	National University of sciences and Technology
TDS	Total dissolved solids
Ti	Titanium
TSS	Total suspended solids

ABSTRACT

Water scarcity and water pollution pose a critical challenge in many developing countries including Pakistan. One of the solutions to this issue is the reuse of wastewater after suitable level of treatment. Wastewater treatment is continually refined to improve its performance and meet stringent disposal standards. A range of physical, chemical and biological methods have been used for wastewater treatment. Alum and Iron salts are traditionally used as coagulants for water and wastewater treatment in chemical process. Search for new and efficient coagulants have always been on, to improve efficiency of process. In this study, coagulation and flocculation processes with Titanium tetrachloride ($TiCl_4$) for wastewater treatment are investigated in terms of turbidity, COD, BOD and TSS removal at different coagulant dosages and pH values. The competency of this coagulant is investigated by comparing with the traditionally used coagulants such as Aluminum sulfate ($Al_2(SO_4)_3$) and Ferric chloride ($FeCl_3$). All experiments were performed on laboratory scale with Jar Test Apparatus. Titanium tetrachloride was found better in COD, BOD, TSS and turbidity removal in all pH values especially at pH 5-7. Titanium tetrachloride showed the highest COD removal (85%) at pH 5. Titanium tetrachloride showed 77-84% TSS removal and 88-97% turbidity removal at pH 5-7. With the development of titanium industry, titanium salts are gradually becoming comparable in price to the conventional coagulants. Titanium tetrachloride is found to be an effective new coagulant in wastewater treatment in terms of organic matter removal. It’s sludge is also a resource rather than a burden.

Chapter 1

INTRODUCTION

1.1 BACKGROUND

Reuse of treated wastewater for agricultural purposes is in practice since early ages. But, planned reuse of wastewater has gained importance as water demands increased due to population growth, technological advancement and urbanization, which has put stress on natural water cycle. The high population growth and rapid spread of water pollution have led to an unbalanced situation between water demand and natural recharge. Water usage is increasing approximately at the rate of three times of the world population growth (Vigneswaran *et al*., 2004). Over 2.6 billion people around the globe are living without adequate sanitation facilities and nearly 900 million people do not have access to drinking water from improved water resources (UN-Water, 2010). Developments of human societies are dependent upon availability of water in adequate quantity with suitable quality for variety of uses, ranging from domestic to industrial supplies. Agricultural, chemical and Industrial wastes are the main causes of ground and surface water contamination. During the last century, wastewater treatment processes were continually refined to improve its performance and meet stringent disposal standards (Shon *et al*., 2007). These treatment processes have used various physical, chemical and biological methods.

Coagulation and Flocculation are the chemical processes used for water and wastewater treatment. The addition of some particular chemicals (coagulants) causes the coagulation or agglomeration of contaminant particles in large flocs (Okour *et al.*, 2007) and these flocs settled down in the form of sludge. Comparably good quality treated wastewater is produced by chemical process which can be used for secondary purposes. The chemical process is relatively less energy intensive and easy to operate.

Alum ($Al_2(SO_4)_3$) and Ferric chloride ($FeCl_3$) as coagulants are generally used for water and wastewater treatment in the world but these coagulants produce large amount of sludge and the handling of this sludge is a major problem. Generally, this sludge is disposed off in engineered landfills. The disposal of sludge into landfills is no longer acceptable, because it can cause secondary contamination due to landfill leachate. The sludge produced by alum may be used for better crop growth but at low concentration because excess Al^{3+} in soil enters root zone, resulting the reduction of plant vigor and yield (Yi-fan *et al.*, 2011).

To overcome sludge handling problem, world need a coagulant that may produce less amount of sludge or more reusable sludge. Titanium tetrachloride ($TiCl_4$) is an emerging chemical coagulant which can be used for water and wastewater treatment. Titanium tetrachloride produces a small amount of sludge as compared to other traditional coagulants. The second main advantage of titanium compound is the recovery of Titanium dioxide (TiO_2) from sludge. A large amount of functional TiO_2 may be produced from wastewater sludge, generated by the Ti-salt flocculation. TiO_2 is produced by incineration of sludge at 600°C (Shon *et al.*, 2007).

Upton and Buswell (1937) are the pioneers which explored the titanium salts as a coagulant for water treatment but due to high cost of titanium this coagulant was not considered at that time. At this time, the cost of titanium salts is comparable due development in the industries of titanium.

Recently, some studies have been carried out by (Shon *et al*., 2009), (Lee *et al*., 2009), (Zhao *et al*., 2014) and (Okour *et al*., 2007) to examine the performance of titanium tetrachloride for water and wastewater treatment and they found better results in terms of COD, DOC, TSS and Color removal. But in these studies mostly synthetic wastewater was selected as a sample to evaluate the behavior of coagulant. Due to significance of wastewater treatment by coagulation/flocculation process, the actual wastewater was preferred for this study.

The performance of an emerging coagulant ($TiCl_4$) is investigated for its effectiveness for wastewater treatment by physico-chemical process. The performance of Titanium tetrachloride ($TiCl_4$) is evaluated by comparing its results with the traditional chemical coagulants such as Alum ($Al_2(SO_4)_3.18H_2O$) and Ferric chloride ($FeCl_3$) in term of COD, BOD, TSS and turbidity removal.

The wastewater of septic tank constructed at the back side of IESE building was selected to perform the experimental work in laboratories of IESE building. After availing residence time of one day in septic tank, this sewage water enters in the main sewage line of NUST (Saadat, 2012).

1.2 CHARACTERISTICS OF TITANIUM TETRACHLORIDE

Titanium tetrachloride is the inorganic compound with the formula $TiCl_4$.Molar mass of $TiCl_4$ is 189.679 g/mol and density is 1.726 g/cm^3. $TiCl_4$ is a dense, colorless liquid. $TiCl_4$ is one of the rare transition metal halides that are liquid at room temperature. Upon contact with air, it forms spectacular opaque clouds of Hydrogen chloride (HCl) and Titanium dioxide (TiO_2).

$TiCl_4$ is produced by the Chloride process, which involves the reduction of Titanium oxide ores (typically $FeTiO_3$) with carbon under flowing Chlorine at 900°C.

$$2FeTiO_3 + 7Cl_2 + 6C \rightarrow 2TiCl_4 + 2FeCl_3 + 6CO$$

During the coagulation/flocculation process, the chemical coagulant ($TiCl_4$) changes into $TiOCl_2$ in wastewater. Depending on pH, the $TiOCl_2$ hydrolyses to $Ti(OH)_4$. As the zeta potential of the negatively-charged organic matter is broken by $Ti(OH)_4$, organic matter aggregates with the $Ti(OH)_4$. Titanium tetrachloride is quadrivalent cation due to which it is better in aggregation than the trivalent Aluminum or iron ion particularly for Fluoride removal (Shon and Yousef, 2007).

1.3 APPLICATIONS OF TITANIUM TETRACHLORIDE

The world's supply of titanium metal, about 250 Kilotons per year, is made from $TiCl_4$. The conversion takes place by the reduction of the Chloride with

Magnesium metal, and yields Titanium metal and Magnesium chloride. This procedure is known as the Kroll process.

$$2Mg + TiCl_4 \rightarrow 2MgCl_2 + Ti$$

Around 90% of the $TiCl_4$ production is used to make the Titanium dioxide (TiO_2). The most important application areas of Titanium dioxide are paints, plastics, paper, printing inks, rubber, fibers and foodstuffs etc. For the production of titanium dioxide the conversion involves hydrolysis of $TiCl_4$ (Hans, 2006).

$$TiCl_4 + 2H_2O \rightarrow TiO_2 + 4HCl$$

In some cases, $TiCl_4$ is oxidized directly with oxygen:

$$TiCl_4 + O_2 \rightarrow TiO_2 + 2Cl_2$$

Keeping in mind, the aforementioned problems of sludge handling and the introduction of titanium tetrachloride as an emerging coagulant for wastewater treatment, we have focused in this work on Titanium tetrachloride for wastewater treatment because Titanium tetrachloride produces a small amount of sludge as compared to other traditional coagulants (Shon *et al*., 2007).

1.4 OBJECTIVES OF THE STUDY

The objectives of the study are:

- Performance investigation of chemical coagulants (Alum, Ferric chloride and Titanium tetrachloride) for wastewater treatment in terms of COD, BOD, TSS and Turbidity removal.

- To evaluate the effect of pH values on the performance of these three coagulants.

- Cost comparison between $TiCl_4$ and traditional coagulants i.e., Alum and $FeCl_3$.

1.5 SCOPE OF THE STUDY

The scope of the study includes:

- Monitoring the performance of Physico-chemical process for wastewater treatment in laboratory scale by using the Jar Test Apparatus and sand filtration columns.

- Analyze the emerging coagulant (Titanium tetrachloride) performance for wastewater treatment in terms of physical and chemical parameters.

- Comparison of titanium tetrachloride with Alum and Ferric chloride in terms of cost and efficiency.

Chapter 2

LITERATURE REVIEW

In recent years, the effluent standards for treated wastewater have become stringent to preserve the existing water resources for sustainable development. Due to dwindling natural resources, the application of reuse of treated wastewater for the secondary purposes i.e., watering lawns, cleaning, fire fighting is increasing day-by-day.

2.1 WASTEWATER TREATMENT BY BIOLOGICAL PROCESS

The use of biological (aerobic and anaerobic) treatment process for wastewater treatment can be traced back to the late nineteenth century (Visvanathan *et al.*, 2010). Since then, these aerobic and anaerobic biological processes have been commonly used to treat wastewater. Biological methods are very effective for wastewater treatment and during various treatment stages, approximately all harmful chemical materials become dissociated. In these processes, the organic matters (exists mainly in soluble form) is converted into CO_2, H_2O, NH_4^+, NO_2^-, NO_3^-, CH_4 and biological cells. The end products are dependent on the presence of oxygen (Visvanathan *et al.*, 2010). There are several biological methods which can be used for wastewater treatment e.g., Activated sludge, trickling filters, anaerobic degradation etc. Table 2-1 demonstrates the advantages and disadvantages of different biological wastewater treatment methods.

Table 2-1: Advantages and disadvantages of different biological wastewater treatment methods (Nazaroff and Alvarez, 2001)

Technology	Applications	Advantages	Disadvantages
Activated sludge	Low conc. organics, Some inorganics	○ Removal of dissolved constituents ○ Low maintenance ○ Destruction process	○ Volatile emissions ○ Waste sludge disposal area ○ High energy costs ○ Requires technically skilled manpower
Trickling filters, Fixed-film reactors	Low conc. organics, Some inorganics	○ Low maintenance ○ Destruction process ○ Relatively safe ○ Reduced sludge generation	○ Volatile emissions ○ Susceptible to shocks and toxins ○ Susceptible to seasonal changes ○ Relatively high capital and operating cost
Aerated lagoons, Stabilization ponds	Low conc. organics, Some inorganics	○ Removal of dissolved constituents ○ Low maintenance ○ Destruction process ○ Relatively safe ○ Low capital costs	○ Produce effluent with a high suspended solids concentration ○ Volatile emissions ○ Susceptible to shocks and toxins ○ High land requirement ○ No operational control
Anaerobic degradation (septic systems)	Low conc. organics, Chlorinated organics, Inorganics	○ Removal of dissolved constituents ○ Treatment of chlorinated wastes	○ Susceptible to shocks and toxins ○ Susceptible to seasonal changes ○ Relatively high capital and running cost

Consequently, sedimentation tanks of large volume offering several hours for residence time for treated water are required to obtain adequate liquid/solid separation (Fane *et al.*, 1978).

2.2 WASTEWATER TREATMENT BY MBR (MEMBRANE BIOREACTOR)

This process consists on combination of membranes and the biological reactor system. MBR system is relatively new technology which is being used for wastewater treatment. The function of membrane is defined as a thin wall which has processing capability by selective resistance to transfer of different constituents of a fluid through it.

The material of membranes should be of reasonable mechanical strength which can maintain a high through put of desired permeate with the high degree of selectivity (Ben *et al.*, 2010).

Membrane fouling is in the list of key issues which strongly effects the operation and maintenance cost of MBR. Membrane fouling is the deposition of fouling layer and this layer limits the permeate flux. Membrane fouling leads to frequent cleaning and/or the replacement of membrane, which increased the operating cost (Rousseau, 2011). Table 2-2 shows the advantages and disadvantages of MBR.

Table 2-2: Advantages and disadvantages of MBR (Rousseau, 2011)

Advantages of MBR	Disadvantages of MBR
Small footprint	Membrane surface fouling
No settlement problems	Membrane channel clogging
No further polishing required for disinfection/clarification	High capital and operational cost
No equalisation of hydraulic and organic loadings required	Process complexity

2.3 WASTEWATER TREATMENT BY PHYSICO-CHEMICAL PROCESS

Natural organic matters are usually associated with humic substances, degradation products in decaying wood, and soil organic matters. These substances are objectionable because these substances impart the color in water; act as a vehicle for transporting the toxic substances and form carcinogenic by-products by reacting with chlorine. The coagulation/flocculation process can remove these substances very efficiently. Coagulation/flocculation processes are commonly used to remove the suspended solids, suspended organic matter and color (DeWolfe *et al*., 2003). The competency of coagulation process to remove organic material is also dependent on matter type, present in wastewater. Generally, species of lower molecular weight e.g., fulvic acids are difficult to remove by coagulation process as compared to species of higher molecular weight e.g., humic acids (Beddow and Sun, 2010).

2.4 COAGULANT

Coagulants, when added into water/wastewater, the metal ions (Al, Fe and Ti) hydrolyze rapidly and form a series of metal hydrolysis species. The rapid mixing, the coagulant dosage and the pH determine hydrolysis species which is more effective for water/wastewater treatment. Different kinds of coagulants are used for water and wastewater treatment e.g., chemical and synthetic.

2.4.1 Synthetic Coagulants

There are many kinds of synthetic coagulants (polymers) which are used for water or wastewater treatment. Synthetic coagulants (Polymers) are the organic chemicals of long chain and higher molecular weight. Generally synthetic coagulants are used as a coagulant aids.

Following are the reasons to use synthetic coagulants:

- To enhance the aggregating efficiency to achieve better coagulating effect;
- To reduce the dosage requirement; and
- To increase the settling velocity.

Usually, negatively charged (Anionic) polymers are used with metal coagulants. Positively charged (Cationic) polymers of low and medium molecular weight may be used alone and these polymers may also be used in combination with aluminum/iron type coagulant.

These coagulants are able to function efficiently over a wide range of temperature and pH. Comparatively, small dosage is required to achieve goal and lower sulfate or chloride residuals are produced. A large range of natural and synthetic polymers are available which are macromolecular water soluble compounds. Table 2-3 shows the advantages and disadvantages of different synthetic coagulants.

Table 2-3: Advantages and disadvantages of different synthetic coagulants (Dgrsol, N.D)

Chemical Class	Chemical	Advantages	Disadvantages
Pre-Hydrolyzed Metal Salts	PACl / PAC	Floc is tougher Less sensitive to pH, operating range exists between pH 4.5 to 9.5. Mixing time is not very critical.	Generally on-site production plant is required for production of this synthetic coagulant.
	Polyiron Chloride	Suitable for high color applications.	Generally on-site production plant is required for production of this synthetic coagulant.
Synthetic Cationic Polymers	Epichlorohydrin di-methylamine Aminomethyl poly-acrylamide Poly-alkylene Poly-amines	Produce sludge of low density. Generally low amount of dosage is required. Economically beneficial because very lower dosage is required especially when used with combination of metal salts.	Poor in adsorbing the NOM. Difficult to determine the exact ratio of inorganic for proper mixing.

Polymers are several times more expensive than inorganic coagulants. Usually, the selection of the proper polymer for the required purpose is also very difficult task because a huge work on Jar Test Apparatus under the simulated plant conditions, followed by pilot scale is required.

All polymers must be approved by regulatory agencies before use for potable water. Toxicity is the common issue of synthetic polymers, which is generally produced due to unreacted residual monomers.

Gao (2002) used Aluminum-silicate polymer to investigate the floc size development, coagulant stability and the effect of pH value on turbidity removal. The results indicate that Aluminum-silicate polymer composite may enhance the aggregating efficiency, but weaken charge effectiveness in the coagulation process, when stored for longer time, especially at higher basicity (OH/Al ratio) and lower Al/Si ratio. It was observed that the coagulating effect of synthetic coagulant (Aluminum-silicate polymer composite) is linked to the preparation method

2.4.2 Chemical Coagulants

Generally, chemical coagulants fall into two categories: those which are based on aluminum and those which are based on iron. The aluminum coagulants include aluminum sulfate (alum), sodium aluminate and aluminum chloride. The iron coagulants include ferric chloride, ferric chloride sulfate, ferric sulfate and ferrous sulfate. On the other side, there are some emerging chemical coagulants (titanium tetrachloride, titanium sulfate, ferrate (VI), and Magnesium chloride), which are gaining their importance day by day due to some specialty on traditional coagulants (aluminum and iron).

2.4.2.1 Traditional coagulants, (Alum & Ferric)

Aluminum sulfate ($Al_2(SO_4)_3$) and Ferric chloride ($FeCl_3$) are the most commonly used coagulants. Approximately, Alum as a coagulant is used about more than 72% for water/wastewater treatment (DeWolfe *et al*., 2003). Alum is the cheapest coagulant, easily available and the handling of alum is very easy. Its main drawback is that it is most effective over a limited pH range of 6 to 8 (Adin *et al*., 1998).

Ferric chloride as a coagulant is also very famous and about 23% is used for water/wastewater treatment. Ferric chloride is effective over a wide range of pH 4 to 10. The Ferric hydroxide floc is heavier than the Aluminum floc which improves its settling characteristics. But Ferric chloride leaves the color behind in effluent.

The color removal characteristic of Ferric chloride is poor as compare to other coagulants. Ferric chloride is difficult to handle than alum. These traditional coagulants produce large quantity of sludge (DeWolfe *et al*., 2003).

