Development of polyaluminum chloride-based coagulants from aluminum scrap for the treatment of textile wastewater

A Dissertation Submitted to University of Dhaka for the Partial Fulfillment of the Requirements of the Degree of Doctor of Philosophy in Environmental Science

Submitted by

Shamima Akther Eti

Registration no: 24

Session: 2017-18

Department of Soil, Water & Environment

University of Dhaka

Dhaka-1000, Bangladesh

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Declaration

Experiments described in this thesis were carried out by the author of this thesis in the Department of Soil, Water & Environment, University of Dhaka, Dhaka-1000, Bangladesh. This work has not been presented and will not be presented for any other degree.

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Abstract

High volumes of wastewater generation have become a serious concern over the last few decades worldwide. The discharge of untreated textile wastewater has severely polluted water and soil, threatening the entire environment. The treatment of this wastewater is important in preventing environmental pollution. The most effective methods to treat textile wastewater are coagulation and flocculation. In chemical coagulation, positively charged ions of metal salts are added for charge neutralization and destabilization of colloidal particles. Polyaluminum chloride (PAC) is a highly effective coagulant that has gained popularity over the last few decades for the treatment of textile wastewater because of its apparent cost-effectiveness and availability. In the present study, PAC was synthesized using aluminum scraps as a raw material. For the synthesis of PAC, AlCl3 solution was vigorously mixed with NaAlO2 solution for 3 h in an automated synthesis system at 70 °C. The synthesized PAC was characterized using Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry (SEM-EDX), wavelength dispersive X-ray fluorescence (WD-XRF) spectrometry, X-ray diffraction (XRD), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), Zetasizer. The synthesized PAC was also characterized for its basicity and Al2O3 content.

To determine the coagulation behavior of scrap-derived PAC coagulant, a batch study was conducted with a commercially used anionic dye (Novacron Navy S-G). The optimized parameters of the PAC dosage, pH, contact time, shaking speed and sedimentation time were found to be 2.5 mg, 6.0, 20 min, 150 rpm and 35 min, respectively. At optimum conditions, the synthesized PAC coagulant was found to remove 83.37 to 94.11% of dye from 50 mL of dye-containing wastewater. The effectiveness of PAC and conventional alum for the reduction of turbidity and chemical oxygen demand (COD) in textile wastewater has also been investigated. Batch studies were performed to optimize different parameters for the successful removal of turbidity and COD. The parameters tested in the batch studies were coagulant dosage, pH, contact time, mixing speed and sedimentation time. Results revealed that at optimum conditions, PAC removed 97 to 99% of turbidity and alum removed 94 to 98% of turbidity. On the

other hand, the reduction of ii COD was found to be 42 to 51% with PAC and 33 to 45% with alum. Even though the coagulants demonstrated more or less similar performance with respect to turbidity and COD removal, the scrap-aluminum-derived PAC performed at a lower dosage. Therefore, scrap-derived PAC might be a potential coagulant and good alternative to alum for raw textile wastewater treatment.

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(Shamima Akther Eti)

DEDICATION

To my parents and beloved family members

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List of Abbreviations and Symbols

BOD= Biological Oxygen Demand

COD= Chemical Oxygen Demand

% = Percent

PAC= Polyaluminum chloride

EDX= Energy Dispersive X-ray

WDXRF= Weavelength Dispersive X-Ray Fluroscence

TGA= Thermogravimetric Analysis

DSC= Differential Scanning Calorimetry

SEM= Scanning Electron Microscope

DI= De-ionized Water

FTIR= Fourier Transform Infrared Spectroscopy

XRD= X-Ray Diffraction

et al., = Association

g= gram

mg= Miligram

min= Minute

hrs= Hours

kg= Kilogram

ml= Mililitre

No. = Number

rpm= Rotation per minute

mg/l= Milligram per litre

mv= Milivolt

^{o}C= Degree Celsius

Chapter-1

INTRODUCTION

1. INTRODUCTION

1.1. Background

Textile industries are the most important exporting industry in Bangladesh, which is evident by the increasing growth over the last few decades (Hasan et al., 2016). The importance of this industry cannot be overemphasized. For Bangladesh, the bulk of the export earning originates from textile and textile-related goods. The industry's contribution is 12% towards the gross domestic product (GDP) of Bangladesh (Ahmed et al., 2015). The textile production industry is a longstanding industry in the country and it has become sophisticated over the years. The industry requires a lot of water which is determined by the type of raw materials used in a textile industry. As a result, some of the industries generate a lot of wastewater. Textile mills have been flourishing due to the increasing demand of a growing population. Consequently, the volume of wastewater these industries generate is causing one of the major water pollution problems in the world. To give a perspective, a significant amount (around 10-15%) of dyes are released into wastewater while the dyeing process is carried out (Gita et al., 2017). In addition to dyes, other organic and inorganic pollutants are also being emitted from different industries and contaminating water, soil and other niches of the environment. Some of these pollutants are known to be hazardous for humans. There is an association between the rate of economic development and the rate at which fresh water is being contaminated (Tetteh & Rathilal, 2019). As industrialization is the driving force for the development in both developed and developing countries, pollution-causing industries cannot be shut. Rather, new strategies are required to tackle the pollutants emitted from industries of different types.

There are escalated concerns stemming from untreated or partially treated textile effluents because organic compounds and heavy metals present in the effluents may pose toxicity towards aquatic and terrestrial plants and animals, including humans (Gita et al., 2017). The effluents released from the dyeing industry are characterized in terms of color, pH, COD, temperature and biodegradability. The dyeing effluents were found to reduce the oxygen concentration drastically because of the presence of hydrosulfides (Gita et al., 2017; Hassaan et al., 2017). The effluents with color and turbidity are also known to block the passage of light in water bodies (Azanaw et al., 2022). Reduced light affects the

photosynthesis process negatively (Kamal et al., 2016). As wastewater poses detrimental effects to humans and other organisms, novel water-related technologies and materials development have become a priority in the scientific community and people associated with industries. Based on the treatment systems, different technologies are in use in different water treatment plants. Factors such as water quality, the aim of water treatment, economy, etc. determine as to which technology will be used in a treatment plant (Khishdoost B et al., 2014). However, water quality varies from time to time and the deficiency in treatment facilities may lead to reduced efficiency of a treatment plant, which may, in turn, increase the cost of production (Tetteh & Rathilal, 2019).

The effluents released from textile industries contain various colors and a number of inorganic and organic constituents. The constituents are widely variable because of the variability in clothes types. The dyes are also variable structurally. The dyes may be acidic, basic, metal complex, azo, diazo, and reactive in nature (Kumar & Saravanan, 2017). The effluents also include other contaminants such as suspended solids, acids, bases, pigments, surfactants, sizing chemicals, oxidizing, and reducing agents (Badani et al., 2005; Mahmoued, 2010; Yadav et al., 2013). These chemicals and additives are added during the wet processing technique. The textile effluents are generally alkaline in nature and are characterized by having high pH, biochemical oxygen demand (BOD) and chemical oxygen demand (COD). The effluent contains some refractory compounds. As a result, the effluents cannot be subjected to biological treatment processes directly (Yadav et al., 2013).

The color and turbidity of textile wastewaters are difficult to remove by the sedimentation process (Kumar et al., 2016). Turbidity may reduce the efficiency of the filtration system by clogging the system prematurely. Turbidity can also strain the chemical disinfection process by increasing the oxidant demand. UV irradiation is also affected by turbidity and color from reduced light transmission. Turbidity also decreases the efficiency of UV irradiation by providing protection to microbes (Soros et al., 2019). Therefore, high-level turbidity in textile wastewaters must be removed by other techniques so that clean water can be obtained (Ramavandi, 2014). Removing turbidity not only decreases the loads of organic matter and other organic and inorganic constituents but also removes some

microbes. As a result, the efficacy of the downstream treatment processes is increased to a great extent.

The textile industry requires a huge amount of water for dyeing and washing purposes. A variety of dyes are used in different stages for coloring purposes. Dyeing and washing stages require ~30-40%, and 60-70% of water, respectively (Dey & Islam, 2015). Wastewater containing dyes pose toxicity to aquatic ecosystems.

Considering all the facts, it is imperative that wastewater be treated before its discharge into the environment. Wastewater treatment involves the removal of substances deemed hazardous for aquatic and terrestrial ecosystems, including humans. Industrialists generally seek cheaper technology while treating their effluents (Theodoro et al., 2013). A number of techniques such as adsorption, ion exchange, precipitation, oxidation, membrane process, biological degradation process, etc. are employed for treating wastewater. Each of these techniques has their own merits and demerits (Rana & Suresh, 2017). Among the above-mentioned technologies, precipitation using the coagulation and flocculation processes is still the most prevalent method in treatment plants because of its cost-effectiveness. Coagulation and flocculation are routinely used in water and wastewater treatment plants (Islam & Mostafa, 2018; Pal et al., 2011; Rao, 2015; Sahu & Chaudhari, 2013). As such, technologies came and went over the years, but the demand and application of coagulation never waned. This fact demonstrates the indispensability of the coagulation process in providing us the clean water for consumption and treating the wastewater for safe discharge into the environment. Coagulation chemistry involves destabilization and agglomeration of colloidal particles into larger aggregates. The larger aggregates readily settle down to be separated from the water (Ang & Mohammad, 2020).

In the past, many researchers investigated the coagulation process with real and synthetic textile wastewaters. A number of chemicals such as aluminum sulfate, ferric sulfate, and ferric chloride were tested. Factors such as pH and dosage of chemicals were found to determine the coagulation efficiency (Yang et al., 2016). In water, colloidal particles are generally negatively charged. Coagulants generate positively charged species on hydrolysis. The positively charged species get adsorbed on to the colloidal particles to neutralize the charge. The repulsive interaction between colloids dissipates and then the

colloids grow in size and settle (Yadav, 2013). The entire mechanism is presented in **Figure 1.1** and will be referred to in the following sections.

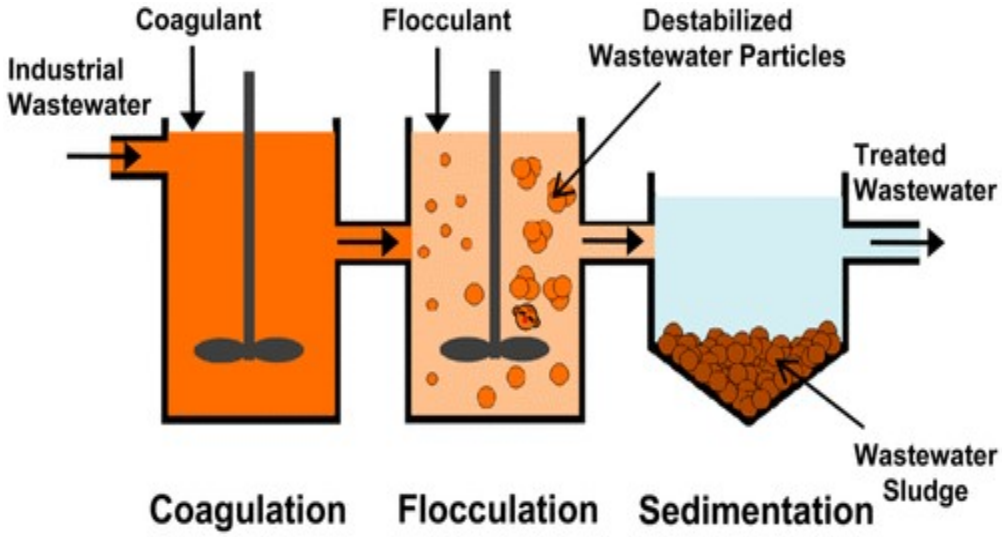

Figure 1.1. Coagulation-Flocculation Mechanism (Teh et al., 2016)

The coagulation and flocculation processes are controlled by many factors. The type of coagulants, their dosage, and operational parameters govern the coagulation and flocculation processes. The parameters are optimized for the efficient removal of suspended particles. When the dosage is not in the optimum range, the suspended particles remain stable. Below the optimum amount, the coagulant is inadequate to destabilize the particles. When the amount is beyond the optimum range, the coagulant acts as a chemical coating that re-stabilizes the particle (Watkinson et al., 2007).

Coagulation is also affected by variables such as pH and alkalinity. Color removal is promoted when water is acidic in nature. On the other hand, alkaline water responds better to technologies intended for turbidity removal. Therefore, controlling pH is vitally essential in the coagulation process. pH also helps to achieve the minimum level of residual aluminum in the clean water. The coagulation efficiency was found to reduce with increasing total hardness (Wang et al., 2010). Mixing time is another factor influencing the efficiency of the removal of particulate matter. Insufficient mixing times lead to poor agglomeration of particles. Low temperature may affect the coagulation process by modifying the solubility of coagulants, the viscosity of water, and the kinetics of hydrolysis reactions (Sahu, 2016). Yu et al. (2007) also observed a reduced coagulation process in

low temperatures. Similar findings were reported by Gao et al. (2007). They obtained higher efficiency in coagulation by PAC in higher temperatures.

As industrial pollution has been increasing over the years and coagulation has been the mainstay in water and wastewater treatments in terms of particulate matter removal, escalated attention has been given to coagulation research concomitantly. The research activities have essentially centered around the improvement of coagulation efficiency in water treatment plants.

The chemistry of conventional coagulants (e.g., alum, $Al_2(SO_4)_3$) such as aluminum salts has been studied extensively and the partial polymerization of these coagulants has been recommended for enhanced efficiency of the coagulation process. Subsequently, a range of pre-polymerized aluminum solutions was produced. Included among them are poly-aluminum chlorides (PAC), poly-aluminum sulfates (PAS), aluminium chlorohydrate (ACH), polyaluminium chlorohydrate, and poly-aluminum chloro-sulfates (PACS) with variable degrees of polymerization. These solutions have been in use in treatment plants around the world over the past two decades. These coagulants were extensively studied and found to be more effective in lower dosages and higher pH, temperature and colloidal range compared to the conventional ones (Zouboulis & Tzoupanos, 2010). The pre-hydrolyzed polyaluminium coagulants possess high basicity (ratio of hydroxyl to aluminum ions) resulting in low alkalinity consumption in the coagulation process, thereby having little impact on pH (Umar et al., 2016). PAC, a polynuclear form of $AlCl_3$, has been employed extensively worldwide with an ever-increasing demand (Aydın et al., 2018). Previous studies reported higher removal of turbidity and TOC using PAC. PAC was found to be less sensitive to temperature and thereby more suitable for application at lower temperatures (Zhang et al., 2018). Aluminum exists in water solutions and at pH values <3 as a six-coordinated Al^{3+} ion. Velasco et al. (2007) conducted a comparative study between PAC and alum and obtained higher removal of particulate matter with PAC under both high and low alkalinity–hardness conditions. The superiority of PAC over alum in cold water was reported by other scientists (Şirin et al., 2012). Among the polyaluminum coagulants, $[AlO_4Al_{12}(OH)_{24}(H2O)_{12}]^{7+}(Al_{13})$, one of the Al_b polymeric species, is the most effective coagulation species (Jiao R et al., 2016).

The pre-polymerized coagulants are produced by partial neutralization of an Al solution through the addition of a base solution. Many parameters govern the properties of the final product. Factors such as the base addition rate, the stirring speed, the synthesis temperature, the presence of other anions (e.g., Cl^-, SO_4^{2-}, CO_3^{2-}), the aging time, etc. determine the properties of a pre-polymerized coagulant. However, the most important parameter is the molar ratio of bound hydroxide to the concentration of metal cations (i.e., the OH/Al molar ratio), termed as basicity. The basicity is employed to indicate the degree of polymerization of coagulant agents (Gao et al., 2005). The fact that it is pre-hydrolyzed means that it consumes less alkalinity, forms highly charged polymeric aluminum species and functions rapidly in the coagulation process. The polymeric aluminum species include $Al_2(OH)_2^{4+}$, $Al_3(OH)_4^{5+}$, and $Al_{13}O_4(OH)_{24}^{7+}$ (Kumar N & Balasundaram N, 2017).

The raw material used for the synthesis of aluminum chloride, a precursor of PAC, is expensive. It is imperative to seek other available resources as raw materials that are cheaper and that contain high aluminum (Hesain, 2015). If the raw material is some recyclable waste, that will help protect the environment and reduce the cost of production by a significant amount (Hesain, 2015). Aluminum beverage cans may be a good source of aluminum and raw materials for the production of aluminum chloride. The cans are one of the most recycled material owing to their high value. Moreover, aluminum retains its properties from start to finish. Feng et al. (2007) studied the effects of temperature on the aluminum formats synthesized in the PAC preparation process. The highest polymeric aluminum was obtained at 80 ℃. In the past, for the preparation of PAC, an alkaline solution was slowly added into an aluminum chloride ($AlCl_3$) solution. Aluminum (Al^{3+}) was found to react with OH^- to form high Al_{13} content PAC (Cheng et al., 2008).

A great many studies have been performed on textile wastewater treatment. Most of the studies were conducted with simulated textile wastewater. However, the conditions at which the synthetic or simulated textile wastewater was treated differ significantly from the real textile wastewater conditions. Therefore, more research is required on real-world textile wastewater alongside simulated wastewater to optimize the process of coagulation with PAC and other coagulants.

The research work described in this dissertation included the synthesis and characterization of PAC from wasted scrap aluminum beverage can as a source of aluminum. The study also included the coagulation performance of the synthesized PAC for the removal of reactive dye, turbidity, and COD from the textile wastewater. The dissertation also included comparative removal study by using conventional coagulant, alum. Sludge produced after coagulation study was also characterized to ensure proper waste management.

1.2. Need Statement

Textile industry and the associated wastewater is a huge problem worldwide. The problem arises when untreated effluent is discharged directly into the aquatic ecosystems. The hazardous and toxic chemicals in the wastewater pose problems to the aquatic lives as well as the organisms, including humans, dependent on them. There is a paradigm shift in wastewater treatment. Circular economy concept is triggering everyone to look for cost-effective and cyclable resources for the treatment of textile wastewater and wastewaters of other types, for that matter.

1.3. Research Objectives

The broader goal of this research is to develop a pre-polymerized coagulant, polyaluminum chloride (PAC) using waste aluminum scraps for the treatment of textile wastewater. The specific objectives of this study are:

- Development of a cost-effective technology by exploring the locally available scrap/waste aluminum for the synthesis of PAC to be used as a coagulant for the treatment of textile wastewater,
- Characterization of prepared PAC with FT-IR, SEM with EDX, XRD, TGA,
- Investigation of the feasibility of practical uses of PAC for the treatment of synthetic and real-world textile wastewater manipulating different parameters,
- Study of the performance of prepared PAC and commercially available conventional coagulants, and
- Development of appropriate technology for the recovery and use of PAC sludge generated during the treatment of wastewater to ensure proper waste management.

1.4. Hypotheses

- Scrap-aluminum-derived PAC coagulant might be helpful to reduce treatment cost.
- Scrap-aluminum-derived PAC will perform at a lower dosage.
- Synthesized PAC might be a good alternative to other conventional coagulants.
- Findings of the present study will contribute new knowledge on the use of coagulants in treating textile wastewater.

1.5. Dissertation Organization

Chapter 1 is an outline of the research problem, need statement, objectives and hypotheses of the research work. **Chapter 2** discusses the synthesis of polyaluminum chloride (PAC) by locally available waste scrap aluminum and characterization of scrap-derived PAC by various state-of-the-art technologies. **Chapter 3** describes the dye (Navacron Navy S G) removal from both aqueous solution and real textile wastewater using scrap-derived PAC. **Chapter 4** presents a comparative study of turbidity removal from textile wastewater by the synthesized PAC and alum. **Chapter 5** describes the Chemical Oxygen Demand (COD) removal study by using both the synthesized PAC and alum. **Chapter 6** presents the characterization of generated sludge after coagulation experiments. **Chapter 7** is the conclusions and recommendations for future research.

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2. Synthesis and Characterization of Polyaluminum Chloride Coagulant from Scrap Aluminum

2.1. Abstract

Of late, polyaluminum chloride (PAC), an inorganic polymer, has been used as an alternative to conventional alum for the treatment of wastewater. The present study proposed a novel method to use scrap aluminum as raw materials for the preparation of PAC. For the synthesis of PAC, scrap-aluminum-derived $AlCl_3$ solution was vigorously mixed with $NaAlO_2$ solution for 5 h in an automated synthesis system at 70 ^oC. Various state-of-the-art techniques were used to characterize the synthesized PAC. The PAC was characterized to reveal its degree of polymerization such as basicity, functional groups, chemical composition, morphology, and charge neutralization capacity. Basicity and Al_2O_3 contents of the synthesized PAC were also determined, which were found to be 37.89% and 51.1%, respectively. Fourier Transform Infrared Spectroscopy indicates PAC was successfully prepared and showed characteristic peaks of an inorganic polymer. From the zeta potential analysis, the synthesized PAC was found to have a value of +42.9 millivolts (mV), indicating that the PAC has good stability behavior with colloidal particles. XRD pattern shows that PAC is an amorphous rather than a crystalline substance. The SEM image exhibited the presence of some white salts (sodium chloride) and some random aggregates that are largely amorphous in character; this may have originated from water absorption in the air. Thermogravimetric analysis confirms that PAC has good thermal stability and showed a sharp endothermic peak.

2.2. Introduction

The discharge of wastewater, with or without inadequate treatment, may pose a number of environmental problems (Hernández-Sancho et al., 2015). As a result, the countries incur a significant amount of loss associated with the environment. In order to treat wastewater, different physical, chemical, and biological treatment technologies are employed. Current wastewater treatment systems have significant flaws, including a high energy requirement, inadequate pollutant removal, and the formation of harmful sludge (Ferroudj et al., 2013). For chemical treatments, an astronomical amount of synthetic organic and inorganic substances is used every day all over the world. In most cases, these chemicals are expensive. As the chemicals are

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SYNTHESIS AND CHARACTERIZATION OF POLYALUMINUM CHLORIDE COAGULANT FROM SCRAP ALUMINUM

required in higher doses, the chemical treatment technologies are not cost-effective. Developing countries such as Bangladesh incur a lot of expenses to import these chemicals for wastewater treatment. Therefore, it is imperative to develop an environmentally friendly, cost-effective, and efficient technique for the treatment of wastewaters.

Coagulation is a common and widely used wastewater treatment technique (Pal et al., 2011; Wang et al., 2009). Coagulation-flocculation is a chemical water treatment technology used to enhance the capacity of a treatment process to remove undesired particles before sedimentation and filtration (e.g., quick sand filtration). The types of coagulants used in coagulation are crucial in determining the efficacy of treatments (Zheng et al., 2008; Zheng et al., 2011). In recent years, extensive research has been conducted on coagulation processes. A number of coagulants have been tested in wastewater treatment plants. The currently employed inorganic coagulants are primarily Al-based coagulants (e.g., aluminum sulfate or alum), Fe-based coagulants (e.g., ferric sulfate, ferric chloride), and metal-based composite coagulants (e.g., poly-ferric-aluminum- silicate-sulfate) (Chen et al., 2014; Gao et al., 2005). Both Al-based coagulants and Fe-based coagulants have advantages and disadvantages. The use of aluminum coagulants, for example, may leave a residual concentration of Al in the treated water, which could be hazardous to human health (Jarvis et al., 2012). Despite this, aluminum salts, specifically alum [$Al_2(SO_4)_3$14-H_2O], are the most commonly used coagulant in water and wastewater treatment. Alum is preferred since it was found to be beneficial in a wide range of water types while being reasonably inexpensive (Edzwald, 1993; McCurdy et al., 2004; Wang et al., 2009).

In recent years, research on prehydrolyzed aluminum coagulants (e.g., polyaluminum chloride, denoted as PAC, and polyaluminum sulfate, denoted as PAS) has gained momentum, based on traditional aluminum salts ($AlCl_3$ and alum). When compared to standard flocculants, polyaluminum chloride was shown to be more efficient and cost-effective (Buffle et al., 1985; Edzwald, 1993; Tang & Luan, 1995). The features of these prehydrolyzed aluminum coagulants have been thoroughly investigated, and they have been discovered to be more effective at lower dosages (Sinha et al., 2004; Crittenden et al., 2005). As the dosage requirement is smaller, it

leaves lower residual aluminum.

Coagulation is a common and widely used wastewater treatment technique (Pal et al., 2011; Wang et al., 2009). Coagulation-flocculation is a chemical water treatment technology used to enhance the capacity of a treatment process to remove undesired particles before sedimentation and filtration (e.g., quick sand filtration). The types of coagulants used in coagulation are crucial in determining the efficacy of treatments (Zheng et al., 2008; Zheng et al., 2011). In recent years, extensive research has been conducted on coagulation processes. A number of coagulants have been tested in wastewater treatment plants. The currently employed inorganic coagulants are metal-based composite coagulants (e.g., poly-ferric-aluminum- silicate-sulfate) (Chen et al., 2014; Gao et al., 2005).

Both Al-based coagulants and Fe-based coagulants have advantages and disadvantages. The use of aluminum coagulants, for example, may leave a residual concentration of Al in the treated water, which could be hazardous to human health (Jarvis et al., 2012). Despite this, aluminum salts, specifically alum [$Al_2(SO_4)_3$14-H_2O], are the most commonly used coagulant in water and wastewater treatment. Alum is preferred since it was found to be beneficial in a wide range of water types while being reasonably inexpensive (Edzwald, 1993; McCurdy et al., 2004; Wang et al., 2009). In recent years, research on prehydrolyzed aluminum coagulants (e.g., polyaluminum chloride, denoted as PAC, and polyaluminum sulfate, denoted as PAS) has gained momentum, based on traditional aluminum salts ($AlCl_3$ and alum). When compared to standard flocculants, polyaluminum chloride was shown to be more efficient and cost-effective (Buffle et al., 1985; Edzwald, 1993; Tang & Luan, 1995). The features of these prehydrolyzed aluminum coagulants have been thoroughly investigated, and they have been discovered to be more effective at lower dosages (Sinha et al., 2004; Crittenden et al., 2005). As the dosage requirement is smaller, it leaves lower residual aluminum (Yan et al., 2007).

The prehydrolyzed aluminum coagulants were also found to be working in a wide range of pH, conductivity, temperature, and colloids compared to the conventional ones (Matsui et al., 1998; Matsui et al., 2003; Sinha et al., 2004; Crittenden et al., 2005; Zouboulis & Tzoupanos, 2010; Zhou et al., 2019). They were also reported to

produce less sludge compared to conventional aluminum salts (Matsui et al., 2003). The less sludge production is associated with the fact that the prehydrolyzed aluminum coagulants (e.g., PAC) have higher charge density, which in turn leads to a decreased coagulant dose and solid's production (McCurdy et al., 2004). This polymeric metal coagulant is also of lower alkalinity which is a significant advantage (Choy et al., 2014). Polyaluminum chloride (PAC) may be produced by first separately making two aluminum-containing solutions and then mixing them together. First, a basic aluminum chloride solution is produced by mixing an aluminum-containing raw material (e.g., Al_2O_3) with a concentrated acid (e.g., HCl) under aggressive conditions (e.g., high temperature, extended contact time, etc.) (Zouboulis & Tzoupanos, 2010). The second solution, sodium aluminate (generally formulated as $NaAlO_2$, $Na_2O.Al_2O_3$, or $Na_2Al_2O_4$ in solid state), is made by dissolving an aluminum- containing raw material in a strong alkaline solution (e.g., NaOH, KOH, etc.) (Zouboulis & Tzoupanos, 2010).

The synthesis of PAC is done by slowly adding a sodium aluminate solution into a basic aluminum chloride solution under stirring. When HCl is employed, the resultant product has the empirical formula $Al_n(OH)_mCl_{3n-m}$, where $0<m<3n$ (Shen & Dempsey, 1998; Zouboulis & Tzoupanos, 2010). PAC contains a variety of pre-formed Al(III) hydrolysis species of greater quality and structure, which are more stable for further hydrolysis, resulting in increased coagulation efficiency (Wu et al., 2007). When PAC stock solutions are added to raw water, a variety of species can form (Shen and Dempsey, 1998). Al(III) hydrolysis species can be classified into three categories using ^{27}Al NMR spectroscopic methods: monomeric and dimeric aluminum species (denoted as Al_{mono}), $Al_{13}O_4(OH)_{24}$ (Al_{13} for short), and big polymer aluminum species and solid-phase $Al(OH)_3$ (denoted as Al_{other}) (Wang et al., 2009).

Previous research has shown that the Al(III) hydrolysis species found in PAC are primarily responsible for the coagulation performance and mechanism of aluminum salts (Yan et al., 2007). The polymeric aluminum Al_{13} ($[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$) species has been reported to be the active species responsible for coagulation or precipitation in treatment plants (Stumm & O'Melia, 1968; Wang & Hsu, 1994). These aluminum

species react to generate insoluble aluminum poly-hydroxides, which form large volumetric flocs. The flocs bind to suspended contaminants in the water, which are precipitated by the PAC and easily removed (Matsui et al., 1998). It reduces the coagulant dose and the amount of sludge produced during the treatment process (Zouboulis et al., 2010).

Aluminum beverage cans are the most recycled packaging material on account of their high value and ease of collection. In scrap aluminum, aluminum retains its properties, unlike other materials. The act of recycling aluminum beverage cans aids in eliminating waste. Moreover, recycling saves energy, reduces pollution, and reduces the use of landfills in cities, as well as provides additional cash to recyclers (AlSaffar & Bdeir, 2008). In the present study, scrap aluminum was used for preparing PAC. The proposed process will contribute significantly to recycling wasted resources and protecting the environment. The process may reduce production costs by lowering the cost of purchasing raw materials for coagulants (Lee et al., 2011). Also, the characterization of scrap derived PAC was done by using state-of-the-art technologies.

2.3. Experimental

2.3.1. Materials

Spent beverage cans, made of aluminum, were collected from local scrap markets and used as the source of aluminum in this research work. To eliminate undesired debris, the collected cans were washed with copious amounts of water and then washed with an acidic or basic solution. The cans were then cut into little pieces to facilitate the intended chemical reactions. Hydrochloric acid (35.9% purity) and 0.1 M solution of sodium hydroxide (>98% purity) was collected from Merck, Germany and reagents utilized in this experiment were all of the analytical grade. All of the solutions were made with deionized (DI) water with a conductivity of less than 0.05 μS/cm.

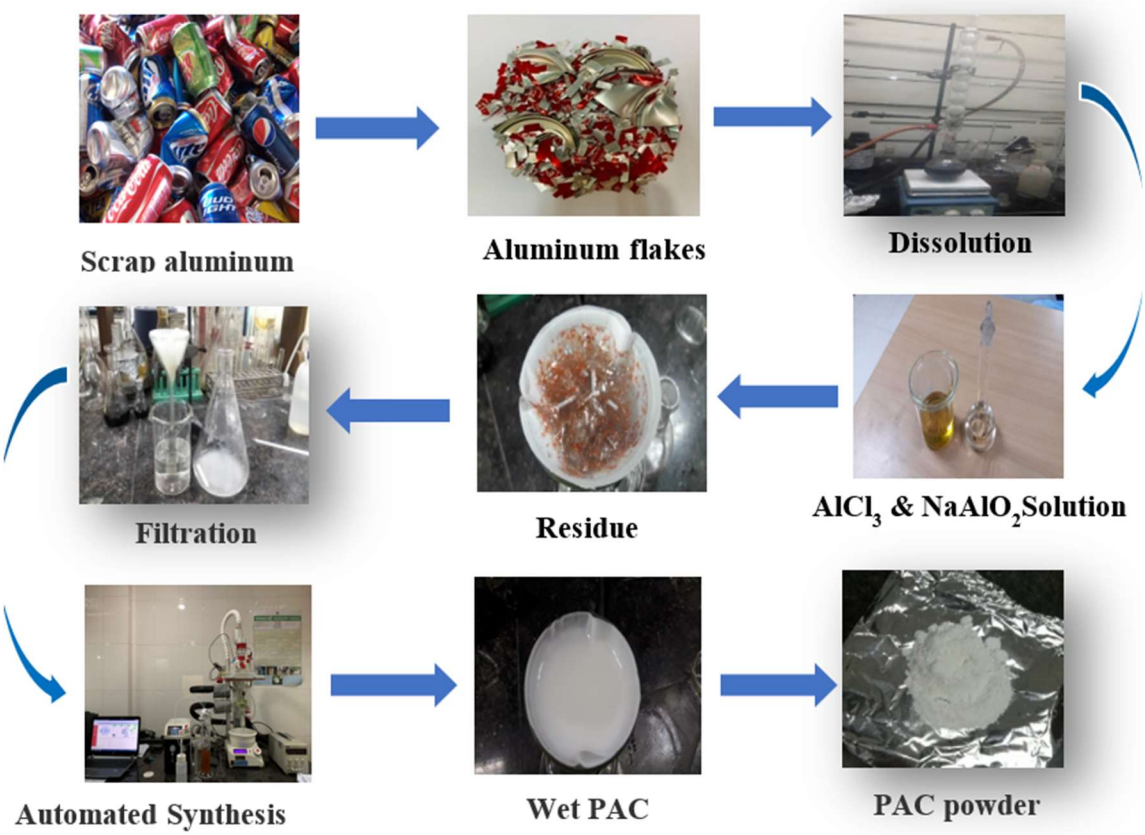

Figure 2.1. Schematic of PAC synthesis in the laboratory.

