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PULP AND PAPER WASTEWATER COLOR REMOVAL

by

Parsa Pezeshk

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Abstract

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Pulp and paper industries generate highly-colored wastewaters, the color of which is not removed by conventional biological treatment. As a result, the persistent color of the wastewater can potentially disrupt the aesthetic appearance of the receiving stream as well as releasing potentially toxic components to the environment. Coagulation and flocculation is a chemical treatment practiced to remove color from pulp mill wastewaters. The main focus of this work was to study the color removal efficiency of coagulation/flocculation treatment on a specialty pulp and paper mill wastewater located in the State of Tennessee. In this regard, the effect of coagulant, coagulant aid, and flocculent dosages as well as the wastewater pH and temperature on color removal process were examined. Furthermore, bentonite clay and powdered activated carbon (PAC) effectiveness for color removal were tested.

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1. Introduction

1.1 Pulp and paper industry

United States pulp and paper industry is a world leader in the production of pulp and paper’ producing approximately 26 billion tons of pulp every year, which accounts for 35% of the pulp produced in the world. The pulp and paper industry is considered the fifth largest industry and the third largest polluter in the United States. The wastewater can be characterized in terms of measurable factors such as solids (suspended, colloidal and dissolved), adsorbable organic halides (AOX, a measure of halogenated organic compounds), chemical oxygen demand (COD), biochemical oxygen demand (BOD), color, and alkalinity.

More than 250 chemicals have been identified in the effluents of pulp and paper mills. Chlorinated dibenzo-p-dioxins (CDDs) and chlorinated dibenzofurans (CDFs) – by-products of chemical reactions taking place in pulp bleaching – are examples of highly toxic persistent organic pollutants (POPs), which are resistant to degradation and have been classified as “priority pollutants” by the EPA *(USEPA 1993)*. These compounds are found to be toxic to aquatic life and able to induce genetic changes in exposed organisms (*Nestmann 1985*).

Existence of toxic constituents to the microorganisms also imposes the need to pre-treat the wastewater in case it is to be treated biologically. Several studies have shown that exposure to pulp and paper wastewaters has adverse effects on phytoplankton and zooplankton, and causes respiratory stress, oxidative stress, liver damage, and genotoxicity on animals living in the waters that receive the effluent *(Ericson and Larsson 2000; Johnsen et al. 1998; Leppanen and Oikari 1999; Lindström-Seppa et al.*

1998; Owens et al., 1994; Vass et al. 1996; Schnell et al., 2000). Wood extractives at even low concentration may bring about toxic and hormonal effects in aquatic environments *(Lehtinen et al. 1999; Mörck et al. 2000*; *Oikari et al. 1983).* On the other hand, halogenated organic compounds (HOCs) can accumulate in fish tissues and aquatic organism cells (bioaccumulation), which can bring about concerns in the food chain (biomagnifications) and pose risks to humans consuming fish products.

Furthermore, it has been reported that exposure to dioxins and furans can cause skin disorders, cancer, and detrimental effects on human reproductive and immune system *(EPA Pulp and Paper Fact Sheet 1997).* Dioxin is recognized as a human carcinogen by the World Health Organization. It has also been reported that pulp and paper wastewater discharged to the environment can cause health impacts such as diarrhea, vomiting, headaches, nausea, and eye irritation in children and workers exposed *(Mandal and Bandana 1996).*

Finally, thermal impacts caused by releasing the wastewater into the stream can lead to the reduction of oxygen solubility in water, which in turn endanger the aquatic life.

1.2 Overview of the wastewater color problem

On Average, pulp and paper industry produces about 20,000 to 60,000 gallons of highly-colored brownish wastewater per ton of product *(Pokhrel and Viraraghavan 2004).* Color – as a nonconventional pollutant and the main focus of this study – interferes with aquatic life balance by limiting the light transmittance through the water. Secondly, colored wastewater can reduce the aesthetic quality of the receiving stream and bring about an objectionable appearance. An increase in public awareness regarding the fate and effects of pulp and paper industry wastewaters is leading the authorities to apply more stringent regulatory limits to the effluents of this industry in order to control both the detrimental and aesthetic effects of the wastewater.

