Effect of Coagulant Aid (P-Floc) in treatment of dye wastewater

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***Abstract*— This study was conducted to investigate the effect of solution pH and dosage of cationic polyelectrolyte, P-floc as a flocculant in treatment of dye wastewater and to characterize the quality of treated dye wastewater. For removal dyes in wastewaters, different treatment ways such as adsorption, coagulation-flocculation, chemical oxidation, photo-degradation and biological exchange are useful. Among the above methods, the process of coagulation-flocculation is widely used in the manufacture of dyes from industrial waste water. Typically, alum or a grounded metal used to treat dye wastewater. But the manufacture of aluminium alum are contributing to the pollution of wastewater that can negatively affect our ecosystem, especially to aquatic life. Natural flocculants is very useful to solve this problem. Therefore, p-floc is very useful in the treatment of dye wastewater instead of alum to prevent the use of metal-based. The experiment was conducted using Jar test method to determine the optimum pH value, coagulant and flocculant dose. In this research, the study was conducted by varying p-floc dosage in between 1.0 ml to 3.5 ml in order to study their effect in flocculation and the optimum condition for each parameter. Parameters such as turbidity, Chemical Oxygen Demand (COD), Total Suspended Solid (TSS), Colour, Phosphate, Sulfate, DPD Total Chlorine, DPD Free Chlorine and heavy metals have been evaluated. It is discovered that decolourization of dye was occurred between pH 6 to 8 and between dosage P-Floc 2.5 to 3mL. The results obtained were based on turbidity, Chemical Oxygen Demand (COD), Total Suspended Solid (TSS), Colour, Phosphate, Sulfate, DPD Total Chlorine, DPD Free Chlorine and heavy metals. Based on this fact, P-Floc has a big potential to become as a coagulant aid to treat dye wastewater.**

Keywords—coagulant, P-Floc, dye wastewater, coagulation-flocculation, Jar Test

I. INTRODUCTION

One of the most important industry in Malaysia is a textile dyeing which is ranked in the dyeing and finishing processes in the textile dyeing industry, however, the impact in the generation is produced large quantities of wastewater coloured dye [5]. The untreated colour wastewater that discharge into the colour can be very damaging ecosystems of bodies of water distribution. Typically, the dye waste water which is untreated from the fabrication of dyestuff and dyeing industry have many diverse colours and difficult to biodegrade because of a complex chemical structure. Discharge of waste water into the color of the body of water can reduce the penetration of light and at that point can interrupt the process of photosynthesis in an aquatic life [4]. In addition, the adverse effects of the dye are cancer on human health, an allergy, dermatitis as well as skin irritation [4].

In recent years, the widespread contamination of aquatic ecosystems has been increased due to improper disposal of waste water dyes including particularly in developing countries [12]. Textile dyeing process is the most environmentally unfriendly due to industrial waste water highly polluted with dyes, textile auxiliaries and chemicals used [9]. In the textile industry, the main environmental issue is wastewater and other minor problems such as solid waste, waste of resources and employment, health and safety. Preliminary studies indicate that the wastewater from the textile industry poses a danger to the environment in which large parts of the world. Therefore, the dye bath effluent has been treated before it being released into the environment or urban treatment plants [10].

Textile dye molecules with different structures within low or no biodegradability. The elimination of the colour connected with the breakup of conjugated unsaturated bonds in the molecule. Therefore, some chemical treatment process has been widely used to treat wastewater of textile. Most of the research, such as activated carbon adsorption by photocatalytic oxidation, chemical precipitation, ozonation and oxidation of Fenton emphases on the colour removal even if it is effective, but it is expensive plus it also can promote secondary pollution. The jar test techniques is used in the water treatment plant to determine the optimal coagulant concentration and turbidity of the water balance. Moreover, the matter which are dissolved, suspended, colloidal and cannot be set down are reduced in a physical-chemical treatment plus colouring of the dye. After improving the operating conditions for instance pH, coagulants and flocculants concentration, the oxygen demand of the chemical (COD) of the effluent textiles can be reduced between 50% and 70%, but it depends on the characteristics of wastewater [14].