2.3.2. Synthesis of polyaluminum chloride coagulant

2.3.2.1. Preparation of solutions

Aluminum Chloride ($AlCl_3$) solution was prepared by dissolving approximately 35 g of scrap samples in 400 mL 37% of hydrochloric acid in a 1000 mL beaker. Then this beaker was heated at 70℃ using a hot plate with magnetic stirrer. The reaction was performed under a fume hood. Sodium aluminate ($NaAlO_2$) solution was prepared in the same way but without heating. This solution is prepared by dissolving 33 g of scrap sample in 1 M 500 mL Sodium Hydroxide solution in a 1000 ml beaker. After the reaction was completed, both the solutions were filtered using a Whatman 42 filter paper. The filtration was done to remove the suspended particles and for a clear solution.

2.3.2.2. Preparation method of PAC

The synthesis of PAC coagulant was performed in an Automated Synthesis System (Atlas, Syrris, UK). The qualities of the final product may be affected by parameters such

as the base addition rate, stirring speed, and synthesis temperature. The $AlCl_3$ solution was first introduced into the reaction chamber. To synthesize PAC, a pipette was used to slowly add $NaAlO_2$ solution to the reaction chamber. The base addition rate was 0.2 mL/min, with an 800-rpm stirring speed. The $AlCl_3$ to $NaAlO_2$ solution had a 1:1 ratio. The polymerization procedure was carried out at 70 °C for around 5 h. After the reaction was completed, the liquid PAC was collected from the reaction chamber and allowed to settle for more than 24 h. Then, the supernatant was discarded, and the deposit was collected and rinsed three times with copious amounts of deionized water. After that, the PAC in suspension was placed in an oven at 100 ℃ for 18 h. The final product was obtained as white powder form by granulation. **Figure 2.1** depicts the preparation of PAC from scrap aluminum on a laboratory scale. **Table 2.1 and Figure 2.2** show the polymerization reaction condition and properties of the synthesized PAC, respectively.

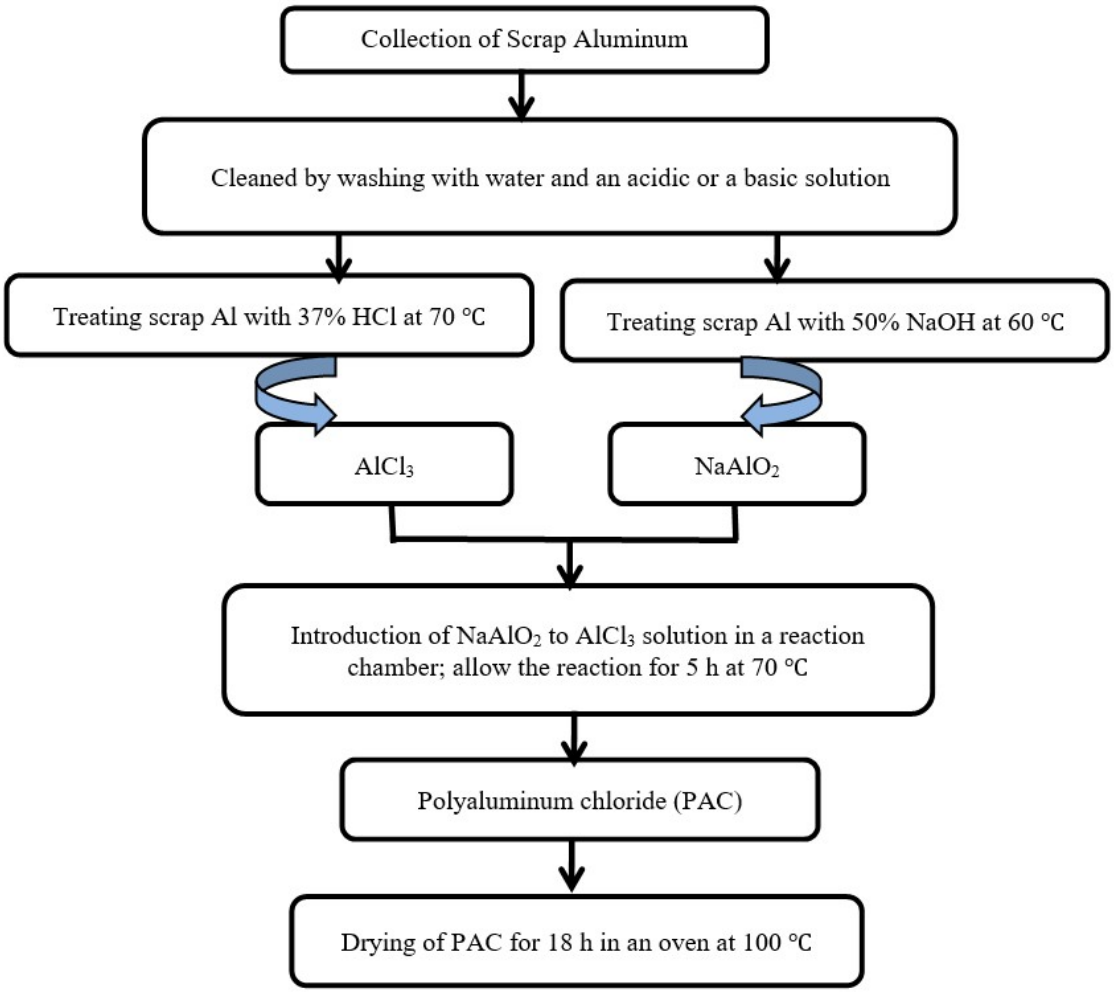

Figure 2.2. Method of preparation of PAC from scrap aluminum

Table 2.1. The Parameters and conditions in polymerization process.

Parameters	Conditions
Polymerization Temperature (TP)	70° C
Polymerization Time (HP)	3hrs
Ratio of $AlCl_3$ to $NaAlO_2$solution	1:1
Stirring speed	800 rpm
Base addition rate	0.2 mL/min

2.3.3. Characterization of synthesized PAC

Various state-of-the-art techniques were used to characterize the synthesized PAC. The PAC was characterized to reveal its degree of polymerization such as basicity, functional groups, chemical composition, morphology, and charge neutralization capacity.

2.3.3.1. Determination of basicity

Basicity is a key indicator that indicates the degree of polymerization of PAC, which influences its coagulant properties. Basicity is defined as the mol proportion of OH- and Al in PAC. PAC is characterized by two primary numbers: their strength (usually in % alumina) and their basicity. Al_2O_3 content (% w/w) and the basicity (%) of PAC were determined following the American Water Works Association (AWWA) standards (AWWA, 1999). **Table 2.2** shows the composition of synthesized PAC.

Table 2.2. Composition of synthesized PAC

Particulars	PAC value
Description	White powder
Alumina as Al_2O_3% (w/w)	51.1
Basicity %	37.89
pH Value (1% Solution)	3.7
Sp. Gravity at 20 °C	1.06
Density	1.27
Water Insoluble %	≤1.5

2.3.3.2. Fourier-Transform infrared spectroscopy

The synthesized PAC was analyzed qualitatively with FT-IR to determine the

functional groups present (Frontier Perkin Elmer, UK). FT-IR samples of the solid coagulants were prepared as potassium bromide (KBr) pellets. The interval of the measured wavenumbers was from 400 to 4000 cm^{-1} (Farmer, 1974).

2.3.3.3. Zeta potential analysis

To assess the surface charge of the synthesized coagulant, a zeta potential study was done using a Zeta Potential Analyzer (Nanopartica SZ-100, HORIBA Scientific Ltd., Japan). Ultrapure water was used to dissolve the PAC coagulant. The concentration of the solution was 1 g/L.

2.3.3.4. X-ray diffraction analysis

Using a Bruker D8 Advance Diffractometer, an X-ray diffraction (XRD) examination of the PAC coagulant was performed to reveal the XRD patterns of the synthesized PAC (Bruker AXS GmbH, Germany). The sample was scanned with CuKα radiation at a speed of 2 deg/min. The current and voltage in operation were 40 mA and 40 kV, respectively.

2.3.3.5. Scanning electron microscopy (SEM) analysis

A scanning electron microscope (SEM) was employed to determine the high-resolution image of morphology of the synthesized PAC. SEM images were taken at a magnification of 3000× (EVO18, Carl Zeiss NTS GmbH, Germany).

2.3.3.6. Identification of elemental composition

To know the elemental composition in the prepared PAC, Energy Dispersive X-ray (EDX) (EDAX, Ametek, Germany) analysis was done. ~0.5 g sample was taken and placed into the machine to analyze the elemental composition. To understand the elemental composition more accurately the Wavelength Dispersive X-Ray Fluorescence, WDXRF (Rigaku ZSX Primus IV, Japan) analysis was also conducted. In this case, about 0.5 g sample was taken for the analysis.

2.3.3.7. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of synthesized PAC was carried out by using a simultaneous thermal analyzer, STA

(NETZSCH STA 449 F5, Germany) under nitrogen atmosphere with the heating rate of 10K min.

2.4. Results and discussion

2.4.1. Characterization of PAC

2.4.1.1. Basicity

Basicity is the most important parameter which is defined as the molar ratio of bound hydroxide to metal cation concentration (i.e., the OH/Al molar ratio). It is a term for the degree to which coagulant agents polymerize (Tzoupanos et al., 2008; Zouboulis & Moussas, 2008). Basicity can influence the properties of PAC and as a result the performance of coagulation (Lei et al., 2009). Previously number of investigations have studied the effect of PAC basicity on coagulation performance. However, there have been reports of contradictory results. In a study, PAC with higher basicity was found to exhibit an enhanced coagulation efficiency (McCurdy et al., 2004). The basicity of PAC was shown to be closely related to the residual Al concentration (Yang et al., 2011). As a result, basicity could be a useful technique for not only improving coagulation performance but also lowering residual Al levels (Zhang et al., 2018). AWWA standards were used to determine the Al_2O_3 concentration (percent w/w) and basicity (percent) (AWWA, 1999). **Table 2.3** shows properties of the synthesized PAC.

Table 2.3. The properties of the synthesized PAC.

Parameter	Description
Appearance	White powder
Alumina as Al_2O_3% (w/w)	51.1
Basicity (%)	37.89
pH Value (1% Solution)	3.7
Specific Gravity at 20 ℃	1.06
Water Insoluble (%)	≤1.5

2.4.1.2. Fourier-Transform Infrared spectroscopic analysis

FT-IR spectra was used to examine the chemical bonds in PAC. The potassium bromide (KBr) pellet method was employed to analyze PAC using an FTIR spectrophotometer. The spectra were in the 4000-400 cm^{-1} region. Briefly, the PAC

sample was dried in an oven at 105 ℃ and then ground into a fine powder. **Figure 2.3** shows that FT-IR spectra exhibited a broad absorption peak in the range of 3200-3650 cm^{-1}. The absorption peaks at 3339 cm^{-1} could be attributed to the stretching vibration of the -OH group (Liu et al., 2017). On the other hand, the absorbance peak at 1620 cm^{-1} (1600-1700 cm^{-1}) could be ascribed to the bending vibrations of water; the water might have been absorbed, polymerized, and crystallized in the synthesized coagulant (Zhou et al., 2014). The bending vibration of the Al-OH-Al groups may be responsible for the band at 1044 cm^{-1} (Gong & Feng, 2015). The bending vibration of Al-OH_2 could be assigned to the bands at 1167 and 1136 cm^{-1} (Tzoupanos et al., 2009). The symmetric stretching mode of the Al-O bond of the central AlO_4^- in the Al_{13} molecule may account for the wavelength at 671 cm^{-1} (Zouboulis et al., 2008). The presence of all the mentioned peaks indicates that the PAC was properly synthesized, as described by Zouboulis et al. (2008).

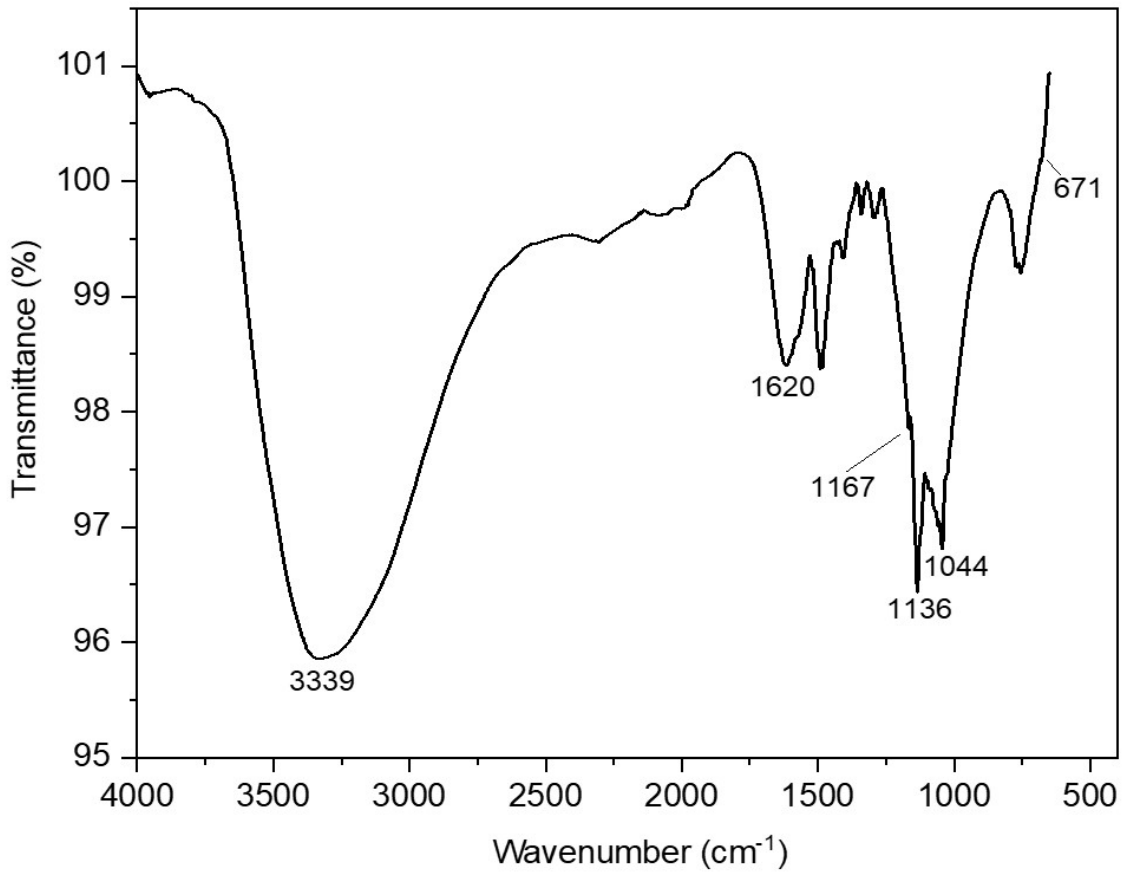

Figure 2.3. FT-IR spectra of synthesized PAC

2.4.1.3. Zeta Potential Analysis

The zeta potential measurement is crucial because its value indicates the stability of colloidal dispersions. In the water treatment, the charge density of the coagulant has an impact on its charge neutralization process. The tendency of the aggregates determines the surface charge (Arumugam et al., 2016). As a result, the synthesized PAC's aggregation behavior could be accurately predicted using zeta potential analysis. Hence, colloids with high positive or negative zeta potential are electrically stabilized, whereas colloids with a low zeta potential have a tendency to coagulate or flocculate (Greenwood & Kendall, 1999; Hanaor et al., 2012). From the zeta potential analysis, the synthesized PAC was found to have a value of +42.9 millivolts (mV), indicating that the PAC has good stability behavior with colloidal particles (Kumar & Dixit, 2017). The higher value also implies that the synthesized PAC has a larger impact on the charge of particulates, and that it will have a higher basicity and coagulant charge, resulting in more effective charge neutralization, colloids destabilization, and hence improved coagulation performance (Zouboulis et al., 2010). **Table 2.4** indicates the stability behavior of the colloid based on zeta potential value (Kumar & Dixit, 2017).

Table 2.4. Stability behavior of the colloid based on zeta potential value (Kumar & Dixit, 2017).

Zeta potential value (mV)	Stability behavior
0 to ± 5	Flocculation or coagulation
±10 to ± 30	Incipient instability
±30 to ± 40	Moderate stability
±40 to ± 60	Good stability
Greater than ± 60	Excellent stability

2.4.1.4. X-ray diffraction spectra

The XRD patterns of the synthesized PAC sample are shown in **Figure 2.4**. The diffractive peaks of Al_{13} are typically thought to appear at the 2-theta values of 5-25º (Hu et al., 2012). However, the figure shows that there are no peaks in the range of 2-theta value of 5-25º in PAC XRD spectra. The spectra exhibited significant diffraction peaks at the 2-theta values of 30.62º and 44.58º, that match well with NaCl crystal diffraction peaks. It is possible that NaCl was present as a by-product of the Al(III)

polymerization; NaCl remained in the synthesized PAC despite undergoing the separation and purification process. The XRD spectrum is particularly sensitive to NaCl, and even a small amount of NaCl can produce a strong response (Wu et al., 2016). Thus, NaCl signals appeared for the investigated samples at the 2-theta value of >25º. The XRD patterns of PAC showed a weak peak of Al_{13} diffraction peak, which may be explained by the fact that the PAC samples were not purified and that the test findings might have been influenced by additional impurities. As a result, it can be argued that PAC is an amorphous rather than a crystalline substance.

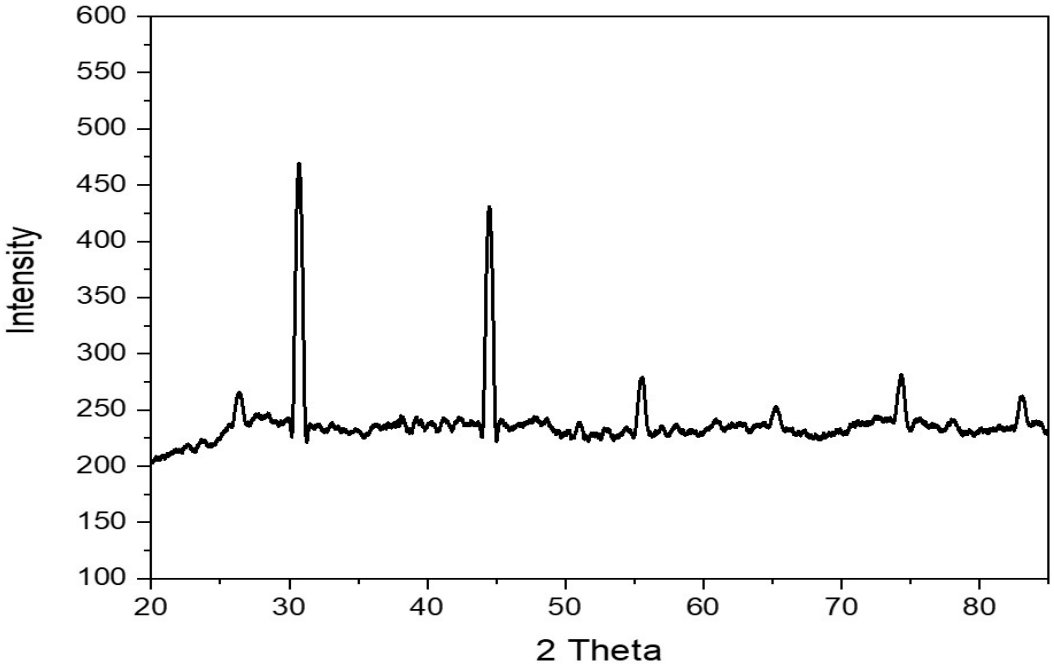

Figure 2.4. XRD spectra of the synthesized PAC.

2.4.1.5. Scanning electron microscopy/energy-dispersive X-ray (SEM)

A scanning electron microscope equipped with an energy-dispersive X-ray (SEM-EDX) was used to understand the microscopic morphology of the powder PAC sample. An X-ray is produced when there is a difference in energy between the higher-energy shell and the lower-energy shell. The analysis was performed at 3000× 15 kV accelerating voltage, and 10.5-mm working distance with the EDAX EDS system. In **Figure 2.5**, the SEM image exhibited the presence of some white salts (sodium chloride) and some random aggregates that are largely amorphous in character; this may have

originated from water absorption in the air. Shi et al. (2007) also examined the SEM images of freeze-dried PAC-Al_{13} particles and obtained no regular crystalline morphology, which can be substantiated by the findings of the present study.

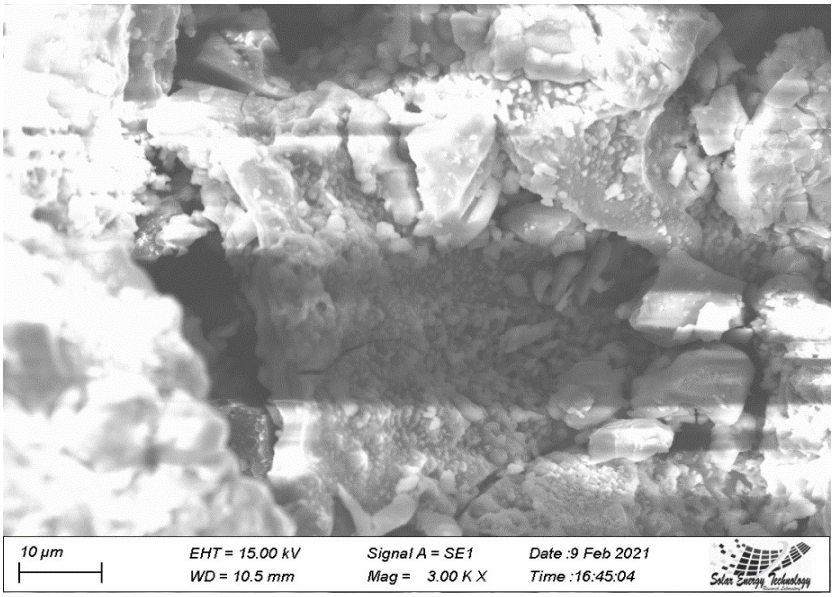

Figure 2.5. SEM image of synthesized PAC.

2.4.1.6. Energy-dispersive X-ray (EDX)

The composition of the synthesized PAC was determined using an energy dispersive X-ray (EDX) analysis. During the EDX analysis, different areas were focused on, and the corresponding peaks are illustrated in **Figure 2.6**.

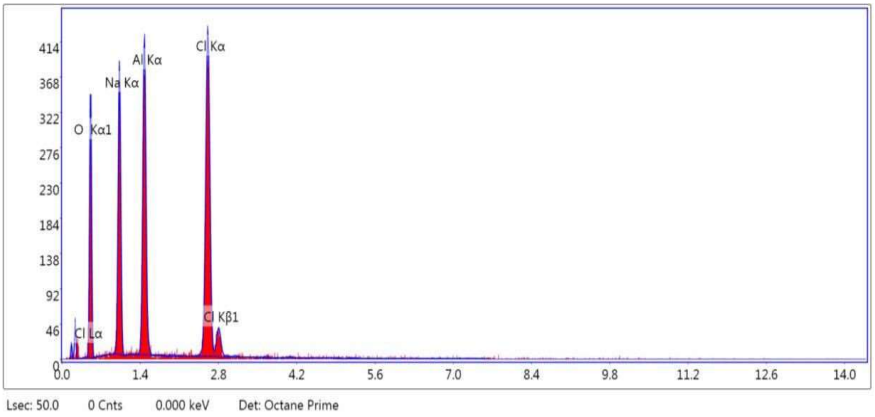

Figure 2.6. EDX spectra of the synthesized PAC.

Among the various elements, the peaks of both aluminum and chlorine were found

in the PAC and a peak of sodium salt was also observed. The elemental composition of the prepared PAC is presented in **Table 2.5.**

Table 2.5. Elemental composition of synthesized PAC by EDX.

Element	Weight%	Atomic%
OK	29.35	42.76
NaK	19.57	19.84
AlK	18.51	15.99
ClK	32.57	21.41

2.4.1.7. Wavelength dispersive X-ray fluorescence analysis

To understand the elemental composition of the prepared PAC in detail, the Wavelength Dispersive X-Ray Fluorescence (WDXRF) analysis was performed. **Table 2.6** shows the elemental composition that are present in the prepared PAC.

Table 2.6. Elemental composition by Wavelength Dispersive X-Ray Fluorescence (WDXRF).

Component	Amount (mass %)	Detection limit	Elemental line	Intensity	w/o normal
Na_2O	14.1	0.01127	Na-KA	10.5152	2.4734
MgO	0.0212	0.00561	Mg-KA	0.0343	0.0037
Al_2O_3	51.1	0.00625	Al-KA	314.2824	8.9473
SiO_2	0.186	0.00156	Si-KA	0.6673	0.0325
P_2O_5	0.0030	0.00106	P-KA	0.0238	0.0005
SO_3	0.0530	0.00312	S-KA	0.3245	0.0093
Cl	34.3	0.01016	Cl-KA	114.6818	6.0028
CaO	0.0605	0.00333	Ca-KA	0.1299	0.0106
Fe_2O_3	0.133	0.00413	Fe-KA	1.0553	0.0233
ZnO	0.0414	0.00229	Zn-KA	1.4716	0.0072
Ga_2O_3	0.0170	0.00251	Ga-KA	0.6600	0.0030

2.4.1.8. TGA- DSC curve

Figure 2.8 shows the thermogravimetric curve of synthesized PAC. Three main stages of thermal decomposition of coagulant, corresponding to their weight reduction, may be observed in **Figure 2.8.** In the initial stage, weight loss of about 3.8% was observed up to 110 ºC. In the second stage, about 29.2% loss was observed in the range of 110-434 ºC. These losses may be ascribed to the water molecules from air which was absorbed by the hydrophilic group of PAC coagulant in the polymerization reaction. In the third stage, the residual mass was found to be 36.3% at 644 ºC due to the presence of aluminum in PAC.

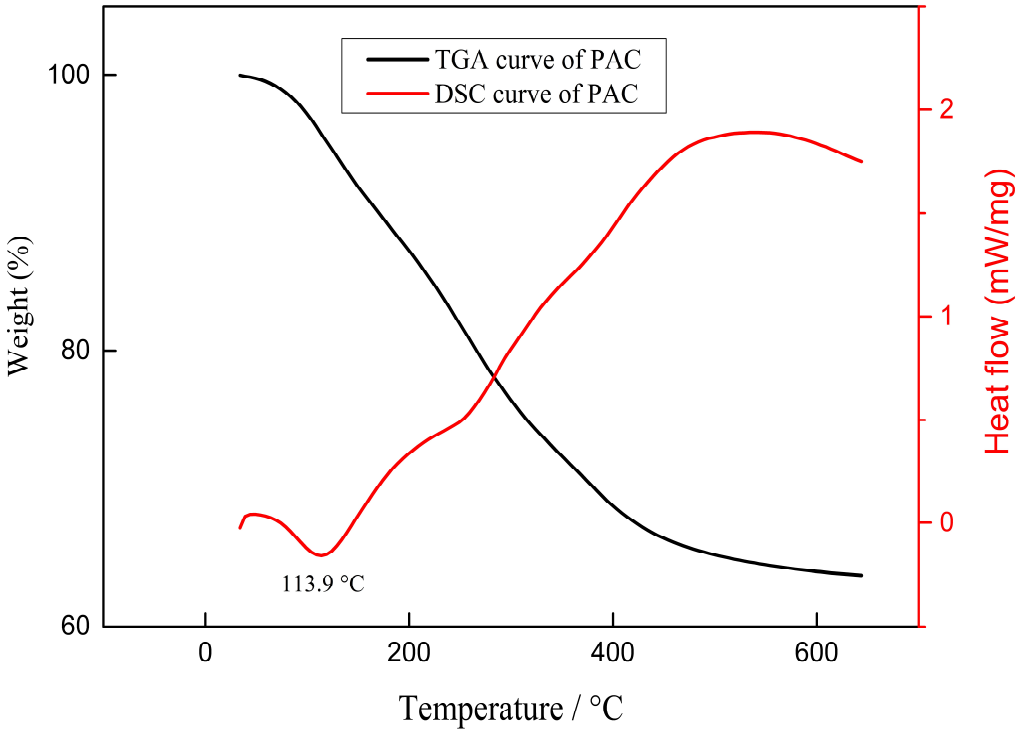

Figure 2.7. Thermogravimetric Analysis of the synthesized PAC.

In **Figure 2.7**, a sharp endothermic peak was observed at 113.9 ºC due to the evaporation of absorbed water from PAC. Çilgi & Cetişli (2009) stated that the thermal decomposition of aluminum sulfate hydrate occurs in four major stages, all endothermic. The study conducted by Lin et al. (2015) reported endothermic peaks at 155 ºC which was caused by the splitting of the surface hydroxyl group of silicon–aluminum–ferric–starch (CSiAFS) flocculant.

2.5. Conclusions

The development of polyaluminum chloride coagulant from recyclable material is one of the promising options for advanced wastewater treatment processes. In the present study, PAC was successfully synthesized from scrap aluminum (used aluminum beverage can), and the parameters for synthesis were also investigated. The synthesized PAC exhibited improved properties such as alumina (Al_2O_3) content of 51.1 % (w/w) and basicity of 37.89% (moderate to high basicity). Thus, the synthesized PAC could be a good alternative to other conventional coagulants for raw water and wastewater treatment. Given the fact that the raw material for the PAC synthesis will be aluminum beverage cans, the cost-effectiveness nature of the PAC appears to be very attractive. Finally, if the described procedure could be scaled up to an industrial scale, the final product may be improved and the method refined. Further studies are needed to determine the applicability of the synthesized PAC for other contaminants.

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Chapter-3

REMOVAL OF ANIONIC DYE (NAVACRON NAVY S G) FROM AQUOUS SOLUTION AND REAL TEXTILE WASTEWATER BY CHEMICAL COAGULATION WITH SCRAP AUMINUM DERIVED POLYALUMINUM CHLORIDE

3. Removal of Anionic Dye (Navacron Navy SG) from Aqueous Solution and Real Textile Wastewater by Chemical Coagulation with Scrap-Aluminum-Derived Polyaluminum Chloride

3.1 Abstract

The textile industry is one of the leading consumers of dyes and chemicals. As a result, this industry releases a huge amount of colorful wastewater. The released wastewater contains dyes and chemicals that may pose toxicity to the environment and living things. Consequently, the effluents released from the textile industry have drawn attention from environmentalists and researchers. In this study, scrap-derived PAC was used as a coagulant for treating dye-containing wastewater. To investigate the efficacy coagulant, different coagulation parameters were tested. The optimum dosage of the prepared PAC was found to be 2.5 mg for 10 mg/L, 50 mL aqueous dye solution. The optimum pH of the aqueous dye solution was found to be 6.0. The ideal contact time was 20 min and the optimum mixing speed was 150 rpm. The optimum settling time after the coagulation was 35 min and the optimum dye concentration was 10 mg/L to treat 50 mL dye solution with 2.5 mg of PAC. Results revealed that the applied process of coagulation achieved a considerable amount of decolorization of reactive dye from aqueous solution and real textile wastewater. The percent removal was 91.3% for synthetic solution and 73.0% for real textile wastewater. It is apparent that the removal efficiency is higher in aqueous solution of dye than in real wastewater at the same concentration under the same condition.