Biological treatment can remove most of the wood extractives (*Kostamo et al. 2004)*. However, these constituents can transform into other toxic compounds during treatment. On the other hand, conventional biological treatment processes have little or no ability to remove the wastewater color. As a result, the biologically-treated wastewater released to the streams will remain highly colored and give rise to an aesthetically unpleasant color to the stream as well as potentially releasing toxic substances to the environment

1.3 Source of color in pulp industry wastewater

The brownish color of the wastewater is due to the existence of lignin and its derivatives and polymerized tannins *(Crooks and Sikes 1990; Goring, 1971; Reeve, 1991; Sankarna and van Lundwig, 1971; Sundman et al., 1981)*. Lignin is a natural amorphous, branched and cross-linked polymer, having several functional groups such as phenolic, hydroxyl, benzylichydroxyl and carbonyl, and aliphatic carboxyl groups *(Srivastava et al. 2005)*. Lignin basic units are linked by at least 10 different linkages. Lignin, the most abundant polymer in nature after cellulose *(Cathala et al. 2003)*, occurs in plant cell wall and act like a glue to hold cellulose fibers together making them rigid. *Goring (1971)* showed that lignin molecules tend to undergo self-condensation reactions particularly in acidic media, which also explained the resistance to degradation. The brown color of lignin solution is found to arise from the double bonds conjugated with an aromatic ring, quinone methides and quinone groups *(Muna Ali and Sreekrishnan 2001)*.

Pulping is the initial stage of the paper making industry and is the largest source of the pollution in the whole papermaking process. In chemical pulping, the wood chips are cooked with appropriate chemicals in an aqueous solution at high temperatures and pressures to break chips into a fibrous mass. In the Kraft process, white liquor is added to dissolve the wood lignin. White liquor is a mixture of sodium hydroxide (NaOH) and sodium sulfide (Na_2S). In order to produce a high-quality paper, lignin polymers should be removed from the fiber *(Ghoreishi and Haghighi 2007)*. Chemical pulping and bleaching processes selectively remove lignin without significantly degrading the cellulose fibers. The white liquor and the chips are heated to a cooking temperature of about 170 °C for about 2 hours. During this treatment, the hydroxide and hydrosulfide anions react with the lignin, causing the polymer to fragment into smaller water/alkali-soluble fragments.

In the next step, the remaining lignin is removed by bleaching. In the bleaching step, elemental chlorine (Cl_2), ozone (O_3), chlorine dioxide (ClO_2), oxygen (O_2), sodium hypochlorite (NaClO), or hydrogen peroxide (H_2O_2) can be used. Chlorine-based bleaching processes produce toxic chlorinated organic compounds and should preferably be substituted by chlorine-free bleaching chemicals. The dissolved lignin is the component giving the wastewater its dark brown color and remains in the solution as colloidal particles. Lignin and its derivatives show high stability to degradation *(Archibald and Roy-Arcand 1995; Liverniche et al. 1983)* due to the presence of carbon-to-carbon biphenyl linkages (*Leiviskä 2009; Muna Ali and Sreekrishnan 2001)*. It is reported that lignin behaves like a hydrocolloid and precipitates as the pH is lowered *(Marton 1964). Pessala et al. (2004)* proposed that lignin may cause growth inhibition of living organisms.

Chemical treatment of pulp and paper mill effluents can be practiced either upstream or downstream of biological treatment. The former alternative is applied when the components in the wastewater are found to interfere with the biological treatment significantly and, as a result, should be removed first. In this case, these components can resist biological degradation or be toxic to the microorganisms that carry out the biological treatment. Consequently, pretreatment before biological treatment enhances the performance of the biological process *(Leiviskä 2009)*. To achieve additional polishing of the wastewater, downstream treatment of pulp and paper wastewater is also practiced to remove recalcitrant compounds *(Stephenson and Sheldon 1996)*.

1.4 Purpose of the Study

Until recently, contribution of pulp and paper mill effluent to the color of water bodies had not been a major problem. As a result, color had been classified as a non-conventional pollutant *(Muna Ali and Sreekrishnan 2001)*. However, the growing public awareness regarding the harmful effects of pulp and paper mill effluents on the environment and consequently the introduction of stringent regulations established by various authorities are forcing the industries to treat their effluents to the required compliance levels before discharging them into the environment. The main purpose of this study was to develop treatment approaches that can lead to more than 90% color removal from the undiluted wastewater samples of a pulp industry.