In industrial wastewater treatment, coagulation and flocculation process is carried out to achieve the maximum removal of chemical oxygen demand (COD), total phenolic content (TP) and total suspended solids (TSS). For that reason, Amudaa and Amoob [3] studied the consequence of coagulant dosage, polyelectrolyte dosing, pH and addition of coagulant aid, polyelectrolyte. Then, they found out the critical parameters for effective treatment of industrial waste water. In coagulation and flocculation process, colloidal particles are detached from water. In the treatment of dye wastewater, P-floc was used as a coagulant aid. Features p-floc is cationic polyelectrolyte molecular weight of the liquid medium. It works effectively as primary coagulants and coagulant aid in water clarification and it can also act as a dewatering aid in the industrial waste sludge.

The jar test is a common laboratory procedure used to determine the optimum operating conditions for water or wastewater treatment. This method allows adjustments in pH, variations in coagulant or polymer dose, alternating mixing speeds, or testing of different coagulant or polymer types, on a small scale in order to predict the functioning of a large scale treatment operation. A jar test simulates the coagulation and flocculation processes that encourage the removal of suspended colloids and organic matter which can lead to turbidity, odor and taste problems. Testing is done for the reasons such as, correct chemical dosage and pH adjustments, sludge characteristics, turbidity removal, color removal, THM (trihalomethanes) removal, and control chemical costs. In water and wastewater treatment operations, the processes of coagulation and flocculation are employed to separate suspended solids from water. Although the terms coagulation and flocculation are often used interchangeably, or the single term "flocculation" is used to describe both; they are, in fact, two distinct processes. Coagulation and flocculation processes are used to improve removal of solids in both drinking water and wastewater treatment, through destabilization and aggregation of suspended material. Floc formation and electric charges are the basis of coagulation. When a coagulant is added to the water and mixed thoroughly, a thick gelatinous precipitate is formed which is insoluble in water.

Aluminium sulfate (alum), ferrous sulfate, ferric chloride and ferric chlorosulfate were commonly used as coagulants [7]. Additionally, high COD removal capacities have been observed during the combined action of alum and lime for the treatment of stabilized leachates. However, it has been stated out recently that there may be a possibility for aluminium-based coagulants to link with Alzheimer's disease [8]. Hence, a special attention has been given to the environmental friendly coagulant or flocculent, chitosan.

P-floc 77 is a cationic polyelectrolyte that have high level of cationic charge mass, meet the demand cationic suspended particles as well as negatively charged initiate clotting and the formation of flocs. It has a low molecular weight medium that allows a slow building flocs (provided there is sufficient length of time the relationship between floc formed and suspended matter) that provide maximum removal of suspended solids (turbidity maximum reduction). It works effectively as primary coagulants and coagulant aid in water clarification and as an aid in sludge dewatering industrial waste. It is also useful in other solid-liquid separation such as secondary clarifiers, settling the flow of products and explain the emulsion.

Apparently, no major studies have been done to clarify the textile wastewater by using flocculant, P-Floc in coagulation and flocculation process. Therefore, this study was carried out to analyze the effect of coagulant aid, P-Floc in clarifying dye wastewater in flocculation process in different experimental conditions. The optimum pH and dosage needed to achieve the best performance of P-Floc in flocculation process were determined.

II. METHODOLOGY

A. Materials

For this research, the sample of dye wastewater were obtained from the Wastewater Treatment Plant nearby the Pilot Plant, UiTM Shah Alam.