3.2 Introduction

The textile industry is the biggest consumer of the dyestuff market in the world. The textile industry utilizes approximately 10,000 tons of dyestuff per year worldwide (Rodríguez-Couto et al., 2009). The industry releases the maximum amount of dye effluent. As such, more than 50% of dye-related pollution is attributed to this industry (Katheresan et al., 2018). Currently, textile and some other industries such as printing, plastic are booming dye-consuming industries (Lewis, 2014). Reactive dyes are widely used to color wool, cotton, nylon, and silk (Rehman et al., 2015). The consumption of water is high in these industries. For instance, ~150 – 350 L of water is needed for 1 kg of finished apparel (Bilińska et al., 2016).

The dyeing process is not fully efficient. From an estimation, during the dyeing process, ~10 – 15% of the dyes find their way into wastewater (Bilinska et al., 2016). In another estimation, around 40% of the dye was found to be lost during the washing and rinsing steps (Li et al., 2012). The lost dyes eventually make their way to the wastewater. Global economic growth is inversely proportional to the well-being of the environment. The deterioration of natural resources is an inevitable outcome of the inexorable economic progress of the world (Gita et al., 2017; Tetteh & Rathilal, 2019).

Untreated wastewater may pose environmental problems. Different niches of the environment are affected to a significant extent (Gita et al., 2017; Hassaan et al., 2017). The tannery industry releases untreated dyes indiscriminately. The dyes and their breakdown products may cause adverse effects on human health (Lavanya et al., 2014 and Tahir et al., 2016). The effluent stemming from the dyeing industry can be characterized with respect to color, pH, COD, temperature, and biodegradability. The Color Index contains more than 10,000 dyes, which are commercially sold. These colors are recalcitrant compounds because of their complex aromatic structure and synthetic origin (Bogoeva et al., 2008).

When untreated textile effluent is discharged into the environment, the oxygen concentration is significantly reduced because of the presence of hydrosulfides. In addition to this, 40% of colors that are widely used across the world contain organically bound chlorine. Organically bound chlorine is carcinogenic in nature. On the other hand, heavy metals present problems because of their non-biodegradability. As a result, they tend to accumulate in primary organs leading to diseases of various types and long-term health effects (Gita et al., 2017).

As wastewater is known to have detrimental effects, wide attention has been given to developing technologies to treat or mitigate the adverse effects of different toxicants. Coagulation has been the mainstay in water and wastewater treatment processes. However, the coagulation process has been in use since ancient times. People used to employ crushed seeds as coagulating agents for water purification. More specifically, the Egyptians, as early as 2000 BC, would use almonds for the treatment of river water. Interestingly, alum was known to the early Romans. However, it was not until ca. 77 AD that they started using

it as a coagulant. In modern times, alum formally came into application in 1881 in England. After so many years, coagulation and flocculation are still the go-to technologies for water and wastewater treatment (Sahu & Chaudhari, 2013).

Coagulation followed by flocculation is important for suspended particles to settle. Coagulants help to overcome the forces leading to the stabilization of suspended particles. Subsequently, particles collide, and floc grows. Coagulation is one of the most employed methods for treating dyes and pigments released from the textile industry (Gao et al., 2007; Golob et al., 2005). Many researchers have been working on the improvement of the coagulation-flocculation process. After reviewing the chemistry, they have come up with some techniques for the enhanced performance of coagulants. Partial polymerization of regular coagulants produces a number of pre-polymerized aluminum solutions, referred to as poly-aluminum chlorides (PAC), poly-aluminum sulfates (PAS), and poly-aluminum chloro-sulfates (PACS) with variable degrees of polymerization. These pre-polymerized coagulants were found to perform better in lower dosages and at higher pH, temperature, and colloids range in comparison to regular coagulants (Zouboulis & Tzoupanos, 2010).

Poly-aluminum chloride (PAC) chemicals are a class of soluble aluminum products is which aluminum chloride is previously reacted with a base. The basicity is an important factor. In the water and wastewater treatment industries, PAC with 50% basicity is recommended (BM, 2008). The aim of the current study was to use PAC coagulant to decolorize both synthetic and real-world textile wastewater (RTW) containing reactive dyes.

3.3 Materials and methods

This research was performed to examine the dye removal efficiency of the synthesized PAC in an aqueous solution. The experiments were carried out at the Fibre and Polymer Research Division, Bangladesh Council of Scientific and Industrial Research (BCSIR). A series of batch studies were performed to optimize the different parameters to enhance the effectiveness of the PAC for wastewater treatment. The parameters include dosage effect, pH of the dye solution, shaking time or contact time, shaking speed, dye concentration, and settling time.

3.3.1 Wastewater sampling and characterization

This study collected textile effluent from sampling locations of Hemayetpur, Savar, District of Dhaka, Bangladesh. The sample was collected in previously acid-washed one-liter polythene bottles. The bottles were washed with 10% hydrochloric acid before sample collection. At the sampling point, the bottles were rinsed with effluents to be sampled. After collection, the samples were brought to the lab immediately. The sample was analyzed for parameters, including pH, electrical conductivity (EC), total suspended solids (TSS), dissolved oxygen (DO), turbidity, chemical oxygen demand (COD), biological oxygen demand (BOD), bicarbonate (HCO_3^-), chloride (Cl^-), fluoride (F^-), nitrate (NO_3^-), phosphate (PO_4^{3-}) and sulfate (SO_4^{2-}) (Baird et al., 2012). TSS of the effluent's was measured by the gravimetric method. COD was determined by the closed reflux method (HACH, DR3900, USA). BOD was determined by incubating the sample at 20 °C for 5 days followed by titration. Bicarbonate, chloride, and sulfate were determined by ion chromatography. The turbidity of each sample was measured by a turbidity meter (HACH, 2100Q, USA).

3.3.2. Preparation of Standard Solution

Navacron Navy SG dye was collected from a textile industry located in an industrial zone in Savar, Dhaka, Bangladesh. The standard solution of Navacron Navy dye was prepared to investigate the removal of dye after adding PAC. Firstly, 20 mg/L, 100 mL mother solution was prepared by adding 2 mg of dye in deionized water. After that 10 mL, 0 mg/L, 2 mg/L, 4 mg/L, 8 mg/L, and 16 mg/L solution was made from the mother solution to conduct the removal studies and standard curve (λ_{max} = 595 nm). UV–Visible Spectrometer (Perkin Elmer) was used to determine the standard curve and final concentration of dye after the addition of PAC.

3.3.3 Preparation of dye-containing textile wastewater

The dyeing process in the factory is continuous and a number of different reactive dyes are used in the factory. About 10 mg of Navacron Navy SG dye was added to 1000 mL (10 mg/L) of collected wastewater.

3.3.4. Experimental set-up for dye removal study

The dye removal study was investigated by a series of batch studies to identify the optimum conditions to treat both the aqueous solution and the dye-containing wastewater. The batch studies were carried out to observe the effects of dosage, contact time, shaking speed, pH, and optimum dye concentration for a particular PAC concentration. The dye solution was prepared by adding 10 mg of dye into 1000 mL of deionized water.

3.3.4.1 Effect of coagulant dosage

To examine the optimum dose, different amounts of PAC was taken keeping all other parameters constant. The optimum dosage was determined by adding 0 mg, 0.5 mg, 1.0 mg, 1.5, mg, 2.0 mg, 2.5 mg, 3.0 mg, 3.5 mg, and 4.0 mg of PAC to 50 mL, 10 mg/L dye solution in a 100 mL Erlenmeyer flask. The other parameters such as contact time, pH, shaking speed, dye concentration, and settling time were 15 min, 6.35, 200 revolutions per minute (rpm), 10 mg/L, and 20 min, respectively. The removal studies were carried out by using a UV-Visible Spectrophotometer (Perkin Elmer).

3.3.4.2 Effect of pH of the dye solution

The optimum pH was determined by conducting a series of batch studies at different pH conditions of the dye solution and by keeping other parameters constant. pH of the dye solution tested for the batch studies included 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0, and 8.5. Different pH values were adjusted by using 0.1 N NaOH and 0.1 N HCl. The dye concentration and volume used for the batch studies were 10 mg/L and 50 mL, respectively. 2.5 mg of PAC was added as a coagulant to the solution.

3.3.4.3 Effect of contact time and kinetic study

The kinetic study was performed by adding 2.5 mg of PAC to the 10 mg/L, 50 mL dye solution and by keeping the pH of the solution at 6.0. The optimum contact time was determined by shaking the dye solution with PAC for 1 min, 5 min, 10 min, 15 min, 20 min, and 25 min. The dye solutions were shaken by an orbital shaker. The shaking speed was set at 200 rpm.

3.3.4.4 Effect of shaking speed

The shaking speed was determined by using an orbital shaker. Different shaking speed was maintained to investigate the optimum shaking speed. The shaking speed tested was 0 rpm, 20 rpm, 50 rpm, 100 rpm, 150 rpm, and 200 rpm. 2.5 mg of PAC sample was added to the 10 mg/L, 50 mL dye solution. The pH and contact time were maintained at 6.0 and 20 min, respectively.

Figure 3.1 Shaking of aqueous solution with the help of Orbital Shaker.

Figure 3. 2 Shaking of wastewater sample with the help of Orbital Shaker.

3.3.4.5 Effect of Settling Time

After shaking with the help of an orbital shaker, the dye solution was allowed to settle down as sludge. Different times were considered to investigate the optimum settling time. The experimental settling time was 0 min, 5 min, 15 min, 25 min, 35 min, and 45 min. The 10 mg/L, 50 mL dye solution was added 2.5 mg of PAC sample, and the pH of the solution was maintained at 6.0. The contact time and shaking speed were 20 min and 150 rpm, respectively.

3.3.4.6 Determination of Coagulation Isotherm

To determine the coagulation isotherm, a standard solution and different concentrations of dye solution were prepared.

3.3.4.7 Preparation of Standard Solution

10 mg of Navacron Navy S-G dye was measured and added to 100 mL deionized water to make 100 mg/L mother solution. From the mother solution, 0 mg/L, 12 mg/L, 24 mg/L, 48 mg/L, and 96 mg/L solution was prepared as standard solutions.

3.3.4.8 Coagulation Kinetics

Coagulation kinetics was determined by adding 2.5 mg of PAC into 5 mg/L, 10 mg/L, 20 mg/L, 40 mg/L, and 60 mg/L dye solution. From these solutions, the solution from which the highest amount of dye was removed was considered the appropriate dye concentration for 2.5 mg of PAC. The final concentration of the dye solution after adding PAC was determined by UV–visible Spectrophotometer (Perkin Elmer).

3.3.4.9 Determination of Equilibrium Time

Coagulation equilibrium can be defined as a state of stable condition at which the process of coagulation almost ceases. The point after which no significant increase in coagulation occurs was taken as the equilibrium time of a coagulation process.

3.3.5 Statistical analysis

The results are presented as the mean ± SD (n = 3). The raw data was checked for homogeneity of variance. A one-way analysis of variance (ANOVA) was performed

followed by a Tukey's pairwise comparison test. All statistical analysis was performed on Minitab version 21. Significance was determined using p-values of 0.05.

3.4 Results and discussion

3.4.1 Characteristics of collected wastewater

Characteristics of the collected textile wastewater are given in **Table 3.1**. 100 mL of the dye containing wastewater sample was used in the coagulation experiment. The dye removal was measured at a maximum absorbance wavelength (λ_{max} = 595 nm).

Table 3.1 Characteristics of the collected textile wastewater sample

Test Parameter	Unit	Result
Electrical Conductivity (EC)	µs/Cm	18050
Biological Oxygen Demand (BOD)	mg/L	21.3
Dissolved Oxygen (DO)	mg/L	1.15
Turbidity	NTU	260
Total Suspended Solid (TDS)	mg/L	8800
Chemical Oxygen Demand (COD)	mg/L	6128
pH	-	12.02
Fluoride (F)	mg/L	7.63
Chloride (Cl^-)	mg/L	4817
Nitrate (NO_3^-)	mg/L	44.2
Phosphate (PO_4^-)	mg/L	-
Sulfate (SO_4^-)	mg/L	74.5

3.4.2 Effect of PAC dosage on Dye Removal

Coagulant dosage is a very important factor in the coagulation process. Batch studies were conducted to determine the optimum dose of the PAC. Different quantities of PAC (0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, and 4.0 mg) were used for determining the optimum dosage. The other factors (contact time, shaking speed, pH, and settling time) that affect the coagulation process were kept constant. Based on the PAC dosage study, the lowest dye concentration was obtained at 2.5 mg of PAC dosage, and at this stage, the concentration of dye solution was 1.14 mg/L, whose initial concentration was 10 mg/L (**Figure 3.5 (a)**). At the beginning of the coagulation process, the reaction was faster; thus, there is a sharp decline in the graph. After achieving the optimum PAC dosage, with the increase in the amount of PAC, the concentration of the dye solution was found to increase.

Beyond the optimum condition, the coagulant itself contributed to the solution turbidity (**Figure 3.5 (a)).**

The removal percentage of dye from the aqueous solution was the highest at 2.5 mg of PAC dosage and it was 88.64% (**Figure 3.5 (b)).** The control sample (0.0 mg of PAC) indicates that 18.23% dye was settled down automatically and with increasing the amount of PAC dosage, the removal percentages were increasing. After the optimum condition was achieved, the removal percentage of dye solution started decreasing with the additional load of PAC (**Figure 3.5 (b)).**

Figure 3.3. Prepared dye solution before addition of PAC.

Figure 3.4. Removal of dye at equilibrium condition after addition of PAC.

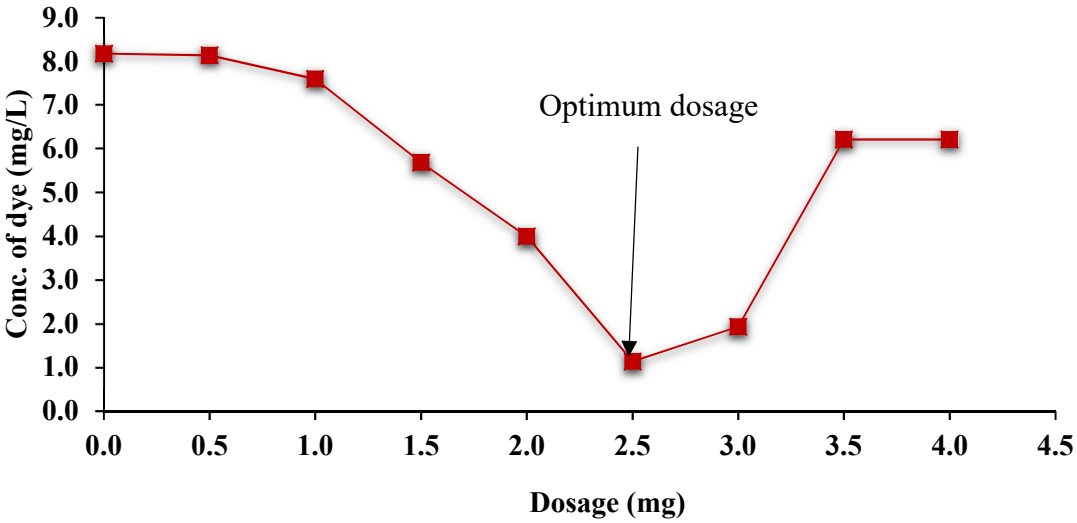

Figure 3.5(a). Effect of PAC dosage on dye (Navacron Navy S-G) removal by the application of PAC at 25 ± 2 ℃. Initial concentration of dye solution = 10 mg/L, Amount of dye solution = 50 mL, pH = 6.35 (unadjusted), Contact time = 20 min, Shaking speed = 200 rpm, and Settling time = 40 min.

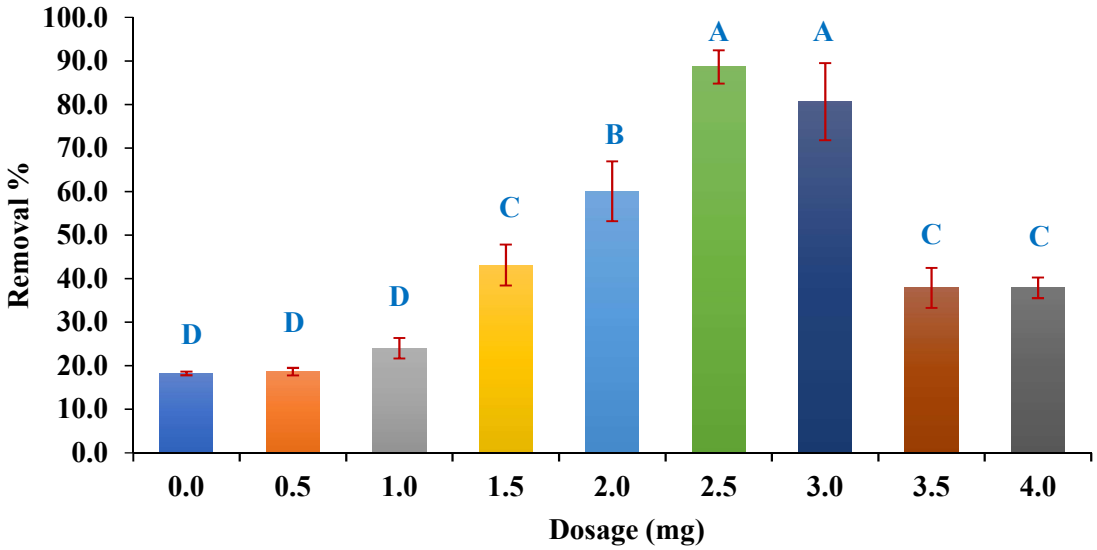

Figure 3.5(b). Dye removal percentage by the application of different PAC dosage at 25 ± 2 ℃. Initial concentration of dye solution = 10 mg/L, Amount of dye solution = 50 mL, pH = 6.35 (unadjusted), Contact time = 20 min, Shaking speed = 200 rpm, Settling time = 40 min. Differences were determined by a one-way ANOVA followed by Tukey's pairwise comparison ($p<0.05$). Different letters above the bars indicate the significance of differences between non-identical coagulant dosages.

3.4.3. Effect of pH on Dye Removal

pH is considered one of the significant factors for the treatment of wastewater containing dye. To investigate the optimum pH, a batch study was performed to examine

the optimum pH condition. Different pH values, namely 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0, and 8.5 were tested in the batch study. To study the optimum pH, other factors (coagulant dosage, contact time, settling time, shaking speed, and concentration of dye solution) related to the coagulation process were kept constant. Based on **Figure 3.6(a)**, it was apparent that the optimum pH condition for PAC was 6.0. In this condition, the dye concentration after the PAC treatment was the lowest and the concentration reduced from 10 mg/L to 1.63 mg/L. When the pH of the dye solution was adjusted to 3.0, the efficacy of PAC was reduced and removed a very little amount of dye from the solution. With the increase in pH values, the efficiency of the PAC was found to increase, and the optimum condition was achieved at pH 6.0 for the treatment of wastewater containing Navacron Navy S-G dye.

The removal percentage of dye was the highest when the pH of the solution was maintained at 6.0 and it was 83.70%. The removal percentage was the lowest at low pH (3.0). With the increase of the pH, the PAC became efficient, and it was found to remove the highest amount of dye when the pH of the solution was 6.0 (**Figure 3.6(b)**).

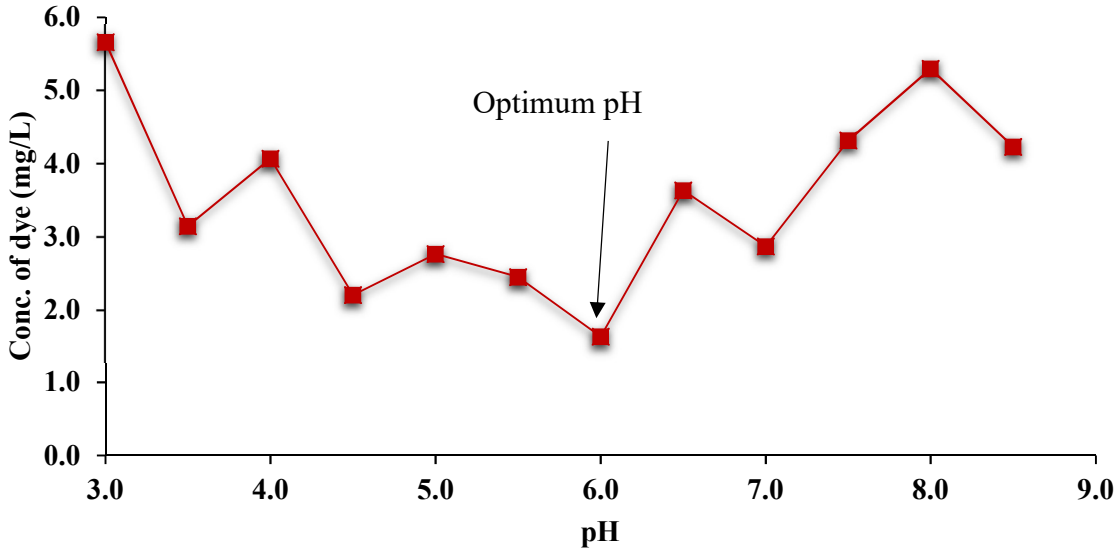

Figure 3.6(a). Effect of pH on dye (Navacron Navy S-G) removal by the application of PAC at 25 ± 2 °C. Initial concentration of dye solution = 10 mg/L, Amount of dye solution = 50 mL, PAC dosage = 2.5 mg, Contact time = 20 min, Shaking speed = 200 rpm, Settling time = 40 min.

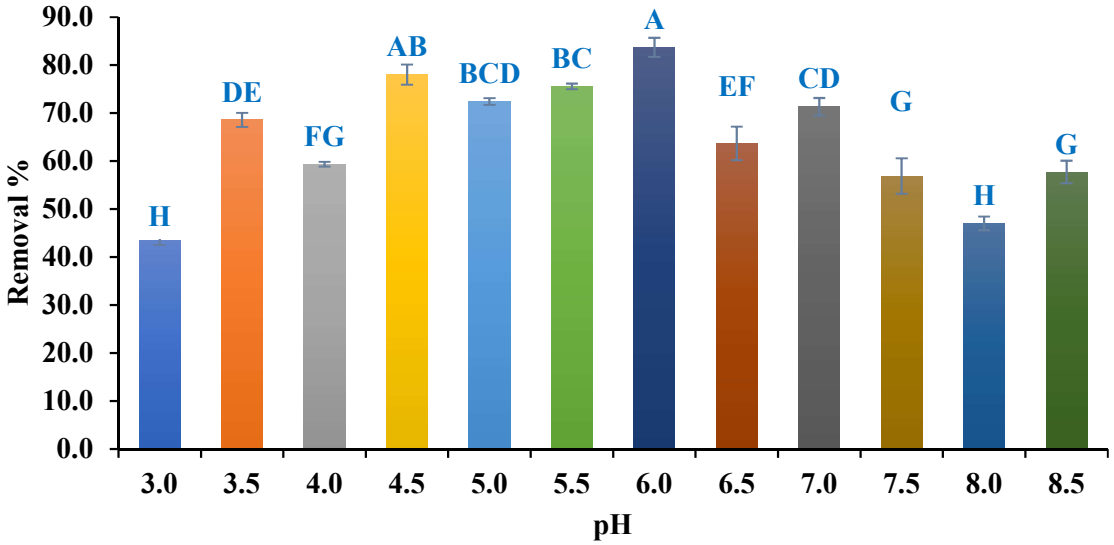

Figure 3.6(b). Dye removal percentage by the adjustment of different pH at 25 ± 2 ℃. Initial concentration of dye solution = 10 mg/L, Amount of dye solution = 50 mL, PAC dosage = 2.5 mg, Contact time = 20 min, Shaking speed = 200 rpm, Settling time = 40 min. Differences were determined by one-way ANOVA followed by Tukey's pairwise comparison ($p<0.05$). Different letters above the bar indicate the significance of differences between distinct pH of aqueous dye solution.

3.4.4. Effect of contact time on dye removal

Contact time between coagulant and dye solution is a very important factor in the coagulation process. To examine the optimum contact time for PAC and dye solution, a batch study was performed where different contact time (1, 5, 10, 15, 20, and 25 min) was maintained for the investigation of optimum contact time. The other factors (coagulant dosage, pH, settling time, shaking speed, and concentration of dye solution) in the coagulation process were kept constant for determining the optimum contact time. From **Figure 3.7 (a)**, the lowest concentration of dye solution was obtained when the contact time between PAC and dye solution was 20 min and the concentration was reduced from 10 mg/L to 1.2 mg/L. When the contact time was 1 min, the concentration of dye was reduced from 10 mg/L to 3.35 mg/L and when the contact time was 5 min, the final concentration of dye solution was 3.08 mg/L. The PAC removed varied amount of dye because the contact time was different in each case.

When the contact time between the PAC and dye solution was for 20 min, the highest removal percentage of dye was observed, and it was 87.37%. When the contact

time was for 1 min and 5 min, the PAC removed 66.5% and 69.19% dye from the dye solution, respectively. For the contact time of 10, 15, and 25 min, the PAC removed the approximately equal amount of dye compared to 20 min contact time (**Figure 3.7(b)**).

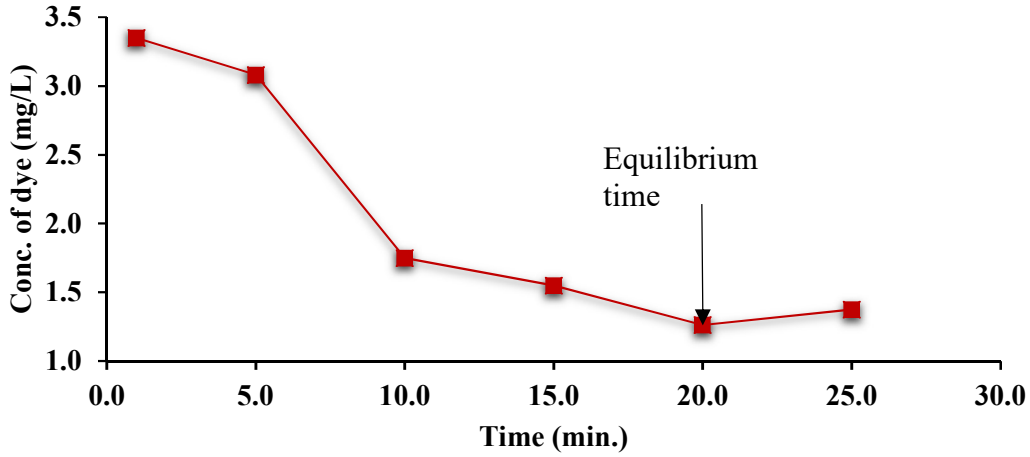

Figure 3.7 (a). Effect of contact time on dye (Navacron Navy S-G) removal by the application of PAC at 25 ± 2 ℃. Initial concentration of dye solution = 10 mg/L, Amount of dye solution = 50 mL, PAC dosage = 2.5 mg, pH = 6.0, Shaking speed = 200 rpm, Settling time = 40 min.

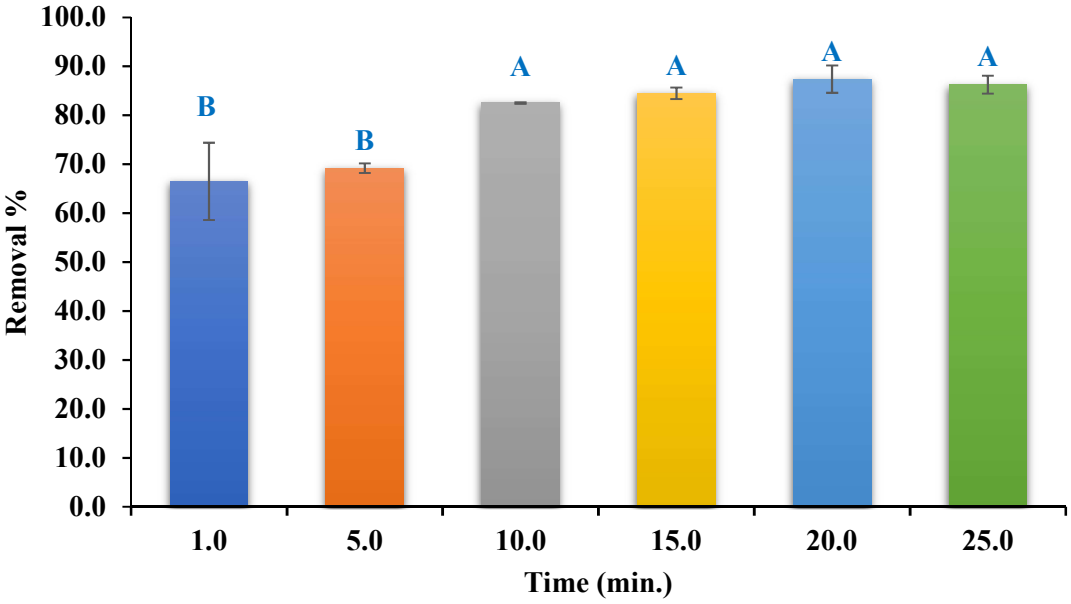

Figure 3.7 (b). Dye removal percentage by contact time at 25 ± 2 ℃. Initial concentration of dye solution = 10 mg/L, Amount of dye solution = 50 mL, PAC dosage = 2.5 mg, pH = 6.0, Shaking speed = 200 rpm, Settling time = 40 min. Differences were determined by

one-way ANOVA followed by Tukey's pairwise comparison ($p<0.05$). Different letters above the bars indicate the significance of differences between different contact times.

3.4.5. Effect of shaking speed on dye removal

In the coagulation process, shaking speed is a significant factor. Without adequate shaking speed, it is not possible to remove dyes as per the coagulant efficiency. A batch study was done to identify the optimum shaking speed. The ideal shaking speed was determined by testing out several shaking speed (0, 20, 50, 100, 150, and 200 rpm). The other factors (coagulant dosage, pH, settling time, contact time, and concentration of dye solution) that affect the coagulation process were kept constant. The lowest concentration of dye was seen when the shaking speed was maintained at 150 rpm and the lowest concentration of dye was 0.9 mg/L where the initial concentration was 10 mg/L (**Figure 3.8(a)**). At the initial stage of this study, when the shaking speed was kept at 0, 20, and 50, a small amount of dye was removed by the PAC. When the shaking speed was maintained at 200 rpm, it removed the same amount as it did at 150 rpm. The low shaking speed was not enough for the PAC to reduce the mass transfer resistance for approaching the dye molecules. As a result, a very small amount of dye was removed at that stage. When the shaking speed was beyond the optimum condition, the amount of dye removal was the same as was obtained for the optimum level (**Figure 3.8 (a)**).

The removal percentage of dye was the greatest when the shaking speed was maintained at 150 rpm and the removal percentage was 90.99. When the shaking speed was 0, 20, 50, and 100 rpm, the dye removal percent was 27.47, 35.98, 42.25, and 76.68, respectively. At the shaking speed of 200 rpm, the removal percentage of dye was approximately the same (90.90%) as it was at 150 rpm (**Figure 3.8(b)**).