1.5 Features of the Study

The challenging feature that distinguishes this work from other studies carried out in the past to remove the pulp and paper wastewater color is the high intensity of the wastewater, which is about 30,000 Pt.Co. units. From an overview of the literature, it can be seen that if not all, many of the previous authors have failed to report the intensity of the original wastewater color being studied and have only reported the percent removals of color achieved. However, the author believes that the results reported will not have a practical value for future research unless the value of original sample color is reported in conjunction with the percent removal. The argument is based on the fact that, in coagulation and flocculation, there is no linear relationship between the dosage of the coagulant and the amount of color removed, which necessitates the performance of jar tests to observe the trend. In other words, the amount of color removed can be considered a function of both the coagulant dosage and the original sample color.

The second distinguishing feature of this work is utilizing a combination of a coagulant, coagulant aid, and flocculent. Most of the studies done before in this respect are focused mainly on finding the proper coagulant type and dosage to remove color from pulp and paper wastewaters. However, in this study, different combinations of coagulant, coagulant aid, and flocculants were tested systematically as well as pH, temperature, and other variables in order to gain better understanding. Moreover, the pulp wastewater used in this study was process wastewater from a specialty pulping process.

1.6 Contribution of the study

Despite the fact that pulp and paper industries are required to provide some level of treatment to remove the effluent color to some extent so that it does not produce an "objectionable color" in the receiving stream, there is still a lack of generally-agreed upon definition of "objectionable color." As a result, the author strongly believes that further work is needed in order to define limits for pulp and paper effluent with respect to color.

2. Literature review

2.1 Colloids

Colloidal particles in wastewater are solids in aqueous dispersion which do not settle by the force of gravity, are considered to be stable in solution, and, as a result, cannot be removed by conventional physical treatments *(Hammer and Hammer 1997)*. These particles are roughly 1 nm to 1 μm in diameter *(Reynolds and Richards 1996)* and are responsible for a portion of color and turbidity of a solution. Colloidal particles present in wastewater can be either hydrophobic or hydrophilic. The hydrophobic types – such as clay – have no affinity for the liquid medium and are, consequently, susceptible to coagulation. On the other hand, hydrophilic colloids – such as proteins – are attracted to water molecules that retard the coagulation process *(Eckenfelder 2009)*. Most naturally-occurring colloidal particles are believed to bear negative charges. Consequently, when in suspension, these particles repel each other, which is considered the reason they stay in solution, do not form flocs spontaneously, and, therefore, do not settle.

2.2 Coagulation/Flocculation

Coagulation is the chemical treatment used in order to give these particles the ability to coalesce and form flocs by adding certain chemicals to the wastewater followed by rapid mixing in order to provide the contact required to interact with the particles. It is believed that these chemicals which carry positive charges – called coagulants hereafter –

have the ability to destabilize the colloidal negative surface charges when added to the water or wastewater so that they can subsequently coalesce and form heavy flocs. In the next step, flocculation, slow mixing of the water for about 30 minutes provides more contact time for the destabilized particles to form strong floc particles. In the final step, the flocs formed are allowed to settle (usually within 2-4 hours), and are removed as sludge.

There are two main types of chemicals that are used in coagulation/flocculation processes *(Bratby 2008; Stechemesser and Dobias 2005):*

1. Inorganic and organic coagulants:
    - 1-1. Mineral additives: lime, calcium salts, etc.
    - 1-2. Hydrolyzing metal salts: aluminum sulfate, ferric chloride, ferric sulfate, etc.
    - 1-3. Pre-hydrolyzed metals: polyaluminum chloride, polyaluminumsilicate sulfate, etc.
    - 1-4. Polyelectrolytes (coagulant aids)
2. Organic flocculants:
    - 2-1. Cationic and anionic polyelectrolytes
    - 2-2. Non-ionic polymers
    - 2-3. Amphoteric and hydrophobically-modified polymers
    - 2-4. Naturally-occuring flocculents: starch derivatives, tannins, alginates, etc.

Usually, aluminum and iron salts with different basicities and counter-ions (e.g. chloride, sulfate, etc.) are available to use *(Leiviskä 2009)*.