B. Chemicals

Ferric chloride ($FeCl_3$) was used as a coagulant, while the cationic polyelectrolyte (P-Floc) was used as a coagulant aid. In the process of coagulation-flocculation, sodium hydroxide (NaOH, alkaline) and hydrogen bromide (HBr, acidic) was used as an agent of pH regulating. Distilled water is used to formulate all solutions dyes, thickeners and coagulant aid solution.

C. Instruments

ICP-OES (Perkin Elmer OES Optima 8000) was used to determine the heavy metal such as cadmium and lead and essential elements such as calcium, potassium and sodium. The COD test was performed by calorimetric method using Spectrophotometer HACH Model DR/2000. It is used to measure the oxygen demand for the oxidation of organic matters by a strong chemical oxidant which is equivalent to the amount of organic matters in sample. Moreover, turbidity was measured by using turbiditimeter which the sample was filled into a sample cell and put into the cell holder for measurement. While the Total Suspended Solid (TSS), Colour, Phosphate, Sulfate, DPD Total Chlorine, DPD Free Chlorine were measured by using UV-Vis Spectrophotometer.

D. Jar test

Each beaker were filled with the 500 ml dye wastewater. The 6 beakers were adjusted by varies the pH and were marked with 1 to 6. First, dye pH was adjusted to pH 5, 6, 7, 8, 9 and 10, correspondingly via 1.0 M HBr or 1.0 M NaOH to adjust the desired pH, because pH disturbs the structure of the dye molecules, then change the amount of the solution. Then, 1 ml of $FeCl_3$ with 0.5 ml P-Floc was added to each beaker and stirred in the mixing gently for 5 minutes for allowing the floc occurred then carry on with speedy mixing about 100 rpm for 30 minutes. After that, the mixer was switched off and the beaker is leaved to settle down for 30 minutes. The final turbidity and color in each beaker is measured and recorded. Final turbidity and color were measured using UV-Vis Spectrophotometer. For the next round of trials, the coagulant, $FeCl_3$ and coagulant aid, 0.5 ml of P-Floc has been added to the waste water which has a pH optimum dye that has been learned from previous experiments. Now, the amount of coagulant was adjusted to 2 ml, 3 ml, 4 ml, 5 ml, 6 ml and 7 ml and once again stirred in the mixing gently for 5 minutes to allow the floc then proceed with the speed of the mixing rapidly about 100 rpm for 30 min. After that, the mixer was turned off and the beakers were permitted to settle down for 30 minutes and the turbidity and color in each beaker were measured and recorded. Then for the third round of jar test, the coagulant aid, P-floc was adjusted to 1 ml, 1.5 ml, 2 ml, 2.5 ml, 3 ml and 3.5 ml with a pH optimum dye wastewater and optimal dose of the coagulant, $FeCl_3$ has been known from previous experiments which is 3mL. Formerly, it was stirred at the mixing gently for 5 minutes to allow the floc then he continued rapid mixing speed of about 100 rpm for 30 min. After that, the beaker is allowed to settle for 30 minutes and the final turbidity and colour in each beaker is measured. For each experiment was repeated three times. Finally, after all the experiments that have been conducted, data collected will be analyzed. In this study, only pH, color, turbidity, chemical oxygen demand (COD), heavy metals and physical characteristic were analyzed.

III. RESULTS AND DISCUSSION

A. Introduction

In this study, coagulation-flocculation process was conducted for the treatment of the dye wastewater. Numerous jar tests were carried out in order to establish a practical understanding of the coagulation performance and to find optimum pH, coagulant dosage and coagulant aid dosage. There are several parameters such as turbidity, Chemical Oxygen Demand, Total Suspended Solid, Colour, Phosphate, Sulfate, DPD Total Chlorine, DPD Free Chlorine and heavy metals have been evaluated. Following figures show the final results of all experiment.