2.4.2.2 Emerging Coagulant

There are many coagulants which are under surveillance to achieve better results in the field of wastewater treatment called emerging coagulants. The detail of few of them is given below:

a) Ferrate (VI)

Ferrate (VI) as coagulant may be used for water and wastewater treatment. In previous studies, it was observed that due to unique properties of ferrate (strong oxidizing potential and simultaneous generation of ferric coagulating species), this salt can disinfect microorganisms and can remove colloidal/suspended particles by single dosing. Ferrate (VI) is found very useful for degradation of the organic and inorganic impurities. But these applications of ferrate (VI) are mostly observed in laboratory scale and these findings have not yet lead to full scale for the water and wastewater treatment due to some difficulties e.g., relatively low yield of ferrate (VI) and instability of the ferrate(VI) which depends on method of preparation (Jiang and Lloyd, 2002).

Jiang *et al.* (2006) evaluated the performance of potassium ferrate (VI) in comparison with that of sodium hypochlorite and that of NaOCl plus ferric sulfate or alum. The results indicate that the potassium ferrate (VI) can remove 10 - 20% more UV_{254} - abs and DOC than NaOCl (plus ferric sulfate) with same dose at pH (6 and 8).

b) Magnesium Chloride ($MgCl_2$)

Tan *et al.*, (2000) investigated the performance of this coagulant to examine the effectiveness in chemical precipitation method for the removal of coloring matters. The results were compared with the results obtained from alum and PAC. The color concentration of the dye solutions were measured by visible spectrophotometer. The effect of coagulant dose, pH and coagulant aid dosage were also included in this study. It was observed that magnesium chloride is more effective in removing the reactive dye than alum and PAC (in terms of settling time and the amount of alkalinity required), and is capable to remove more than 90% coloring material. But this good result was achieved at very high dose of magnesium chloride (4 g /liter) and only at pH 11.

2.5 TITANIUM TETRACHLORIDE ($TiCl_4$)

The use of Titanium salts as a chemical coagulant for water treatment was first proposed by Upton and Buswell in 1937. They reported that coagulation process could be affected by dosing titanium compounds as coagulants, which flocculated easily at low temperatures and these compounds are more effective for color removal, as compared to traditional coagulants.

Shon *et al*. (2007) reported the use of Ti-salt as a new coagulant is efficient not only in terms of organic matter removal, but also in sludge reduction. They studied Titanium tetrachloride to remove dissolved organic matter and particulate from wastewater and observed that Titanium tetrachloride successfully removed organic matter to the same extent as Ferric and Aluminum salts. They found 70% organic matter removal with optimum dose 9.8 Ti-mg/L. Lokshin and Belikov (2003) also investigated Ti-salt flocculation and found that wastewater can be efficiently purified to remove Fluoride ions with Titanium (IV) compounds.

Okour *et al*. (2009) performed flocculation process for wastewater treatment by Titanium as coagulant. The performance of this coagulant was investigated in terms of DOC removal, turbidity removal, particle size and zeta potential. The results were compared with Alum and Ferric chloride. They found 60 to 67% organic removal at pH range 4-8. He found that Aluminum sulfate did not remove the turbidity at pH 4. This may be due to solubility of Aluminum hydroxide at this pH value. On the other hand, better removal by titanium tetrachloride was recorded at pH less than 5. As shown in the Table 2-4, at pH 5, the Ferric chloride showed 75 % removal in turbidity, whereas Titanium tetrachloride showed better 77% removal in turbidity. At pH 6, the optimum dose for the Aluminum sulfate and Ferric chloride were 30mg/L and 20mg/L for 76% and 75% removal in turbidity respectively. Titanium tetrachloride showed better removal in turbidity about 77% at optimum dose of 30 mg/L. At pH 8, Titanium tetrachloride showed 76% turbidity removal. At pH 10, all coagulants except alum showed similar turbidity removal with turbidity ratio of 0.29 (71% turbidity removal).

Table 2-4: Turbidity removal by Ti, Fe and Al salts at different pH (Okour et al., 2009)

Coagulant	**Turbidity Removal (%) at pH 5**	**Turbidity Removal (%) at pH 6**	**Turbidity Removal (%) at pH 8**	**Turbidity Removal (%) at pH 10**
Titanium tetrachloride	77	77	76	71
Ferric chloride	75	75	72	71
Aluminum sulphate	Nil	76	76	71

Shon and Vigneswaran (2009) performed the work on flocculation process for wastewater treatment by using coagulants aids with primary coagulant titanium tetrachloride. $Al_2(SO_4)_3$, $FeCl_3$ and $Ca(OH)_2$ were the chemicals which were used as coagulant aid. The prime purpose of this study was to analyze any improvement in the photoactivity of Titanium dioxide (TiO_2) produced from the sludge after flocculation and increment in pH value of resulting wastewater. They found in their results an effective increase in pH value of the supernatant and better DOC removal, when coagulants aids are used with Titanium tetrachloride. At optimum concentration 8.4 Ti-mg/L (without coagulant aids), the 70 % DOC removal and pH 3.25 of supernatant was recorded. To increase the pH value, the use of coagulant aids $FeCl_3$, $Ca(OH)_2$ and $Al_2(SO_4)_3$ with $TiCl_4$ was included. Table 2-5 represents the DOC removal and pH value of treated wastewater by Titanium tetrachloride with different coagulants aid.

At optimum concentration 4.2 mg/L of Ti and 6.9 mg/L of Fe, 70% DOC removal and pH 4.7 were recorded. The optimum concentration 4.2 Ti-mg/L and 8.0 Al-mg/L was recorded when Al is used as a coagulant aid with Ti. The DOC removal and pH value at the optimum concentration of Ti and Al salts were 72% and 4.5, respectively. The optimum concentration 6.3 Ti-mg/L and 15.0 Ca-mg/L was recorded when Ca is used as a coagulant aid with Ti. The DOC removal and pH value at the optimum concentration of Ti and Ca were 70% and 7.6, respectively.

Shon and Vigneswaran (2009) also observed an increase in surface area, especially when alum is used as a coagulant aid with titanium. They noted that surface area of Al/TiO_2 flocs was $136 m^2/g$, whereas the surface area of TiO_2flocs only was $122\ m^2/g$.

Table 2-5: DOC removal and pH by $TiCl_4$ with/without Coagulant aid (Shon et al., 2009)

Coagulants	pH of Supernatant	DOC Removal %
Titanium tetrachloride without coagulant aid	3.25	70
Titanium tetrachloride with Aluminum sulfate	4.5	72
Titanium tetrachloride with Ferric chloride	4.7	70
Titanium tetrachloride with Calcium hydroxide	7.6	70

Okour *et al*. (2009) observed the effect of coagulation process on color removal and investigated the efficiency of different coagulants on color removal. Given figures show the results of color removal, which clearly explain that the percentage of color removal is approx. directly proportional to coagulant's doses. Titanium sulfate ($Ti(SO_4)_2$) showed 100% color removal in supernatant at all pH with dose ≥50 mg/L. All coagulants performed very well at pH 10 and color removal 92% to 97% was achieved.

As shown in the Figure 2-1, titanium tetrachloride has a minimum color ratio of 0.04 (96% color removal) at pH 4 and 6. Ferric chloride showed only 70% color removal at pH 6 and aluminum sulfate showed only 76% color removal at pH 6. Titanium tetrachloride and aluminum sulfate have the same color ratio of 0.10 at pH 8 with doses of 40 and 50 mg/L respectively.

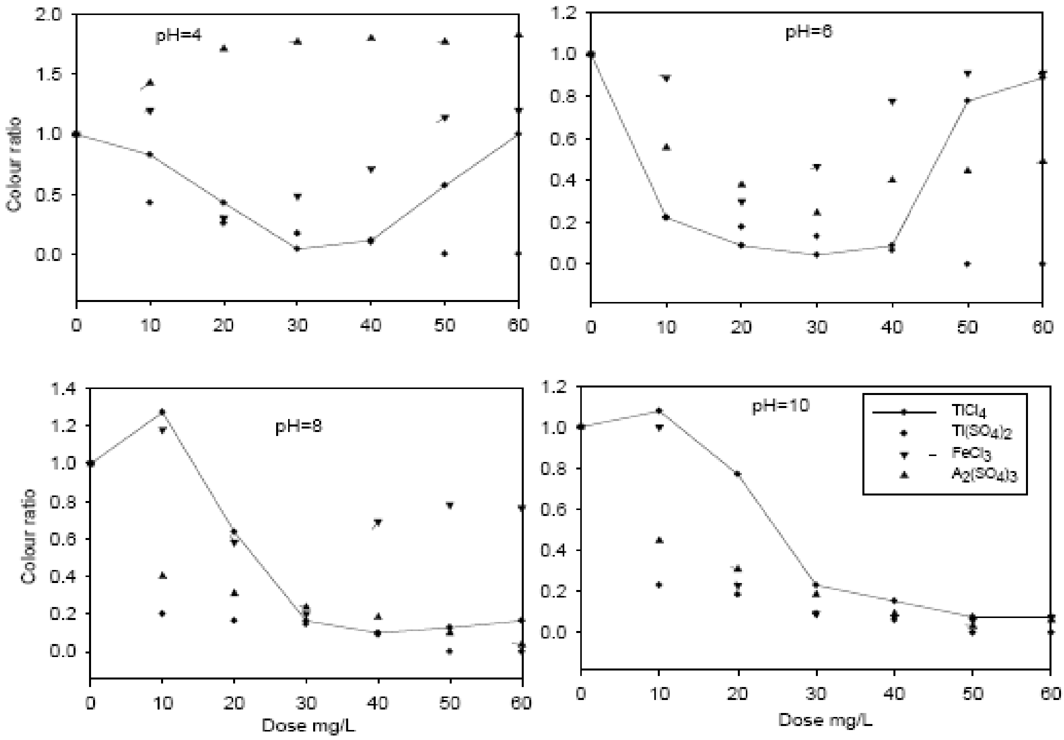

Figure 2-1: Variation in residual color ratio as a function of coagulant doses at different pH (Okour *et al.*, 2007)

Shon *et al.*, (2007) represented the very beneficial information regarding the production of highly valued recycled Titanium dioxide (TiO_2) by the incineration of sludge produced from coagulation/flocculation processes by using Titanium salts as a coagulant. This is very novel solution to overcome the sludge handling problem. Titanium dioxide is the most widely used metal oxide (Kaneko and Okura, 2002). Upto 40 mg-TiO_2 nanoparticles/L of wastewater may be produced from the wastewater sludge. Titanium dioxide produced by this process is quite valuable. The production of TiO_2 by this process can be very beneficial due to huge market demand of Titanium dioxide. In addition, it is observed that the photocatalytic activity of recycled TiO_2 is better than the commercially available TiO_2.The supernatant toxicity after $TiCl_4$ flocculation is very low even nil toxicity is observed when 100mg/L dose of coagulant is used. The TiO_2 nanoparticles regenerated from flocculated sludge also indicate very low amount of toxicity as compared to commercially available TiO_2 nanoparticles (Lee *et al.*, 2009).

Zhao *et al.*, (2010) compared the performance of Titanium tetrachloride with commonly used coagulants such as Poly aluminum chloride (PACl), Alum, Ferric chloride and Poly ferric sulfate (PFS) for the treatment of water in terms of dissolved organic carbon (DOC), UV_{254} and turbidity. In their study, they reported that $TiCl_4$ flocculation achieved 84% removal in (DOC), 98% removal in UV_{254} and 93% removal in turbidity. A pilot scale plant study was conducted by Okour *et al*. (2007) to demonstrate the feasibility of novel process using Titanium tetrachloride ($TiCl_4$) flocculation with dye wastewater. It was found that the removal ratio of the chemical oxygen demands (COD) with $TiCl_4$ flocculation was comparable to traditional coagulants.

Zhao *et al.*, (2011) reported that removal of organic matter (of different molecular weight) by Ti-salt flocculation is similar to that of Al-salt and Fe-salt flocculation. During physico-chemical process, small increase in shear force give rise to flocs breakage. The rate of sedimentation of flocs will decrease and smaller particles will travel with supernatant. These smaller particles will affect filtration efficiency because some particles will block the pores of filter and remaining particles which will pass through the filter will affect the overall efficiency of the process. Therefore, the flocs strength and recoverability are important parameters that should be well controlled for overall process optimization. According to previous study performed by P.T. Spicer, the flocs that form at a low velocity gradient, if broken into smaller flocs, due to increase in shear force, can re-form in their original size, if same low velocity gradient is reapplied and is known as reversible breakage. However, Zhao *et al.* (2011) has concluded in their results that original size of floc cannot be attained after breakage. The flocs aggregation and re-growth characteristics depend on the characteristics of coagulant, water and as well as on various other parameters e.g., applied shear force and shear exposure time. Yukselen and Gregory (2002) reported that, the flocs formed by alum for the coagulation of kaolin particles have the poorest re-growth characteristics after shear and reaching only a third of their previous size.

Zhao *et al*., (2011) investigated the flocs strength and re-growth properties of flocs produced by Alum, Ferric Chloride and Titanium tetrachloride. Flocs strength and re-growth properties were measured through breakage and subsequent re-growth potential by increasing the shear force. A laser diffraction particle sizing device was used to examine the floc growth, breakage (flocs strength) and re-growth of $Al_2(SO_4)_3$, $TiCl_4$ and $FeCl_3$.He found that the flocs strength of titanium tetrachloride is higher than other two coagulants. The order with respect to flocs strength was $TiCl_4 > FeCl_3 > Al_2(SO_4)_3$.

2.6 Septic Tank

Septic tank is the system that allows the onsite treatment for wastewater at residential or small commercial units. The quiescent condition inside the septic tank allows the portions of suspended solid to settle, floatable to rise up and provides storage space for biological activity (Clearinghouse, 2000).

The first reported application of domestic use of septic tank was in France in 1860 A box was located among the house and the cesspool trapped excrement, which reduced the solids and generated treated wastewater, that entered the soil more quickly. In America, household septic tank was first used in 1883 which had two section tank designs. After that the septic tank use increased rapidly and now it is implemented in many parts of the world (Butler *et al*., 1995).

Conventional septic system mainly consists on a septic tank and soil absorption system, septic system is preferable for on-site wastewater treatment because septic system operation and maintenance are not expensive. If septic system was installed properly in suitable soil, it can be used for many years. Table 2-6 shows the wastewater characteristics of typical sewage & septic tank, and their comparison with National Environmental Quality Standards (NEQS).

Table 2-6: Characteristics comparison of typical sewage with septic tank & NEQS(PEPC)

Parameter	**Typical Sewage**	**Septic Tank**	**Inland Water NEQS**	**Coastal Area NEQS**
Biochemical Oxygen Demand (BOD_5)	200-300 mg/l	50-100 mg/l	80 mg/l	80 mg/l
Chemical Oxygen Demand (COD)	350-500 mg/l	90-170 mg/l	150 mg/l	400 mg/l
pH	6.0-8.5	6.5-8.0	6-9	6-9
Total Suspended Solids	200-300 mg/l	80-120 mg/l	200 mg/l	200 mg/l

The sewage/wastewater of septic tank is selected as a sample to perform experiments. Table 2-7 shows the approximate sewage generation rate at IESE.

Table 2-7: Sewage generation rate at IESE (Saadat Ali, 2012)

Designations of Persons	**Numbers**	**Production of Wastewater per Capita per day (Liters)**	**Total Volume of Water per Day (Liters)**
Teachers	15	20	300
Students	150	20	3000
Staff	30	20	600
Total			3900 liters/day

Chapter 3

METHODOLOGY

3.1 SAMPLING SOURCE

The septic tank constructed near IESE building at NUST campus, H-12, Islamabad was selected as source of wastewater. Figure 3.1 represents the cross section view of septic tank.

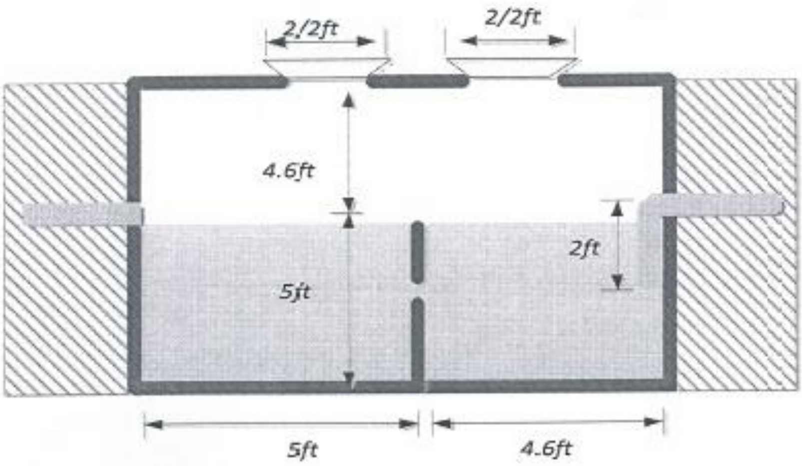

Figure 3-1: Cross section view

3.2 SAMPLE COLLECTION AND ANALYSIS

A pump was installed on the septic tank. The suction point for the pump was at the level of 6″ below the surface of wastewater in septic tank. A piping network was established from septic tank to IESE laboratory. The discharge line of pipe was opened at a small tank placed in laboratory.

Cleaning of all jars and small tank, and the drainage of water from pipe, were always taken care of during every performance/experiment. Figure 3-2shows the sketch of experimental set-up.