When a coagulant is added to a water or wastewater, destabilization of the colloids occurs mainly due to three mechanisms: charge neutralization, sweep flocculation, and patching and bridging *(Leiviskä 2009).*

The first mechanism causes the colloidal particles to form flocs due to the neutralization of their surface charges so that they can aggregate. In this case, overdosing the coagulant will result in re-stabilization of the particles by reversing their surface charges from negative to positive, which in turn leads to the emergence of electrostatic repulsion forces between the particles. The second mechanism is the case when insoluble precipitates form upon adding the coagulant to the water that can enmesh/sweep the colloidal particles during mixing.

In the third mechanism, the coagulant has the ability to adsorb to the colloidal particles via hydrogen or ion bonding *(Bolto and Gregory 2007)* and create local positive charges that can interact with the negative charges. Also, divalent positive metal ions are able to act as a bridge between the anionic polymer and the negative charges on the particles (*Berg et al. 1993*). As a result, when positively charged metal coagulants are added first followed by adding a long chain polymer having negative charges, the assembly of long-chain polymers connected to the particles via metal ions will settle more rapidly.

As a coagulant salt added to water dissociates, the metallic salt is hydrolyzed and creates positively charged polyvalent hydroxo-metallic ion complexes that are able to adsorb to the surface of negative colloidal solids achieving particle destabilization. It is believed that the hydrolysis products tend to undergo polymerization reactions *(Stumm* *and Morgan 1962; Stumm and O'Melia 1968)*. General hydrolysis reaction of trivalent metal salts is shown below *(Ching et al. 1994)*:

$$mM^{3+} + nH_2O \rightarrow M_m(OH)_n^{(3m-n)+} + nH^+$$

As shown by the reaction, M^{3+} ions dissolved in water remain in the solution in very acidic conditions. As the pH or the coagulant concentration is raised, the reaction is directed to the right by hydrolysis and several polymeric species of MOH^{2+}, $M(OH)_2^{+}$, $M_2(OH)_2^{4+}$, $M(OH)_4^{5+}$, $M(OH)_3$ (solid), and $M(OH)_4^{-}$ are formed. These interactions explain the existence of an optimum characteristic pH for each coagulant that leads to the most desired results. The positive polymeric species are found to have amorphous structures with very large surface areas *(Rankte 1988)*, are absorbed onto the anionic particle surfaces (in the water), and become insoluble *(Dentel and Gosset 1988)*. Flocs formed in water/wastewater coagulation processes are believed to assume fractal structures *(Thomas et al. 1999)*. Generally, the effectiveness of coagulation process depends on the coagulant type and dosage, the solution pH and ionic strength, concentration and the nature of the organic compounds in water, and the mixing intensity *(Amirtharajah and O'Melia 1990; Dentel 1991; Rankte 1988;)*.

2.3 Coagulant aids

The addition of some chemicals will usually enhance coagulation by promoting the growth of large, rapid-settling flocs. Polyelectrolytes are high-molecular-weight polymers which contain adsorbable groups and can be used as coagulant aids, which are found to improve the coagulation process by polymer bridging and adsorption, or by charge neutralization *(Bolto 1995; Bratby 2008; Levine 1981; Stechemesser and Dobias 2005).*

Three types of polyelectrolytes are cationic, anionic, and nonionic. Cationic polyelectrolyte adsorbs on a negative colloid or floc particle. An anionic polyelectrolyte replaces the anionic groups on a colloidal particle and the polymer. Finally, a nonionic polyelectrolyte adsorbs and flocculates by hydrogen bonding between the solid surfaces and the polar groups in the polymer *(Eckenfelder et al. 2009)*. Generally, polymers with different molecular weights are available and are categorized as low MW (less than 10^5), medium MW ($10^5 – 10^6$), and high MW (more than 10^6) *(Bolto and Gregory 2007).* Large flocs (0.3 to 1 mm) are created when small dosages of polyelectrolyte (1 to 5 mg/L) are added in conjunction with the coagulant. Compared to inorganic coagulants, lower dosages of polymers are needed, which leads to the formation of less precipitates. However, organic polymers are more expensive compared to inorganic coagulants *(Leiviskä 2009).* Cationic polyelectrolytes are found to be more toxic to aquatic life than anionic or nonionic ones (*Bolto and Gregory 2007*).