B. *Effect of pH on coagulation*

In the coagulation-flocculation process, pH is very important since the coagulation occurs within a specific pH range for each coagulant. In this study, a wide range pf pH between 5 to 10 was selected. To determine optimum pH value, dosage of $FeCl_3$ and P-Floc were constant. pH is an important parameter for coagulation process since it controls hydrolysis species. When a coagulant such as ferric salt is added to water, a series of soluble hydrolysis species are formed. These hydrolysis species have positive or negative charges depending on the water pH. They are positively charged at low pH (< 6) and negatively charged at high pH. The positively charged hydrolysis species can absorb onto the surface of colloidal particles and destabilize the stable colloidal particles. This mechanism is called 'charge neutralization'. A precipitate of ferric hydroxide is formed at sufficiently high coagulant dosage. These precipitates can physically sweep the colloidal particles from the suspension. This mechanism is called 'sweep-floc coagulation' [10]. In this study, after addition of $FeCl_3$ as a coagulant, mechanism of coagulation showed properties of sweep-floc coagulation due to the high pH in operation.

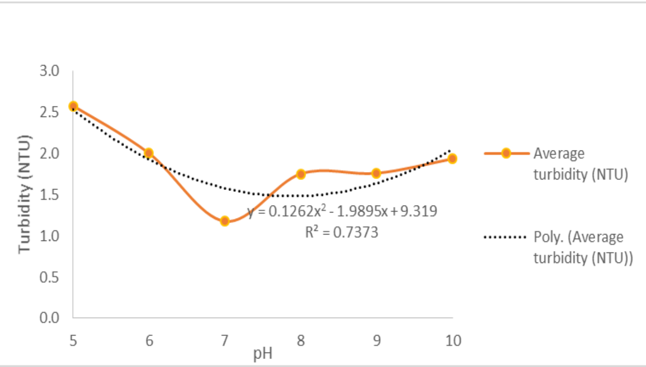

Figure 1.1: The effect of pH on the turbidity

The effect of pH value on the turbidity using P-Floc as a coagulant aid is shown in Figure 1.1. The volume of $FeCl_3$ that have been used was 1mL and 0.5 mL of P-Floc. It can be clearly seen that the optimum range of pH in term of turbidity is 7 for the coagulation-flocculation process. The turbidity at pH 7 is the lowest which is 1.18 NTU. Figure 1.1 show the trend line, $R^2 = 0.7373$, which is a relatively good fit of the line to the data. The turbidity shows a decrease at pH 5 to 7. Turbidity is a measure of the degree to which the water loses its transparency due to the presence of suspended particulates. The more total suspended solids in the water, the murkier it seems and the higher the turbidity. Turbidity is considered as a good measure of the quality of water. There are various parameters influencing the cloudiness of the water which makes the turbidity becomes highest. Some of these are phytoplankton, sediments from erosion resuspended sediments from the bottom (frequently stir up by bottom feeders like carp), waste discharge, algae growth and urban runoff.

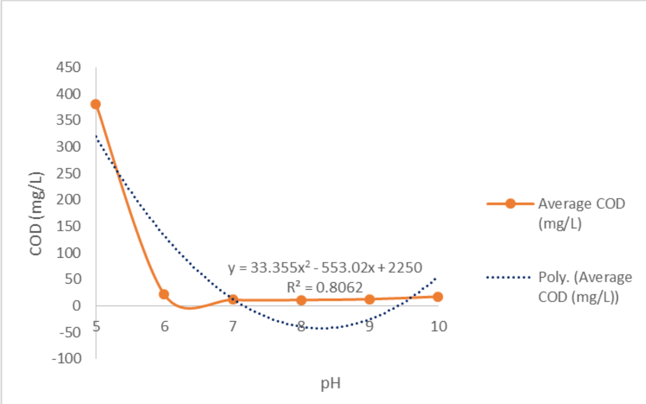

Figure 1.2: The effect of pH on Chemical Oxygen Demand (COD)