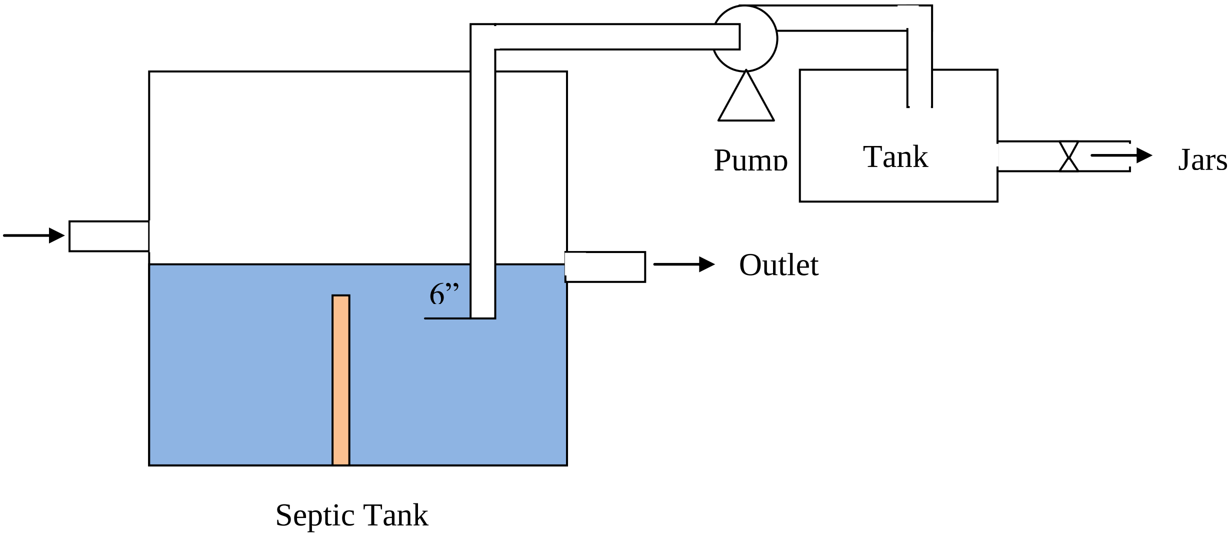

Figure 3-2: Sketch for sampling process

3.3 WASTEWATER CHARACTERIZATION

The wastewater characterization of the collected samples was done in the IESE laboratory using Standards Methods (Eaton, 2005).

The parameters for which wastewater were analyzed before and after the physico-chemical process along with the corresponding analysis methods are listed in Table 3-1. All types of the solutions required to measure the value of COD and BOD were freshly prepared for these experiments.

Table 3-1: Analytical parameters, methods and equipments

Sr. no.	Parameter	Technique	Equipment/ Material	Chemicals/ Reagents
1	COD	Closed reflux	COD tube, oven (150˚C)	i. Potassium dichromate digestion solution ii. Sulfuric acid reagent iii. Ferroin indicator solution iv. Ferrous ammonium sulfate
2	BOD_5	Dissolved oxygen method	Glass bottles (300ml), Incubator (20˚C)	i. Magnesium sulfate solution ii. Phosphate buffer solution iii. Ferric chloride solution iv. Calcium chloride solution
3	TSS	Filtration-Evaporation	1.2µm (GF/C, Whatman), oven (103˚C)	
4	Turbidity	Nephelometric method	HACH Turbidimeter 2100N	
5	pH	acidity or alkalinity of solution	pH meter	

3.4 PREPARATION OF COAGULANTS STOCK SOLUTIONS

3.4.1 Preparation of Alum Stock Solution

Alum in the form of flakes ($Al_2(SO_4)_3.18H_2O$) was used in this study. Alum stock solution was prepared by weighing accurately 50 grams of Alum and was dissolved in the distilled water. The volume of alum stock solution was made up to the mark in one liter volumetric flask. Since 1000ml of alum stock solution contains 50000mg of alum, therefore 1ml of alum stock solution would contain 50mg of alum. Alum stock solution was then preserved in a refrigerator for subsequent use.

3.4.2 Preparation of Ferric Chloride Stock Solution

Anhydrous ferric chloride in the powder form was used in this study. Ferric chloride stock solution was prepared by weighing accurately 50 grams of ferric chloride and was dissolved in the distilled water. The volume of ferric chloride stock solution was made up to the mark in one liter volumetric flask. Since 1000ml of ferric chloride stock solution contains 50000mg of ferric chloride, therefore 1ml of ferric chloride stock solution would contain 50 mg of ferric chloride. Ferric chloride stock solution was then preserved in a refrigerator for subsequent use.

3.4.3 Titanium Tetrachloride

$TiCl_4$ in the form of liquid (98% pure) was used in this study. Titanium tetrachloride is highly reactive with water and produce HCl in response of reaction with water. Therefore as per standard procedure for handling of Titanium tetrachloride, this chemical was injected directly in jars by creating inert atmosphere by using nitrogen gas.

3.5 JAR TESTAPPARATUS

The coagulation, flocculation and settling process were performed on laboratory scale with the help of JARTESTER, Model No. PB-700^{TM} manufactured by PHIPPS&BIRD, USA.

The removal of COD, BOD, TSS and Turbidity from wastewater were examined by using each coagulant independently at different pH values. The pH values 5, 6, 6.5, 7, 8 and 9 were selected to examine the performance of each coagulant. On the basis of removal of COD, BOD, TSS and Turbidity from wastewater, the optimum dosage was evaluated for each coagulant at each pH. The following range of dosages for each coagulant was selected for this study:

- Alum ($Al_2(SO_4)_3.18H_2O$): 0 to 600mg/l
- $FeCl_3$: 0 to 200 mg/l
- $TiCl_4$: 0 to 200 mg/l

These ranges of dosages were selected on the basis of previous studies by (Okour *et al*., 2007), (Shon *et al*., 2007) and (Lee *et a*l., 2009).All results achieved from the experiments were compared with one another at each pH value to draw a complete sketch of their performance. On the basis of the comparisons of each coagulant at each pH, the cost comparison is also generated between these coagulants at each pH value. All tests were performed with samples, collected from running sewage system. Therefore the values of COD, BOD, Turbidity and TSS of samples were found approximately always different. So, it is difficult to represent actual optimum dosages of each sample for each coagulant and actual removal in mg/l of COD, BOD, Turbidity and TSS in wastewater with each coagulant. Therefore all results are drawn in term of percentage removal of BOD, COD, TSS and turbidity.

3.6 PROCEDURE FOR THE DETERMINATION OF OPTIMUM COAGULANT DOSAGE

Standard Jar Test method was carried out for the determination of optimum coagulant dosage of Alum, Ferric chloride and Titanium tetrachloride. The coagulation, flocculation and settling process were performed on laboratory scale with the help of Jar Test Apparatus. The main steps of the procedure were as follows:

- Equal volumes i.e., 2L of the representative wastewater from septic tank was taken into each of the six jars

- COD, TSS and Turbidity of sample were measured before experiment.

- The required pH of the wastewater was adjusted in jars with 0.1N H_2SO_4orNaOH solutions

- Different concentrations of coagulant were added to each of the six jars i.e. 0ml, 4.8ml, 9.6ml, 14.4ml, 19.8ml and 24ml.

- Then, rapid mixing of the contents of the jars was carried out for 1 minute at a speed of 100rpm

- After flash mixing, slow mixing of the contents of the jars were carried out for 20 minutes at a speed of 30 rpm

- After the slow mixing period the paddles were withdrawn from each jar and the contents of the jar were allowed to settle for a period of 30 minutes

- After 30 minutes of sedimentation the COD, TSS and turbidity of the wastewater in each jar were determined by taking waste samples from each jar, extreme care was taken so that the sludge should not be disturbed during the sampling.

- From the COD and TSS values of wastewater in each jar the next dosage of coagulant required to run the jar test was estimated.

- The jar test experiment was repeated for another dosage of coagulant until a value of least COD and TSS were obtained. The dosage of the coagulant which gave least COD and TSS values was considered as the required optimum dosage of the coagulant.

- Similar procedure was used for determination of optimum dose of Alum, Ferric chloride and Titanium tetrachloride.

3.7 FILTRATION

For filtration process, three filtration columns were fabricated using 8 mm thick plastic sheet. The dimensions of filtration columns were 3″x3″x24″. Two layers were established for filtration purpose, top layer consisted on sand of size 0.8-1.2mm with dimensions 3″x3″x6″. The bottom layer was of rocks of size 3-4 mm with dimensions 3″x3″x3″. The column size was suitable for the treatment of 2 liters water at one time. Each filtration column was allocated for individual coagulant. Filtration process was added to investigate the effect of filtration in the removal of COD and TSS. Each column was backwashed for 5 minutes using tap water before introducing new sample.

Chapter 4

RESULTS AND DISCUSSION

As mentioned earlier, the performance of following three chemical coagulants against wastewater was investigated in this study:

i. Alum ($Al_2(SO_4)_3.18H_2O$) as traditional coagulant.

ii. Ferric chloride ($FeCl_3$) as traditional coagulant.

iii. Titanium tetrachloride ($TiCl_4$) as emerging coagulant.

The optimum dose of each coagulant at different pH levels was determined by using Physico-chemical process. Finally the results were compared with one another to evaluate the performance of emerging coagulant (titanium tetrachloride) in term of cost effectiveness and percentage removal of COD, BOD, TSS& Turbidity.

4.1 ALUM ($Al_2(SO_4)_{3.}18H_2O$) AS TRADITIONALCOAGULANT

Chemical Oxygen Demand (COD)

The performance of Alum was investigated in term of COD removal with different doses from 0 to 600 mg/l at different pH values (5, 6, 6.5, 7, 8 & 9) based upon the literature review. First of all, an interval of 120 mg/l was chosen between 0 and 600mg/l. Figure 4-1 represents the COD removal under wider dosage range.

As shown in the figure, that Alum gives better results at doses (240 mg/l & 360 mg/l) at all pH levels except pH 9.

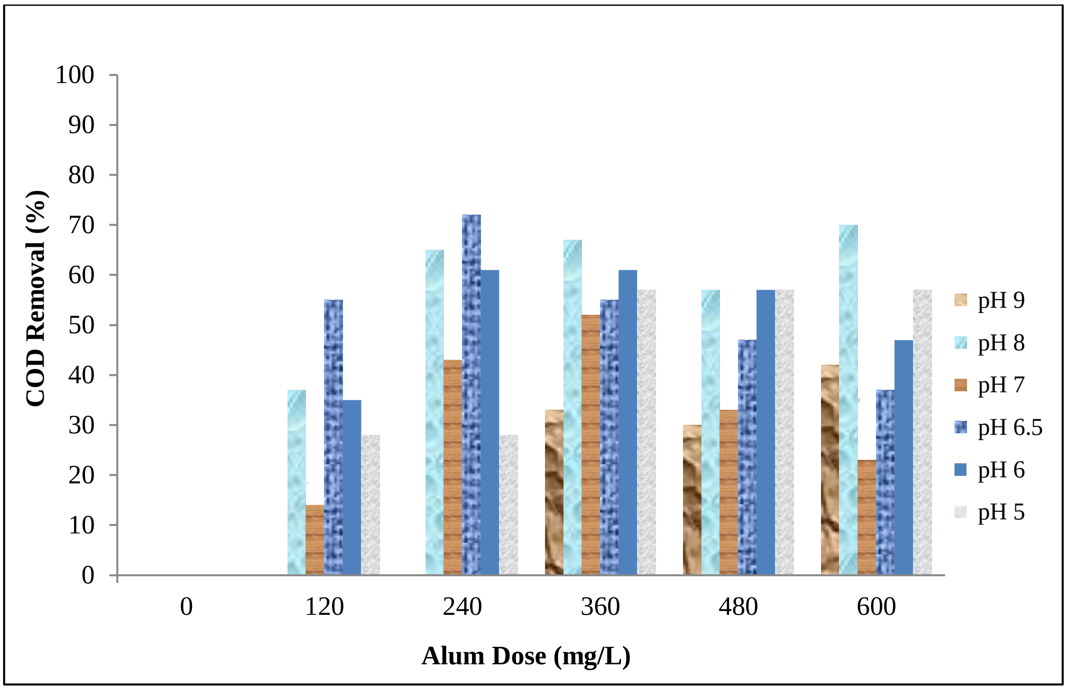

Figure 4-1: COD removal by using Alum as a coagulant

pH 6.5 and pH 8 exhibited better COD removal as compared to other pH levels. This was because these pH levels fall with charge neutralization and sweep floc zones of coagulation (Khan, 1993). To find the optimum dose of Alum and the maximum COD removal, the experiments were again performed but now with small intervals (260mg/l, 280mg/l, 300mg/l, 320mg/l and 340mg/l).As shown in Figure 4-2, max. COD removal of 77% was found at pH 6.5 with 280 mg/l dosage. The up and down trend at different pH levels show that coagulation is effective only under certain pH and dose conditions and effectiveness declines as soon as we go out of that zone.

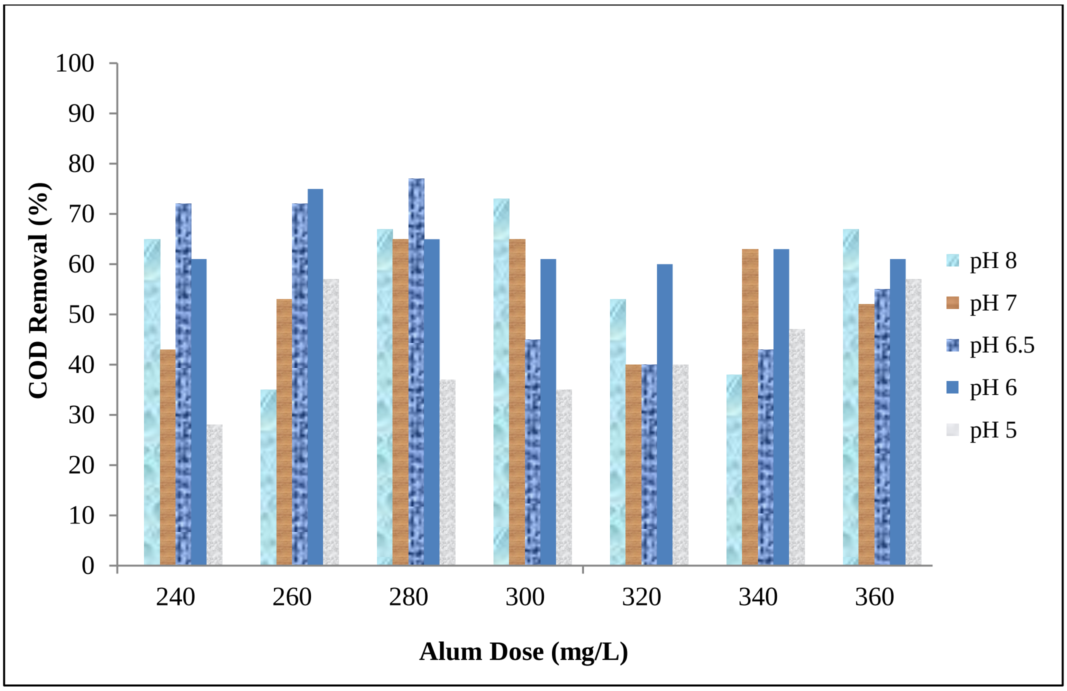

Figure 4-2: Evaluation of optimum dose of Alum for COD removal

Biochemical Oxygen Demand (BOD_5)

More than 200 COD tests were performed for this study. It was difficult to perform as many tests for BOD_5as it takes five days for each test and resources were limited to run several tests at the same time. Therefore, only six tests of BOD_5were performed to develop relationship between BOD_5 and COD. Figure 4-3 represents the relation between BOD and COD.

The BOD_5/COD ratio 0.637 was obtained, which means that if any sample has COD value 100 mg/l then its BOD_5 value would be approximately 63.7mg/l. This factor (0.637) was used to find out the BOD_5 value for the remaining samples.

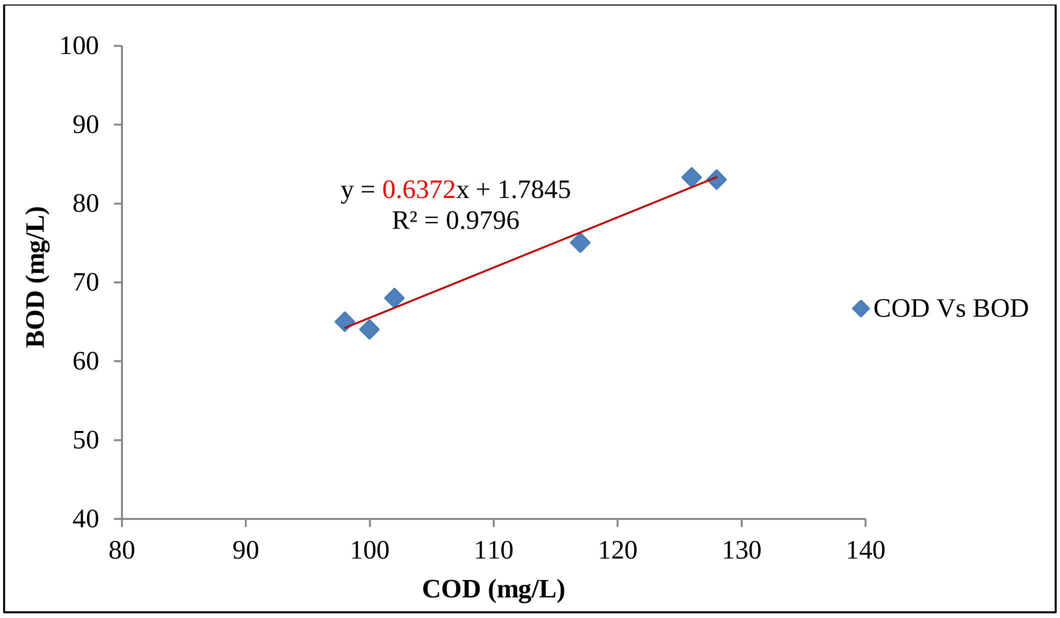

Figure 4-3: Development of COD & BOD_5relationship

Based on above mentioned factor and COD values (which were all found out experimentally), the BOD_5 removal trends are shown in Figure 4-4.