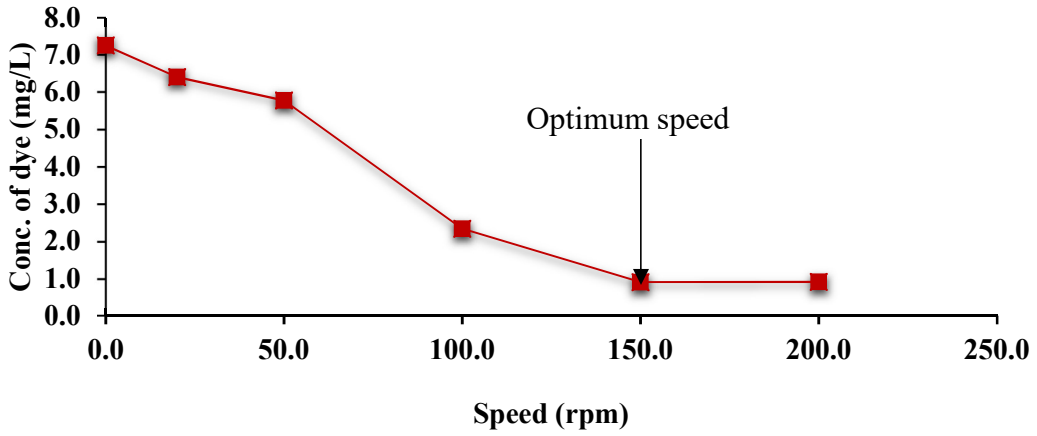

Figure 3.8 (a). Effect of shaking speed on dye (Navacron Navy S-G) removal by the application of PAC at 25 ± 2 ℃. Initial concentration of dye solution = 10 mg/L, Amount of dye solution = 50 mL, PAC dosage = 2.5 mg, pH = 6.0, Contact time = 20 min, Settling time = 40 min.

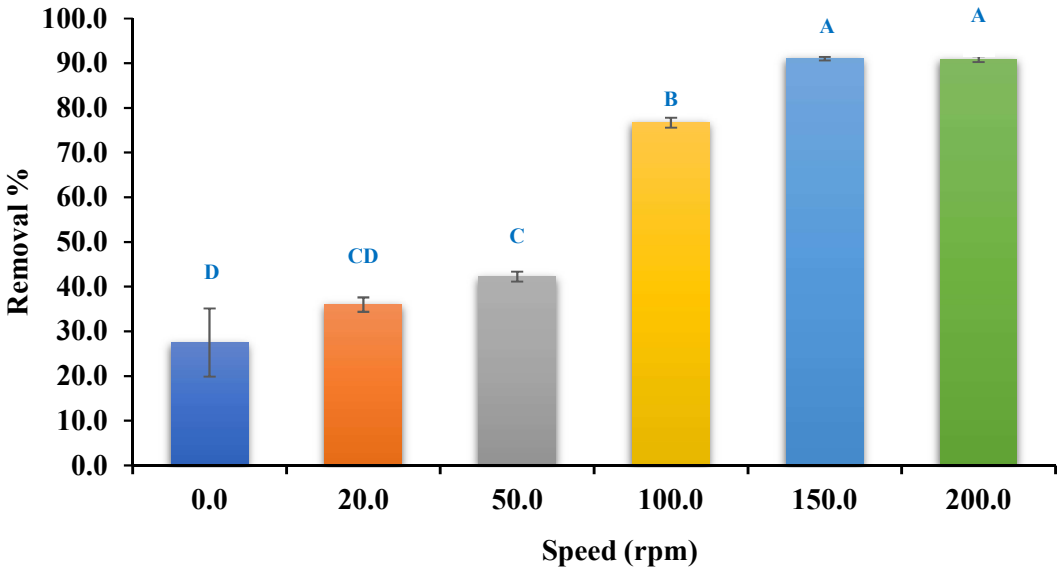

Figure 3.8 (b). Dye removal percentage by shaking speed at 25 ± 2 ℃. Initial concentration of dye solution = 10 mg/L, Amount of dye solution = 50 mL, PAC dosage = 2.5 mg, pH = 6.0, Contact time = 20 min, Settling time = 40 min. Differences were determined by one-way ANOVA followed by Tukey's pairwise comparison ($p<0.05$). Different letters above the bars indicate the significance of differences between distinct shaking speeds.

3.4.6 Effect of settling time on dye removal

Settling time is also an important factor in the coagulation process because the sludge produced in coagulation take time to settle down. If the sludge does not get enough time to settle down, they remain in the suspended condition in the solution which results an incomplete water treatment process. To examine the ideal settling time, different settling times (0, 5, 15, 25, 34, and 45 min) were maintained and the other factors (coagulant dosage, pH, shaking speed, contact time, and concentration of dye solution) that influence the coagulation process were kept constant. From **Figure 3.9(a)**, the lowest concentration of dye (1.2 mg/L) was detected when the settling time was maintained for 35 min. At the settling time of 45 min, the amount of settled down sludge was approximately the same as the 35 min settling time. At the beginning of the batch study, when the settling time was maintained for 0 min, the quantity of suspended sludge was high and thus the removal of dye from the solution was low. With increasing settling time, more sludge was settled down and the equilibrium settling time was found at 35 min settling time (**Figure 3.9(a)**). The sharp decline of dye quantity indicates that the sludge settled down at a faster rate. From the conducted experiment, different amounts of sludge settled down at a different time, and with increasing time, the amount of sludge was increased and concomitantly more dye was removed from the aqueous solution. After achieving the equilibrium condition, though the settling time was extended, the amount of removed dye was the same (**Figure 3.9 (a)**).

The removal percentage of dye was 87.68 and 87.97% when the settling time was maintained 35 and 45 min, respectively. The lowest amount of dye removal (55.94%) was identified when the maintained settling time was 0 min (**Figure 3.9 (b)**).

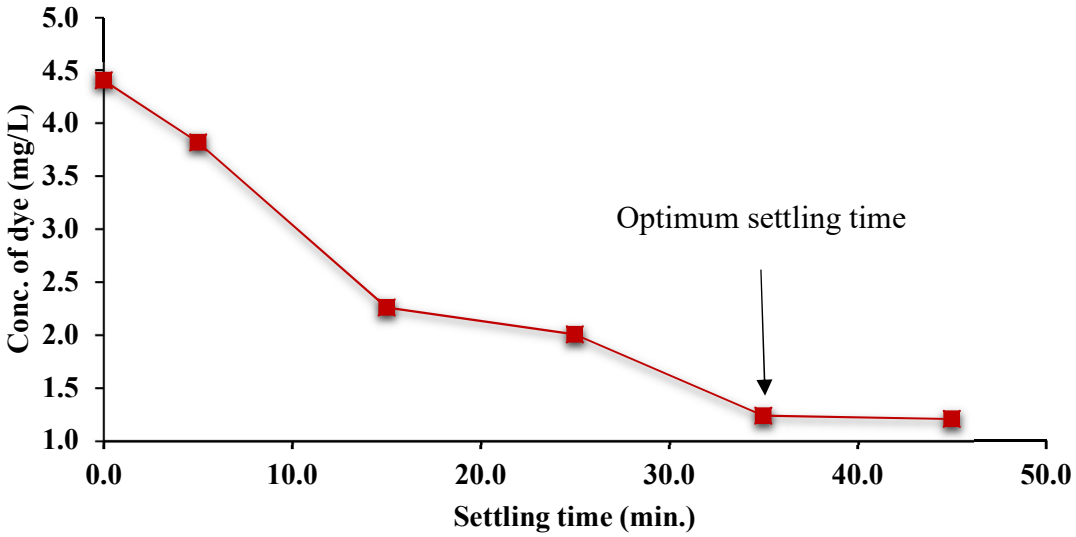

Figure 3.9 (a). Effect of settling time on dye (Navacron Navy S-G) removal by the application of PAC at 25 ± 2 ℃. Initial concentration of dye solution = 10 mg/L, Amount of dye solution = 50 mL, PAC dosage = 2.5 mg, pH = 6.0, Contact time = 20 min, Shaking speed = 150 rpm.

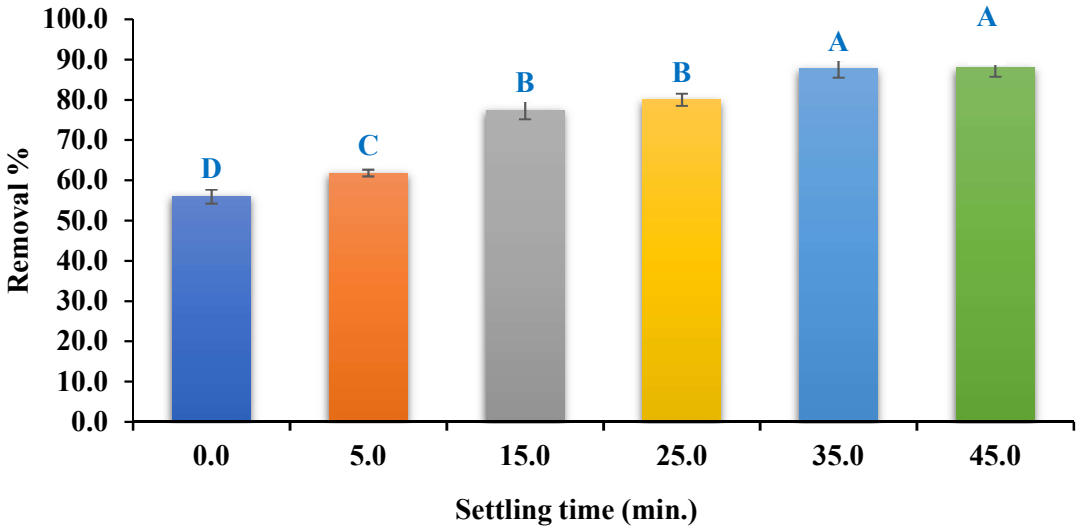

Figure 3.9 (b). Dye removal percentage by settling time at 25 ± 2 ℃. Initial concentration of dye solution = 10 mg/L, Amount of dye solution = 50 mL, PAC dosage = 2.5 mg, pH = 6.0, Shaking speed = 150 rpm. Differences were determined by one-way ANOVA followed by Tukey's pairwise comparison ($p<0.05$). Different letters above the bars indicate the significance of differences between different settling times.

3.4.7. Effect of Dye Concentration on Coagulation Process

The concentration of dye is a fundamental factor to determine the amount of coagulant needed for the treatment of wastewater. Different concentration of dye solution cannot be treated equally by a particular amount of PAC. To determine the optimum dye solution for a particular amount of PAC, different concentration of aqueous dye solution (5, 10, 20, 40, and 60 mg/L) was taken. The other factors were kept constant that have influence on coagulation process. 2.5 mg of PAC was taken for the treatment of different dye solutions containing different concentrations. From the graph (**Figure 3.10(a)**), the highest amount of dye removed from 10 mg/L dye solution and the later, with the increase of dye solution, the removal of dye from the solution was decreased. When the PAC applied to 5 mg/L dye solution, the final concentration was reduced to 3.4 mg/L. In this case, the amount of PAC exceeded the optimum limit for 5 mg/L dye solution, thus the PAC itself created turbidity. The lowest concentration of dye was detected in treated water when 2.5 mg of PAC was applied to the 10 mg/L of dye solution and the final concentration was 0.6 mg/L. When the same amount of PAC was added to the 20, 40, 60 mg/L dye solution, the removal of dye from was reduced gradually. The lowest amount of dye was removed from 60 mg/L dye solution, where the final concentration was detected 54.5 mg/L (**Figure 3.10(a)**).

The removal percentage of dye from different dye solution was different. From the 5 mg/L dye solution, the removal percentage was 24.41%. The removal percentage was 94.11% when the dye solution was 10 mg/L before the treatment. For the solution of 20, 40, and 60 mg/L, the removal of dye was 21.38, 11.77 and 9.16%, respectively (**Figure 3.10(b)**).

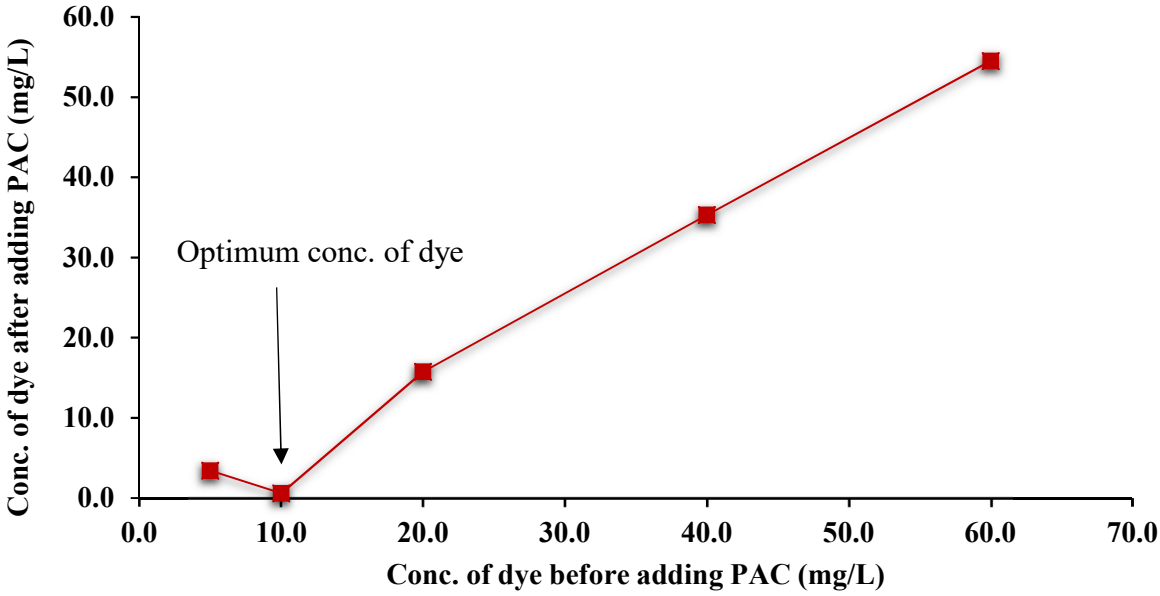

Figure 3.10(a). Effect of dye (Navacron Navy S-G) concentration on coagulation process by the application of PAC at 25 ± 2 ℃. Amount of dye solution = 50 mL, PAC dosage = 2.5 mg, pH = 6.0, Contact time = 20 min, Shaking speed = 150 rpm, Settling time = 35 min.

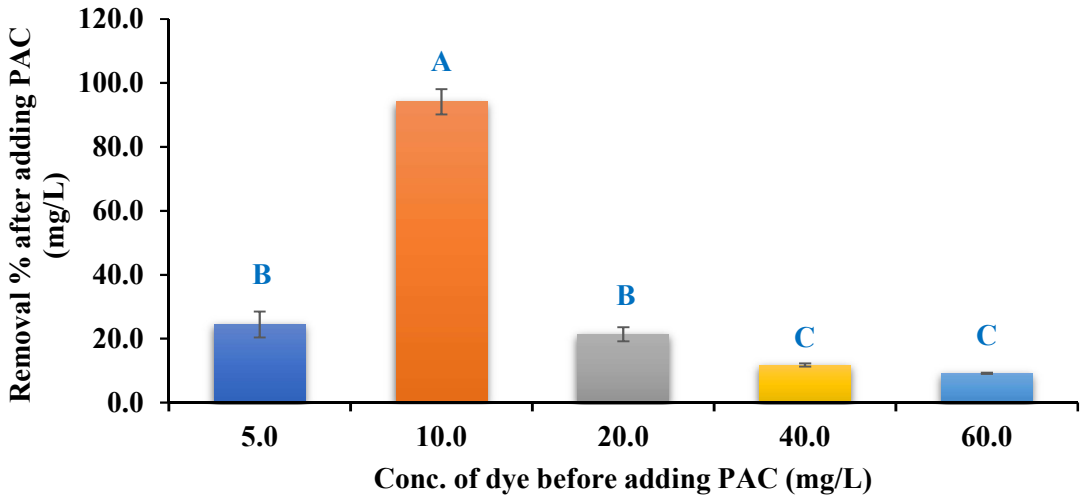

Figure 3.10(b). Dye removal percentage from different concentration of dye solution at 25 ± 2 ℃. Amount of dye solution = 50 mL, PAC dosage = 2.5 mg, pH = 6.0, Contact time = 20 min. Shaking speed = 150 rpm, Settling time = 35 min. Differences were determined by one-way ANOVA followed by Tukey's pairwise comparison ($p<0.05$). Different letters above the bar indicate the significance of differences between different concentrations of dye solution.

3.4.8 Coagulation with dye containing real textile wastewater

The optimum reaction conditions were determined for synthetic wastewater i.e; initial concentration, solution pH, contact time, coagulant dosage, shaking speed and sedimentation time were considered for dye-containing real textile wastewater.

The reduction of dye by the PAC coagulants showed the variation as the dye reduction obtained with synthetic wastewater which was 91.3%. The coagulation studies were carried out with 100 mL of real textile dye containing wastewater at pH = 6 and 25°C. The percent dye reductions are shown in **Fig 3.11.** In contrast to the observation made for the synthetic wastewater, PAC coagulant showed comparatively less dye reduction at the dosage of 2.5 mg and showed the reduction of 73% dye present in the wastewater. The experiment with real textile wastewater showed lower dye removal efficiencies, most likely due to the probable presence of a considerable amount of pollutants and dyes in the wastewater sample. Based on the dye reduction performance, PAC coagulant at the 2.5 mg dosage is the most effective coagulation conditions to treat the real textile wastewater containing reactive dye.

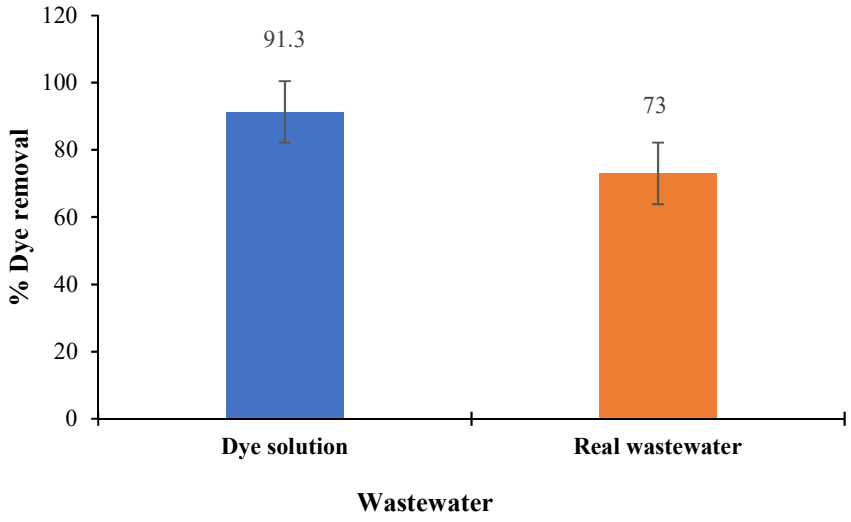

Fig 3.11 Dye removal percentage both from dye solution and dye containing wastewater at 25 ± 2 ℃. Amount of dye solution and wastewater= 50 mL, PAC dosage = 2.5 mg, pH = 6.0, Contact time = 20 min. Shaking speed = 150 rpm, Settling time = 35 min.

3.5 Conclusions

The presence of dye effluents originating from textile industry is a major environmental problem. In this study the coagulation behavior of Navacron Navy SG dye from synthetic wastewater onto the PAC was examined using initial concentration, solution pH, contact time, coagulant dosage, shaking speed and sedimentation time. Results revealed that applied process of coagulation achieved a considerable amount of decolorization of reactive dye from aqueous solution and real textile wastewater was 91.3% and 73.0% respectively. Based on the dye reduction performance, it can be concluded that the PAC coagulant at the 2.5 mg dosage is the most effective coagulation condition to treat the aqueous solution and real textile wastewater containing anionic dye. The removal efficiency is higher in the aqueous solution of dye than in real wastewater at the same concentration under the same condition.

3.6 References

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Chapter-4

REMOVAL OF TURBIDITY OF TEXTILE WASTEWATER USING SCRAP DERIVED POLYALUMINUM CHLORIDE

4. Removal of Turbidity of Textile Wastewater Using Scrap-Derived Polyaluminum Chloride

4.1. Abstract

The textile industry generates huge quantities of wastewater containing suspended solids and turbidity. The untreated textile waters have been polluting both terrestrial and aquatic ecosystems over the years. Humans are also at the receiving end of these pollution events. Therefore, treating these pollutants-loaded wastewater is imperative considering the hazardous nature of the toxicants. Polyaluminum chloride (PAC) has gained attention as a coagulant for the treatment of wastewater because of its cost-effectiveness and compatibility in wider conditions. In this study, PAC was synthesized from scrap aluminum and analyzed for its aluminum content, basicity, and charge neutralization capacity. The coagulant was further characterized using FTIR spectroscopy, scanning electron microscopy (SEM) with Energy Dispersive X-ray (EDX) and X-ray diffraction (XRD) analysis, Wavelength Dispersive X-ray Fluorescence (EDXRF) and Thermogravimetric analysis (TGA). The study was an attempt to assess the level of pollution because of textile wastewater. The study also assessed the coagulant efficiency of PAC and alum (aluminum sulfate) for treating textile wastewater. A series of coagulation tests were conducted to optimize the coagulant dose, pH, and operating conditions such as contact time, shaking speed, and settling time. The optimum dose was determined for each of them that give less turbidity and a higher removal percentage. The optimum coagulant dose and pH were found to be 2.5 mg and 6.0 for PAC and 5 mg and 7.0 for alum, respectively. Results revealed that at optimum conditions, PAC removed 97 to 99% of turbidity and alum removed 94 to 97% of turbidity. Even though the coagulants demonstrated more or less similar performance with respect to turbidity removal from textile wastewater, scrap-aluminum-derived PAC performed at a lower dosage. Therefore, scrap-derived PAC might be a good alternative to alum for textile wastewater treatment.

4.2. Introduction

The activities of different industries cause pollution to different niches of the environment (Singh et al., 2020, Dil et al., 2016). The textile industry is one of the booming industries which is polluting the environment through discharging untreated effluents. The

industry requires a huge amount of water and a wide variety of eight thousand chemicals (Saravanan et al., 2016). The effluents the textile industry release contain an array of toxic substances stemming from activities such as dyeing and finishing processes. As a result, the effluents need to be treated to ensure compliance with the local standards set by the Department of Environment, Bangladesh (Gasmi A et al., 2022).

Colloids present in wastewater are tiny particles and cannot be settled because of their light weight. These tiny particles are responsible for turbidity. The colloidal particles have light scattering properties which give rise to the turbidity phenomenon. Water containing excessive colloidal particles becomes very cloudy. The cloudiness of water is an aesthetic problem (Šćiban et al., 2021). Turbidity is measured by an SI unit Nephelometric Turbidity Units (NTU). Turbidity or the high presence of colloidal particles may stem from different physical, chemical, and biological factors (Andrianova & Prakash, 2014). Metals and organic compounds of synthetic origin are sometimes responsible for turbidity. When these happen, turbidity may be a significant source of diseases for humans and other organisms, both terrestrial and aquatic. Turbidity may trigger the growth of algae as it hinders light into deep waters (de Oliveira Cardoso Nascimento et al., 2021). The suspended particles causing turbidity may also enhance the temperature of the water by dint of its ability to absorb heat. Considering all the facts, it is essential that turbidity be removed from wastewater for better-quality water for different purposes (Januário et al., 2021).

The removal of turbidity from wastewater can be advantageous as it is likely to solve a number of problems associated with turbidity. Various coagulants of organic and inorganic types are able to remove turbidity. The level of turbidity indicates the efficiency of a treatment plant (Mohammed & Shakir, 2018). Removal of turbidity is vitally important because of its potentially hazardous nature. A number of treatment processes such as screening, pre-sedimentation, coagulation-flocculation, and filtration are available for the removal of suspended particles causing turbidity (Mohammed & Shakir, 2018).

Among the various methods, coagulation followed by flocculation is the most widely used. The chemistry of coagulation involves the addition of an oppositely charged ion which neutralizes the charges of colloidal particles. Coagulants cause the double layer

to compress leading to charge neutralization of the colloidal particles (Putra, 2020). When coagulants are added, they undergo hydrolysis. The positive charges form aggregates. The aggregates interact with each other, and the dissolved and suspended particles and flocs develop. Eventually, precipitates are formed, and they settle. The precipitates may be taken away by sedimentation or filtration (Ahmad, 2016). The ability of a coagulant to remove impurities depends on a number of factors, including water properties (e.g., pH, color, turbidity, temperature, etc.) and the dosage of coagulants.

Conventional coagulants such as aluminum sulfate, ferric sulfate, ferric chloride, etc. are generally used in water and wastewater treatment plants (Yang et al., 2016). In Bangladesh, aluminum salts are mainly used as coagulants in wastewater treatment plants, including textile industry. Aluminum salts are used for their cost-effectiveness and accessibility. Until the recent past, the application of alum worked quite well. However, as the water related guidelines became stringent, the utility of alum has gone down (Pathak et al., 2015). Of late, the use of PAC as coagulant has gained popularity. Polyaluminum chloride with formula $Al_2(OH)_nCl_{6-n}$ is a polymeric coagulant, which is very effective in eliminating turbidity from water at small doses. Moreover, they operate under varied pH ranges (Bae et al., 2007).

In this study, PAC was used for the treatment of real-world textile wastewater. The conventional coagulant alum was also used for comparison purposes. This study was an attempt to remove turbidity of wastewater under different experimental conditions. Two series of coagulation experiments were carried out to optimize the parameters for both PAC and alum. Subsequently, the performance of the two coagulants was assessed for comparison purposes. Five parameters were tested for determining their optimum conditions: coagulant dose, pH, contact time, shaking speed and sedimentation time.

4.3. Materials and methods

The experiments were carried out at the Fibre and Polymer Research Division, BCSIR Laboratories, Dhaka, Bangladesh Council of Scientific and Industrial Research (BCSIR) to examine the turbidity removal efficiency by the scrap-derived PAC.

4.3.1. Chemicals and reagents

The chemicals and reagents used in this study were of analytical grade. Hydrochloric acid (35.9% purity) and 0.1 M solution of sodium hydroxide (>98% purity) was collected from Merck, Germany. Deionized (DI) water containing no higher than 0.5 µS/cm was used for preparing all the solutions.

4.3.2. PAC synthesis and characterization

This research was conducted to synthesize PAC from aluminum scraps and analyzed for its aluminum content, basicity, and charge neutralization capacity. Scrap derived PAC was analyzed for determining its aluminum content, basicity, and charge neutralization capacity. PAC was further characterized by using state-of-the-art technologies such as FTIR spectroscopy, scanning electron microscopy (SEM) with Energy Dispersive X-ray (EDX), and X-ray diffraction (XRD) analysis, Wavelength Dispersive X-ray Fluorescence (EDXRF) and Thermogravimetric analysis (TGA).

4.3.3. Wastewater sampling and characterization

The study was performed using real-world textile wastewater collected from a textile industry located in Hemayetpur, Savar, Bangladesh. The sample was collected in a one-liter plastic bottle. Prior to sampling, every bottle was rinsed with 10% hydrochloric acid followed by double distilled water. At the sampling point, the bottles were first rinsed with wastewater to be sampled. The samples were brought to the laboratory immediately and some parameters were measured instantaneously using different meters. **Table 4.1** presents the characteristics of wastewater sample determined following different standard methods (AWWA, APHA,1998). Some major parameters of the textile wastewater were determined including pH, dissolved oxygen (DO), electrical conductivity (EC), total suspended solid (TSS), chemical oxygen demand (COD), biological oxygen demand (BOD), turbidity, bicarbonate (HCO_3^-), chloride (Cl^-), fluoride (F^-), nitrate (NO_3^-), phosphate (PO_4^{3-}), and sulfates (SO_4^{2-}). The gravimetric method was used for measurement of total suspended solids. For effluent, 5 days BOD was also determined by incubation followed by titration. COD was also estimated by the closed reflux method (HACH, DR3900, USA). Bicarbonate, chloride, fluoride, nitrate, phosphates, and sulfates were determined by ion chromatography. The turbidity of the sample was measured by a

turbidity meter (HACH, 2100Q, USA). The analytical results of the wastewater sample were then assessed following the norms prescribed under EPA standards.

Table 4.1. Characteristics of the real textile wastewater sample.

Test Parameter	Unit	Result
Electrical Conductivity (EC)	µS/cm	18050
Biological Oxygen Demand (BOD)	mg/L	21.3
Dissolve Oxygen (DO)	mg/L	1.15
Turbidity	NTU	260
Total Suspended Solid (TDS)	mg/L	8800
Chemical Oxygen Demand (COD)	mg/L	6128
pH	-	12.02
Fluoride (F^-)	mg/L	7.63
Chloride (Cl^-)	mg/L	4817
Nitrate (NO_3^-)	mg/L	44.2
Phosphate (PO_4^-)	mg/L	-
Sulfate (SO_4^{2-})	mg/L	74.5

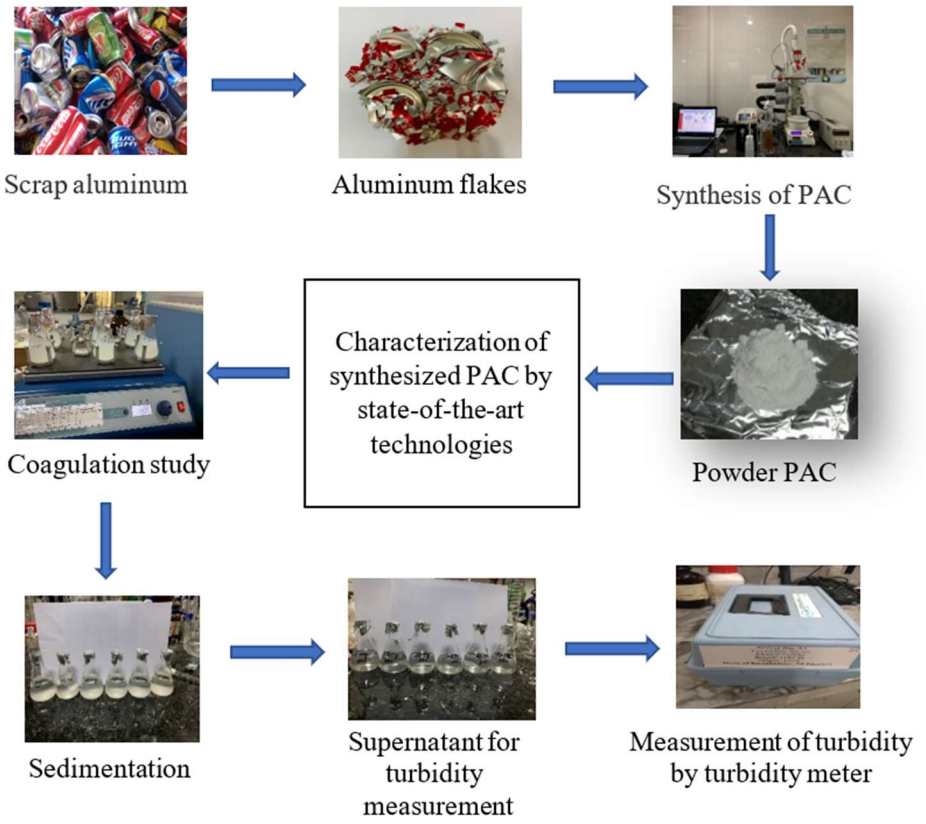

Figure 4.1. Turbidity removal experiment set-up.

4.3.4. Coagulation study with both synthesized PAC and alum

A series of batch studies were performed to optimize the different parameters to enhance the effectiveness of the PAC for wastewater treatment. For adjusting pH of wastewater sample, 0.1 M solution of hydrochloric acid and sodium hydroxide were used with a pH meter (HACH, PH31, USA)

Figure 4.1 presents the turbidity removal experiment set up by both PAC and alum. The collected sample was treated with PAC and alum coagulants. The optimized parameters include effect of dose (1-40 mg), pH (3-8) of sample solution, contact time (1-25 min), shaking speed (0-200 rpm) and settling time (0-35 min). An orbital shaker (SHO-2D, Korea) was employed to ascertain the optimum condition for all the variables. For batch studies, original pH (12.02) of the wastewater sample was used. At first, a certain amount of both coagulants was added to the 100 mL of wastewater in a beaker and mixed with a magnetic stirrer at 150 rpm for 20 min. The contents were then allowed to settle for 35 min. The batch studies were conducted at room temperature (25±2 ℃). About 50 mL

sample was withdrawn from 1.0 cm below the surface of the test sample for turbidity measurement and expressed in nephelometric turbidity unit (NTU). The optimal dosage giving lowest turbidity was then determined for each coagulant. **Figure 4.2** presents the steps of the chemical coagulation process. All the analyses were performed in triplicates and the mean values were reported. Finally, the reaction kinetics was determined for the turbidity removal at the optimum conditions. Experimental characteristics for the coagulation experiments in this research were summarized in **Table 4.2.** The efficiency of turbidity removal, R% was computed using the following formula:

$$R\% = \frac{C_0 - C}{C_0} \times 100$$

where,

Co is the initial turbidity, NTU

C is the final turbidity, NTU

Table 4.2. Experimental characteristics for coagulation experiments conducted.