The results of the study showing the effect of pH on COD when P-Floc was used as coagulant aid is presented in Figure 1.2. When pH increased from 5 to 8, the COD value decreased from 381 mg/L to 11.22 mg/L. At pH 9 to 10, the COD value increased. It is clear that optimum pH was 8 for the coagulation-flocculation process. Figure 1.2 show the trend line, $R^2 = 0.8062$, which is a relatively good fit of the line to the data. The Chemical Oxygen Demand (COD) method determines the quantity of oxygen required to oxidize the organic matter in a waste sample, under specific conditions of oxidizing agent, temperature, and time. Higher COD levels mean a greater amount of oxidizable organic material in the sample, which will reduce dissolved oxygen (DO) levels. A reduction in DO can lead to anaerobic conditions, which is deleterious to higher aquatic life forms.

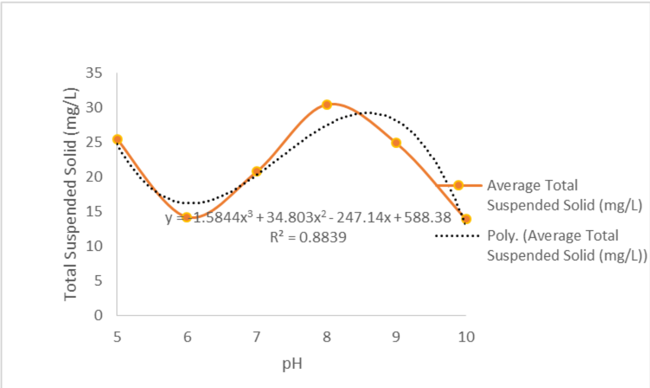

Figure 1.3: The effect of pH on Total Suspended Solid (TSS)

Figure 1.3 show the effect of pH on Total Suspended Solid (TSS) when P-Floc was used as coagulant aid. Total suspended solid is the solid which are present in suspended form and are attributed to the present of different dyestuffs used in the textile industry. In the present research, the optimum pH is 6 which is the TSS value is 14.22 mg/L. TSS can include a wide variety of material, such as silt, decaying plant and animal matter, industrial wastes, and sewage. High concentrations of suspended solids can cause many problems for stream health and aquatic life. Total suspended solids are a significant factor in observing water clarity [9]. The more solids present in the water, the less clear the water will be.

C. *Effect of dosage of cationic polyelectrolyte, P-floc as a flocculant*

Dosage was one of the most important parameters that been considered to determine optimum condition for the performance of P-Floc in coagulation and flocculation. Basically, insufficient dosage or overdosing would result in the poor performance in flocculation. Therefore, it was crucial to determine the optimum dosage in order to minimize the dosing cost and obtain the optimum performance in treatment. Polyelectrolytes are commercial coagulant aids. Synthetic polyelectrolytes are currently the most widely used chemicals in the treatment of industrial wastewaters. Generally, a little amount of polyelectrolyte dosage is enough to reach high efficiency. Because of they have some advantages including the possibility of structuration in response to specific requirements, greater purity, higher quality, stability and greater efficiency [1]. With polyelectrolytes as coagulant aids, the metal coagulant dosage can be reduced without cutting down the performance [6]. Yu et al, [15] reported that the charge density and molecular weight of polyelectrolyte play important role in the coagulation.$FeCl_3$ was used as coagulants coupled with cationic polyelectrolyte, P-Floc as a coagulant aid (flocculant).

The effect of flocculant dosage (1-3.5mL) were separately measured on the dye removal with a fixed dosage $FeCl_3$ (3mL) at initial solution pH 7. The pH was controlled by adding either acid (HBr) or base (NaOH). Also, during this step, the coagulation mixing speed of about 210 rpm for the first 5 minutes followed by slow mixing 100 rpm for 25 minutes and then settling for 30 minutes. The results of the effect by $FeCl_3$ coupled with P-Floc are shown in Figure below.