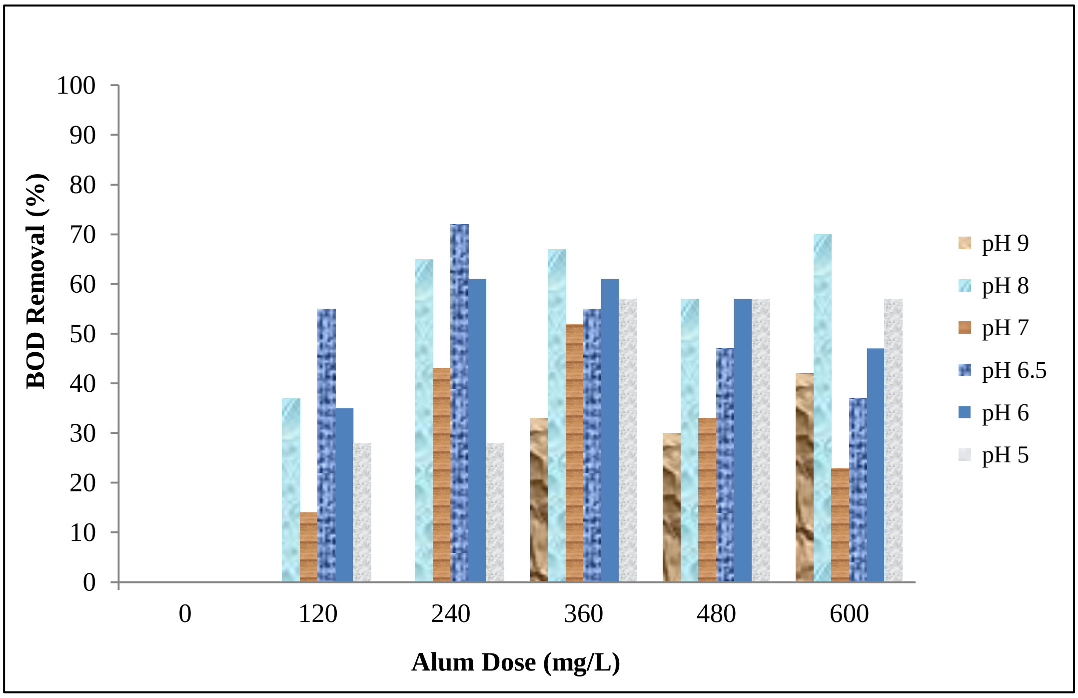

Figure 4-4: BOD removal from wastewater with Alum

Better BOD removal was observed at pH 6.5 and pH 8 as compared to other pH levels. As shown in Figure 4-4, the maximum BOD removal of 72% was found with Alum dose of 240 mg/l at pH 6.5.

Total Suspended Solids (TSS)

The performance of Alum was also investigated in term of TSS removal from wastewater within same dose range (0 to 600 mg/l) at the same pH values (5, 6, 6.5, 7, 8 and 9). Figure 4-5 illustrates the percent removal of TSS using Alum as a coagulant.

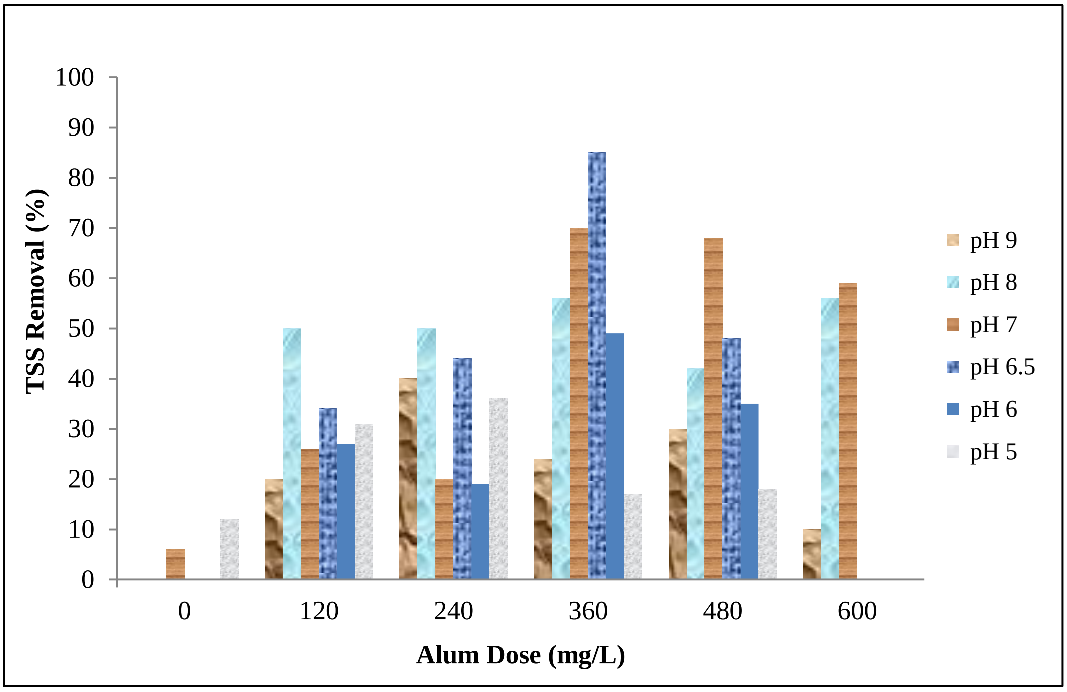

Figure 4-5: TSS removal using Alum as coagulant

It can be evaluated from figure that Alum gives better TSS removal at pH 6.5, 7 & 8 with an alum dose of around 360mg/l. The maximum of 85% TSS removal was achieved with alum dose of 360mg/l at pH 6.5. This clearly shows that TSS removal by Alum is more effective at lower pH (6-7) and within the charge neutralization zone of coagulation. Figure 4-5 also elucidates that alum is less effective in higher pH condition.

Next, the experiments were performed again with small intervals with doses 320mg/l, 340mg/l and 380mg/l to maintain the doses values around the 360mg/l.

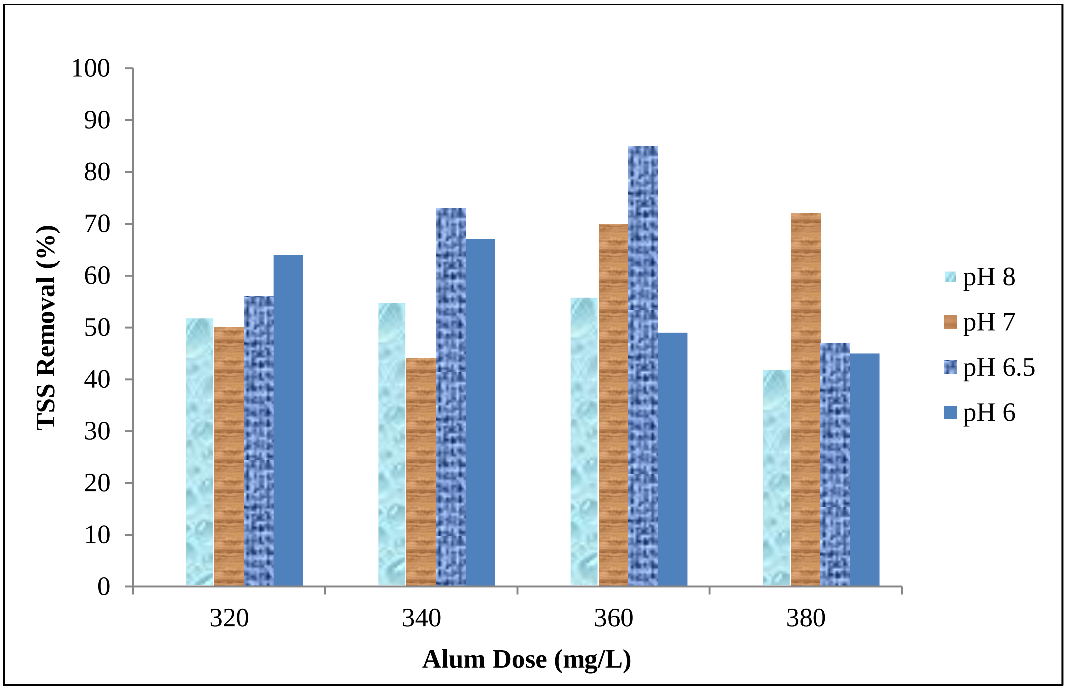

Figure 4-6: Evaluation of optimum dose of Alum for TSS removal

Once again, it is clear that TSS from wastewater can be best removed at a pH of 6.5 using an alum dose of 360 mg/L.

Sand Filtration

To complete the physico-chemical process, filtration was introduced to the process. After completion of coagulation/flocculation and settling process, the supernatant was passed through the filter with hydraulic loading rate of 2gpm/ft^2.As discussed in section 3.7, the dimensions of filtration columns were 3″x3″x24″. Two layers were established for filtration purpose, top layer consisted on sand of size 0.8-1.2 mm with depth of 150 mm. The bottom layer was of rocks of size 3-4 mm with a depth of 75 mm. After filtration, the COD and TSS tests were again performed on filtered wastewater to investigate the impact of filtration on COD and TSS removal. Figure 4-7 represents the overall TSS removal, achieved from coagulation/flocculation and filtration processes.

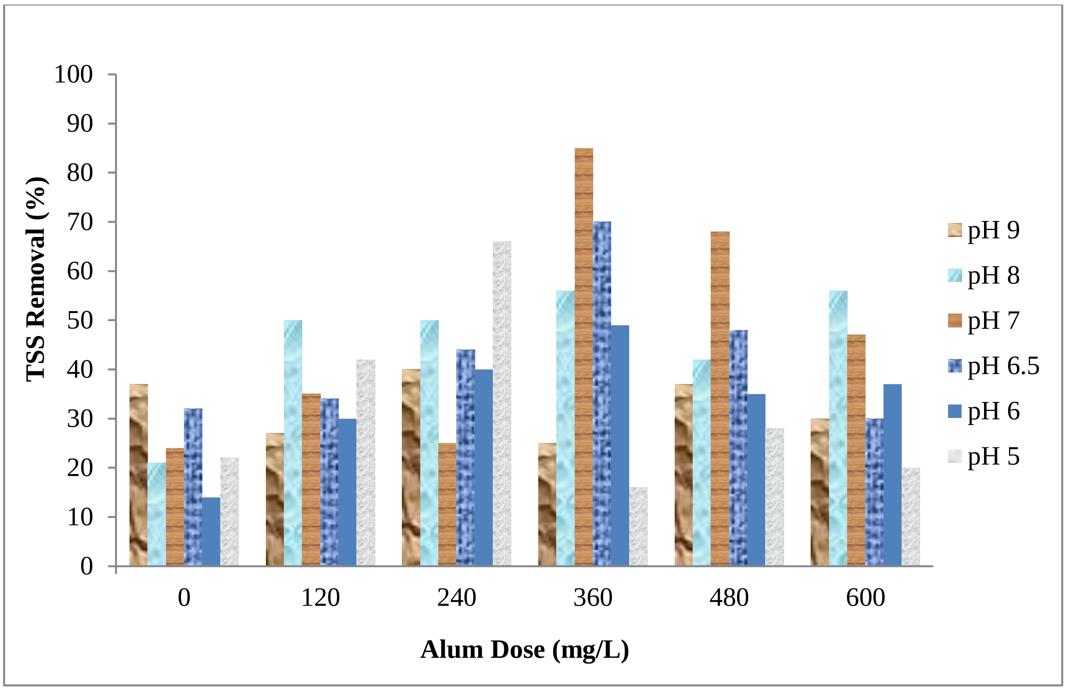

Figure 4-7: TSS removal with Alum and filtration

As for COD, it was concluded that filtration process with above specification did not contribute into COD removal. However, TSS removal after filtration process was observed. By comparing these trends with trends of TSS removal without filtration process, it can be concluded that those samples which had comparatively higher TSS value shows better removal after filtration. Therefore, it can be said that overall efficiency of system becomes improved for TSS removal but this filter did not help significantly for COD and TSS removal. The reason of this performance by filtration may be due to limited depth of sand

and rock layers because that COD and TSS removal may be achieved with sand filter with big layer of sand e.g., 1000 mm (Zaidum, N.D).

Turbidity (NTU)

The supernatant of samples of pH 5, 6, 7 and 8 after coagulation and flocculation process with Alum were evaluated in term of turbidity removal. The results are shown in Fig. 4-8 which illustrates that alum gives better results at pH 5, 6&7 and the maximum turbidity removal of 96% was found with Alum. This clearly shows that turbidity removal by Alum is more effective in acidic condition. At higher pH (pH 8), the decrease in removal of turbidity with Alum coagulant might be attributed to the competition between colloidal particles of negatively charge and hydroxyl ions (Zhao *et al*., 2010).

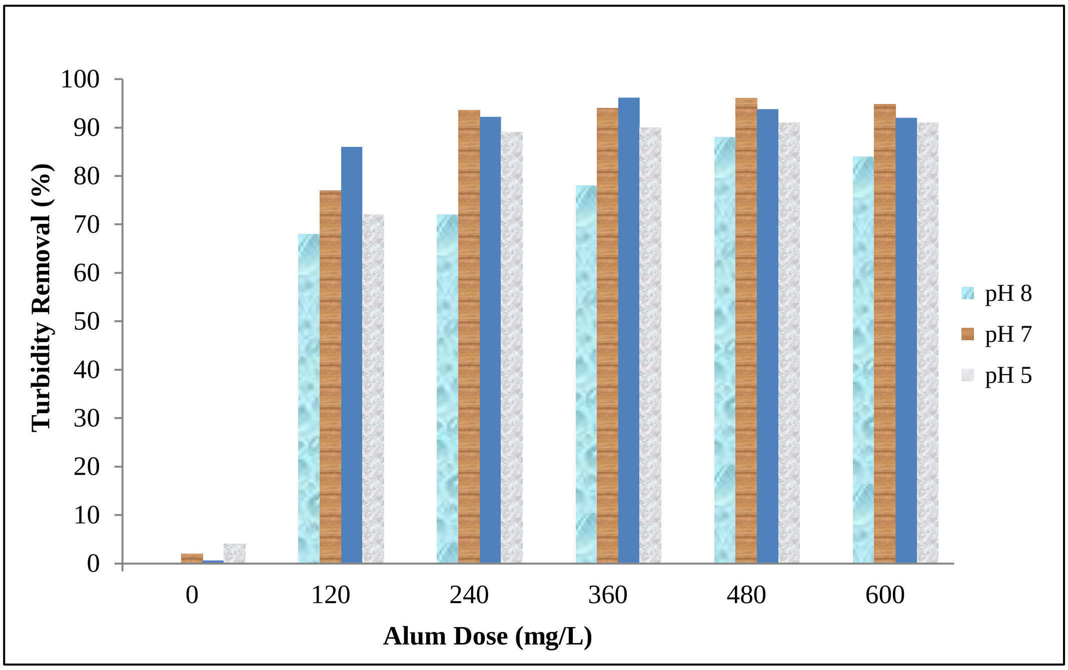

Figure 4-8: Turbidity removal with Alum

4.2 FERRIC CHLORIDE AS TRADITIONAL COAGULANT

Chemical Oxygen Demand (COD)

The performance of Ferric chloride was investigated in term of COD removal with different doses ranging from 0 to 200 mg/l at different pH values (5, 6, 6.5, 7, 8 and 9)based upon the literature review. First of all an interval of 40 mg/l was chosen between 0 and 200mg/l. Figure 4-9 represents the trend of COD percentage removal when Ferric chloride was used as coagulant. As shown in the graph, the Ferric chloride gives better COD removal at low doses. At pH 6, 85% COD removal with dose of 80 mg/L of Ferric chloride was observed, butat pH 9, the performance of Ferric chloride was not appreciable. In these experiments, it was evaluated that Ferric chloride is good in COD removal but removal of color imparted by $FeCl_3$ remains an issue.

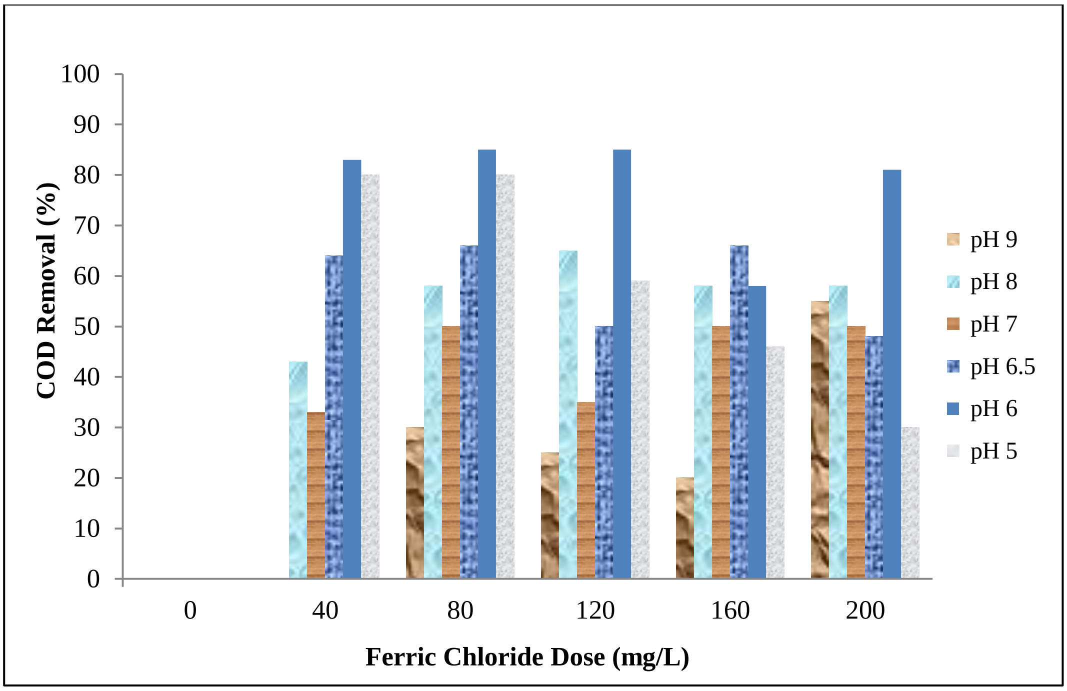

Figure 4-9: COD removal by using Ferric chloride as a coagulant

The experiments were repeated with small intervals with doses 20mg/l, 60mg/l and 100mg/l to maintain the doses values around the 80mg/l. The values of COD removal against the dose 40 mg/l and 80 mg/l of previous experiment were used in Figure 4-10. Dose 20 mg/L was used to reassure that performance of $FeCl_3$ at lower dosages range. Results of these explorations are shown in Figure 4-10. As shown in the figure, that better results of COD removal are obtained with 40mg/l dose, especially at pH 5 and pH 6.In these experiments, it was also observed that Ferric chloride has higher COD removal than alum.