Characteristics	**Description**
Coagulants	PAC and Alum
Coagulant dose range	1 to 40 mg
pH range	3 to 8 (initial pH=12.02)
Initial turbidity	260 NTU
Shaking speed	0-200 rpm
Contact time	1-25 min
Settling time	0-35 min
Temperature	Room temperature (25 ± 2 ℃)

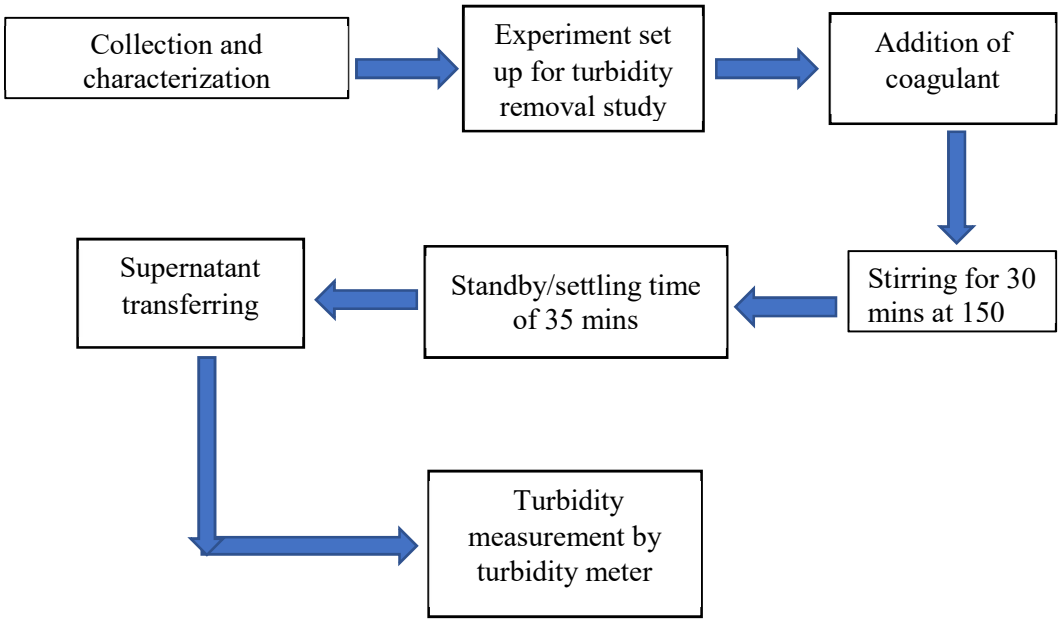

Figure 4.2. Steps of chemical coagulation process.

4.3.5. Statistical analysis

The results are presented as the mean ± SD (n = 3). The raw data was checked for normality and homogeneity of variance. A one-way analysis of variance (ANOVA) was performed using the General Linear Model, followed by a Tukey's pairwise comparison test. All statistical analysis was performed on Minitab version 21. Significance was determined based on p-values 0.05.

4.4. Results and discussion

After synthesis and characterization, PAC coagulant was used in batch studies to assess its efficacy as coagulant in water treatment processes. **Table 4.1** shows a very high level of turbidity in collected textile wastewater sample. Coagulation-flocculation studies depend on several factors. Coagulant and pH were the main variables optimized in the coagulation–flocculation studies. The operational conditions such as contact time, shaking speed, and settling time were also optimized. In this study, orbital shaker was used to optimize five variables in the following sequence: coagulant dose, pH, contact time, shaking speed and settling time. These variables were optimized for both coagulants (PAC and alum). Optimization of these variables was done employing "changing one factor at a

time" strategy. During batch studies, a single factor was varied while the rest of the factors were kept constant at a specific set of conditions. The initial pH of the collected sample was 12.02.

4.4.1. Optimized turbidity removal efficiency

4.4.1.1. Effect of coagulant dosage on turbidity removal

Dosage is a very important parameter for assessing the performance of a coagulant in coagulation-flocculation processes. Underdose or overdose of coagulants result in the poor performance in coagulation and flocculation (Tan & Noor, 2009). The optimum dosage of a coagulant can be determined from an experiment; this is a dose beyond which there will be no significant increase in removal efficiency with further addition of the coagulant (Aziz et al., 2011). Each type of coagulant has its own optimal dosage range. The effects of increasing dosage of coagulants on the wastewater sample were determined. For this purpose, batch studies were performed to determine the optimum dosage of both PAC and alum coagulants. **Figure 4.3(a)** shows optimum dosage of PAC and alum, respectively. Different quantities of PAC and alum (0, 1, 2.5, 5, 10, 20, and 40 mg) were used for determining the optimum dosage. The other factors (pH, contact time, shaking speed, and settling time) that affect the coagulation process were kept constant. Based on the coagulant dosage study, the lowest turbidity was obtained at 2.5 mg of PAC dosage and the turbidity of the treated solution was 2.5 NTU. On the other hand, 6.93 NTU was obtained by applying 5 mg alum dosage whose initial turbidity was 260 NTU (**Figure 4.3(a)**). The turbidity removal efficiency was found to increase with an increase in PAC and alum dosage until reaching the optimum dosage. The positive charge of the coagulants became more pronounced as dosage was increased, which resulted in an electrostatic repulsion between particles. PAC is known to possess a good structure and higher charge density. As a result, dosage requirements and sludge production is less for PAC coagulant (Zainol et al., 2011). Interestingly, the turbidity removal was found to increase up to a certain point and then decrease. This phenomenon could be attributed to the restabilization of colloidal particulates at higher dosage of the coagulant in excess of the optimum value (Daryabeigi & Hoveidi, 2015).

Figure 4.3(a)) shows the decreased turbidity with an increase in the dosage of both types of coagulant. At the beginning of the coagulation process, the reaction was faster,

thus there is a sharp decline in the graph. Beyond the optimum condition, the coagulants themselves contributed to the solution turbidity.

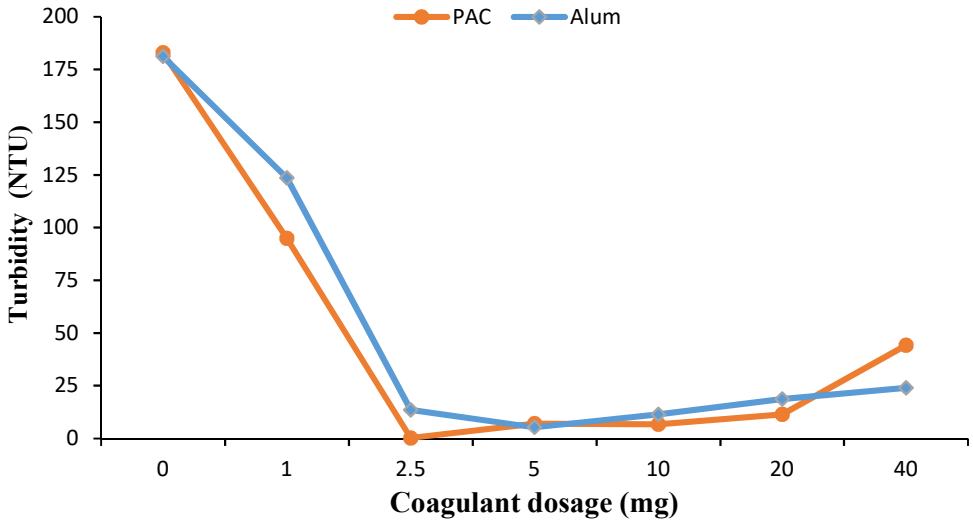

Figure 4.3(a). Effect of coagulant dosage on the removal of turbidity at pH = 12.02 (initial) with 200 rpm shaking speed for 20 min and 40 min settling time at 25 ± 2 °C.

It is clear from Figure **4.3(b)** that the removal percentage of turbidity from the wastewater was the highest at 2.5 mg of PAC dosage (removal was 99.09%) and at 5 mg of Alum dosage (removal was 97.33%). These two treatments were found to be significantly different from the rest of the treatments (one-way ANOVA; $p<0.05$). The lowest removal was found when no coagulants were applied to the wastewater sample. In a similar study by Sinha et al. (2004), the average turbidity removal was 95.30% by PAC and 92.1% by alum. The control sample (0.0 mg of PAC and alum) indicates that 29.61% and 27.74% particulate suspended material settled down automatically and with increasing amount of both coagulant dosages, the removal percentages were increasing. After the optimum condition was achieved, the removal percentage of turbidity started decreasing with the additional load of both coagulants (**Figure 4.3(b)**). Results indicated that turbidity removal efficiency was varied by pH, coagulant dosage and initial turbidity of water.

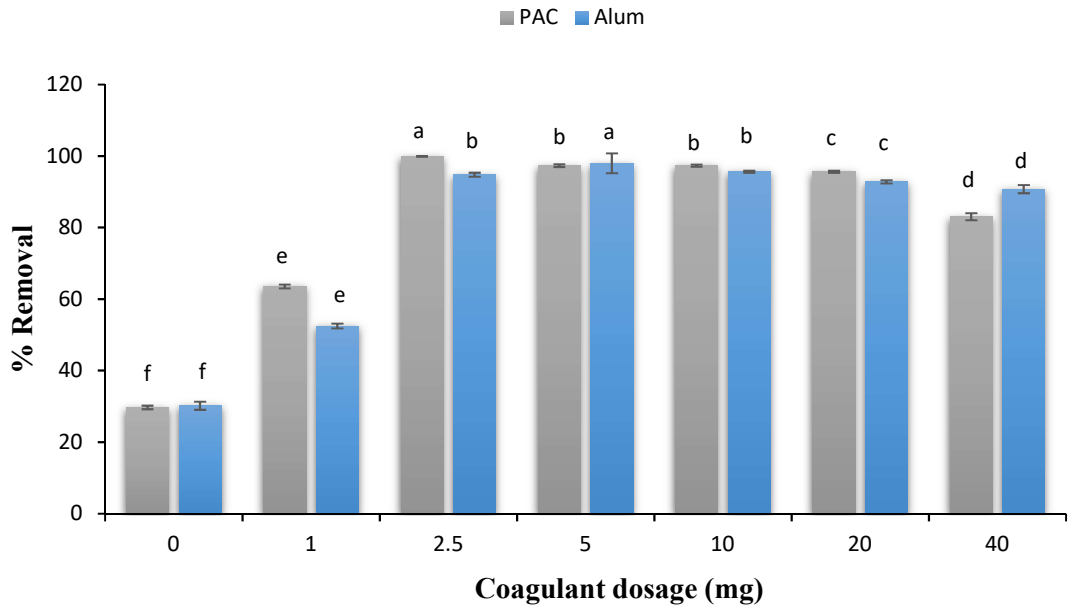

Figure 3.3(b). Percent removal of turbidity at pH = 12.02 (initial) with 200 rpm shaking speed for 20 min and 40 min settling time at 25 ± 2 ℃. Differences were determined by a one-way ANOVA followed by Tukey's pairwise comparison ($p<0.05$). Different letters above the bars indicate significant differences between coagulant dosage.

Results showed that turbidity removal efficiency was higher for PAC in comparison to alum at optimum conditions. However, turbidity removal efficiency showed an almost similar pattern for both PAC and alum which means that PAC has the potentiality to remove turbidity from the wastewater and requirements were less as compared to alum.

4.4.1.2. Effect of pH on turbidity removal

The ideal pH of the coagulant should be ascertained in order to remove the maximum amount of contamination from wastewater because chemical coagulation and precipitation phenomena are highly pH-dependent (Saha et al., 2015). The pH does not only affect the surface charge of coagulants but also affects the stabilization of the suspension. Thus, pH must be controlled to establish optimum conditions for coagulation. Experiments were conducted using the previously obtained optimum coagulant dosage. Thus, to determine the optimum pH range, the fresh batch studies were conducted at different pH values employing the optimum dosage of PAC, 2.5 mg and alum, 5 mg. The pH value of wastewater samples was adjusted using 0.1 N sulphuric acid (H_2SO_4) and 0.1

N sodium hydroxide (NaOH). The pH values tested were between 3.0 and 9.0. The qualities of the treated water, the kind of coagulant employed, and its concentration all affect pH, with the ideal value being dependent on all three (Altaher et al., 2011). To study the optimum pH, other factors (coagulant dose, contact time, shaking speed and settling time) related to the coagulation process were kept constant. Effects of pH on turbidity removal from wastewater were found to be interesting. **Figure 4.4(a)**, it was evident that the optimum pH values for PAC and alum were 6.0 and 7.0, respectively. In this condition, the turbidity after the PAC treatment was the lowest and the concentration reduced from 260 NTU to 3.93 NTU and alum from 260 NTU to 11.39 NTU. At pH 3, the efficiency of both PAC and alum was reduced and removed a very little amount of turbidity from the wastewater. As illustrated by **Figure 4.4(a)** with the increase in pH values, the efficiency of the PAC was found to increase, and the optimum condition was achieved at pH 6.0. A similar trend was observed for alum, but optimum condition was achieved at pH 7.0. In the present study, turbidity removal was maximum in pH values between 6 and 8 because $Al(OH)^{2+}$ and $Al(OH)_2^{+}$ are positively charged inside this range. Insoluble $Al(OH)_3$ species are also predominant in this range. These cations will cause the neutralization of the solution charge since the colloidal particles are negatively charged (Gasmi et al., 2022).

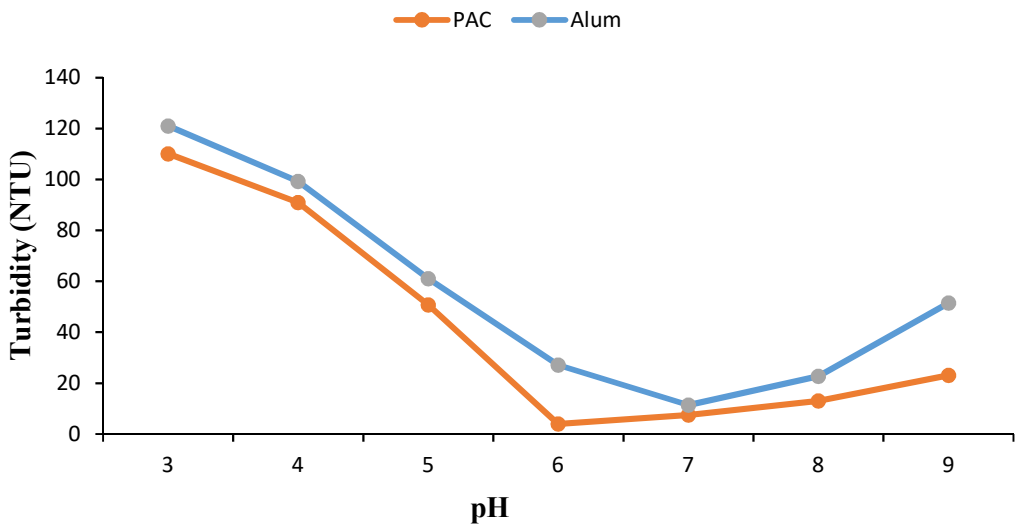

Figure 4.4(a). Effect of pH on the removal of turbidity with optimum coagulant dose with 200 rpm shaking speed for 20 min and 40 min settling time at 25 ± 2 °C.

The findings in this study are in agreement with those obtained by Volk et al. (2000). They reported that the pH of coagulation was the most influential parameter controlling NOM removal from water (Volk et al., 2000). López-Grimau et al. (2006) proposed an optimum pH of 8 for 400 mg/L of coagulant dosage. In this study, the removal percent was the lowest at low pH (pH 3). At that pH, turbidity removal for PAC was higher than in case of alum. Turbidity removal for PAC (98.49%) was more than that achieved with using alum (95.62%). In the current study, pH above 9 is not efficient in the coagulation process for turbidity removal. These observations showed the treatment of wastewater is highly dependent on pH value of wastewater sample.

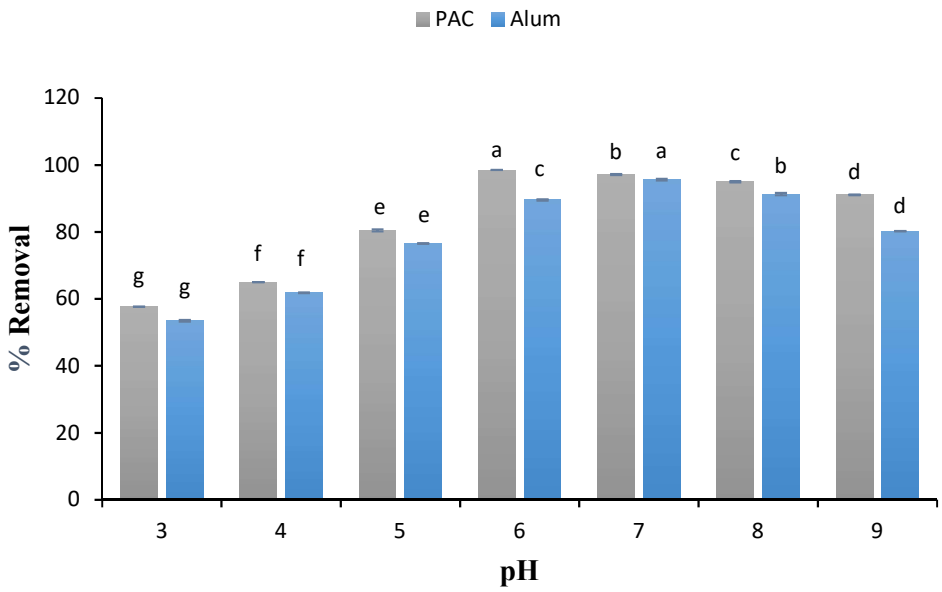

Figure 4.4(b). Percent removal of turbidity with optimum coagulant dose with 200 rpm shaking speed for 20 min and 40 min settling time at 25 ± 2 °C. Differences were determined by one-way ANOVA followed by Tukey's pairwise comparison. Different letters above the bars indicate the significance of differences between pH values of tested sample.

Significant differences were found in the abilities of PAC and alum to remove turbidity ($p<0.05$). Both coagulants work in a wider pH range (5-8) and removes a considerable amount of turbidity from the sample but the optimum dose was attained at pH 6 with PAC and alum at pH 7, because at this stage, the efficiency of both coagulants was the highest.

4.4.1.3 Effect of contact time on turbidity removal

The effect of contact time on the turbidity removal efficiencies was also examined. Contact time is an important factor in that it plays an important role in aggregation of colloidal particles. On application, polymeric coagulant disperses throughout the medium and adsorbs onto the colloidal particle surfaces for inter particle bridging or charge neutralization during the mixing period. If the mixing time is too short, the collisions between the coagulants and colloids are not sufficient to precipitate suspended solids in wastewater. In this study, the effects of contact time were analyzed at optimum dosage of PAC (2.5 mg) and alum (5 mg), pH 6 for PAC and 7 for alum at 150 rpm and 40 min of settling time for a range of contact time which varied from 1 to 25 mins.

From **Figure 4.5(a)**, the lowest turbidity of test sample was obtained when the contact time between PAC and wastewater sample was 20 min and turbidity was reduced from 260 NTU to 2.12 NTU. In the case of alum, turbidity was reduced from 260 NTU to 11.47 NTU. When the contact time was 1 min, the turbidity was reduced from 260 NTU to 123.62 NTU for PAC and 260 NTU to 144.94 NTU.

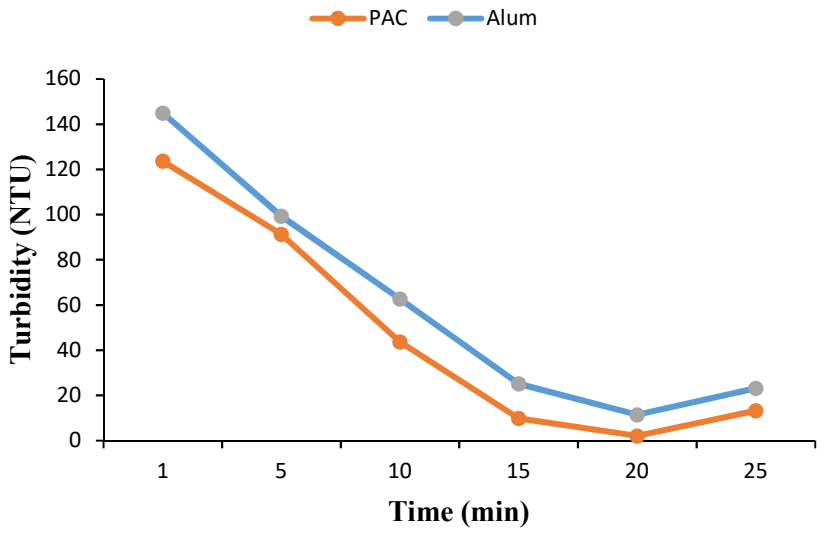

Figure 4.5(a) Effect of contact time on the removal of turbidity by optimum coagulant dosage and pH with 200 rpm shaking speed and 40 min settling time at 25 ± 2 ℃.

When the contact time between the PAC and wastewater was for 20 min, the highest removal percentage of turbidity was observed (99.18%). When the contact time was for 1 min and 5 min, the PAC removed turbidity of 52.40% and 64.92% respectively. For the contact time of 10, 15, and 25 min, the PAC removed the approximately equal amount of turbidity compared to 20 min contact time indicated the potentiality of the PAC coagulant **(Figure 4.5(b)).** Similar trends were observed for the coagulation study of alum with wastewater.

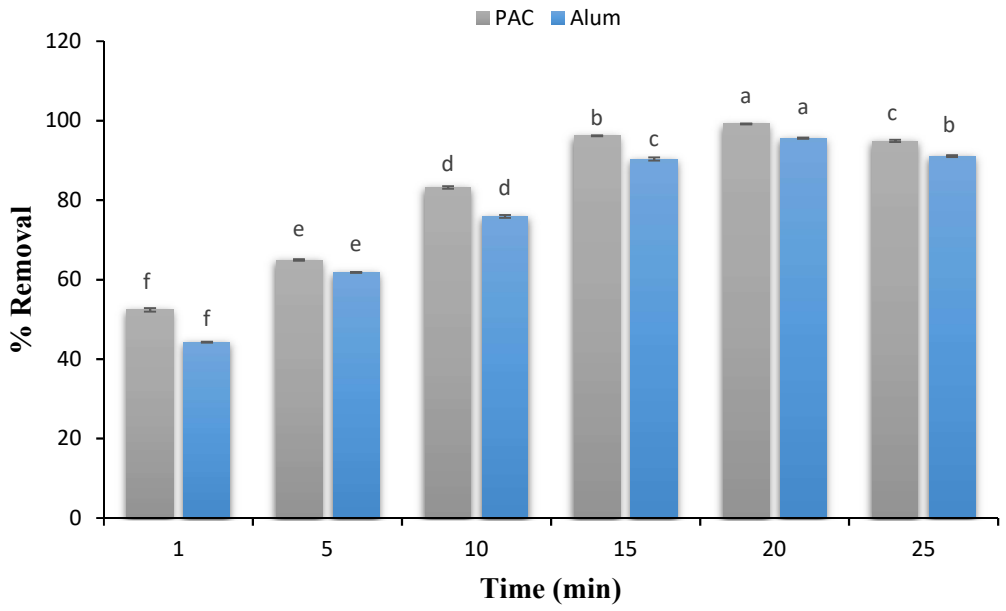

Figure 4.5(b). Percent turbidity removal by optimum coagulant dose and pH with 200 rpm shaking speed and 40 min settling time at 25 ± 2 ℃. Differences were determined by one-way ANOVA followed by Tukey's pairwise comparison ($p < 0.05$). Different letters above the bars indicate the significance of differences between different contact times.

4.4.1.4. Effect of shaking speed on turbidity removal

A series of tests were conducted with PAC and alum as coagulants to study the effect of shaking speed on the removal performance of turbidity. **Figure 4.6(a)** shows the effect of shaking speed (0, 20, 50, 100, 150, and 200 rpm) on the removal performance for PAC and alum dosages of 2.5 mg and 5 mg, respectively. The other factors (coagulant dosage, pH, settling time, contact time, and settling time) that affect the coagulation process

were kept constant. The lowest amount of turbidity was seen when the shaking speed was maintained at 150 rpm and the lowest turbidity was 7.14 NTU by treatment with PAC and 15.35 NTU by alum where the initial turbidity was 260 NTU. At the initial stage of this study, when the shaking speed was kept at 0, 20, and 50, a small amount of turbidity was removed by the PAC. When the shaking speed was maintained at 200 rpm, it removed the same amount as it did at 150 rpm. When the shaking speed was beyond the optimum condition, the turbidity removal was the same as was obtained for the optimum level (**Figure 4.6(a)**). A similar pattern of results was observed for alum. The removal percentage of turbidity was the greatest when the shaking speed was maintained at 150 rpm. The highest turbidity removal was achieved using an optimum dosage of PAC (97.25%) compared with using alum (94.09%). At the shaking speed of 200 rpm, the removal percentage was 95.89% by PAC and 92.60% by alum, as it was at 150 rpm (**Figure 4.6(b)**). The lowest removal was found when no speed was applied to the wastewater sample. The removal efficiency of PAC was found to decrease gradually as the mixing speed increased. This could be attributed to the floc formation and breakage at higher mixing speed (Xu et al., 2010).

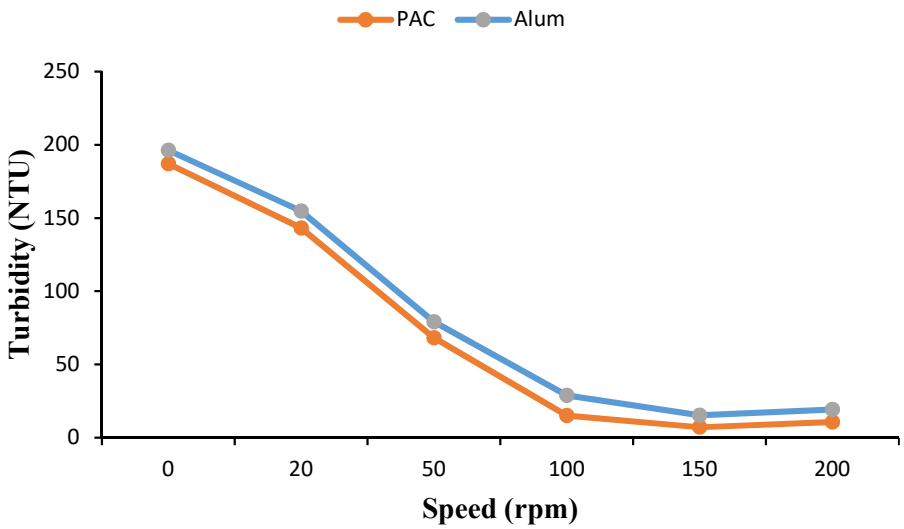

Figure 4.6 (a). Effect of shaking speed on the removal of turbidity using optimum coagulant dose and pH for 20 min and 40 min settling time at 25 ± 2 °C.

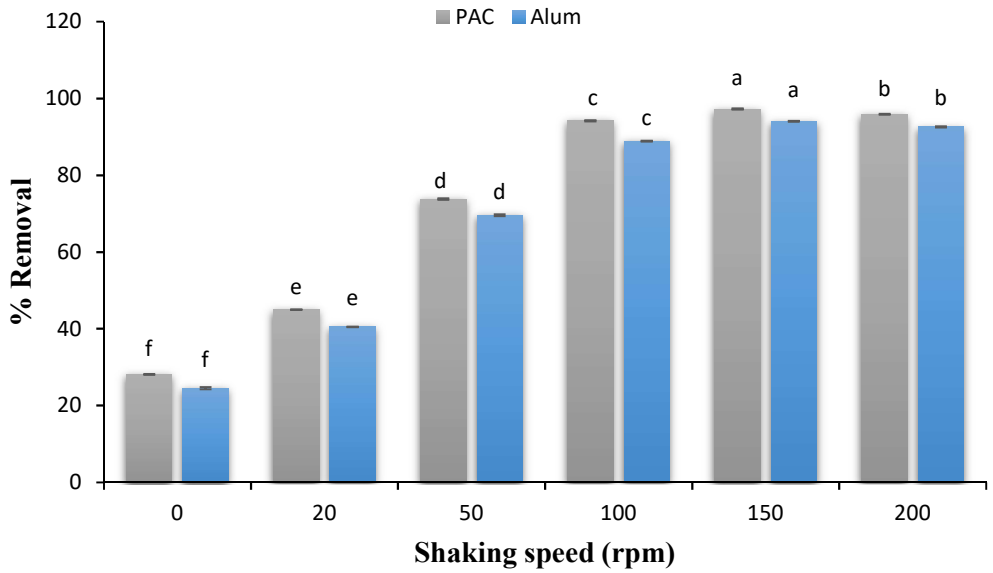

Figure 4.6(b). Percent turbidity removal using optimum coagulant dose and pH for 20 min and 40 min settling time at 25 ± 2 ℃. Differences were determined by one-way ANOVA followed by Tukey's pairwise comparison ($p < 0.05$). Different letters above the bars indicate the significance of differences between different shaking speeds.

4.4.1.5. Effect of settling time on turbidity removal

Settling time is an important factor in the coagulation process because the sludge produced in coagulation take time to settle down. If the sludge does not get enough time to settle down, it remains in the suspended condition in the solution, which results in an incomplete water treatment process. Thus, the effect of settling time on the turbidity removal efficiencies was also examined. To examine the ideal settling time, different settling times (0, 5, 15, 25, 35, and 45 min) were maintained and the other factors (coagulant dose, pH, shaking speed, and contact time) that influence the coagulation process were kept constant. **Figure 4.7(a)** shows the effect of settling time at the optimum PAC and alum dosages. The optimum percentage of removals for turbidity using PAC were 99.14% and when compared with using alum were 96.88 %.

From **Figure 4.7(a)**, the lowest turbidity (2.24 NTU) was detected when the settling time was maintained for 35 min. At the settling time of 45 min, the amount of settled down

sludge was approximately the same as the 35 min settling time. At the beginning of the batch study, when the settling time was maintained for 0 min, the quantity of suspended sludge was high and thus the removal of turbidity from the sample was low. With increasing settling time, more sludge was settled down and the equilibrium settling time was found at 35 min settling time (**Figure 4.7(a)**). The sharp decline of turbidity indicates that the sludge settled down at a faster rate. From the conducted experiment, different amounts of sludge settled down at a different time, and with increasing time, the amount of sludge was increased, and concomitantly more suspended solids were removed from the wastewater sample. After achieving the equilibrium condition, though the settling time was extended, the turbidity was the same (**Figure 4.7(a)**). The settling time of the flocs treated with PAC and Alum are about the same.

The removal percentage of turbidity by PAC was 99.14 and 99.12% when the settling time was maintained 35 and 45 min, respectively. In the case of alum, the removal percentage of turbidity was 96.88 and 96.77% when the settling time was maintained 35 and 45 min respectively. The lowest amount of turbidity removal (57.39% by PAC and 53.04% by alum) was identified when the maintained settling time was 0 min (**Figure 4.7(b)**). Results showed that as the settling time increases, the removal of turbidity increases.