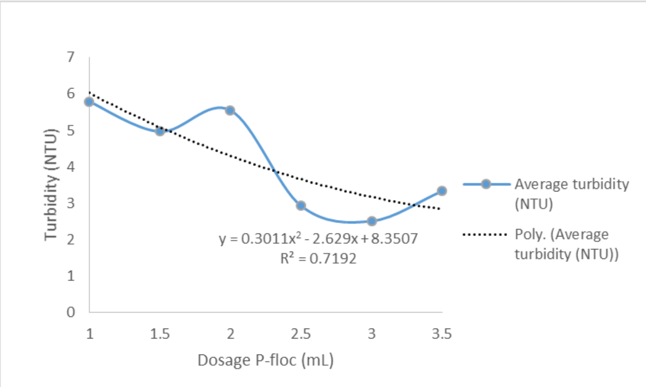

Figure 1.4: The effect of dosage P-Floc on the turbidity

The effect of dosage P-Floc on the turbidity is shown in Figure 1.4. The volume of $FeCl_3$ that have been used was 3mL and pH value was at 7. It can be clearly seen that the optimum range of dosage P-Floc in term of turbidity is 3mL for the coagulation-flocculation process. The turbidity at dosage P-Floc 3mL is the lowest which is 2.51mL. Figure 1.6 show the trend line, $R^2 = 0.7192$, which is a relatively good fit of the line to the data. The turbidity shows a decrease at 2mL to 3mL.

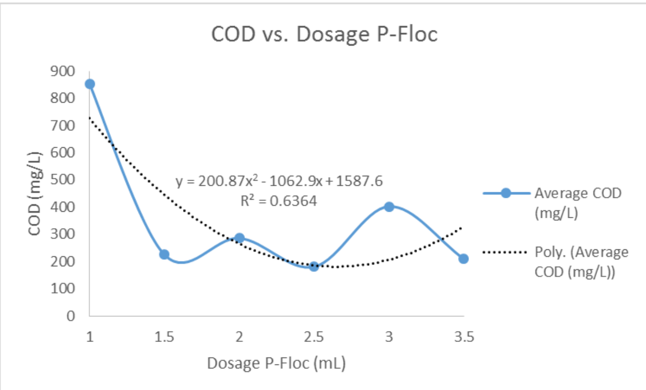

Figure 1.5: The effect of dosage P-Floc on the COD

Effect of P-Floc dosages on the COD value is shown in Figure 1.5. Coagulation-flocculation was performed between dosages P-Floc 1 to 3.5 mL. At a dosage 2.5 mL, the COD value was 181mg/L that was accepted as the optimum dosage. At high coagulant doses, metal hydroxides are produced and organic substances are removed by incorporation into or sorption onto hydroxide flocs [7].

At the lowest concentration of polyelectrolyte, COD value was 851.67 mg/L which is the highest value of COD. With increase in polyelectrolyte concentration, COD decreased to 210 mg/L. At a concentration 181 mg/L, effluent COD decreased thus 2.5 mL polyelectrolyte dosage was accepted as optimum dosage. Optimum concentration of polyelectrolyte forms a bridge between particles and cause good flocculation. However high concentration of polyelectrolyte forms an envelope on the suspending particles and causes them to remain in suspension thus removal efficiency decreases [7]. Similar result was obtained from this study and when the polyelectrolyte concentration was increased, process performance was decreased.