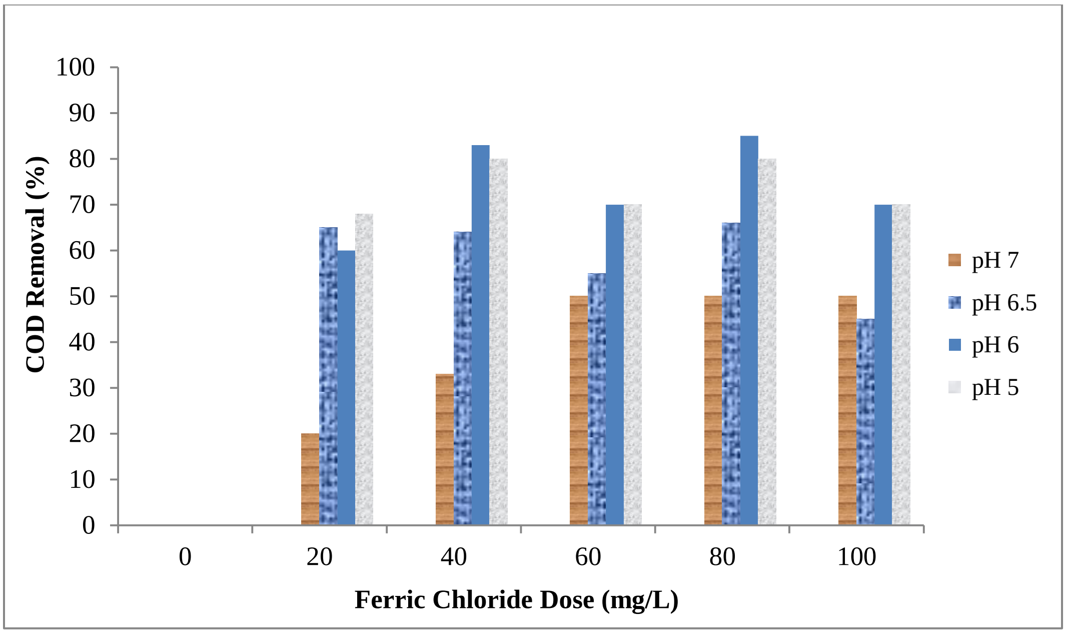

Figure 4-10: Evaluation of optimum dose of Ferric chloride for COD removal

Biochemical Oxygen Demand (BOD_5)

BOD removal was found by using the same factor (0.6372) of COD and BOD relation. Maximum BOD removal was achieved at pH 6, approximately with all doses rate. Figure 4-11 shows the result of BOD_5 removal with Ferric chloride.

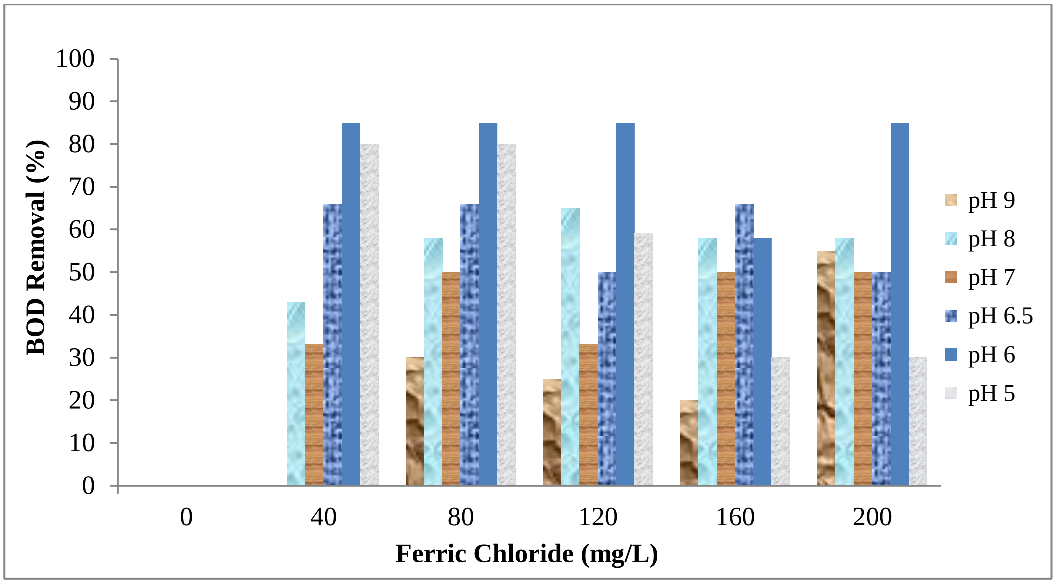

Figure 4-11: BOD removal with Ferric chloride

Total Suspended Solids (TSS)

The performance of Ferric chloride was also investigated in term of TSS removal from wastewater with same doses range (0 to 200 mg/l) at the same pH values (5, 6, 6.5, 7, 8 and 9) used for COD removal.

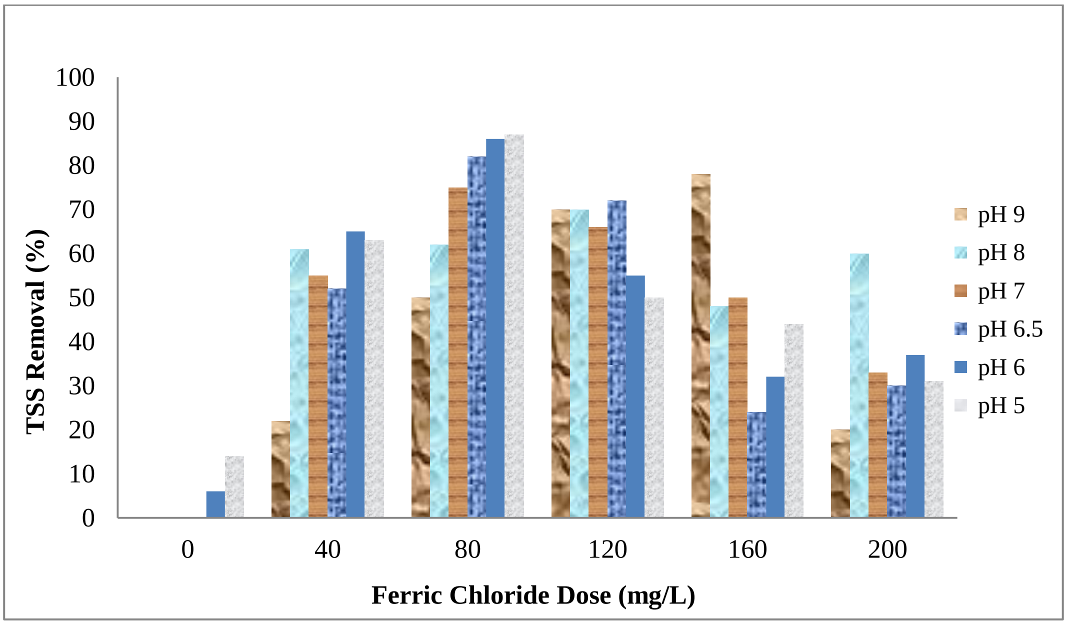

Figure 4-12: TSS removal with Ferric chloride

As shown in the Figure 4-12, the maximum TSS removal 87% was observed by Ferric chloride. This removal was obtained at pH 5 with dose rate 80 mg/l.

Therefore, the experiments were again performed with dose rate 60mg/l and 100mg/l to maintain the doses values around the 80mg/l. The values of TSS removal against the dose 80 mg/l and 120 mg/l of previous experiment were used in Figure 4-13. As shown in the Figure 4-13, better TSS removal was obtained with dose 80mg/l.

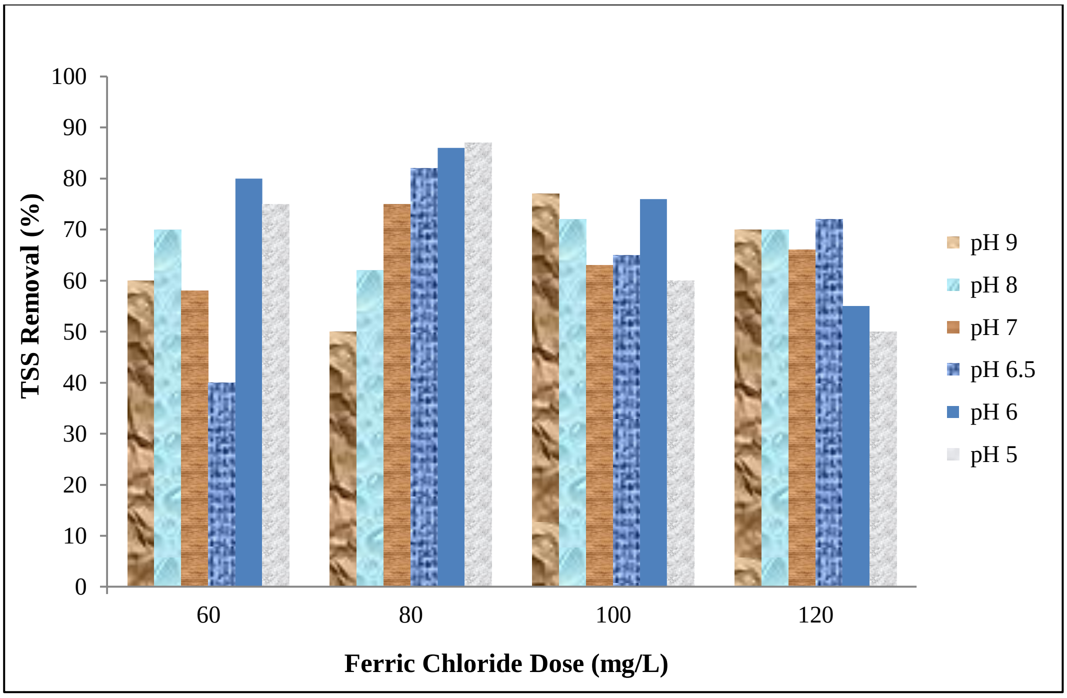

Figure 4-13: Evaluation of optimum dose of Ferric chloride for TSS removal

Approximately same type of trends was observed at all pH values. Ferric chloride gave better removal at low pH values (pH 4 – pH 6) as compare to higher pH levels. This indicates that adsorption and charge neutralization is dominating the coagulation process and colloidal restabilization takes over at higher pH.

Sand Filtration

After coagulation/flocculation process, the supernatant was passed through a new filtration column. COD and TSS tests were performed to investigate the impact of filtration on COD removal and TSS removal. It was observed that filtration process did not participate in COD removal. However, TSS removal was recorded in some of those samples which had comparatively higher TSS value. Figure 4-14 represents the overall TSS removal, achieved from coagulation/flocculation by using Ferric chloride as coagulant and filtration process.

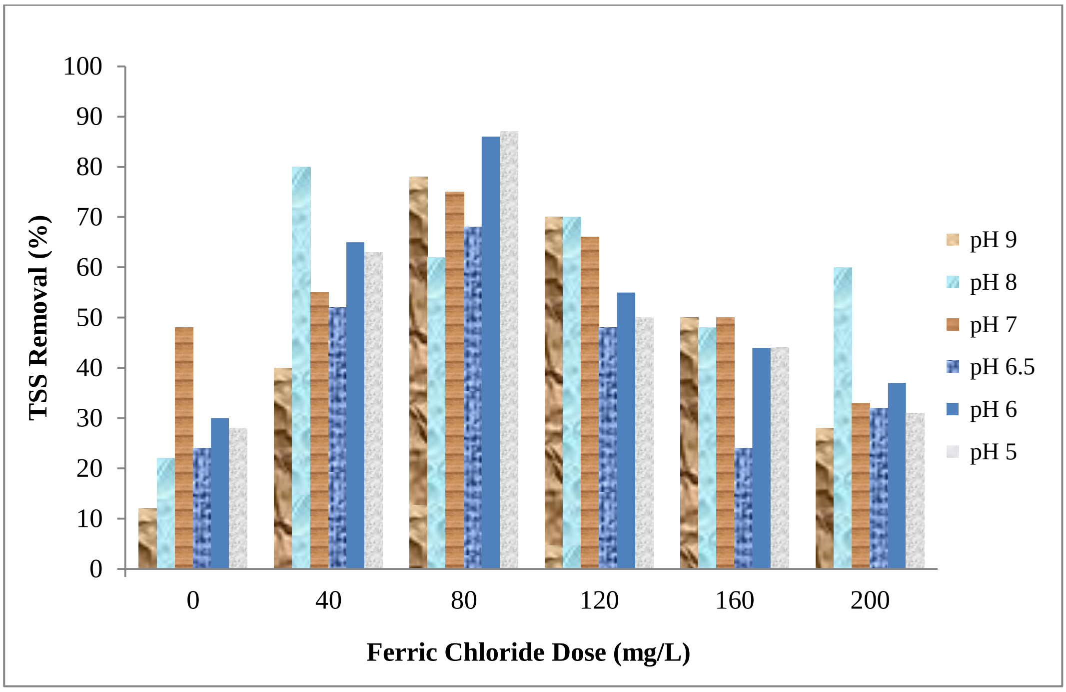

Figure 4-14: TSS removal with Ferric chloride and filtration

Turbidity (NTU)

After coagulation/flocculation process, turbidity of supernatant of samples was checked to evaluate the impact of processes on turbidity removal. The measurement of turbidity is a good parameter to investigate the performance of coagulant. Maximum 96% turbidity removal was recorded. As shown in the Figure 4-15, which illustrates that Ferric chloride gives better results at pH 5, 6&7. This clearly shows that turbidity removal by ferric chloride is more effective in acidic condition.

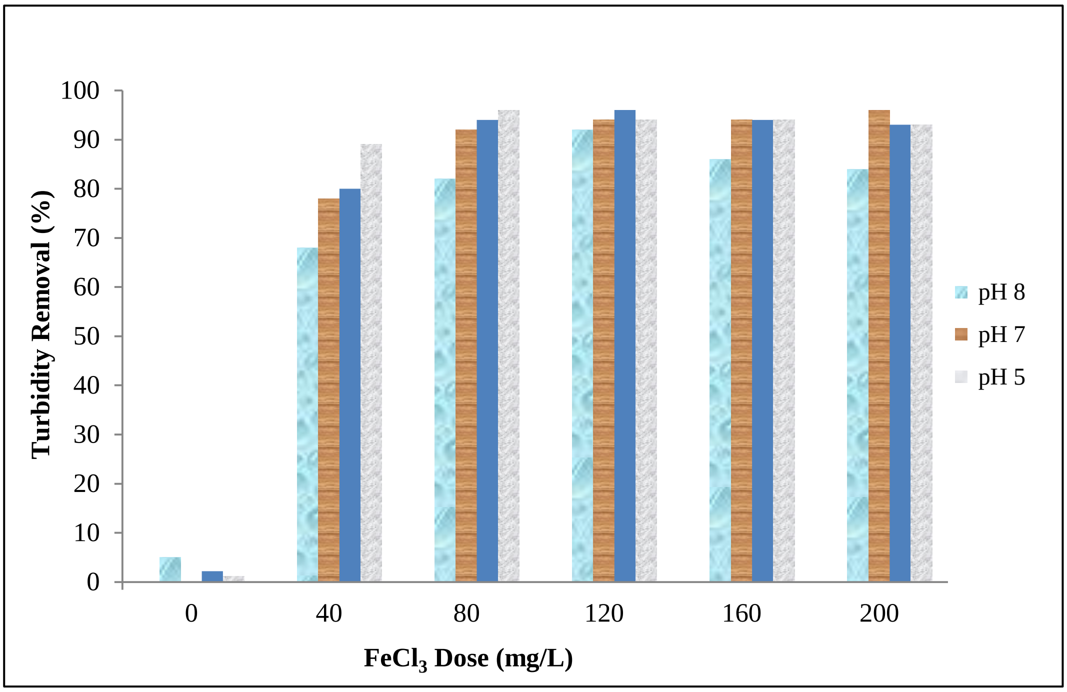

Figure 4-15: Turbidity removal with Ferric chloride

4.3 TITANIUM TETRACHLORIDE AS EMERGING COAGULANT

Chemical Oxygen Demand (COD)

The performance of Titanium tetrachloride was investigated in term of COD removal with different doses ranging from 0 to 200 mg/l at different pH values (5, 6, 6.5, 7, 8 and 9), firstly an interval of 40 mg/l was chosen.