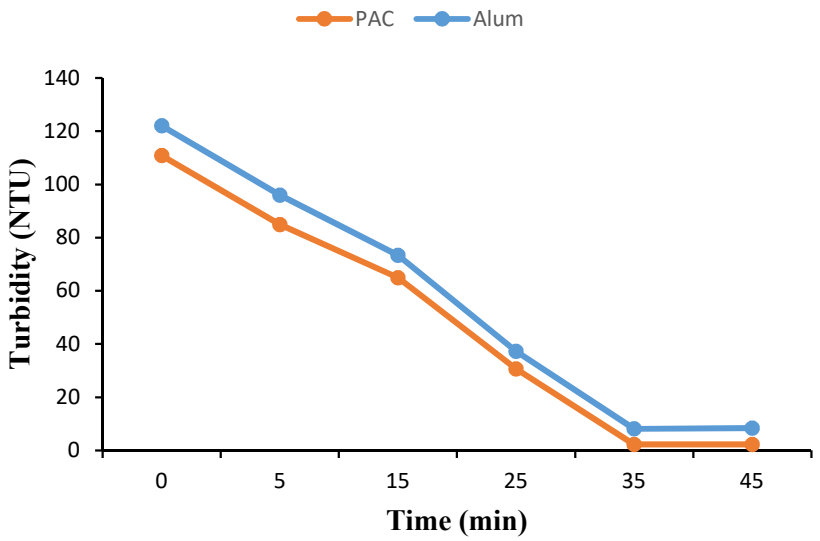

Figure 4.7(a). Effect of settling time on turbidity removal by the application of PAC at 25 ± 2 ℃. PAC dose = 2.5 mg and alum dose 5 mg, pH = 6.0 for PAC and 7 for alum, Contact time = 20 min, shaking speed=150 rpm.

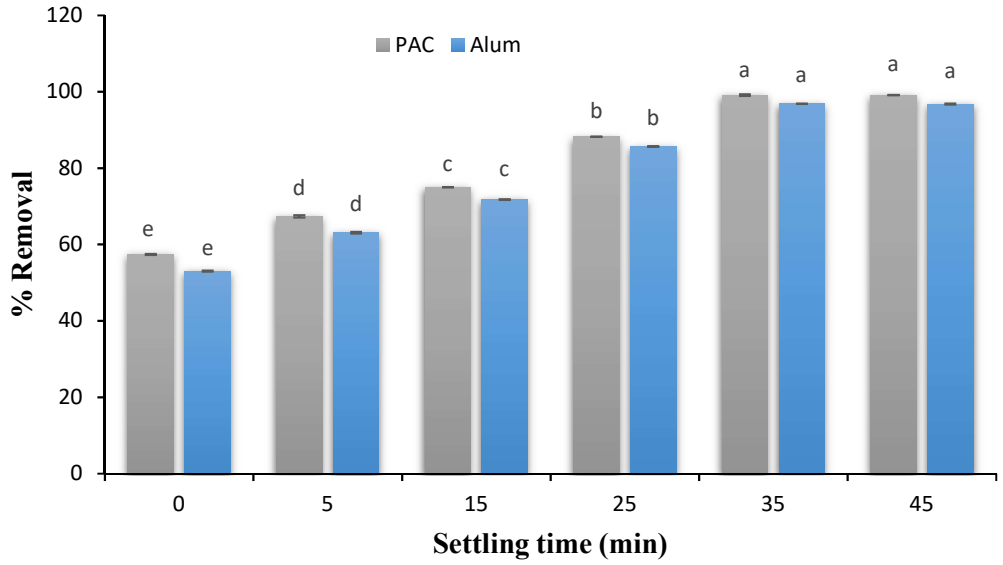

Figure 4.7(b). Percent turbidity removal by settling time at 25 ± 2 ℃. PAC dose = 2.5 mg and alum dose 5 mg, pH = 6.0 for PAC and 7 for alum, Contact time = 20 min, shaking speed=150 rpm. Differences were determined by one-way ANOVA followed by Tukey's pairwise comparison ($p < 0.05$). Different letters above the bars indicate the significance of differences between different settling times.

4.4.2. Turbidity removal efficiency of PAC in comparison with alum

Turbidity removal percentages measured at each stage of the stepwise optimization processes are presented in **Table 4.3.** Different values of the optimum conditions were obtained for PAC and alum. It is revealed from **Table 4.3** that PAC proved higher turbidity removal efficiency in terms of alum. However, PAC was almost two-fold more effective than alum coagulant at removing turbidity.

Table 4.3. Percentage removal of turbidity at the optimum condition of each step.

Step of optimization	PAC		Alum		DoE standard
	Optimum value	% turbidity removal	Optimum value	% turbidity removal	
Coagulant dose (mg)	2.5	99.90	5	97.33	<5 NTU
pH	6	98.49	7	95.62	
Contact time (min)	20	99.18	150	95.59	
Shaking speed (rpm)	150	97.25	20	94.09	
Settling time (min)	35	99.14	35	96.88	

Table 4.3 indicates that as the coagulant dose increases, turbidity removal efficiency increases in such that turbidity removal of 99.90 % with confidence of 95 % at 2.5 mg of PAC was obtained. In the cases of alum, 97.33 % with confidence of 95 % at 5 mg of alum was obtained. Regarding the results of one-way ANOVA followed by Tukey's pairwise comparison test ($p< 0.05$) a significant difference can be found between coagulant dosage and turbidity reduction. The higher dosages were not economically viable and no significant difference was found between the highest dose and the next to highest dose in terms of pollutant removal (Asrafuzzaman et al., 2011). However, regarding the results, optimum PAC dosage was 2.5 mg, pH 6, 20 min of contact time, shaking speed of 150 rpm and settling time of 35 mins. Optimum alum dosage was 5 mg, pH 7, 20 min of contact time, shaking speed of 150 rpm and settling time of 35 mins were used for the purpose of this study. At the optimum values of the parameters, the turbidity removal efficiency of 99.90% and 97.33% was observed for PAC and Alum, respectively. Current study observed that as compared to alum, PAC coagulant has shown better turbidity removal efficiency than alum. Results indicated that after treating the wastewater with PAC, the turbidity in the sample was 0.25 which found lower than the Department of Environment (DOE) standard discharge limits (<5 NTU) for industry.

Both coagulants were found to be effective for turbidity removal from real textile wastewater. However, the polymeric coagulants required less dosages with respect to alum. PAC fared better compared to alum and might be a good alternative to alum for raw water and wastewater treatment. Despite the fact that a high removal efficiency is always sought for, the quality of finished treated water is also important vis-à-vis residual material. Aluminum (or iron), sulfate, and other anions induced by the coagulant itself may be present in high concentrations in treated water. These metals and anions are harmful (GilPavas et al., 2018). In addition to that, the idea of recycled purified water must be taken into consideration because the textile industry is to use large quantity of tap water for various operational processes.

4.5. Conclusions

High level turbidity of the wastewater needs to be treated to get the clean water with low turbidity. In this study, the effectiveness of PAC and alum was evaluated at different pH values and coagulant dosage in order to find optimal operational conditions for wastewaters. The study results showed turbidity removal as highly dependent on the pH, coagulant dosage, as well as initial turbidity of water for both the coagulants. Optimum coagulant dosages for PAC and alum were 2.5 mg and 5 mg respectively. Apparent from those, turbidity removal was also dependent on contact time, shaking speed, and settling time. Maximum turbidity removal efficiency was obtained with a maximum shaking speed 150 rpm for 20 mins and a settling time of 35 mins. The results highlight the applicability of the chemical coagulation process in the treatment of textile wastewater. And PAC coagulant could be an alternative solution for sustainable wastewater management over the alum. Further studies are required for a better understanding of performance of coagulation mechanisms using PAC.

4.6. References

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Chapter-5

EFFECTIVENESS OF SCRAP DERIVED POLYALUMINUM CHLORIDE FOR THE TREATMENT OF CHEMICAL OXYGEN DEMAND (COD) OF TEXTILE WASTEWATER

5. Effectiveness of Polyaluminum Chloride for the Treatment of Chemical Oxygen Demand (COD) of Textile Wastewater

5.1. Abstract

Coagulation is an extremely important process for the removal of organic and inorganic pollutants. Colloidal particles are difficult to handle because of their lightweight and stability. As a result, novel and economically feasible technology is needed to remove colloidal pollutants. In this study, a relatively new coagulant, a scrap-derived polyaluminum chloride, was tested for its ability to remove high-content chemical oxygen demand (COD) from wastewater. The effectiveness of the conventional coagulant was also assessed for comparison purposes. Batch studies were conducted to find the optimal coagulant dose, pH, contact time, shaking effect, and sedimentation time for both coagulants. Results revealed that both scrap-derived polyaluminum chloride (PAC) and alum are able to remove COD from high-COD-containing wastewater. The removal was found to be mainly dependent on coagulant dose, pH and the initial COD content in the wastewater. The highest COD removal efficiency was found to range from 42 – 51% for polyaluminum chloride and 33 – 45% for alum. Even though both the coagulants exhibited promising performance vis-à-vis COD removal from wastewater, polyaluminum chloride demonstrated slightly better performance. Results of this study may be useful for people involved in textile wastewater treatment facilities.

5.2. Introduction

Industrial development has increased the load of different contaminants in the environment. Specifically, water bodies are being seriously polluted by the indiscriminate discharge of industrial wastewater (Kaur, 2021). Industries discharge a wide array of contaminants, including suspended solids, organic matter, inorganic salts, heavy metals, surfactants, etc. When these pollutants make their way into water bodies, the receiving water becomes unsuitable for drinking and irrigation purposes (Gupta, & Singh, 2019). The water bodies pose problems to aquatic life as well. Humans sitting at the top of the food chain are also vulnerable to diseases associated with these contaminants. In Bangladesh, 97% population has access to water. However, the quality is of water is always

questionable (Hasan, et al., 2019). Therefore, management of wastewater at the highest level is essential to ensure the quality of water in the country.

Wastewater released by various industries contains both organic and inorganic matter. As industries use a number of chemicals during processing of the respective products, the wastewater released has color, suspended solids, high chemical oxygen demand (COD), and biological oxygen demand (BOD) (Mazumder, 2011). COD refers to the amount of oxygen required for chemical oxidation of organic and inorganic compounds (Joanna et al., 2020). Morshed et al. (2016) estimated the COD of untreated textile effluents to be between 301 and 359 mg/L.

Previously a good deal of methods has been tested for the removal of COD from textile wastewater. Reduction of COD is an important index typically used to assess the efficacy of a wastewater treatment plant. As a result, a lot of attention has been directed towards the development of technology for the efficient removal of COD worldwide. (Dotto et al., 2019; Zand & Hoveidi, 2015). Previous studies exhibited the deficiency of traditional biological purification as not being efficient in removing toxic heavy metals and the total organic matter content (Rana & Suresh, 2017). At times, some metabolites form which are even more persistent and toxic (Michaelet al., 2015). Thus, it is imperative that other treatment processes be adopted for the complete removal of different toxicants present in wastewater. Coagulation is an important technology for COD removal. It has been used in other industries with good effects. Previously, the pulp industry employed aluminum, ferric chloride, ferrous sulphate and polyaluminum chloride for the treatment of COD in released wastewater (Yang et al., 2019). Presently, novel and cost-effective technologies are required for the treatment of wastewater for its COD level.

Coagulation process has been very popular for many years because of its simplicity and cost-effectiveness. The application of the right coagulant, the right dosage, and other operational parameters govern the performance of a coagulant. Alum is the widely employed coagulant because of its availability and cost-effectiveness (Aydın et al., 2018).

Of late, polymerized forms of metal coagulants such as polyaluminum chloride (PAC) has gained popularity in water and wastewater treatment processes. The escalated use of these coagulants can be attributed to their better coagulation performance in wide

pH values and cost-effectiveness compared to their regular counterpart (Tzoupanos et al., 2009). PAC has an edge over its conventional counterpart because it possesses good structure and higher charge density. These properties result in a decreased dose requirements and consequently lesser sludge production (Zainol et al., 2011). A group of researchers obtained 77.9% removal of COD using the polyaluminum chloride coagulant (Yateh et al., 2020). Another group of researchers worked with paper mill wastewater, and they reported high removal of color and COD using PAC (Chaudhari et al., 2010). PAC was touted to be superior coagulant because of its lower alkalinity consumption and lesser sludge production (Zhai et al., 2017).

In Bangladesh, very few industries employ effluent treatment plants (ETP) to treat their wastewater. The reluctance of these industries may be attributed to the requirement of huge capital for their initial set-up. Consequently, virtually all industries have been releasing their effluent to the environment without any treatment. The environment has been degrading over the years with the flourishing of these industries. Therefore, considering the present needs of Bangladesh in this sector, this study was carried out. The study is a comparative study between PAC and alum coagulants for their comparative performance in the treatment of textile wastewater.

5.3. Materials and methods

This research was undertaken to synthesize PAC from scrap aluminum and to examine the COD removal efficiency of the synthesized PAC in collected textile wastewater. The experiments were carried out at the Fibre and Polymer Research Division in Bangladesh Council of Scientific and Industrial Research (BCSIR), Dhaka, Bangladesh.

5.3.1. Chemicals and reagents

All the chemicals and reagents used in this study were of analytical grade. Hydrochloric acid (35.9% purity) and 0.1 M solution of sodium hydroxide (>98% purity) was collected from Merck, Germany. Deionized water with no more than 0.5 μS/cm conductivity was used for preparing all the solutions.

5.3.2. PAC Synthesis and characterization

This research was conducted to synthesize PAC from aluminum scraps and analyzed for its aluminum content, basicity and charge neutralization capacity. Scrap derived PAC was characterized by using state- of- the- art technologies such as FTIR spectroscopy, scanning electron microscopy (SEM) with energy dispersive x-ray (EDX), and x-ray diffraction (XRD) analysis, wavelength dispersive x-ray fluorescence (WDXRF) and thermogravimetric analysis (TGA).

5.3.3. Wastewater sampling and characterization

Textile effluent sample was collected from Hemayetpur, Savar, Dhaka, Bangladesh. Before going to the field, each bottle was washed with 10% hydrochloric acid followed by copious amounts of double distilled water. At the sampling station, before sample collection, the bottles were rinsed with effluents to be collected. The sample was brought to the laboratory and some sensitive parameters were measured immediately. The sample was analyzed for some major parameters of the textile effluents, including pH, electrical conductivity (EC), total suspended solids (TSS), chemical oxygen demand (COD), biological oxygen demand (BOD), bicarbonate (HCO_3^-), chloride (Cl^-), fluoride (F^-), phosphate (PO_4^{3-}) and sulfates (SO_4^{2-}) (Baird et al., 2012). Total suspended solids was measured using an oven and employing the gravimetric method. Biological oxygen demand at day 5 (BOD_5) was also estimated using the Winkler method (Carpenter, 1965). Chemical oxygen demand COD was measured by the closed reflux method (HACH, DR3900, USA). The anions were determined by ion chromatography. Turbidity was measured by a turbidity meter (HACH, 2100Q, USA).

5.3.4. Coagulation study

The collected textile effluent sample was treated with scrap-derived coagulant PAC. For adjusting the pH of the wastewater sample, 0.1 M hydrochloric acid and 0.1 M sodium hydroxide were used.

An orbital shaker (SHO-2D, Korea) was used to perform the coagulation study under different conditions. Different parameters were optimized step by step. The COD removal efficiency of PAC and alum was determined by varying the parameters such as

dosages (0- 40 mg), pH (3.0 to 9.0), agitation speed (0 to 200 rpm), contact time (1-25 min) shaking speed (0-200 rpm) and settling time (0-35 min). The pH of the wastewater sample was kept at 5.36, the original pH of the sample. To start with, a definite amount of PAC and alum was added to the 100 mL of wastewater into a beaker. The contents were readily mixed with a magnetic stirrer at 150 rpm for 20 min and the mixed solution was allowed to settle for 35 min. All tests were carried out at room temperature (25±2 ℃).

For the COD measurement, about 50 mL sample was withdrawn from 1.0 cm below the surface of the test water. The measurement was performed using the closed reflux method (HACH DR3900, USA) and the value was expressed in mg/L. The optimal dosage for lowest COD was determined for both coagulants. All the analyses were done in triplicates and the mean values were presented in this dissertation. Finally, the reaction kinetics of the COD removal at the optimum condition was determined.

The removal of pollutant (%) in terms of COD (mg/L) from the wastewater was calculated using the following relationship:

$$COD\ reduction\ (\%) = \frac{COD_i - COD_f}{COD_f} \times 100$$

Where, COD_i is the initial COD (mg/L), COD_f is the final or equilibrium COD (mg/L).

Figure 5.1. shows the steps of chemical coagulation process. All the analyses were performed in triplicates and the mean values were reported. Experimental parameters for the coagulation test are summarized in **Table 5.1.**

Table 5.1. Coagulants and the parameters for jar test experiments conducted in this study

Characteristics	Description
Coagulants	PAC and Alum
Coagulant dose range	0-40 mg
pH range	3-9 (Initial pH =5.36)
Initial COD	315 mg/L
Shaking speed	0-200 rpm
Contact time	1-25 min
Settling time	0-45 min
Temperature	Room temperature (25 ± 2 ℃)

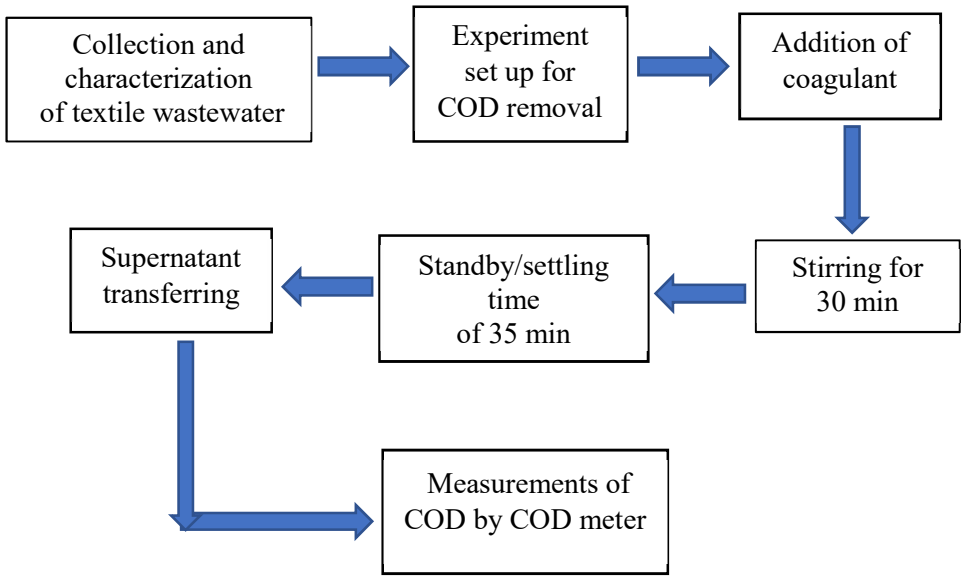

Figure 5.1. Schematic description of treatment process used in this study.

5.3.5. Statistical analysis

The results are presented as the mean ± SD (n = 3). The raw data was checked for normality and homoscedasticity (homogeneity of variance). A one-way analysis of variance (ANOVA) was performed using General Linear Model, followed by a Tukey's pairwise comparison test. All statistical analysis was performed on Minitab version 21. Significance was determined based on p values being 0.05 or not.

5.4 Results and discussion

After the preparation and characterization stage, the coagulation test was performed for better understanding of the removal mechanism. The test was also carried out to determine the optimum conditions for COD removal from the collected textile wastewater by adding scrap aluminum derived PAC. The coagulation process depends on many factors that can influence its efficiency and operation (Tang et al., 2014; Zand & Hoveidi, 2015). Parameters including coagulant dosage, pH, contact time, shaking speed, and settling time were studied. Some physicochemical parameters of textile dyeing effluents were also subjected to analysis and the results were compared with the national standard (DoE) discharge limits of the effluents. **Table 5.2** shows the characteristics of wastewater samples determined following different Standard Methods (AWWA & APHA,1998).

Table 5.2. Characteristics of the textile industry raw wastewater before coagulation treatment.

SL. No	Test Parameter	Unit	Result
1	Electrical Conductivity (EC)	µS/cm	12.13
2	Biological Oxygen Demand (BOD)	mg/L	21.3
3	Dissolved Oxygen (DO)	mg/L	1.15
4	Turbidity	NTU	30.2
5	Total Suspended Solid (TDS)	mg/L	608
6	Chemical Oxygen Demand (COD)	mg/L	**315**
7	pH	-	**5.36**
8	Mercury (Hg)	mg/L	bdl
9	Copper (Cu)	mg/L	0.01
10	Iron (Fe)	mg/L	0.59
11	Manganese (Mn)	mg/L	1.54
12	Lead (Pb)	mg/L	bdl
13	Cadmium (Cd)	mg/L	0.003
14	Nickel (Ni)	mg/L	0.04
15	Zinc (Zn)	mg/L	0.48
16	Fluoride (F^-)	mg/L	0.45
17	Chloride (Cl^-)	mg/L	18.41
18	Nitrate (NO_3-)	mg/L	0.36
19	Phosphate (PO_4^-)	mg/L	0.50
20	Sulfate (SO_4^{2-})	mg/L	297.43

***bdl=below detection limit**

5.4.1 Optimized COD removal efficiency

Table 5.2 shows very high level of turbidity in the collected textile wastewater sample. As the operating variables are important for a successful coagulation process, the operating variables were optimized by performing a series of batch studies. The variables optimized include the dosage of coagulant and pH, which is a master variable in water. In addition to these, contact time, shaking speed and settling time were also manipulated for an optimized coagulation process. An orbital shaker was used to optimize the five selected variables. The variables were optimized in the following sequence: coagulant dose, pH, contact time, shaking speed, and settling time. Before treatment, the initial pH of the collected sample was 5.36.

5.4.1.1. Effect of coagulant dosage on COD removal

The effect of coagulant dosage on COD removal from the wastewater was studied by conducting a batch study (**Figure 5.2(a)**). Initially, optimization was done to determine the optimum coagulant dosage for COD removal. **Figure 5.2(a)** represents the effect of PAC and alum coagulants dosage on COD removal. Different dosage of both coagulants was applied keeping pH at the initial value of the real wastewater (5.36). The removal was found to increase with an increase in coagulant dosage until it reached an optimum value and then the removal was found to be reduced. That removal decreased after an optimum value could be attributed to the restabilization of colloidal particulates when coagulants are applied at dosages in excess of the optimum value (Daud et al., 2015). As indicated in **Figure 5.2(a)**, the COD reduction shows an increase with the PAC dose and reaches a maximum at 10 mg. With the increase in PAC dosage, the COD values were found to decrease significantly.

The performance of a conventional coagulant (alum) on COD removal in textile wastewater was also studied. A similar trend was obtained for alum coagulant. Morshed et al. (2016) reported COD values between 301 and 359 mg/L for an untreated textile effluent. As shown in **Figure 5.2(a)**, both PAC and alum exhibited better removal performance for COD. At the optimum dosage of PAC and alum the COD values reduced to 153, and 173 mg/L, respectively. **Figure 5.2(b).** shows that at the 10 mg coagulant dosage, the maximum 47% COD reduction observed for PAC and 45% reduction was for alum. When the PAC and alum dose was increased to 40 mg, COD reduction dropped to

42% and 33% respectively. Verma et al. (2012) observed that coagulation is less effective in the reduction of COD with respect to the color reduction.

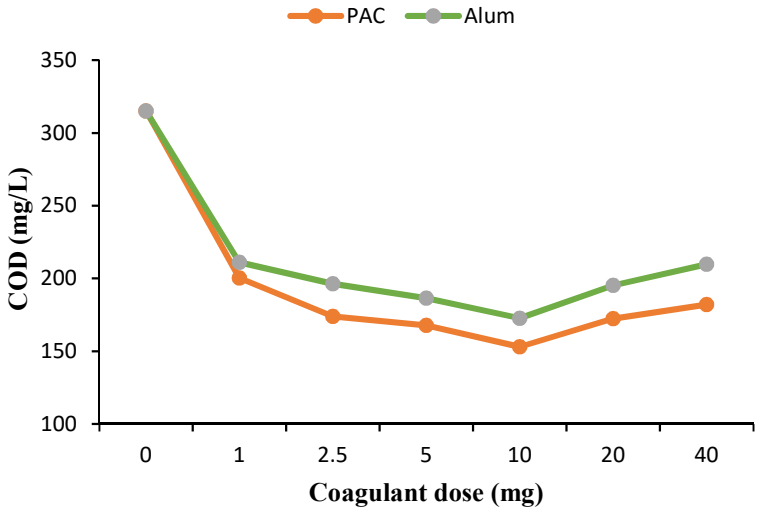

Figure 5.2(a). Effect of coagulant dosage on the removal of COD at pH = 5.36 (initial) with 200 rpm shaking speed for 20 min and 40 min settling time at 25 ± 2 ℃.

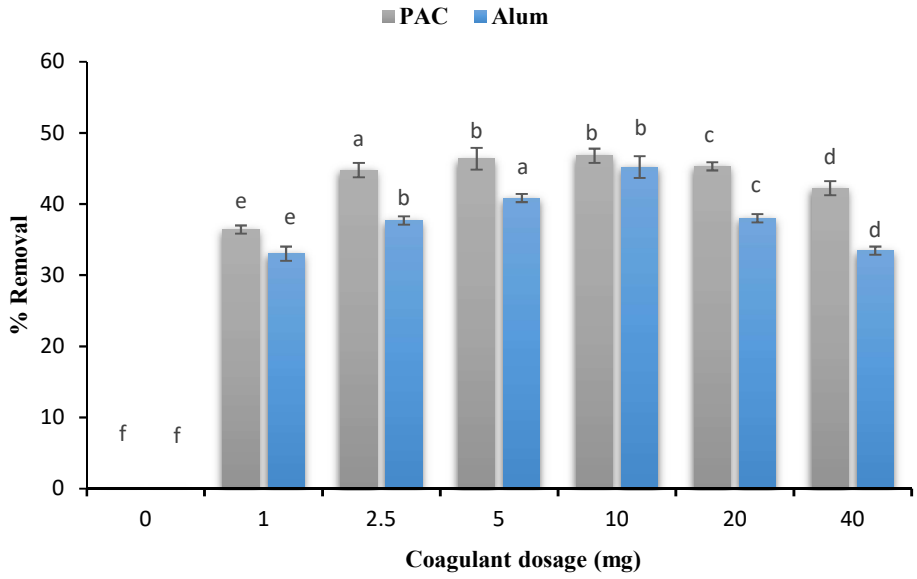

Figure 5.2(b). Percent removal of COD at pH = 5.36 (initial) with 200 rpm shaking speed for 20 min and 40 min settling time at 25 ± 2 ℃. Differences were determined by a one-way ANOVA followed by Tukey's pairwise comparison ($p<0.05$). Different letters above the bars indicate significant differences between coagulant dosage.

5.4.1.2. Effect of pH on COD removal

To understand the effect of pH on COD removal in wastewater, another batch study was carried out. Initial pH of wastewater was 5.36 and the coagulation study was carried out within the pH range of 3–9 and the results are shown in **Figure 5.3(a).** The initial pH of the wastewater was kept fixed in the ranges of 3 to 9. Then the optimal dosages of the coagulants were added to the wastewater samples. The COD values were estimated using the same procedure described in the previous tests. To study the optimum pH, other factors (coagulant dose, contact time, shaking speed and settling time) related to the coagulation process were kept constant. **Figure 5.3 (a)** shows the effect of pH changes on the efficiency of the coagulation process. The removal efficiency was found to increase with increasing pH. The maximum COD removal was at pH = 6 and the minimum COD removal efficiency was at pH = 3. The values were 50.90% and 42.36%, respectively.

As illustrated by **Figure 5.3(a)** with the increase in pH values, the efficiency of the PAC was found to increase, and the optimum condition was achieved at pH 6.0. Similar trend was observed for alum, but optimum condition was achieved at pH 7. In this condition, the amount of COD after the PAC treatment was the lowest and the concentration reduced from 315 mg/L to 154.67 mg/L and alum from 315 mg/L to 173 mg/L. At pH 3, the efficiency of both PAC and alum was reduced and removed a very little amount of COD from the wastewater.

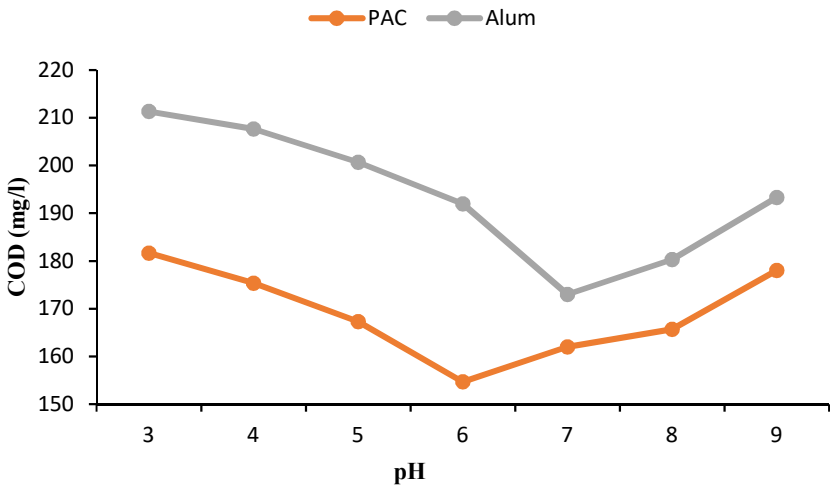

Figure 5.3(a). Effect of pH on the removal of COD with optimum coagulant dose with 200 rpm shaking speed for 20 min and 40 min settling time at 25 ± 2 °C.

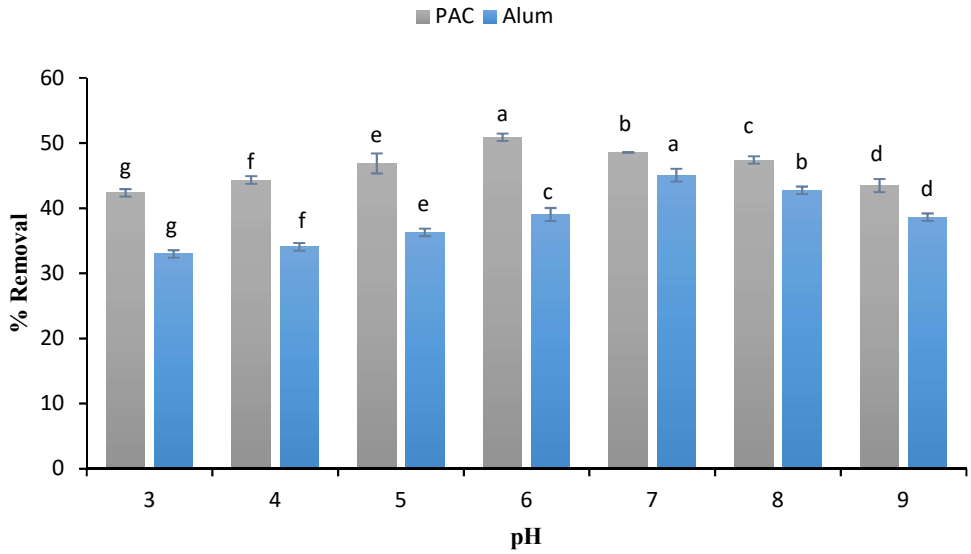

Figure 5.3(b). Percent removal of COD with optimum coagulant dose with 200 rpm shaking speed for 20 min and 40 min settling time at 25 ± 2 °C. Differences were determined by one-way ANOVA followed by Tukey's pairwise comparison. Different letters above the bars indicate the significance of differences between pH values of tested sample.

From Figure **5.3(b)** it is evident that COD removal for PAC were higher than corresponding values obtained with alum. In the current study, pH above 9 is not efficient in the coagulation process for COD removal. These observations show that the treatment of wastewater is highly dependent on pH value of wastewater sample. Al Mubaddal F et al. (2009) found that the acidic values of pH harm the settling of the particles and may encourage corrosion in real applications. Therefore, the optimum values of pH should be in the range of 6–8.