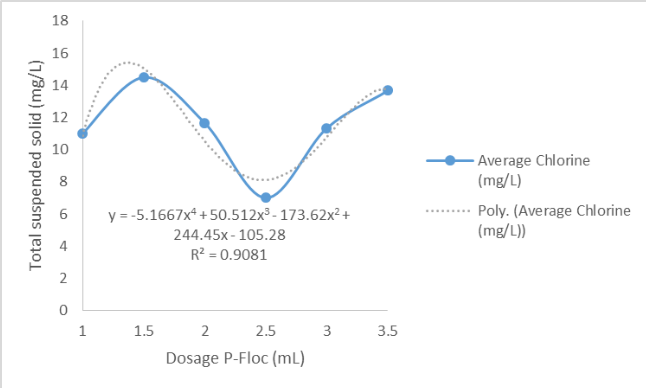

Figure 1.6: The effect of dosage P-Floc on the TSS

Figure 1.6 show the effect of dosage P-Floc on the total suspended solid. Based on the result, dosage of 2.5 mL was accepted as an optimum dosage. Environmental waters may contain a variety of solid or dissolved impurities. In quantifying levels of these impurities, suspended solids is the term used to describe particles in the water column. Practically, they are defined as particles large enough to not pass through the filter used to separate them from the water. Smaller particles, along with ionic species, are referred to as dissolved solids. In considering waters for human consumption or other uses, it is important to know the concentrations of both suspended and dissolved solids. The most common pollutant in the world is “dirt” in the form of TSS.

The implications of total suspended solids (TSS) are high concentrations of suspended solids may settle out onto a streambed or lake bottom and cover aquatic organisms, eggs, or macro-invertebrate larva and this coating can prevent sufficient oxygen transfer and result in the death of buried organisms. Furthermore, the high concentrations of suspended solids decrease the effectiveness of drinking water disinfection agents by allowing microorganisms to “hide” from disinfectants within solid aggregates. This is one of the reasons the TSS, or turbidity, is removed in drinking water treatment facilities.

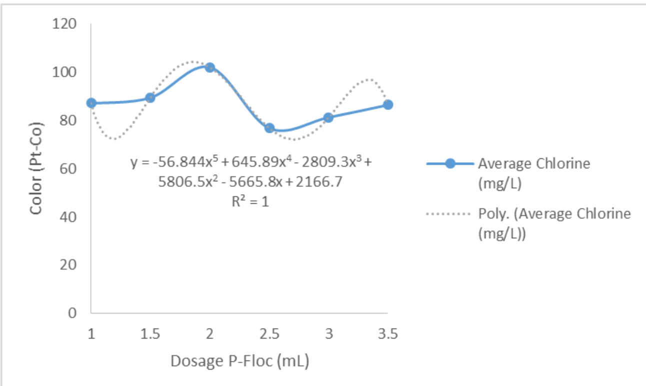

Figure 1.7: The effect of dosage P-Floc on colour

Figure 1.7 show the effect of dosage P-Floc on colour in treatment of dye wastewater. A gradual decrease in color removal was observed dosage P-Floc 2 to 2.5 mL. Beyond dosage 2.5 mL, there was minimal change in colour removal. Between dosage 2 mL and 3 mL, it shows that there exists an optimum dosage for color removal. At a dosage 2.5mL, the color removal was about 76.83. Any increase in dosage beyond 2.5mL, did not result in significant color removal. From Figure 1.7 it is evident that our study followed the trend as depicted in the charge neutralization zone and did not show any significant color removal in the sweep coagulation zone.

IV. CONCLUSION

In treatment of dye wastewater that contains relatively high COD, coagulation process can be used as a pretreatment process. In this study, $FeCl_3$ had the lowest COD value when it was used with P-Floc and it was determined that addition of cationic polyelectrolyte, P-Floc as coagulant aids, improved the COD. The effect of P-Floc as a coagulant aid, was evaluated on the improvement of coagulation flocculation process with $FeCl_3$ for the treatment of dye wastewater. When P-Floc was used in combination with $FeCl_3$, the color removal was increased at 3mL of doses of coagulants. Based on the results and possibilities, using P-Floc as coagulant aid accompanied with $FeCl_3$ can be advisable and more economical option for the treatment of dye wastewater since it can lower the value of turbidity, COD, Total Suspended Solid and Colour. In this study, P-floc is very useful in the treatment of dye wastewater instead of alum to prevent the use of metal-based and it is environmental friendly.

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