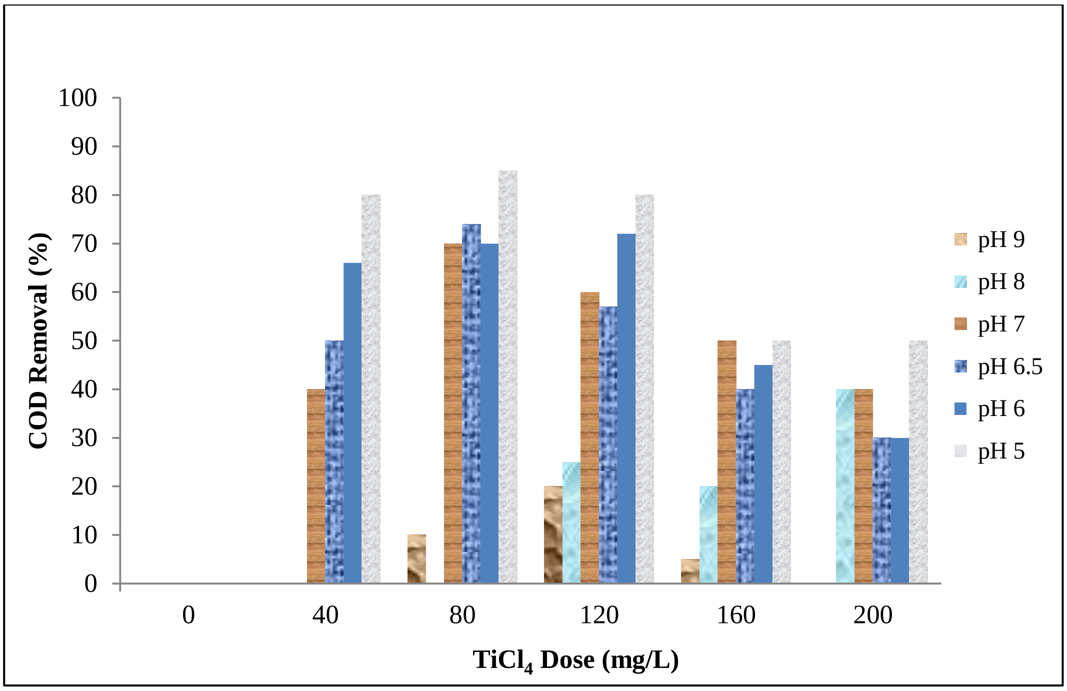

Figure 4-16: Removal of COD by using Titanium tetrachloride as a coagulant

The results are shown in the Figure 4-16. Better results were achieved with dosage 80mg/l. The experiments were again performed with doses 60mg/l and 100 mg/l to create a trend with small intervals (40 mg/l, 60 mg/l, 80 mg/l, 100 mg/l and 120 mg/l). The experiments were again performed only at pH 5, 6, 6.5 and 7 because only at these pH values better results of COD removal were achieved.

Figure 4-17 is representing the results of COD removal. The maximum 85% removal is found with dose 60 mg/l at pH 5 and negligible removal is found at pH 8 and pH 9 even at high dose of coagulant.

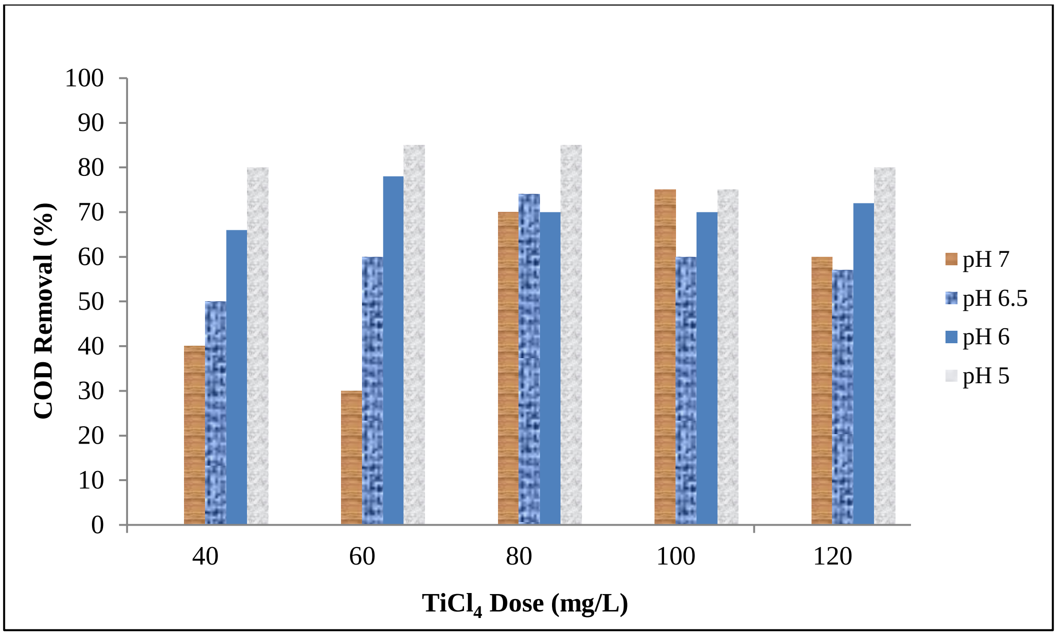

Figure 4-17: Evaluation of optimum dose of Titanium tetrachloride for COD removal

Biochemical Oxygen Demand (BOD_5)

Figure 4-18 is representing the BOD removal by using Titanium tetrachloride as a coagulant.

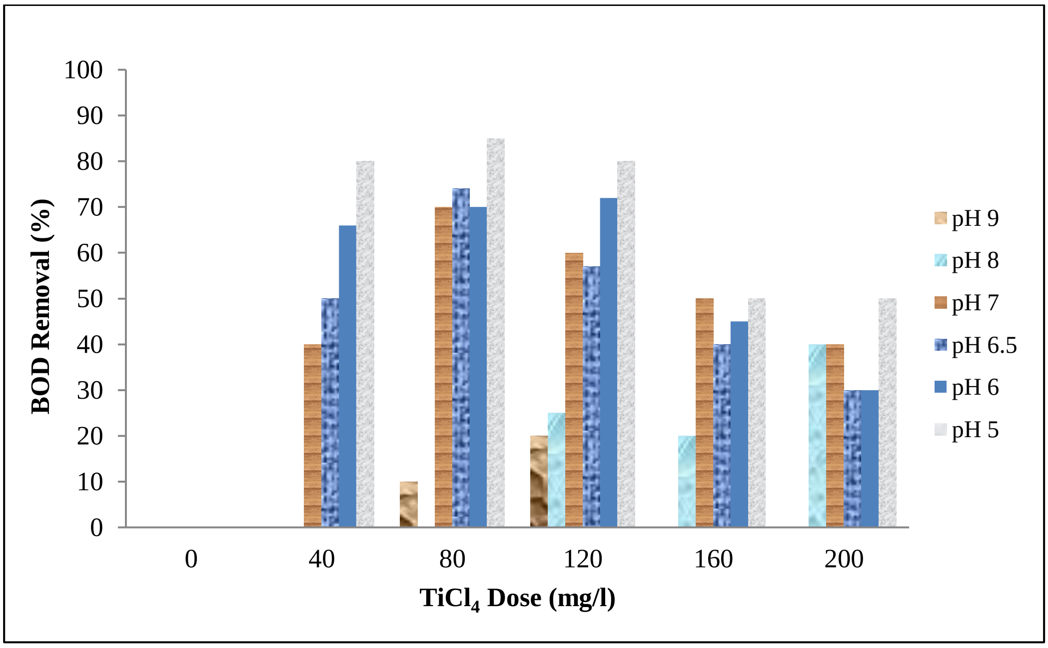

Figure 4-18: BOD removal with Titanium tetrachloride

BOD removal was found by using the same factor (0.6372) of COD and BOD relation. Better BOD removal results were achieved at pH 5 and pH 6 at low dose rate of Titanium tetrachloride. Insignificant removal is found at pH 8 and pH 9 even at high dose of coagulant

Total Suspended Solids (TSS)

The performance of Titanium tetrachloride was also investigated in term of TSS removal from wastewater. Figure 4-19 is representing the percent removal of TSS. It is clearly shown, that Titanium tetrachloride gives better results at approximately at all pH levels with fewer doses. These results indicate that charge neutralization is the main phenomena in $TiCl_4$ flocculation. Positive charge became more dominant due to further increase in coagulant dosage which creates the repulsion (electrostatic) between the particles (Sharp *et al*., 2006).

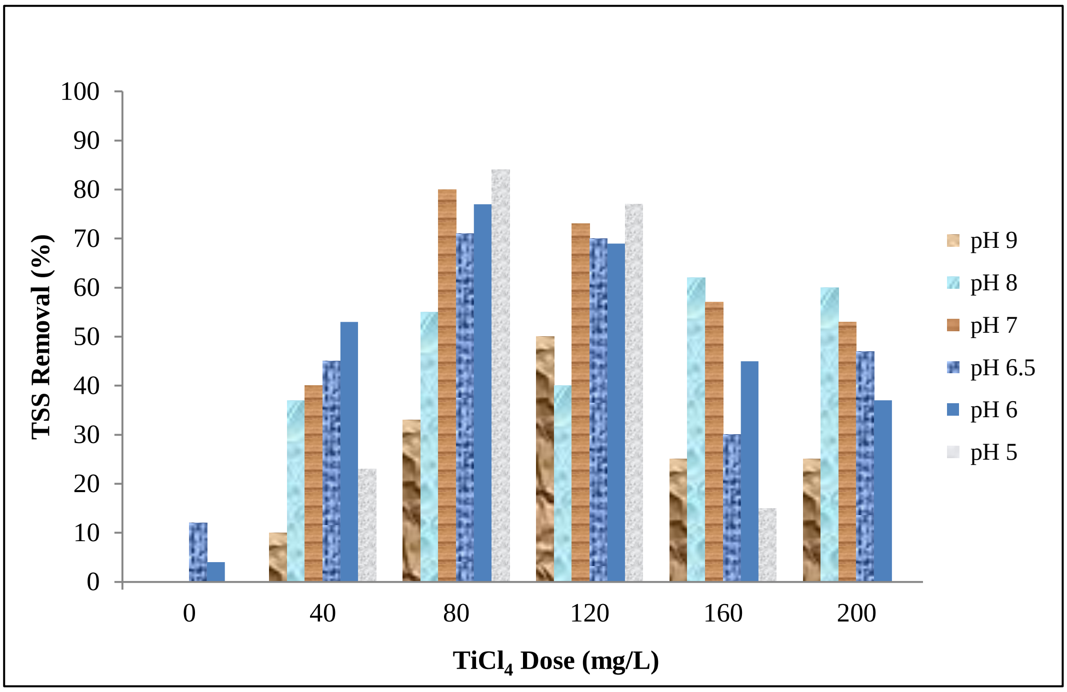

Figure 4-19: TSS removal with Titanium tetrachloride

Therefore, second time, the experiments were performed with small intervals to find the optimum dose for each pH. Figure 4-20 is representing the results of percentage removal in TSS. The maximum 84% TSS removal was found with dose 80 mg/l at pH 5 and relatively less removal was achieved at pH 8 and pH 9.

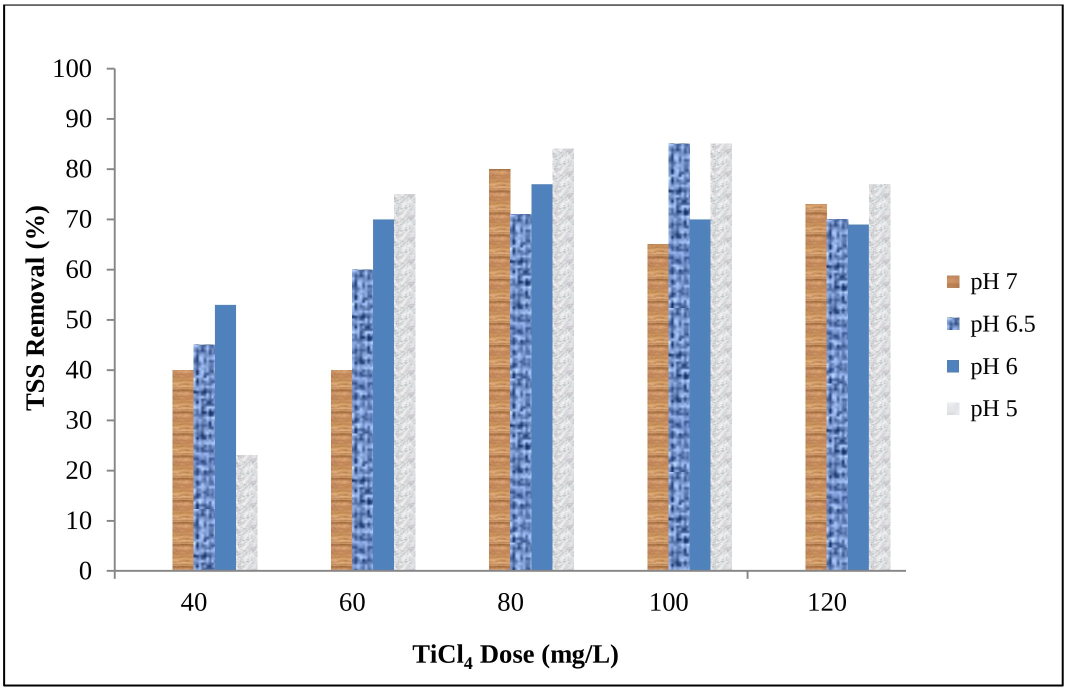

Figure 4-20: Evaluation of optimum dose of Titanium tetrachloride for TSS removal

Sand Filtration

After coagulation/flocculation process, the supernatant was passed through a new filtration column. COD and TSS tests were performed to investigate the impact of filtration on COD removal and TSS removal. It was observed that filtration process did not participate in COD removal. However, TSS removal was recorded in some of those samples which had comparatively higher TSS value Figure 4-21 represents the overall TSS removal, achieved from coagulation/flocculation and filtration processes.

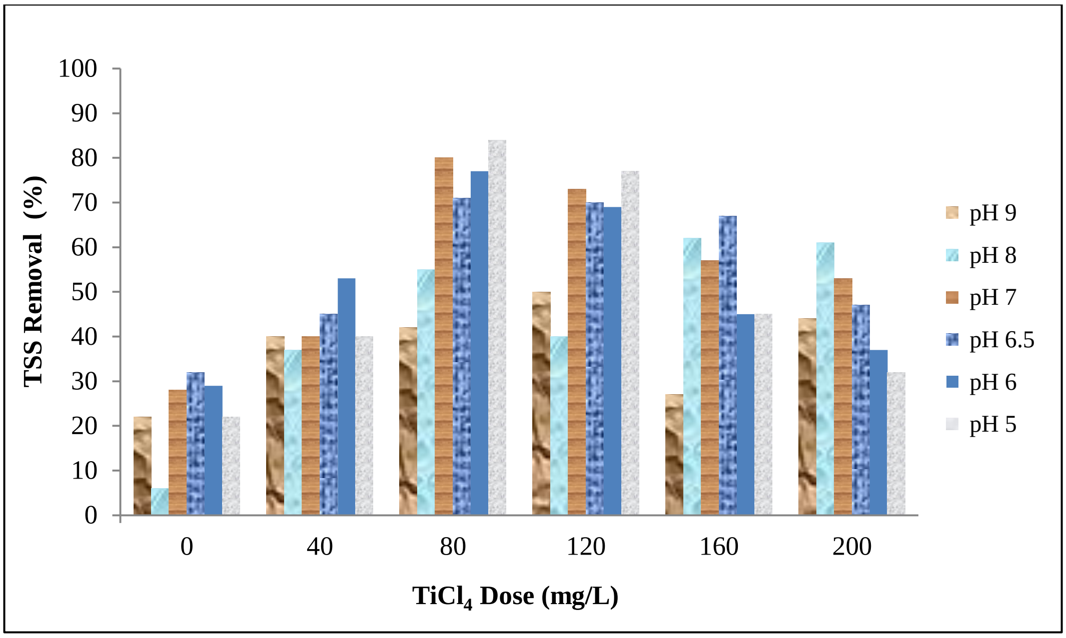

Figure 4-21: TSS removal with Titanium tetrachloride and filtration

Turbidity (NTU)

As shown in Figure 4-22,Titanium tetrachloride gives good results in turbidity removal at all pH levelsandupto97.5% removal was recorded even at pH 8.It was observed that the turbidity removal by all coagulants is effective in acidic condition.

At pH value greater than 7, titanium tetrachloride showed better removal in turbidity as compare to alum and ferric chloride. Titanium tetrachloride showed high and stable removal in turbidity at higher pH values because this coagulant is gradually hydrolyzed as compare to other two coagulants (Zhao *et al.*, 2010). The figure illustrates that the turbidity removal with Titanium tetrachloride is in the range of (90-97%) which indicates that this coagulant is most effective than Ferric chloride and Alum in turbidity removal.

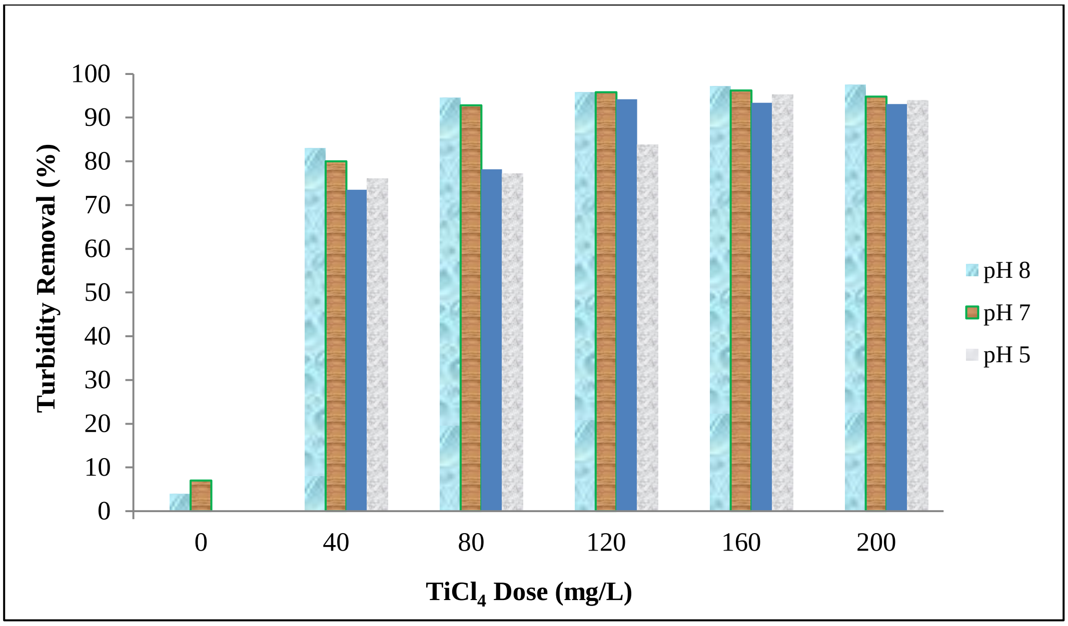

Figure 4-22: Turbidity removal with Titanium tetrachloride as coagulant

4.4 COST COMPARISON

A general cost comparison (irrespective of pH values) among three coagulants is represented in Figure 4-23 which is explained by considering a wastewater treatment plant of capacity 50,000 gallons per day. Then per day consumption of coagulants for wastewater treatment with respect to results achieved during studies is as follows:

- Alum = 53kg/day (280mg/L), 280mg/L is the dose rate at which better removal results are found during experiments.
- $FeCl_3$ = 15kg/day (80mg/L), 80mg/L is the dose rate at which better removal results are found during experiments.
- $TiCl_4$ = 12kg/day (60mg/L), 60mg/L is the dose rate at which better removal results are found during experiments.