It also can be said that significant differences in the abilities of both PAC and alum to remove COD ($p<0.05$). Both coagulants work in a wider pH range (6-7) and removes a considerable amount of COD from the sample but the optimum dosage was attained at pH 6 with PAC and alum at pH 7, because at this stage, the efficiency of both coagulants was the highest. It was found that PAC had more efficiency in removing COD compared with alum under the specified conditions.

5.4.1.3. Effect of contact time on COD removal

The effect of contact time on the turbidity removal efficiencies was also examined. Because agitation time is important to promote good coagulation/flocculation, it should be long enough (20 min) to receive sufficient kinetic energy for the colloidal particles in the wastewater to aggregate (Baraoidan et al., 2007). Insufficient agitation time will lead to incomplete coagulation/flocculation. In this study, the effects of contact time were analyzed at optimum dosage of PAC and alum (10 mg), pH 6 for PAC and 7 for alum at 150 rpm and 40 mins of settling time for a range of contact time which varied from 1to 25 mins.

From **Figure 5.4(a)**, the lowest COD of test sample was obtained when the contact time between PAC and wastewater sample was 20 min and COD was reduced from 315 mg/L to 153.33 mg/L. In the case of alum, COD was reduced from 315 mg/L to 197.67 mg/L. When the contact time was 1 min, the turbidity was reduced from 315 mg/L to 188.67 mg/L for PAC and 315 mg/L to 197.67 mg/L.

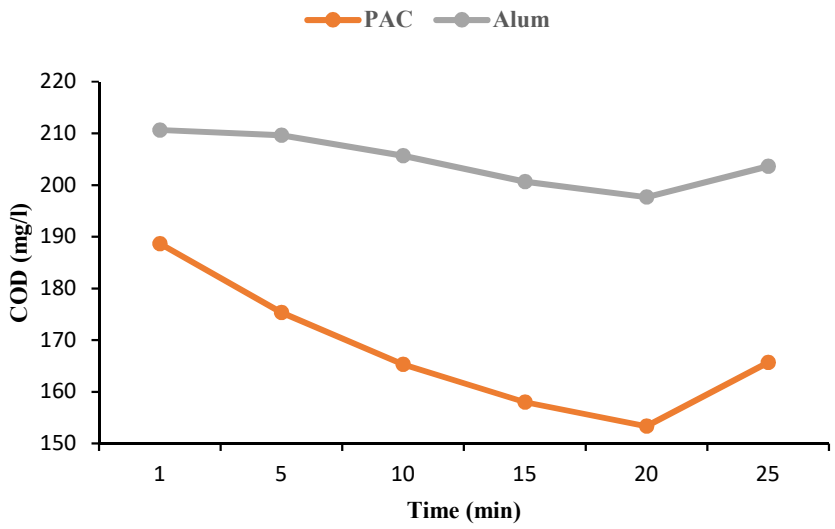

Figure 5.4(a). Effect of contact time on the removal of COD by optimum coagulant dose and pH with 200 rpm shaking speed and 40 min settling time at 25 ± 2 °C.

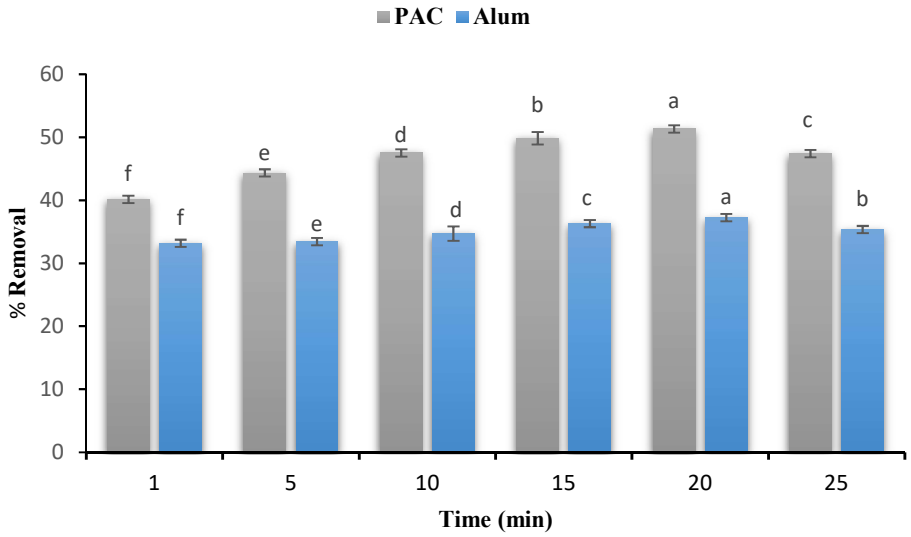

Figure 5.4(b). Percent COD removal by optimum coagulant dose and pH with 200 rpm shaking speed and 40 min settling time at 25 ± 2 ℃. Differences were determined by one-way ANOVA followed by Tukey's pairwise comparison ($p < 0.05$). Different letters above the bars indicate the significance of differences between different contact times.

Figure 5.4(b) illustrates that when the contact time between the PAC and wastewater was for 20 min, the highest removal percentage of COD was observed (51.3%). A similar study was conducted by Rao (2015) who found the optimum mixing time for effective coagulation and flocculation process as 20 min. When the contact time was for 1 min and 5 min, the PAC removed turbidity of 40.1% and 44.3% respectively. For the contact time of 10, 15, and 25 min, the PAC removed the approximately equal amount of turbidity compared to 20 min contact time indicated the potentiality of the PAC coagulant. Similar trends were observed for coagulation study of alum with wastewater.

5.4.1.4. Effect of shaking speed on COD removal

Batch studies were conducted with PAC and alum as coagulants to investigate the effects of shaking speed on the removal performance of COD. **Figure 5.5(a)** shows the effect of shaking speed (0, 20, 50, 100, 150, and 200 rpm) on the removal performance of PAC and alum with a dosage of 10 mg. The other factors (coagulant dosage, pH, settling time, contact time and settling time) that affect the coagulation process were kept constant. Significant differences were seen at all mixing speeds with the optimum rapid mixing speed

for PAC being 150 rpm. The lowest amount of COD was seen when the shaking speed was maintained at 150 rpm and the lowest COD was 156.67 mg/L by treatment with PAC and 178 mg/L by alum where the initial COD was 315 mg/l. At the initial stage of this study, when the shaking speed was kept at 0, 20, and 50, a small amount of COD was removed by the PAC. When the shaking speed was maintained at 200 rpm, it removed the same amount as it did at 150 rpm. When the shaking speed was beyond the optimum condition, the COD removal was the same as was obtained for the optimum level (**Figure 5.5(a)**). A similar pattern of results was observed for alum. The removal percentage of COD was the greatest when the shaking speed was maintained at 150 rpm. The highest COD removal was achieved using optimum dosage of PAC (50.26%) compared with using alum (43.49%). At the shaking speed of 200 rpm, the removal percentage was 49.42% by PAC and 41.80% by alum, as it was at 150 rpm (**Figure 5.5(b)**). It is clear that the lowest removal was found when no speed was applied to the wastewater sample.

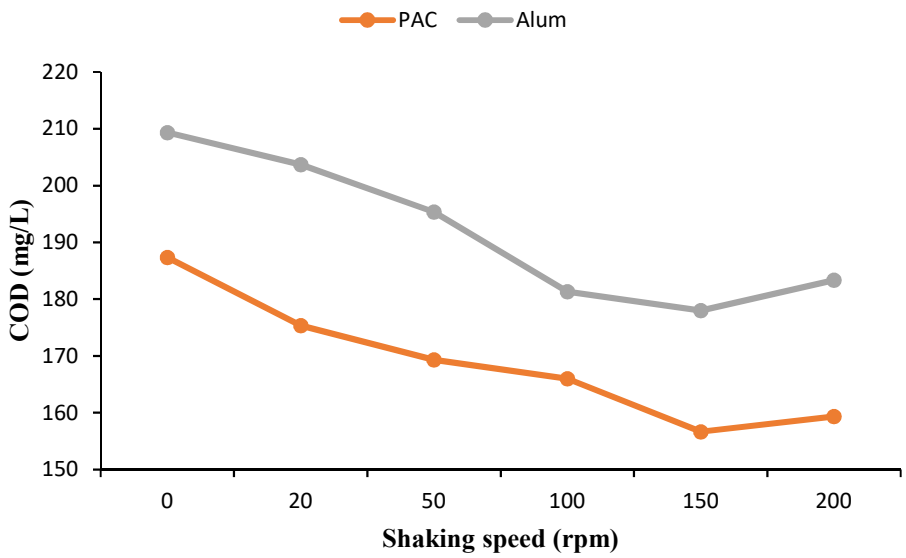

Figure 5.5(a). Effect of shaking speed on the removal of COD using optimum coagulant dose and pH for 20 min and 40 min settling time at 25 ± 2 ℃.

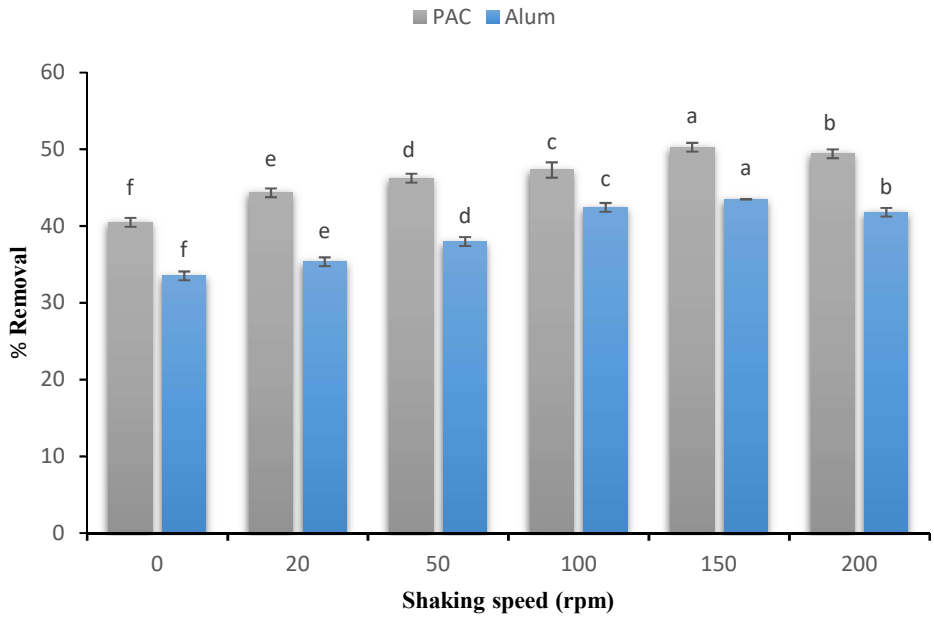

Figure 5.5(b). Percent COD removal using optimum coagulant dose and pH for 20 min and 40 min settling time at 25 ± 2 ℃. Differences were determined by one-way ANOVA followed by Tukey's pairwise comparison ($p<0.05$). Different letters above the bars indicate the significance of differences between different shaking speeds.

5.4.1.5. Effect of settling time on COD removal

Settling time is another important factor in the coagulation process because the sludge generated in coagulation take time to settle down. If the sludge does not get enough time to settle down, they remain in the suspended condition in the solution which results an incomplete water treatment process. Therefore, the effect of settling time on the turbidity removal efficiencies was also investigated. To examine the ideal settling time, different settling times (0, 5, 15, 25, 35, and 45 min) were maintained and the other factors (coagulant dose, pH, shaking speed and contact time) that influence the coagulation process were kept constant. The reduction of COD is also dependent on the settling time as reflected in Figure **5.6(a)** and shows the effect of settling time at the optimum PAC and alum dosages.

From **Figure 5.6(a)**, the lowest content of COD (153 mg/l) was detected when the settling time was maintained for 35 min. At the settling time of 45 min, the amount of

settled down sludge was approximately the same as the 35 min settling time. At the beginning of the batch study, when the settling time was maintained for 0 min, the quantity of suspended sludge was high and thus the removal of COD from the sample was low. With increasing settling time, more sludge was settled down and the equilibrium settling time was found at 35 min settling time (**Figure 5.6(a)**). The sharp decline of COD indicates that the sludge settled down at a faster rate. From the conducted experiment, different amounts of sludge settled down at a different time, and with increasing time, the amount of sludge was increased and concomitantly more suspended solids were removed from the wastewater sample. After achieving the equilibrium condition, though the settling time was extended, the turbidity was the same (**Figure 5.6(a)**). The settling time of the flocs treated with PAC and Alum are about the same.

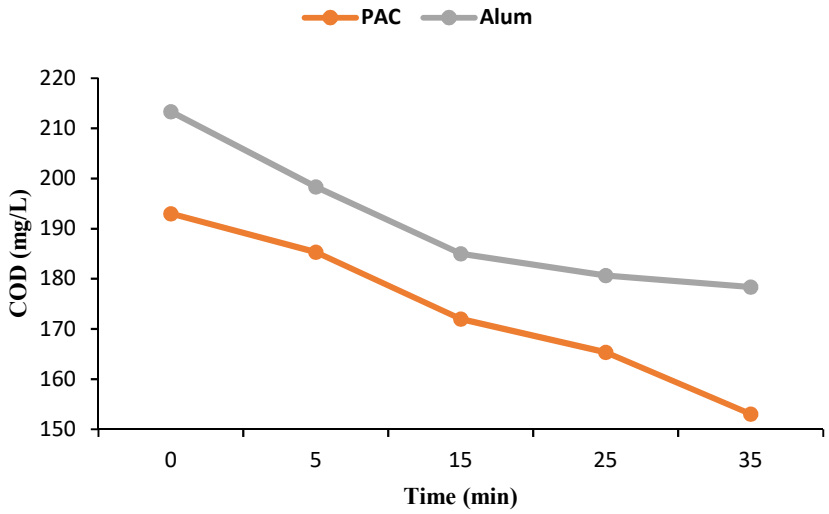

Figure 5.6(a). Effect of settling time on COD removal by the application of PAC at 25 ± 2 ℃. PAC and alum dosage = 10 mg, pH = 6.0 for PAC and 7 for alum, Contact time = 20 min, shaking speed=150 rpm.

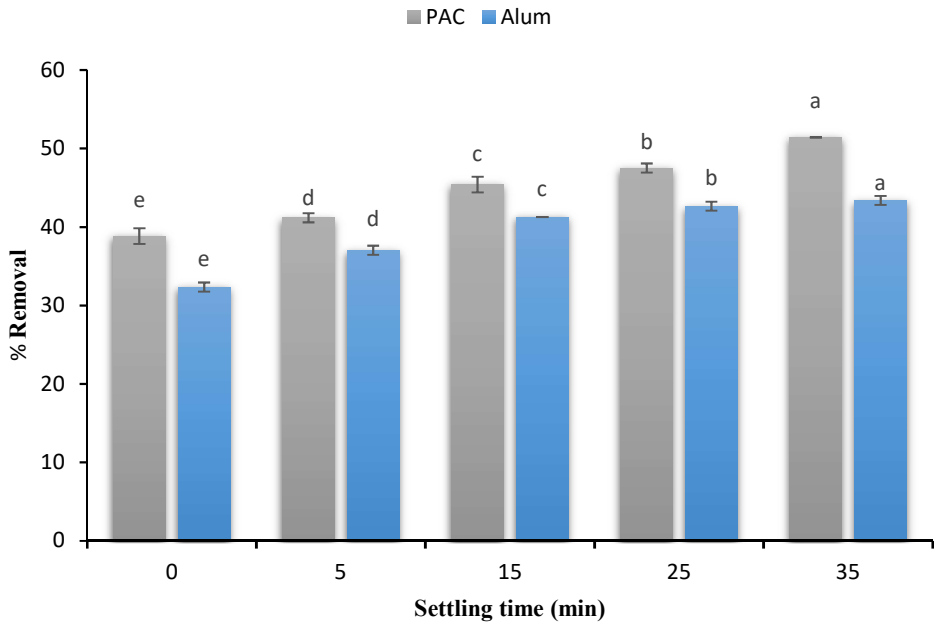

Figure 5.6(b). Percent COD removal by settling time at 25 ± 2 ℃. PAC and alum dosage = 10 mg, pH = 6.0 for PAC and 7 for alum, Contact time = 20 min, shaking speed=150 rpm. Differences were determined by one-way ANOVA followed by Tukey's pairwise comparison ($p < 0.05$). Different letters above the bars indicate the significance of differences between different settling times.

The removal percentage of COD by PAC was 47.51 and 51.43% when the settling time was maintained 35 and 45 min, respectively. In the case of alum, the removal percentage of COD was 42.65% and 43.39 % when the settling time was maintained 35 and 45 min respectively. The lowest amount of COD removal (38.84% by PAC and 32.35% by alum) was identified when the maintained settling time was 0 min (**Figure 5.6(b)**). Result showed that as the settling time increases, the removal of COD increases.

5.4.2. COD removal efficiency of PAC in comparison with alum

Table 5.3 Percentage removal of COD at the optimum condition of each step.

Step of optimization	PAC		Alum		DoE standard
	Optimum value (mg)	% COD removal	Optimum value (mg)	% COD removal	
Coagulant dose (mg)	10	51	10	45	<200 mg/L
pH	6	50.90	7	45.08	
Contact time (min)	20	51.3	20	37	
Shaking speed (rpm)	150	50.26	150	43.49	
Settling time (min)	35	51.43	35	43.39	

Table 5.3 indicates that as the coagulant dose increases, COD removal efficiency increases in such that COD removal of 51 % with confidence of 95 % at 10 mg of PAC was obtained. In the cases of alum, 45 % with confidence of 95 % at 10 mg of alum was obtained. Regarding the results of one-way ANOVA followed by Tukey's pairwise comparison test ($P<0.05$) a significant difference can be found between coagulant dosage and COD reduction. The higher dosages did not significantly increase pollutant removal and were not economically viable (Asrafuzzaman et al., 2011). However, regarding the results, optimum PAC dosage was 10 mg, pH 6, 20 min of contact time, shaking speed of 150 rpm and settling time of 35 mins. Optimum alum dosage was 10 mg, pH 7, 20 min of contact time, shaking speed of 150 rpm and settling time of 35 mins were used for the purpose of this study. Under these optimal values of process parameters, the COD removal efficiency of 51% and 45% was observed for PAC and Alum, respectively. Comparison among the two coagulants reveals that PAC was the most effective coagulant for COD removal from textile wastewater compared to alum. Results indicated that after treating the wastewater with PAC, the COD in the treated sample was 153 mg/L which found lower than the Department of Environment (DOE) standard discharge limits (<200 mg/L) for industry. A similar study conducted by Smoczynski (2014) and found that PAC was a more effective and a more efficient coagulant than alum.

Both coagulants are proven to be effective for COD removal from real textile wastewater. The majority of researchers focuses on the investigation related to how operational factors affect treatment effectiveness. Even though it is important to achieve

high removal efficiency, the researchers should also focus on the quality of treated water in terms of residual material such as aluminum.

5.5. Conclusions

This study was conducted with the aim of investigating COD removal efficiency of scrap-derived PAC in comparison with alum coagulants. The study results revealed that the concentration of COD in textile dyeing wastewater was higher than the standard guidelines for effluent discharged (the initial COD was 315 mg/L). The COD removal efficiency study observed that the coagulant PAC and alum removed COD from ~47% and ~45% respectively at a 10 mg coagulant dose, 20 min of contact time, 150 rpm speed, 25 °C temperature, acidic range between 6 and 7 and settling time of 35 min indicated the potentiality of the coagulant. Result revealed that both coagulants successfully reduced COD from wastewater despite not applying any coagulant aid.

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Chapter-6

STUDIES ON ELEMENTAL, THERMAL AND MORPHOLOGICAL PROPERTIES OF SCRAP ALUMINUM DERIVED POLYALUMINUM CHLORIDE TREATED SLUDGE

6. Studies on Elemental, Thermal, and Morphological Properties of Scrap Aluminum Derived Polyaluminum Chloride Treated Sludge

6.1. Abstract

In the current study, an attempt was made to investigate the elemental, thermal, and morphological properties of scrap aluminum derived polyaluminum chloride treated sludge after removal of an anionic dye, turbidity and COD through the coagulation process. The produced sludge was characterized by using various instrumental analyses such as FT-IR, SEM-EDX, WDXRF, zeta potential analysis and TGA-DSC. FT-IR spectra of produced sludge confirms the presence of hydroxyl group, bending vibration of the oxazine ring, bending vibration of the Al-OH-Al groups, the aromatic C-H out-of-plane bending vibrations of the aromatic ring C-H in-plane bending on 1,4-disubstituted benzene. EDX and WDXRF analysis of the sludge indicates the presence of the carbon, aluminum, sulfur, oxygen, and chlorine. The surface charge of the sludge was 39.0 mV as detected by the Zeta Potential analysis. SEM image showed that produced sludge had non-uniform shape and randomly forming aggregates that are largely in an amorphous structure. From TGA-DSC curve, significant mass losses were observed at different temperatures and a sharp endothermic peak was observed at 109 ^{o}C due to the evaporation of absorbed water from PAC treated sludge. An appropriate technology should be developed for the recovery and reuse of PAC sludges generated during the wastewater treatment process. The PAC sludges could be used as a flocculant aid for further wastewater treatment process to improve the effluent quality of wastewater during primary sedimentation. In order to find the suitability of its application, further detailed studies should be done.

6.2. Introduction

Sludge is the semisolid waste produced in Effluent Treatment Plants (ETPs) and should be treated or disposed of safely. Nowadays, textile sludge management is a vital issue in Bangladesh. Despite the fact that coagulation/flocculation is the appropriate technology for the treatment of textile wastewater, a large amount of sludge is generated from the treatment process (Baraoidan et al., 2007). Disposal of chemical sludge is a knotty problem. The chemical sludge cannot be disposed of in landfills as it can cause secondary

contamination (e.g., landfill leachate). Because of the abovementioned reasons, factory owners find a hard time in handling the sludge originating from treatment plants. Coagulants such as alum and PAC generate sludge containing aluminum residues. Aluminum sludge is considered very problematic because aluminum can pose harmful effects to plants and animals, including humans (Zhao et al., 2011).

Sustainable management of aluminum sludge continues to interest researchers in the water industry. Scientists are now exploring the beneficial uses of aluminum sludge so that the environment can be saved. A number of researchers have presented the possible use of alum sludge as raw materials in different industries. Ferreira & Olhero (2002) proposed a method for modification of aluminum-rich sludge to produce high alumina refractory ceramics. Hsu & Hseu (2011) and Ulen et al. (2012) demonstrated that aluminum-rich sludge can be used in soil as an amendment to reduce the mobility of phosphorus in soil. Some other researchers applied dried aluminum sludge cake for the efficient removal of phosphorus from constructed wetlands (Yang et al., 2006b; Yang, 2011) Although a number of investigations have given insights into the possibility of using aluminum-rich sludge originating from alum, very few studies examined the sludge derived from PAC. It is, therefore, essential to examine the PAC-derived sludge for its possible use in different areas. In the present study, the characterization of PAC-treated sludge was done by using state-of-the-art technologies. A comparative study was performed to see what kind of changes occurred in synthesized PAC after the coagulation treatment.

6.3. Materials and methods

6.3.1. PAC sludge characterization methods

Different state-of-the-art techniques were used to characterize the sludge after the treatment of raw textile wastewater by PAC. The sludge was characterized to reveal its functional groups, morphology, elemental composition, and charge neutralization capacity.

6.3.1.1. Fourier Transform Infrared Spectrometer (FTIR) analysis

The PAC-treated sludge was characterized by identifying the functional groups by FTIR (Frontier Perkin Elmer, UK) using the KBr pellet method. Transmittance of the dry and powdered sludge was recorded in an infrared range between 4000-400 cm^{-1}.

6.3.1.2. Scanning Electron Microscope (SEM) analysis

A scanning electron microscope, SEM (Zeiss, EVO 18, Germany) was used to determine the high-resolution image of the morphology of PAC-treated sludge. The images were taken at 3000 magnifications. After the collection of supernatants, the settled flocs at the bottom of each beaker were transferred to a plastic tray. The tray was then put in an 80 ˚C oven and dried for one day. Samples were collected, scraped off, and placed in a pin-mount sample holder attached with sticky conducting tape. The sample was mounted on the carbon tape, which was taped into aluminum plates and coated with an ultrathin film of gold with a sputter coater. The image was taken to observe the morphology of PAC-treated sludge. The photographs are presented in the results and discussion section.

6.3.1.3. Elemental analysis

To detect the significant elements, present in the produced sludge, Energy Dispersive X-ray EDX, (EDAX, AMETEK, Germany) was done. To understand the elemental composition more accurately the Wavelength Dispersive X-Ray Fluorescence, WDXRF (Rigaku ZSX Primus IV, Japan) analysis was also conducted. In this case, about 0.5 g sample was taken for the analysis.

6.3.1.4. Zeta potential analysis

To assess the surface charge of the PAC-treated sludge, a zeta potential study was done using a Zeta Potential Analyzer (Nanopartica SZ-100, HORIBA Scientific Ltd., Japan). Ultrapure water was used to dissolve the produced sludge. The concentration of the solution was 1 g/L.

6.3.1.5. Thermogravimetric Analysis

The thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC) of PAC-treated sludge was performed by using a simultaneous thermal analyzer, STA (NETZSCH STA 449 F5, Germany) under a nitrogen atmosphere with the heating rate of 10K/min.

6.4. Result and discussion

The settling patterns of alum-derived sludge and PAC-derived sludge was observed in a 2-L capacity measuring cylinder.

6.4.1. Fourier-Transform Infrared Spectroscopy (FTIR)

The possible chemical bonds in PAC treated sludge were investigated by the FT-IR analysis to detect the changes in functional group that have taken place after coagulation. The different peak values in the graph indicate the different chemical compositions originating due to the reaction between the wastewater and PAC. The solid sludge was analyzed by FTIR with the spectrophotometer employing the potassium bromide (KBr) pellet method. The spectra were in the range of 4000-400 cm^{-1}. In the first step, the sludge sample was dried in an oven at 105 ℃ and then ground into fine powder. **Figure 6.1** shows that FT-IR spectra exhibited a broad absorption peak in the range of 3200-3650 cm^{-1}. The absorption peaks at 3391 cm^{-1} which could be assigned to the stretching vibration of -OH groups. These hydroxyl groups exist either in a free state or in a contiguous state with metal ions, indicating that reactions occurred between the coagulants and metal ions present in the wastewater (Liu et al., 2017). The absorbance peaks at 1619 cm^{-1} (1600-1700 cm^{-1}) were attributed to the bending vibrations of water absorbed, polymerized, and crystallized in the sludge. A similar result was found in a study conducted by Zhou et al. (2014). The absorption peak at 1425 cm^{-1} corresponds to the CH_2 bending vibration of the oxazine ring. The band at 1038 cm^{-1} may be attributed due to the bending vibration of the Al-OH-Al groups (Gong & Feng, 2015). The band at 1126 cm^{-1} was assigned to the bending vibration of Al-OH_2 (Tzoupanoset et al., 2009). In the fingerprint region, the aromatic C-H out-of-plane bending vibrations of the aromatic ring are observed at 872 cm^{-1} (Hao et al., 2015). In **Figure 6.1** there are some new peaks in the FT-IR analysis of sludge that were not present in the FT-IR analysis of PAC.

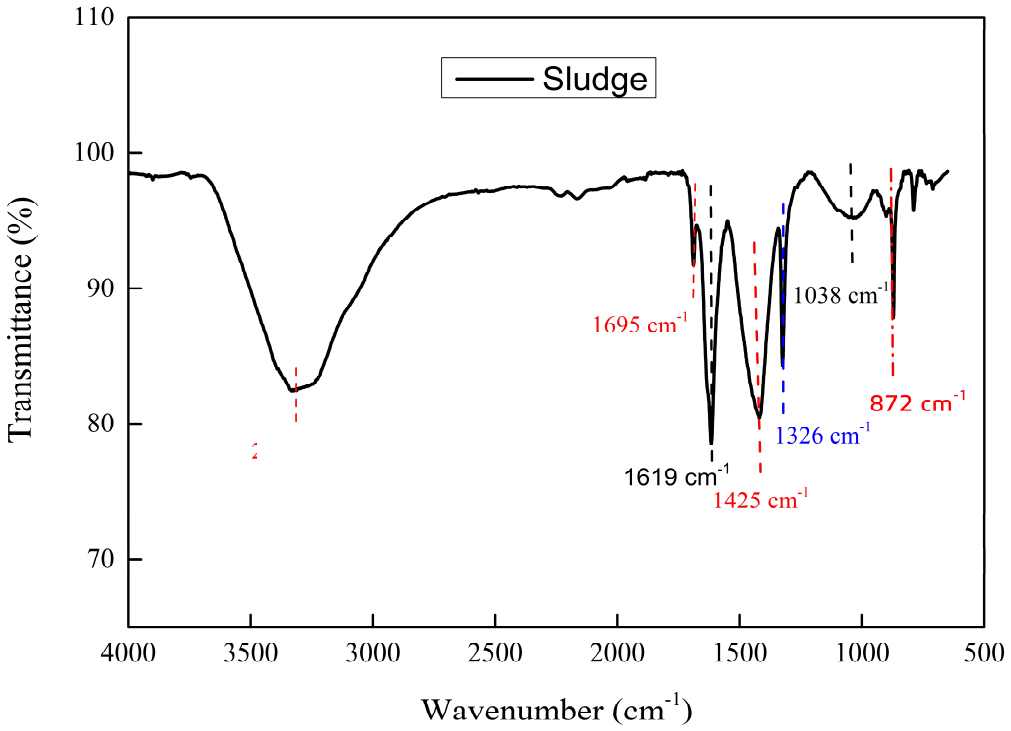

Fig 6.1. FT-IR Spectra of PAC-treated sludge.

6.4.2. Scanning Electron Microscopy (SEM)

To understand the microscopic morphology of the sludge produced after treatment, the SEM micrographs were taken using JEOL, Model JSM-5300, Japan. The SEM is a magnification tool that aids in characterizing the surface structure of materials (Ahmad et al., 2016). An SEM machine was used to observe the floc size characteristics such as surface structure (Robbins, 2015) before and after the treatment. The SEM used in this study was equipped with an energy-dispersive X-ray (EDX). The analysis was performed at 3000 magnifications,15 kV accelerating voltage, and 10.5 mm working distance with the EDX system**.** The SEM images of PAC-treated sludge is shown in **Fig 6.2.** From **Figure 6.2**, the flocs produced after the treatment are hard and compact because colloidal particles are entrapped in these flocs.

In **Figure 6.2,** SEM image showed a non-uniform shape and randomly forming aggregates that are largely in an amorphous structure. This may be caused by the absorption of wastewater. The findings can be substantiated by the findings of Shi et. al. (2012). They

also analyzed the SEM images of freeze-dried PAC-Al_{13} particles and obtained no regular crystalline morphology.

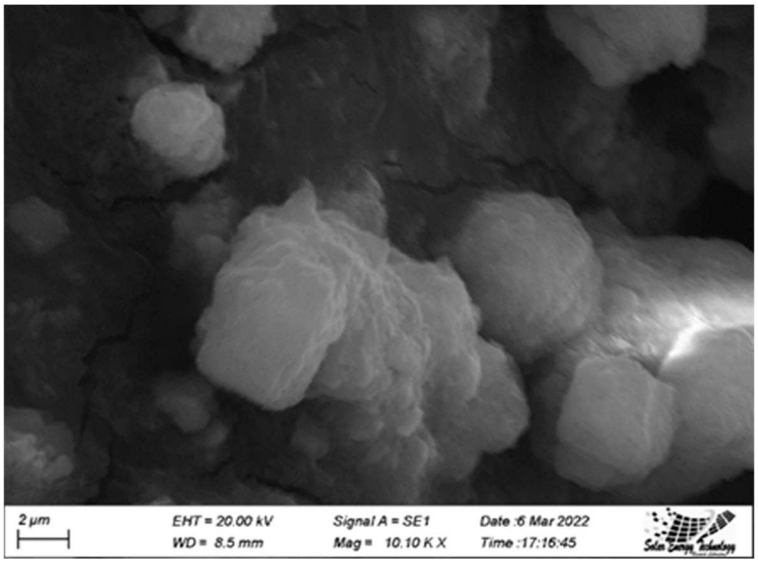

Figure 6.2. SEM images of PAC treated sludge.