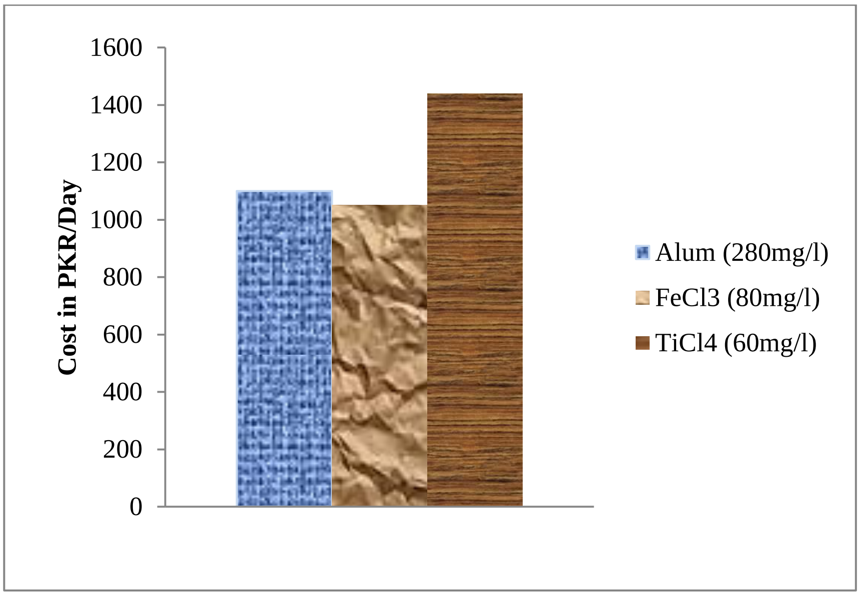

Figure 4-23: Cost comparison between Alum, Ferric chloride and Titanium tetrachloride

Comparison w.r.t. COD Removal

Figure 4-24 is representing the effectiveness comparison between three coagulants in term of COD removal. This graph shows the maximum removal by each coagulant at each pH value irrespective of dose rate.

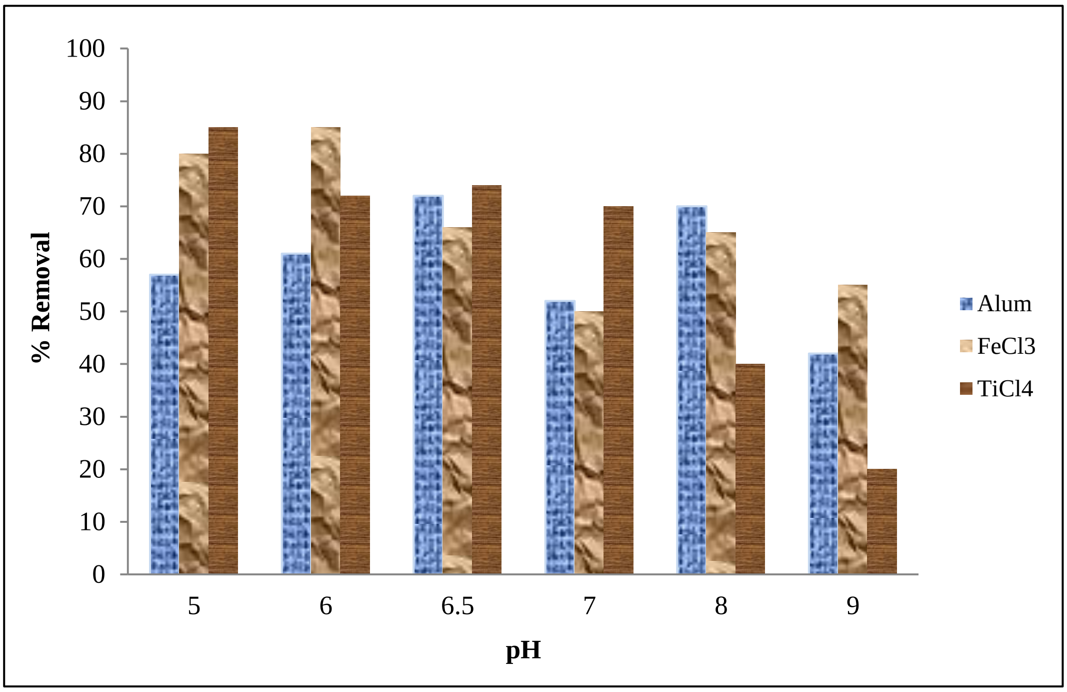

Figure 4-24: Comparison of COD removal by Alum, $FeCl_3$ and $TiCl_4$

Cost Comparison for COD Removal

The Figure 4-25 shows the cost comparison of each coagulant to achieve the COD percent removal which is indicated in the Figure 4-24 for the treatment of 50000 Gallons per day. This graph used the data of dose rate of each coagulant used to attain the COD removal which is indicated above figure.

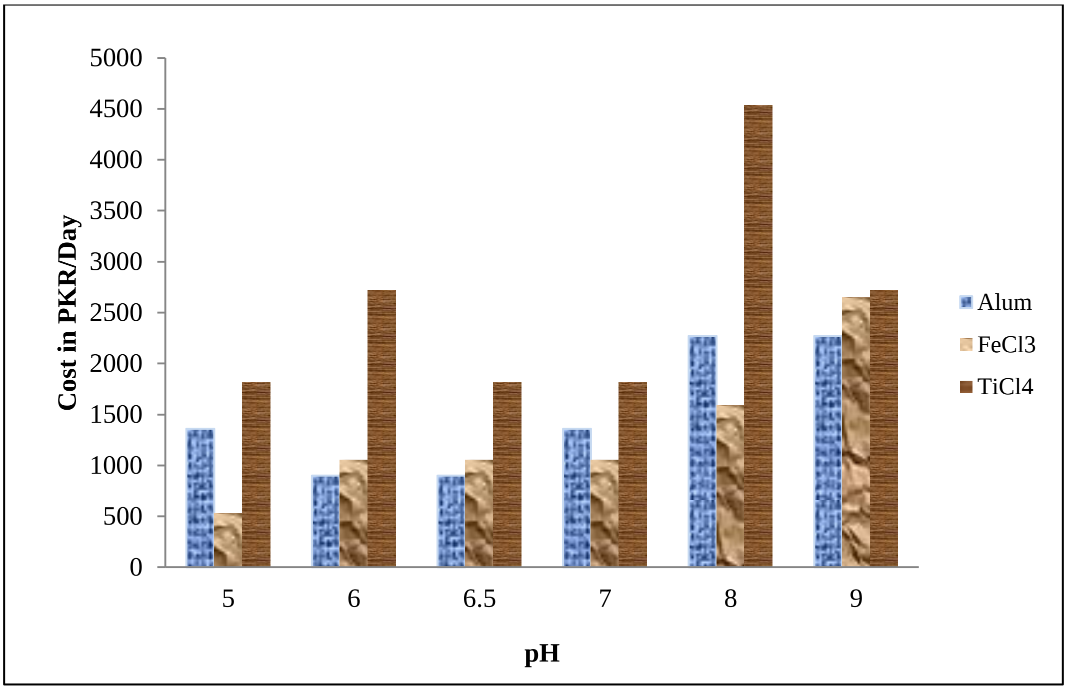

Figure 4-25: Cost comparison between Alum, $FeCl_3$ and $TiCl_4$

Comparison w.r.t. TSS Removal

Figure 4-26 is representing the comparison between coagulants in term of TSS removal.

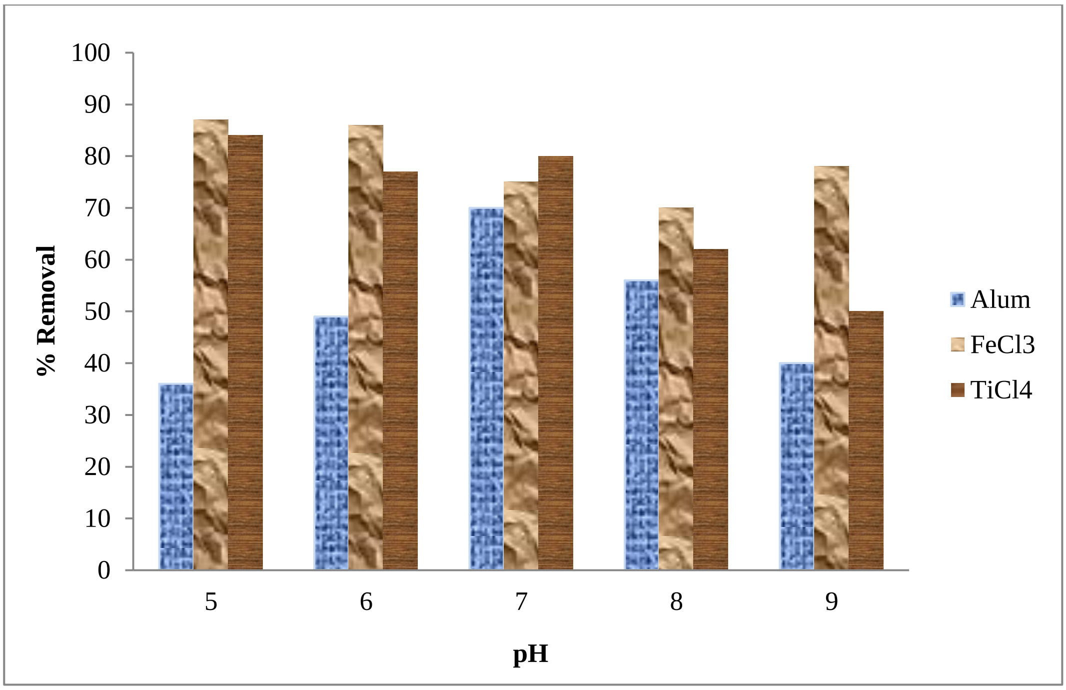

Figure 4-26: Comparison of TSS removal by Alum, $FeCl_3$ and $TiCl_4$

Cost Comparison for TSS Removal

The Figure 4-27 shows the expense comparison of each coagulant to attain the TSS removal which is indicated in the above figure for the treatment of 50000 Gallons per day. This graph used the data of doses of each coagulant used to attain the TSS removal which is indicated in above figure.

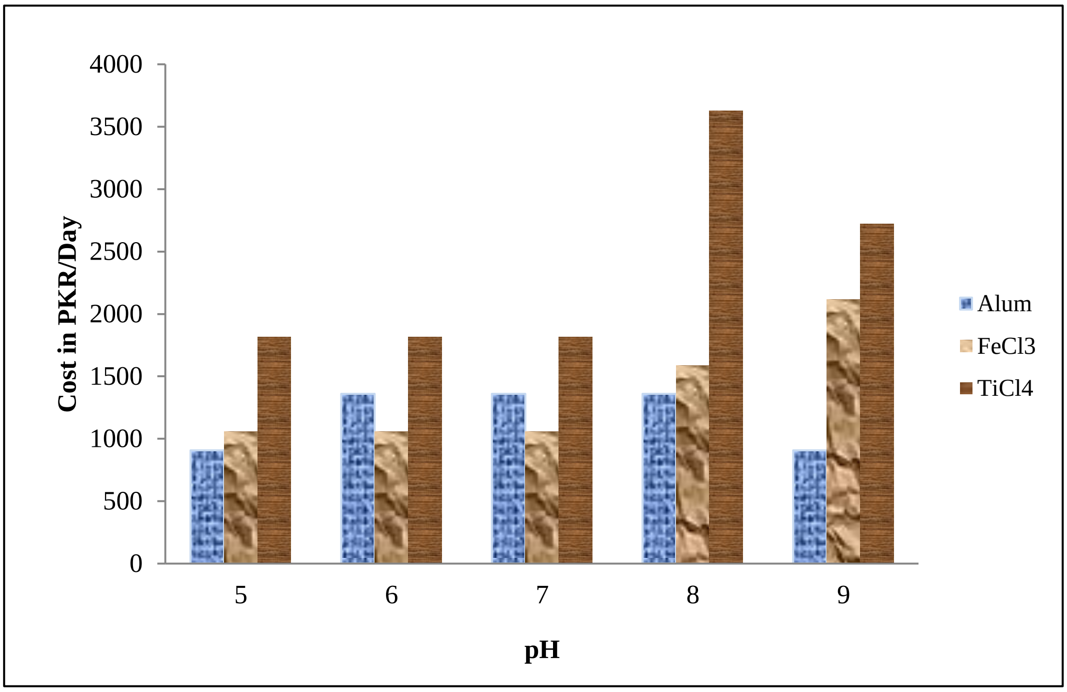

Figure 4-27: Cost Comparison between Alum, $FeCl_3$ and $TiCl_4$

Chapter 5

CONCLUSIONS AND RECOMMENDATIONS

This study was focused on treatment of wastewater by using physico-chemical process. In this study the performance of Aluminum sulfate, Ferric chloride and especially the performance of emerging coagulant “Titanium tetrachloride” were evaluated.

5.1 CONCLUSIONS

Following conclusions are drawn from this study:

The physico-chemical process is sufficient to treat wastewater and no further wastewater treatment is required to satisfy NEQS standards. Coagulation/flocculation is a useful process for the wastewater treatment.

The performance of Titanium tetrachloride is satisfactory for wastewater treatment. Titanium tetrachloride can be confidently used for wastewater at low pH values. This coagulant can be used to obtain upto 85% COD, BOD and TSS removal from wastewater. After obtaining very good results in TSS removal, it can be confidently said, that this coagulant is very suitable for water treatment and wastewater treatment. Table: 5-1 represents the comparison of aforementioned three coagulants performance on the basis of COD, BOD_5, TSS and turbidity removal.

Table 5-1: Coagulants comparison on the basis of COD, BOD_5, TSS & Turbidity removal

Parameters	**Aluminum Sulfate**			**Ferric Chloride**			**Titanium Tetrachloride**		
	Max. % Removal	Optimum Dose (mg/L)	Optimum pH	Max. % Removal	Optimum Dose (mg/L)	Optimum pH	Max. % Removal	Optimum Dose (mg/L)	Optimum pH
COD	77	280	6.5	85	80	6.0	86	60	5.0
BOD_5	72	240	6.5	85	80	6.0	85	80	5.0
TSS	85	360	6.5	87	80	5.0	84	80	5.0
Turbidity	96	360	6.0	96	80	5.0	97	160	8.0

As observed in this study, the required dosage of Titanium tetrachloride is less as compared to other traditional chemicals therefore the cost factor of Titanium tetrachloride is not very significant.

Adin *et al.* (1998) used secondary sewage effluent from activated sludge plant to investigate the flocculation of Ferric chloride. They indicated that turbidity removal of 86% for Ferric chloride occurred at pH 4-5. On the other hand, Musikavong *et al.*, (2005) found the turbidity removal of Ferric chloride at uncontrolled pH was approximately 85% for treated industrial wastewater. Our results are in good agreement with the previous. The turbidity removal for Ferric chloride was mostly in the range of (92-96%).

Mesdaghinia *et al.,* (2006) reported in his study, that the optimum turbidity doses for Ferric chloride and Titanium tetrachloride were always less than Aluminum sulfate, this is due to the fact that Ferric chloride presents more active positive charges than hydrated Aluminum sulfate.

(Zhao *et al.*, 2010) reported that the organic removal efficiency between these coagulants varied in following order: $FeCl_3 > TiCl_4 > Al_2(SO_4)_3$.Our results were approximately of the same order as that of the previous studies.

5.2 RECOMMENDATIONS

Following recommendations are noteworthy for further study.

- The performance of Titanium tetrachloride may be verified for synthetic wastewater, to evaluate the exact optimum dose for each pH.
- The performance of Titanium tetrachloride may be investigated by using Titanium tetrachloride as a coagulant aid with other chemical coagulants.
- The performance of Titanium tetrachloride may be verified for water treatment.

REFERENCES

Adin, A., Y. Soffer and A. R. Ben, (1998).Effluent pretreatment by iron coagulation applying various dose-pH combinations for optimum particle separation.Water Science and Technology, 38(6): 27-34.

Al-Anzi, B., (2012).Assessment of wastewater reuse in Kuwait and its impact on amounts of pollutants discharged into the Sea. Scientific Research: Earth & Environmental Sciences, 3 (8A).

Aziz, H. A., S. Alias, M. N. Adlan, Faridah, Asaari and A. H. Zahari, (2007). Colour removal from landfill leachate by coagulation and flocculation processes, Bioresource technology, 98(1): 218-220.

Beddow V., F. Sun, (2010). Coagulation and flocculation in water and wastewater treatment. http://www.iwawaterwiki.org/xwiki/bin/view/Articles

Chekli, L.,J. Galloux, Y.X. Zhao, B.Y. Gao, H.K. Shon., (2015).Coagulation performance and floc characteristics of polytitanium tetrachloride (PTC) compared with titanium tetrachloride ($TiCl_4$) and iron salts in humic acid–kaolin synthetic water treatment. Separation and Purification Technology. Volume 142: Pages 155–161

Chun-Yang Yin, (2010). Emerging usage of plant-based coagulants for water and wastewater treatment, Process Biochemistry 45 (2010): 1437–1444

Corbitt, R. A., H. B. Crawford and D. Gleason, (1989). Stand Handbook of Environment Engineering, McGraw Hill, New York.

DeWolfe, J., B. Dempsey, M. Taylor and J. W. Potter, (2003).Guidance manual for coagulant changeover. American Water Works Association Press.

Duan. J. M., J. Gregory, Coagulation by hydrolyzing metal salts, Adv. Colloid Interface Sci. 100-102 (2003): 475-502.

Fane, A.G., C. J. D. Fell and M. T.Nor, (1978). Wastewater treatment using a combined activated sludge and ultrafiltration system. Proceedings of Asian Pacific Confederation of Chemical Engineering (APCCHE), Jakarta, 117–129.

Gao, B.Y., H. H. Hahn, E. Hoffmann, (2002). Evaluation of aluminum-silicate polymer composite as a coagulant for water treatment.Journal of Elsevier: 36 (14): 3573–3581.

Hans, G. V.(2006). “Pigments, Inorganic” in Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, 2006

Hussain, S., J. V. Leeuwen, C.W.K. Chow, R. Aryal, S. Beecham, J. Duan, M. Drikas, (2014). Comparison of the coagulation performance of tetravalent titanium and zirconium salts with alum. Chemical Engineering Journal. Volume 254: Pages 635–646

Jiang, J. and B. Lloyd, (2002). Progress in the development and use of ferrate(VI) salt as an oxidant and coagulant for water and wastewater treatment. Water Research, 36 (6): 1397–1408.

Jiang, J., S. Wang, A. Panagoulopoulos, (2006). The exploration of potassium ferrate(VI) as a disinfectant/coagulant in water and wastewater treatment. Chemosphere, 63 (2): 212–219.

Kaneko, M. and I. Okura, (2002). Photocatalysis: Science and Technology, Springer, Tokyo.

Lee, B.C., S. Kim, H.K. Shon, S. Vigneswaran, (2009).Aquatic toxicity evaluation of TiO_2 nanoparticle produced from sludge of $TiCl_4$ flocculation of wastewater and seawater. Journal of Nanoparticle Research., 11 (8): 2087-2096.

Lokshin, E.P. and M.L. Belikov, (2003). Russ. J. Appl. Chem., 76, 466.

Mesdaghinia A., M. T.Rafiee, F.Vaezi, A. Mahvi., A. Torabian and A. Ghasri(2006).Control of disinfection by products formation potential by enhanced coagulation. International Journal of Environmental Science and Technology, 2(4), 335-342

Nazaroff& Alvarez-Cohen (2001), Section 6.E – slightly augmented Biological Wastewater Treatment.

O’Melia C. R., W. C. Becker and Au K. - K. (1999).Removal of humic substances by coagulation. Water Science and Technology. 40(9): 47-54

Okour, Y., H.K. Shon and I. El Saliby, (2009). Characterization of titanium tetrachloride and titanium sulfate flocculation in wastewater treatment. Journal of Water Science & Technology. 59 (12): 2463.

Qadir, M., D. Wichelns, L. Raschid-sally, P.G. McCornick, P. Drechsel, A. Bahri, P.S. Minhas, (2008). The challenges of wastewater irrigation in developing countries. Journal of Agriculture Water Management, vol. 97, p561-568.

Rousseau D., T. Hooijmans, (2011).Membrane bioreactors (MBRs) for wastewater treatment, UNESCO-IHE, Institute for Water Education.

SaadatAli, (2012). Development of membrane based septic tank in treating domestic waste water. IESE, NUST.

Šciban, M., M. Klašnja, M. Antov, Biljanaškrbic, (2009). Removal of water turbidity by natural coagulants obtained from chestnut and acorn. Bioresource Technology, 100 (2009): 6639-6643.

Sharp, E. I., S. A. Parson, B. Jefferson, Coagulation of NOM: linking character to treatment, Water Sci. Technol. 53 (7) (2006): 67-76.

Shon, H.K., S. Vigneswaran, Ins. Kim, J. Cho G.J. Kim, J.B. Kim and J.H. Kim, (2007).Preparation of titanium dioxide (TiO_2) from sludge produced by titanium tetrachloride ($TiCl_4$) flocculation of wastewater. Environmental Science & Technology., 41 (4): 1372-1377.

Shon, H.K., S. Vigneswaran, J. Kandasamy, J.-B.Kim, H.J. Park, S.W. Choi and J.-H.Kim, (2009).Preparation of titanium oxide, iron oxide, and aluminium oxide from sludge generated from Ti-salt, Fe-salt and Al-salt flocculation of wastewater. Journal of Elsevier.

Shon, H.K., S. Vigneswaran, J. Kandasamy, M.H. Zareie, J.B. Kim, D.L. Cho and J.-H. Kim, (2009). Preparation and characterization of titanium dioxide (TiO_2) from sludge produced by $TiCl_4$ flocculation with $FeCl_3$, $Al_2(SO_4)_3$and $Ca(OH)_2$coagulant aids in wastewater. Separation Science and Technology, 44 (7).

Shon, H.K., Y. Okour, Ibrahim el Saliby, J.B. Kim and J.-H.Kim, (2007). Preparation and characterisation of titanium dioxide (TiO_2) produced from Ti-salt flocculated sludge in water treatment. The Journal of the Korean Chemical Society.

Sun, Y., G. Zhou, X. Xiong, X. Guan, L. Li, H. Bao, (2013). Enhanced arsenite removal from water by $Ti(SO_4)_2$ coagulation. Water Research, 47 (2013): 4340-4348.

Tan, B. H., T. T. Teng, A. K. M. Omar, (2000). Removal of dyes and industrial dye wastes by magnesium chloride.Water Research, 34 (2): 597–601.

Vigneswaran, S., M. Sundaravadivel, (2004). Wastewater recycle, reuse, and reclamation - recycle and reuse of domestic wastewater.

Vijayaraghavan, G., T. Sivakumar, A. V. Kumar, (2011). Application of plant based coagulants for waste water treatment. International Journal of Advanced Engineering Research and Studies.

Visvanathan, C., R. B. Aim, and K. Parameshwaran, (2010).Membrane bioreactor applications in wastewater treatment. Taylor & Francis: Critical Reviews in Environmental Science and Technology, 30(1):1–48.

Yi-fan, Wu, Wen Liu, Nai-yunGao, Tao Tao, (2011).A study of titanium sulfate flocculation for water treatment. Water Research 45 (2011): 3704-3711.

Yukselen,M.A and J. Gregory, (2002).Breakage and re-formation of alum flocs. Environ. Eng. Sci. 19(4): 229-236.

Zhao, Y.X., B.Y. Gao,G.Z. Zhang, Q.B. Qi, Y. Wang, S. Phuntsho, J.-H. Kim, H.K. Shon, Q.Y. Yue, Q. Li, (2014). Coagulation and sludge recovery using titanium tetrachloride as coagulant for real water treatment: A comparison against traditional aluminum and iron salts. Separation and Purification Technology. Volume 130: Pages 19–27

Zhao, Y.X., B.Y. Gao, B.C. Cao, Z.L. Yang, Q.Y. Yue, H. K. Shon, J.H. Kim, (2010). Comparison of coagulation behavior and floc characteristics of titanium tetrachloride ($TiCl_4$) and polyaluminum chloride (PaCl) with surface water treatment. Chemical Engineering Journal 166 (2011): 544-550.

Zhao, Y.X., B.Y. Gao, H.K. Shon, B.C. Cao, J.-H. Kim, (2010).Coagulation characteristics of titanium (Ti) salt coagulant compared with Aluminum (Al) and iron (Fe) salts. Journal of Hazardous Materials. 185(11): 1536-1542.

Zhao, Y.X., B.Y. Gao, H.K. Shon, J.H. Kim, Q.Y. Yue, (2011). Effect of shear force, solution pH and breakage period on characteristics of flocs formed by titanium tetrachloride ($TiCl_4$) and polyaluminum chloride with surface water treatment. Journal of Hazardous Materials, 187(2011): 495-501.

Zhao, Y.X., B.Y. Gao, H.K. Shon, J.-H. Kim, Q.Y. Yue, Y. Wang, (2011). Floc characteristics of titanium tetrachloride ($TiCl_4$) compared with aluminum and iron salts in humic acid–kaolin synthetic water treatment. Separation and Purification Technology, 81 (2011), 332-338.

Anonymous (N.D).Coagulants. http://www.dgrsol.com

ANNEXURE A

PERFORMANCE PARAMETERS

Coagulant: $Al_2(SO_4)_3.18H_2O$

i. pH: 5

Dose (mg/L)	TSS (mg/L)	TSS Removal (%)	COD (mg/L)	COD Removal (%)	Turbidity (NTU)	Turbidity Removal (%)
Sample	***168***		***120***		**88**	
0	147	12%	120	0%	84.5	4%
120	116	31%	87	28%	22	75%
240	107	36%	87	28%	9.7	89%
360	145	14%	52	57%	8.96	90%
480	138	18%	52	57%	7.9	91%
600	168	0%	52	57%	7.92	91%

ii. pH: 6

Dose (mg/L)	TSS (mg/L)	TSS Removal (%)	COD (mg/L)	COD Removal (%)	Turbidity (NTU)	Turbidity Removal (%)
Sample	***129***		***90***		**79**	
0	129	0%	90	0%	78.5	0.6%
120	94	27%	58	35%	11	86%
240	105	19%	35	61%	6.2	92.2%
360	66	49%	35	61%	3	96.2%
480	84	35%	38	57%	4.9	93.8%
600	129	0%	48	47%	3.95	92%

iii. pH: 6.5

Dose (mg/L)	TSS (mg/L)	TSS Removal (%)	COD (mg/L)	COD Removal (%)	Turbidity (NTU)	Turbidity Removal (%)
Sample	***116***		***105***			
0	116	0%	105	0%	-	-
120	77	34%	47	55%	-	-
240	65	44%	30	72%	-	-
360	17.4	85%	47	55%	-	-
480	60	48%	55	47%	-	-
600	116	0%	66	37%	-	-

iv. pH: 7

Dose (mg/L)	**TSS (mg/L)**	**TSS Removal (%)**	**COD (mg/L)**	**COD Removal (%)**	**Turbidity (NTU)**	**Turbidity Removal (%)**
Sample	***105***		***108***		**69**	
0	104	6%	108	0%	67.6	2%
120	81	26%	93	14%	15.8	77%
240	105	5%	62	43%	4.4	93.6%
360	31.4	70%	52	52%	4.14	94%
480	35	68%	73	33%	2.75	96%
600	58	47%	83	23%	3.6	94.8%

v. pH: 8

Dose (mg/L)	**TSS (mg/L)**	**TSS Removal (%)**	**COD (mg/L)**	**COD Removal (%)**	**Turbidity (NTU)**	**Turbidity Removal (%)**
Sample	***131***		***93***		**72**	
0	131	0%	93	0%	72	0%
120	66	50%	58	37%	23	68%
240	66	50%	33	65%	20	72%
360	58	56%	31	67%	15.8	78%
480	76	42%	40	57%	8.6	88%
600	58	56%	28	70%	11.5	84%

vi. pH: 9

Dose (mg/L)	**TSS (mg/L)**	**TSS Removal (%)**	**COD (mg/L)**	**COD Removal (%)**	**Turbidity (NTU)**	**Turbidity Removal (%)**
Sample	***97***		***93***			
0	97	0%	93	0%	-	-
120	78	20%	93	0%	-	-
240	58	40%	93	0%	-	-
360	87	10%	62	33%	-	-
480	68	30%	65	30%	-	-
600	87	10%	54	42%	-	-

Coagulant: $FeCl_3$

i. pH: 5

Dose (mg/L)	TSS (mg/L)	TSS Removal (%)	COD (mg/L)	COD Removal (%)	Turbidity (NTU)	Turbidity Removal (%)
Sample	***121***		***127***		**80**	
0	104	14%	127	0%	79	1.2%
40	45	63%	25	80%	8.8	89%
80	16	87%	25	80%	2.6	96%
120	60	50%	52	59%	4.8	94%
160	68	44%	89	30%	4.8	94%
200	84	31%	89	30%	5.6	93%

ii. pH: 6

Dose (mg/L)	TSS (mg/L)	TSS Removal (%)	COD (mg/L)	COD Removal (%)	Turbidity (NTU)	Turbidity Removal (%)
Sample	***132***		***120***		**96**	
0	122	7%	120	0%	93.8	2.2%
40	46	65%	20	83%	19.2	80%
80	19	86%	18	85%	5.7	94%
120	60	55%	18	85%	3.8	96%
160	94	29%	50	58%	5.7	94%
200	83	37%	18	85%	6.7	93%

iii. pH: 6.5

Dose (mg/L)	TSS (mg/L)	TSS Removal (%)	COD (mg/L)	COD Removal (%)	Turbidity (NTU)	Turbidity Removal (%)
Sample	***124***		***98***			
0	124	0%	98	0%	-	-
40	60	52%	35	64%	-	-
80	22	82%	33	66%	-	-
120	34	72%	49	50%	-	-
160	112	10%	33	66%	-	-
200	87	30%	49	50%	-	-

iv. **pH: 7**

Dose (mg/L)	**TSS (mg/L)**	**TSS Removal (%)**	**COD (mg/L)**	**COD Removal (%)**	**Turbidity (NTU)**	**Turbidity Removal (%)**
Sample	***172***		***112***		**106**	
0	172	0%	112	0%	106	0%
40	78	55%	75	33%	23.3	78%
80	43	75%	56	50%	8.4	92%
120	59	66%	75	33%	6.3	94%
160	172	0%	56	50%	6.3	94%
200	115	33%	56	50%	4.2	96%

v. **pH: 8**

Dose (mg/L)	**TSS (mg/L)**	**TSS Removal (%)**	**COD (mg/L)**	**COD Removal (%)**	**Turbidity (NTU)**	**Turbidity Removal (%)**
Sample	***156***		***102***		**87**	
0	156	0%	102	0%	82.6	5%
40	59	61%	58	43%	27.8	68%
80	59	62%	43	58%	15.6	82%
120	47	70%	36	65%	7	92%
160	91	42%	43	58%	12.1	86%
200	62	60%	43	58%	13.9	84%

vi. **pH: 9**

Dose (mg/L)	**TSS (mg/L)**	**TSS Removal (%)**	**COD (mg/L)**	**COD Removal (%)**	**Turbidity (NTU)**	**Turbidity Removal (%)**
Sample	***98***		***96***			
0	98	0%	96	0%	-	-
40	77	22%	96	0%	-	-
80	49	50%	67	30%	-	-
120	30	70%	72	25%	-	-
160	22	78%	77	20%	-	-
200	79	20%	43	55%	-	-

Coagulant: $TiCl_4$

i. **pH: 5**

Dose (mg/L)	TSS (mg/L)	TSS Removal (%)	COD (mg/L)	COD Removal (%)	Turbidity (NTU)	Turbidity Removal (%)
Sample	**141**		***112***		**70**	
0	141	0%	112	0%	70	0%
40	108	23%	22	80%	16.8	76%
80	23	84%	17	85%	15.9	77.2%
120	32	77%	22	80%	11.2	83.8%
160	120	15%	56	50%	3.4	95.2%
200	141	0%	56	50%	4.2	94%

ii. **pH: 6**

Dose (mg/L)	TSS (mg/L)	TSS Removal (%)	COD (mg/L)	COD Removal (%)	Turbidity (NTU)	Turbidity Removal (%)
Sample	**110**		***94***		**89**	
0	106	4%	94	0%	89	0%
40	52	53%	32	66%	23.5	73.5%
80	25	77%	28	70%	19.4	78.2%
120	34	69%	26	72%	5.1	94.2%
160	60	45%	52	45%	5.8	93.4%
200	69	37%	66	30%	6.2	93.1%

iii. **pH: 6.5**

Dose (mg/L)	TSS (mg/L)	TSS Removal (%)	COD (mg/L)	COD Removal (%)	Turbidity (NTU)	Turbidity Removal (%)
Sample	**91**		***98***			
0	81	12%	98	0%	-	-
40	50	45%	49	50%	-	-
80	26	71%	25	74%	-	-
120	27	70%	42	57%	-	-
160	64	30%	59	40%	-	-
200	48	47%	69	30%	-	-

iv. pH: 7

Dose (mg/L)	**TSS (mg/L)**	**TSS Removal (%)**	**COD (mg/L)**	**COD Removal (%)**	**Turbidity (NTU)**	**Turbidity Removal (%)**
Sample	**93**		***90***		**78**	
0	93	0%	90	0%	72.5	7%
40	56	40%	54	40%	15.6	80%
80	18	80%	27	70%	5.6	92.8%
120	25	73%	36	60%	3.3	95.8%
160	62	33%	45	50%	2.8	96.2%
200	43	53%	54	40%	4	94.8%

v. pH: 8

Dose (mg/L)	**TSS (mg/L)**	**TSS Removal (%)**	**COD (mg/L)**	**COD Removal (%)**	**Turbidity (NTU)**	**Turbidity Removal (%)**
Sample	**151**		***87***		**71**	
0	151	0%	87	0%	68.1	4%
40	95	37%	87	0%	12	83%
80	68	55%	87	0%	3.9	94.5%
120	91	40%	65	25%	3	95.8%
160	57	62%	70	20%	2	97.2%
200	60	60%	52	40%	1.8	97.5%

vi. pH: 9

Dose (mg/L)	**TSS (mg/L)**	**TSS Removal (%)**	**COD (mg/L)**	**COD Removal (%)**	**Turbidity (NTU)**	**Turbidity Removal (%)**
Sample	***127***		***98***			
0	127	0%	98	0%	-	-
40	114	10%	98	0%	-	-
80	85	33%	88	10%	-	-
120	64	50%	79	20%	-	-
160	95	25%	98	0%	-	-
200	95	25%	98	0%	-	-