The SEM image of sludge clearly indicates the substantial difference in texture after treatment. Figure also shows some rough texture of sludge.

6.4.3. Energy Dispersive X-Ray (EDX)

To understand and compare the chemical composition between PAC and produced sludge, the EDX analysis was performed. During the EDX analysis, different areas were focused, and the corresponding peaks are shown in **Figure 6.3**. The elemental composition of the PAC sludge is presented in **Table 6.1.** There are various elements present in sludge. Among the elements, carbon was found to be the dominant in sludge. The peak of calcium was found in the sludge that was not found in the synthesized PAC. PAC contained the peak of sodium and aluminum, but peak of these element was not found in produced sludge and also the peak of calcium was found in the sludge which was not present in the synthesized PAC. Thus, some changes occurred in the composition of the PAC when it reacted with dye and wastewater impurities.

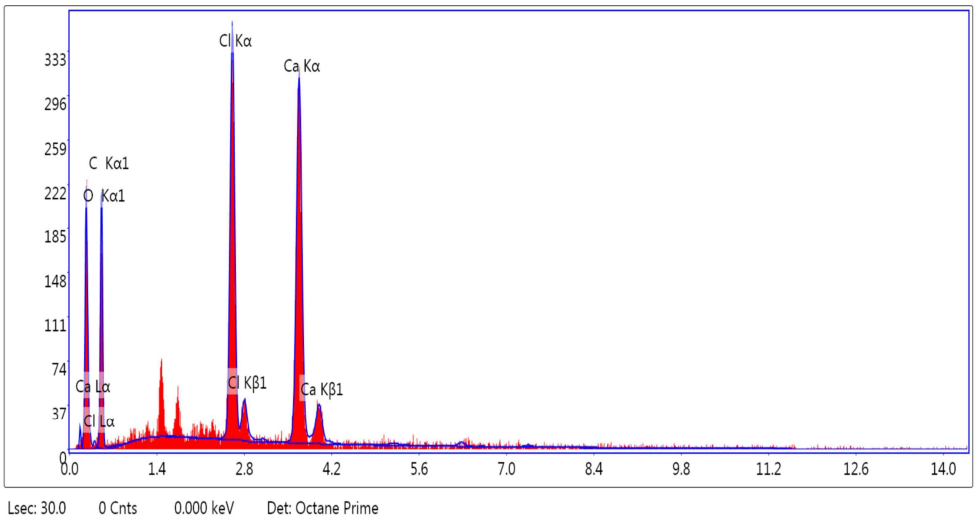

Fig 6.3. EDX spectra of PAC treated sludge.

Table 6.1. Elemental composition of PAC treated sludge by EDX.

Element	Weight %	Atomic %
C K	34.46	49.29
O K	33.97	36.48
ClK	12.43	6.02
CaK	19.14	8.20

6.4.4. Wavelength Dispersive X-Ray Fluorescence (WDXRF)

To understand more accurately, the elemental composition of the sludge, the Wavelength Dispersive X-Ray Fluorescence (WDXRF) analysis was performed. Aluminum sludge has a gelatinous appearance because it contains aluminum with a blend of organic and inorganic materials and hydroxide precipitates. The following table shows the elemental composition that are present in the PAC-treated sludge. It is clear from Table **6.2**, there are various elements present in sludge. Calcium was found to be the dominant element in the sludge. This might be due to the coagulation of PAC with pollutants present in wastewater sample. It was also observed that less aluminum and chloride was found after coagulation treatment with PAC which was found high in scrap-derived PAC coagulant.

Table 6.2. Elemental composition by Wavelength Dispersive X-Ray Fluorescence (WDXRF).

Component	Amount (mass %)	Detection limit	Elemental line	Intensity	w/o normal
Na_2O	0.0000	0.16373	Na-KA	0.0912	0.0000
MgO	0.531	0.00401	Mg-KA	0.3092	0.0389
Al_2O_3	4.76	0.00146	Al-KA	11.1390	0.3492
SiO_2	2.06	0.00119	Si-KA	4.5233	0.1513
P_2O_5	0.320	0.00073	P-KA	1.5153	0.0235
SO_3	0.0530	0.00241	S-KA	2.8341	0.0559
Cl	15.1	0.00501	Cl-KA	34.9072	1.1046
K_2O	0.0941	0.00158	K-KA	0.1492	0.0069
CaO	72.7	0.00500	Ca-KA	75.6768	5.3263
Fe_2O_3	3.23	0.00862	Fe-KA	5.5078	0.2368
ZnO	0.394	0.00483	Zn-KA	2.8329	0.0289
SrO	0.113	0.00375	Ga-KA	3.0733	0.0083

6.4.5. Zeta Potential

To determine the surface charge of the produced sludge, the zeta potential analysis was performed. The value obtained from the analysis for the sludge is +39.0 millivolt (mV). From **Figure 2.4**, the value indicates that the sludge is moderately stable and is very close to good stability. But the surface charge of scrap-derived PAC was found to have a value of +42.9 millivolts (mV) indicating good stability behavior with colloidal particles but the

produced sludge has moderately stable behavior with colloidal particles. This may be because of the coagulation reaction occurring between PAC and wastewater impurities. That is why the surface charge of produced sludge was found to be less than the synthesized PAC.

6.4.6. Thermogravimetric Analysis and Differential Scanning Calorimetry (TGA-DSC)

Figure 6.4 shows the thermogravimetric curve of PAC treated sludge. Three main stages of thermal decomposition of sludge, corresponding to their weight reduction, may be observed in **Figure 6.4.** In the initial stage, weight loss of about 18.1% was observed up to 114 ^{o}C. In the second stage, about 29.2% loss was observed in the range of 114-444 ^{o}C. These losses may be ascribed to the water molecules from air which is absorbed by the hydrophilic group of PAC coagulant in the polymerization reaction. In the third stage, the residual mass was found to be 52.7% at 644 ^{o}C. This indicates that aluminum in the sludge together with some other metal may be present.

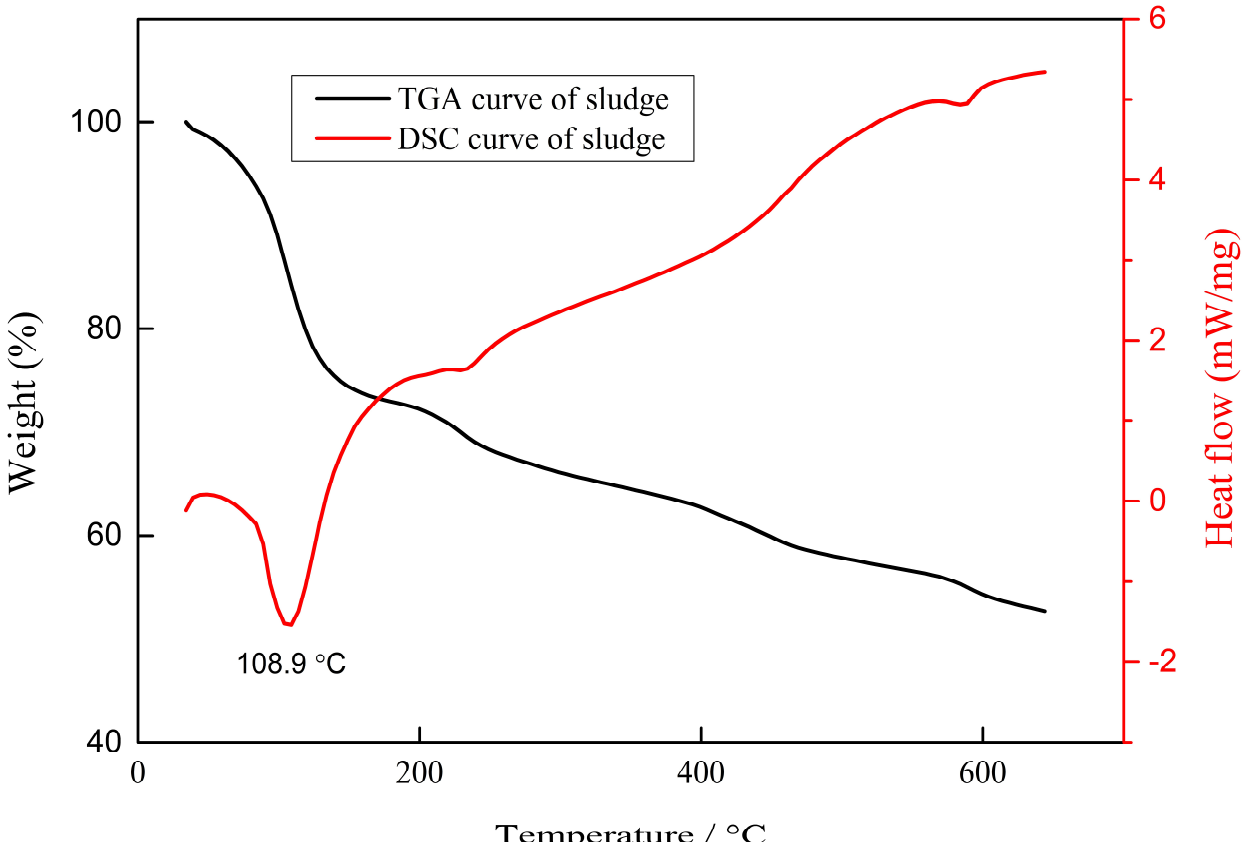

Figure 6.4. TGA-DSC curve of PAC treated sludge.

In **Figure 6.4**, a sharp endothermic peak was observed at 109 ºC due to the evaporation of absorbed water from PAC treated sludge.

6.5. Conclusions

The sludge produced after chemical coagulation of wastewater by scrap-aluminum-derived PAC was investigated by using different types of state-of-the-art technologies. Based on sludge characterization results, differences in elemental composition were observed compared with PAC. Result revealed that sludge contained high carbon value which was not contained in PAC. The morphology of sludge determined by SEM shows non-uniform shape. The differences of charge neutralization capacity were observed between PAC and sludge and sludge showed moderately stable behavior with colloidal particles but scrap derived PAC had good stability. From TGA-DSC curve, a sharp endothermic peak was observed. An appropriate technology should be developed for the recovery and reuse of PAC sludges generated during the wastewater treatment process. The PAC sludges could be used as a flocculant aid for further wastewater treatment process to

improve the effluent quality of wastewater during primary sedimentation which should be evaluated. Further detailed studies must be done in order to find the suitability of its application.

6.6. References

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Chapter-7

CONCLUSIONS AND FUTURE DIRECTIONS

7. CONCLUSIONS AND FUTURE DIRECTIONS

7.1 . Conclusions

In this research, Poly-aluminum Chloride (PAC) was synthesized from aluminum scraps and characterized by using state of the art technologies as well as to see the efficiency of scrap derived PAC as a coagulant for the removal of dye, turbidity and COD from collected textile wastewater sample. The dye used for the experiment was Navacron Navy S-G that was manufactured in Switzerland and collected from textile industry. To synthesize the PAC, aluminum scraps were collected from a local shop. After the collection of the scraps, it was cut down into small pieces so that it can go to the reaction easily. The waste aluminum/ scraps were dissolved into hydrochloric acid and sodium hydroxide to produce aluminum chloride and sodium aluminate solution. The solution of aluminum chloride and sodium aluminate was further reacted with each other under 70 ℃ in a reaction calorimeter. After the completion of the reaction, the liquid PAC was dried in an oven to attain powdered PAC. The basicity (i.e. the OH/Al molar ratio) of the scrap derived PAC was determined by titrimetric method and it was found 37.89% indicates medium basicity PAC.

The characterization of the PAC was performed using various instrumental analyses and techniques. FT-IR spectra of scrap derived PAC shows characteristics absorption peaks i.e., the stretching vibration of the hydroxyl group, C=N stretching, bending vibration of Al-OH_2, symmetric stretching mode of the Al-O bond of the central AlO_4^- in the Al_{13} molecule, bending vibration of the Al-OH-Al groups, and C-H stretch of alkanes.

The elemental composition of synthesized PAC showed carbon, oxygen, Fluorine, Sodium, Aluminum, and Chlorine as identified by EDX analysis. WDXRF analysis showed the presence of Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, SO_3, Cl, CaO, Fe_2O_3, ZnO, and Ga_2O_3 in the PAC. From the zeta potential analysis, the synthesized PAC was found to have a value of +42.9 millivolts (mV), indicating that the PAC has good stability behavior with colloidal particles. In the SEM study, SEM images of scrap derived PAC did not find well-formed crystalline structures and the XRD patterns of synthesized PAC showed significant peaks of NaCl but weak Al_{13} or Al_{30} diffraction peaks, which may result from the fact that the PAC samples were not purified and that the test results could have been affected by

other impurities. TGA-DSC curve showed significant mass losses at different temperatures and a sharp endothermic peak was observed at 113.9ºC due to the evaporation of absorbed water from scrap derived PAC coagulant.

A coagulation experiment was performed with collected wastewater. Batch study was conducted for the removal of Navacron Navy SG dye, turbidity and COD removal from textile wastewater. Evaluation of the factors affecting the removal study including coagulant type, coagulant dosage, pH, contact time, shaking speed, settling time, initial dye concentration, initial turbidity and initial COD of wastewater using oneway ANOVA analysis followed by Tukey's Pairwise comparison for each coagulant indicated that there was a significant effect on the removal of dye, turbidity and COD in wastewater. Result revealed that coagulation study with PAC successfully reduced Navacron Navy SG dye by 94.11 % from aqueous solution and 73.0% from collected textile wastewater. Removal of turbidity was found to be 97-99% and 94-97% by PAC and alum respectively. Result revealed that, after treatment with PAC, final turbidity in the textile wastewater were found lower than the DoE standard (<5 NTU) for the discharge limits of the textile effluents. Removal of COD was found to be 51% and 45% by PAC and alum respectively which were also found lower than the DoE standard (<200 mg/l) for the discharge limits of the textile effluents.

It is difficult to degrade the dyeing effluent using a single treatment unit such as physical, chemical, and biological. Therefore, the study suggested a combination of the units for achieving a higher degradation of the effluents. Based on the nature of wastewater it is decided which type of coagulant will be used before final disposal. However, further research and development activities are required in order to limit the technical, economic, social and environmental impacts. So, it is necessary to ensure the safety, efficacy, quality of the treated wastewater.

The produced sludge was performed using various instrumental analyses. FT-IR spectra of produced sludge showed the presence of hydroxyl group, bending vibration of the oxazine ring, bending vibration of the Al-OH-Al groups, the aromatic C-H out-of-plane bending vibrations of the aromatic ring C-H in-plane bending on 1,4-disubstituted benzene. EDX and WDXRF analysis of the sludge indicates the presence of the carbon, aluminum,

sulfur, oxygen, and chlorine. The surface charge of the sludge was 39.0 mV as detected by the Zeta Potential analysis. SEM image showed that Sludge had non-uniform shape and randomly forming aggregates that are largely in an amorphous structure. From TGA-DSC curve, significant mass losses were observed at different temperatures and a sharp endothermic peak was observed at 109^{o}C due to the evaporation of absorbed water from PAC treated sludge.

Wastewater treatment is the only way to overcome the present situation of environmental pollution caused by textile industry. In the wastewater treatment process, the removal of dyes, physicochemical parameters from wastewater becomes a subject of paramount importance. Today, most industry owners are reluctant to use coagulants for the treatment of wastewater as the cost price is too high. Removal of pollutants by coagulation process using various types of aluminum waste products as a raw material could be an effective as well as economical approach for removing the pollutants present in untreated wastewater sample. It is difficult to degrade the dyeing effluent using a single treatment unit such as physical, chemical, and biological. It is difficult to degrade the dyeing effluent using a single treatment unit such as physical, chemical, and biological. Therefore, the study suggested a combination of the units for achieving a higher degradation of the effluents. Based on the nature of wastewater it is decided which type of coagulant will be used before final disposal. However, further research and development activities are required in order to limit the technical, economic, social and environmental impacts.

7.2 Future directions

The findings of this study have some significant suggestions for practice. The selection of appropriate treatment parameters and technologies is one of the major challenges and significant factors that determines the further development of company, municipality or entire country treatment processes. Further research is necessary to develop a dynamic, economical, and potential coagulant derived from the aluminum scraps. Some recommendations are given below:

1. Future research could possibly take into account molecular formulae, crystal structures and charges on the inorganic particles present in suspension in the water, for easy disposal.

2. This research work was carried out with an industrial wastewater of a single dye system. Studies on a multi-component system using binary, effluents from the garments industry, and multitudinal dyes need to be done to determine the effect of the presence of more than one dye on the coagulation capacity of a specific one.
3. The comparative study was carried out with only one conventional coagulant (alum) as a coagulant. Studies on other conventional coagulants should be done to determine the effectiveness of other coagulants with PAC.
4. Comparative studies with different sources of waste aluminum may be carried out to compare their coagulation capacities.
5. Estimate the residual aluminum after treatment of wastewater by PAC and process it.

Future researchers should conduct more studies on this area to cover the existing gaps and make improvements on the coagulation methods method as well as the choice of coagulant. More research should be needed to investigate combined coagulant (composite coagulant) instead of single coagulant.

Appendix A

A.1. ANOVA Table: Effect of PAC dose on dye removal.

Source	DF	SS	MS	F-Value	P-Value
Dose (mg)	8	16074.0	2009.24	92.27	0.000
Error	18	392.0	21.78		
Total	26	16465.9			

A.2. Tukey Pairwise Comparison: Effect of PAC dose on dye removal.

Dose (mg)	N	Mean	Grouping
2.5	3	88.64	A
3.0	3	80.64	A
2.0	3	60.07	B
1.5	3	43.13	C
4.0	3	37.88	C
3.5	3	37.87	C
1.0	3	24.01	D
0.5	3	18.625	D
0.0	3	18.234	D

Appendix B

B.1. ANOVA Table: Effect of pH on dye removal.

Source	DF	SS	MS	F-Value	P-Value
Solution pH	11	5042.79	458.435	112.29	0.000
Error	24	97.98	4.083		
Total	35	5140.77			

B.2. Tukey Pairwise Comparison: Effect pH on dye removal.

pH	N	Mean	Grouping
6.0	3	83.70	A
4.5	3	78.03	AB
5.5	3	75.581	BC
5.0	3	72.419	BCD
7.0	3	71.35	CD
3.5	3	68.597	DE
6.5	3	63.71	EF
4.0	3	59.369	FG
8.5	3	57.74	G
7.5	3	56.87	G
8.0	3	47.025	H
3.0	3	43.404	H

Appendix C

C.1. ANOVA Table: Effect of contact time on dye removal.

Source	DF	SS	MS	F-Value	P-Value
Time (min.)	5	1250.4	250.07	19.83	0.000
Error	12	151.3	12.61		
Total	17	1401.7			

C.2. Tukey Pairwise Comparison: Effect of contact time on dye removal.

Time (min.)	N	Mean	Grouping
20	3	87.37	A
25	3	86.26	A
15	3	84.496	A
10	3	82.4957	A
5.0	3	69.191	B
1.0	3	66.50	B

Appendix D

D.1. ANOVA Table: Effect of shaking speed on dye removal.

Source	DF	SS	MS	F-Value	P-Value
Speed (rpm)	5	12421.4	2484.27	233.57	0.000
Error	12	127.6	10.64		
Total	17	12549.0			

D.2. Tukey Pairwise Comparison: Effect of shaking speed on dye removal.

Speed (rpm)	N	Mean	Grouping
150	3	92.992	A
200	3	90.895	A
100	3	76.678	B
50	3	42.245	C
20	3	35.977	CD
0	3	27.47	D

Appendix E

E.1. ANOVA Table: Effect of settling time on dye removal.

Source	DF	SS	MS	F-Value	P-Value
Settling time (min.)	5	2691.23	538.247	155.31	0.000
Error	12	41.59	3.466		
Total	17	2732.82			

E.2. Tukey Pairwise Comparison: Effect of settling time on dye removal.

Settling time (min.)	N	Mean	Grouping
45	3	87.97	A
35	3	87.67	A
25	3	79.981	B
15	3	77.43	B
5	3	61.803	C
0	3	55.938	D

Appendix F

F.1. ANOVA Table: Effect of solution concentration on dye removal.

Source	DF	SS	MS	F-Value	P-Value
Solution concentration (mg/L)	4	14878.0	3719.49	500.35	0.000
Error	10	74.3	7.43		
Total	14	14952.3			

F.2. Tukey Pairwise Comparison: Effect of solution concentration on dye removal.

Solution concentration (mg/L)	N	Mean	Grouping
10	3	94.11	A
5	3	24.41	B
20	3	21.38	B
40	3	11.768	C
60	3	9.155	C

Appendix G

G.1. ANOVA Table: Effect of PAC dosage on turbidity removal.

Source	DF	SS	MS	F-Value	P-Value
Dosage (mg)	6	12150.2	2025.04	52569.14	0.000
Error	14	0.5	0.04		
Total	20	12150.8			

G.2. Tukey Pairwise Comparison: Effect of PAC dosage on turbidity removal.

PAC dosage (mg)	N	Mean	Grouping
2.5	3	99.9141	A
10	3	97.4487	B
5	3	97.3205	B
20	3	95.6192	C
40	3	83.017	D
1	3	63.531	E
0	3	29.692	F

G.3. ANOVA Table: Effect of alum dosage on turbidity removal.

Source	DF	SS	MS	F-Value	P-Value
Dosage (mg)	6	12906.6	2151.10	9812.14	0.000
Error	14	3.1	0.22		
Total	20	12909.7			

G.4. Tukey Pairwise Comparison: Effect of alum dosage on turbidity removal.

Alum dosage (mg)	N	Mean	Grouping
5	3	97.969	A
10	3	95.6192	B
2.5	3	94.786	B
20	3	92.797	C
40	3	90.746	D
1	3	52.454	E
0	3	30.171	F

Appendix H

H.1. ANOVA Table: Effect of pH on turbidity removal by PAC.

Source	DF	SS	MS	F-Value	P-Value
pH	6	5098.18	849.697	8450.75	0.000
Error	14	1.41	0.101		
Total	20	5099.59			

H.2. Tukey Pairwise Comparison: Effect of pH on turbidity removal by PAC.

pH	N	Mean	Grouping
6	3	99.8603	A
7	3	97.1192	B
8	3	95.259	C
9	3	90.609	D
5	3	80.4500	E
4	3	64.937	F
3	3	56.974	G

H.3. ANOVA Table: Effect of pH on turbidity removal by alum.

Source	DF	SS	MS	F-Value	P-Value
pH	6	4455.17	742.528	18080.05	0.000
Error	14	0.57	0.041		
Total	20	4455.74			

H.4. Tukey Pairwise Comparison: Effect of pH on turbidity removal by alum.

pH	N	Mean	Grouping
7	3	95.6192	A
8	3	91.046	B
6	3	89.7051	C
9	3	80.321	D
5	3	76.6949	E
4	3	61.692	F
3	3	53.5991	G

Appendix I

I.1. ANOVA Table: Effect of contact time on turbidity removal by PAC.

Source	DF	SS	MS	F-Value	P-Value
Contact time	5	5501.16	1100.23	66203.31	0.000
Error	12	0.20	0.02		
Total	17	5501.36			

I.2. Tukey Pairwise Comparison: Effect of contact time on turbidity removal by PAC.

Time (min)	N	Mean	Grouping
20	3	99.1846	A
15	3	96.2462	B
25	3	94.8679	C
10	3	83.2192	D
5	3	64.9231	E
1	3	52.3859	F

I.3. ANOVA Table: Effect of contact time on turbidity removal by alum.

Source	DF	SS	MS	F-Value	P-Value
Contact time	5	6066.01	1213.20	60362.45	0.000
Error	12	0.24	0.02		
Total	17	6066.25			

I.4. Tukey Pairwise Comparison: Effect of contact time on turbidity removal by alum.

Contact time (min)	N	Mean	Grouping
20	3	95.5897	A
25	3	91.0808	B
15	3	90.3449	C
10	3	75.9231	D
5	3	61.692	E
1	3	44.3487	F

Appendix J

J.1. ANOVA Table: Effect of shaking speed on turbidity removal by PAC.

Source	DF	SS	MS	F-Value	P-Value
Shaking speed	5	13266.3	2653.26	1055021.05	0.000
Error	12	0.0	0.00		
Total	17	13266.3			

J.2. Tukey Pairwise Comparison: Effect of shaking speed on turbidity removal by PAC.

Speed (rpm)	N	Mean	Grouping
150	3	98.4590	A
200	3	95.8859	B
100	3	94.1923	C
50	3	73.7974	D
20	3	44.9782	E
0	3	28.0966	F

J.3. ANOVA Table: Effect of shaking speed on turbidity removal by alum.

Source	DF	SS	MS	F-Value	P-Value
Shaking speed	5	13364.9	2672.98	138769.54	0.000
Error	12	0.2	0.02		
Total	17	13365.1			

J.4. Tukey Pairwise Comparison: Effect of shaking speed on turbidity removal by alum.

Shaking speed (rpm)	N	Mean	Grouping
150	3	95.6333	A
200	3	92.6026	B
100	3	88.967	C
50	3	69.629	D
20	3	40.4974	E
0	3	24.5269	F

Appendix K

K.1. ANOVA Table: Effect of Settling time on turbidity removal by PAC.

Source	DF	SS	MS	F-Value	P-Value
Settling time	5	4466.89	893.378	163743.06	0.000
Error	12	0.07	0.005		
Total	17	4466.96			

K.2. Tukey Pairwise Comparison: Effect of Settling time on turbidity removal by PAC.

Settling time (min)	N	Mean	Grouping
35	3	99.1372	A
45	3	99.1205	A
25	3	88.2115	B
15	3	75.0038	C
5	3	67.3564	D
0	3	57.3874	E

K.3. ANOVA Table: Effect of Settling time on turbidity removal by alum.

Source	DF	SS	MS	F-Value	P-Value
Settling time	5	4953.63	990.726	132010.04	0.000
Error	12	0.09	0.008		
Total	17	4953.72			

K.4. Tukey Pairwise Comparison: Effect of Settling time on turbidity removal by alum.

Settling time (Min)	N	Mean	Grouping
35	3	96.8795	A
45	3	96.773	A
25	3	85.6564	B
15	3	71.7667	C
5	3	63.1038	D
0	3	53.0385	E

Appendix L

L.1. ANOVA Table: Effect of Coagulant dosage on COD removal by PAC.

Source	DF	SS	MS	F-Value	P-Value
Dosage	6	5461.31	910.218	10536.91 10536.91	0.000
Error	14	1.21	0.086		
Total	20	5462.52			

L.2. Tukey Pairwise Comparison: Effect of Coagulant dosage on COD removal by PAC.

Dosage (mg)	N	Mean	Grouping
10	3	51.429	A
5	3	46.772	B
20	3	45.291	**C**
2.5	3	44.762	C
40	3	42.222	D
1	3	36.402	E
0	3	0.0000	F

L.3. ANOVA Table: Effect of Coagulant dosage on COD removal by alum.

Source	DF	SS	MS	F-Value	P-Value
Dosage	6	4034.40	672.400	10007.83	0.000
Error	14	0.94	0.067		
Total	20	4035.34			

L.4. Tukey Pairwise Comparison: Effect of Coagulant dosage on COD removal by alum.

Dosage (mg)	N	Mean	Grouping
10	3	45.185	A
5	3	40.847	B
20	3	37.989	C
2.5	3	37.672	C
40	3	33.439	D
1	3	33.016	D
0	3	0.000000	E

Appendix M

M.1. ANOVA Table: Effect of pH on COD removal by PAC.

Source	DF	SS	MS	F-Value	P-Value
pH	6	165.303	27.5506	416.67	0.000
Error	14	0.926	0.0661		
Total	20	166.229			

M.2. Tukey Pairwise Comparison: Effect of pH on COD removal by PAC.

pH	N	Mean	Grouping
6	3	50.899	A
7	3	48.57	B
8	3	47.407	C
5	3	46.878	C
4	3	44.339	D
9	3	43.492	E
3	3	42.3633	F

M.3. ANOVA Table: Effect of pH on COD removal by alum.

Source	DF	SS	MS	F-Value	P-Value
pH	6	349.579	58.2632	1200.70	0.000
Error	14	0.679	0.0485		
Total	20	350.258			

M.4. Tukey Pairwise Comparison: Effect of pH on COD removal by alum.

pH	N	Mean	Grouping
7	3	45.079	A
8	3	42.751	B
6	3	39.048	C
9	3	38.624	C
5	3	36.296	D
4	3	34.074	E
3	3	32.9806	F

Appendix N

N.1. ANOVA Table: Effect of contact time on COD removal by PAC.

Source	DF	SS	MS	F-Value	P-Value
Contact time	5	242.917	48.5834	1115.65	0.000
Error	12	0.523	0.0435		
Total	17	243.440			

N.2. Tukey Pairwise Comparison: Effect of contact time on COD removal by PAC.

Time (min)	N	Mean	Grouping
20	3	51.323	A
15	3	49.841	B
10	3	47.513	C
25	3	47.407	C
5	3	44.339	D
1	3	40.1411	E

N.3. ANOVA Table: Effect of contact time on COD removal by alum.

Source	DF	SS	MS	F-Value	P-Value
Contact time	5	38.2999	7.65998	155.86	0.000
Error	12	0.5898	0.04915		
Total	17	38.8897			

N.4. Tukey Pairwise Comparison: Effect of contact time on COD removal by alum.

Contact time (min)	N	Mean	Grouping
20	3	37.249	A
15	3	36.296	B
25	3	35.344	C
10	3	34.709	D
5	3	33.439	E
1	3	33.1570	E

Appendix O

O.1. ANOVA Table: Effect of shaking speed on COD removal by PAC.

Source	DF	SS	MS	F-Value	P-Value
Shaking speed	5	252.846	50.5692	1890.40	0.000
Error	12	0.321	0.0268		
Total	17	253.167			

O.2. Tukey Pairwise Comparison: Effect of shaking speed on COD removal by PAC.

Speed (rpm)	N	Mean	Grouping
150	3	50.265	A
200	3	49.418	B
100	3	47.302	C
50	3	46.243	D
20	3	44.339	E
0	3	40.4938	F

O.3. ANOVA Table: Effect of shaking speed on COD removal by alum.

Source	DF	SS	MS	F-Value	P-Value
Shaking speed	5	252.846	50.5692	1890.40	0.000
Error	12	0.321	0.0268		
Total	17	253.167			

O.4. Tukey Pairwise Comparison: Effect of shaking speed on COD removal by alum.

Shaking speed (rpm)	N	Mean	Grouping
150	3	43.49	A
100	3	42.434	B
200	3	41.799	C
50	3	37.989	D
20	3	35.344	E
0	3	33.5097	F

Appendix P

P.1. ANOVA Table: Effect of Settling time on COD removal by PAC.

Source	DF	SS	MS	F-Value	P-Value
Settling time	4	4466.89	893.378	163743.06	0.000
Error	10	0.07	0.005		
Total	14	4466.96			

P.2. Tukey Pairwise Comparison: Effect of Settling time on COD removal by PAC.

Settling time (min)	N	Mean	Grouping
35	3	51.43	A
25	3	47.513	B
15	3	45.397	C
5	3	41.164	D
0	3	38.836	E

P.3. ANOVA Table: Effect of Settling time on COD removal by alum.

Source	DF	SS	MS	F-Value	P-Value
Settling time	4	255.741	63.9351	3058.70	0.000
Error	10	0.209	0.0209		
Total	14	255.950			

P.4. Tukey Pairwise Comparison: Effect of Settling time on COD removal by alum.

Settling time (Min)	N	Mean	Grouping
35	3	43.386	A
25	3	42.646	B
15	3	41.27	C
5	3	37.037	D
0	3	32.3457	E