Furthermore, due to the fact that coagulation process can bring about small or fragile flocs (that would break up) at low temperatures, coagulant aids or polymeric additives are used in conjunction with the primary coagulant to provide better floc quality by enhancing the agglomeration process of the flocs *(Bratby 2008; Renault et al. 2009; Stechemesser and Dobias 2005).*

2.4 Flocculents

Unstable particles formed in the coagulation process due to charge neutralization mechanism are called primary floc (or coagulation floc). Flocculants are typically organic chemicals that are able to improve the coagulation process and cause the primary flocs to grow in size and become stabilized. The larger flocs that are formed as a result of bridging between the smaller flocs are known as secondary floc *(Stephenson et al. 1996)*. Two types of flocculation are micro-flocculation (perikinetic) and macro-flocculation (orthokinetic). In micro-flocculation, particles aggregate as a result of random thermal motions of fluid molecules – known as Brownian motion. On the other hand, macro-flocculation is the aggregation of particles as a result of velocity gradient induced by mixing. Another form of macro-flocculation occurs when large particles with higher settling velocities overtake smaller particles thus forming larger flocs. The purpose of flocculation is to produce larger particles that can be removed by gravity sedimentation or filtration *(Metcalf and Eddy 2003)*.

Inorganic flocculants are not used commonly nowadays due to the following disadvantages *(Bratby 2008; Renault et. al 2009; Stechemesser and Dobias 2005; Türkman and Uslu 1991):*

1. Large amounts are required to obtain the desired flocculation quality.
2. They give rise to large volumes of sludge to deal with.
3. Their performance is highly sensitive to pH.
4. They are not efficient in agglomeration of very fine particles.
5. They are applicable to a limited number of dispersed systems.

However, there are some suggested inorganic flocculants (such as polyferric chloride: PFC, pre-hydrolyzed polyferric sulfate: PFS, etc.) that exhibit higher levels of hydrolysis, which makes them more effective in lower doses compared to the conventional reagents and applicable over a wide range of pH and temperature.

Two types of organic flocculants are synthetic and natural. Synthetic flocculants are polymers composed of various monomeric units (such as acrylamide, acrylic acid, diallyldimethylammonium chloride, etc.). Natural flocculants are natural polymers (such as starch cellulose, alginate, natural gums, tannins, etc.) *(Aesoy and Haraldesen 2003;Takeda et al. 2004)*.

The last step in the coagulation/flocculation process is sedimentation, flotation, or filtration in order to separate the flocs from the clear supernatant *(Leiviskä 2009)*.

2.5 Color removal technologies

Most of the color in pulp and paper wastewaters is the result of chemical pulping and bleaching processes. Conventional activated sludge processes (biological) may not provide satisfactory treatment of pulp and paper wastewater *(Rintala and Lepisto 1992; Schnell et al. 2000)*. As a result, tertiary treatments may be required to further treat the wastewaters in order to meet the effluent discharge standards *(Srivastava et al. 2005)*. Main color removal technologies can be classified as:

1. Physiochemical Treatment
2. Biological Treatment

In physiochemical treatment, removal of suspended solids, colloidal particles, and color is achieved by any of the following treatments:

- Coagulation
- Ozone oxidation
- Activated carbon adsorption
- Membrane separation

The focus of the following part of this text is on physiochemical treatment approaches found in the literature.

2.6 Physicochemical treatment of pulp and paper wastewater

Colored wastewaters of pulp and paper mills are found to be highly anionic. As a result, cationic coagulants are expected to neutralize the wastewater *(Ho et al. 1991).* Furthermore, color removal is dependent on the coagulant dosage until a breakpoint is reached, beyond which the amount of color in the supernatant starts to rise (since the coagulant dose exceeds the coagulant demand, which leads to re-stabilization of the colloidal particles responsible for the color. Generally, hydrolyzing metal salts of aluminum and iron are used widely as primary coagulants in wastewater treatment *(Stephenson and Sheldon 1996)*.

Chemical precipitation and coagulation are highly dependent on pH owing to the fact that the type of polymeric metal species formed when the coagulant is dissolved in water is determined by the pH *(Stumm and Morgan, 1962)*. On the other hand, the effect of pH on coagulation is explained by taking two competitive forces into account (*Randtke 1988)*. First, it is believed that there is a competition between H^+ and metal-hydrolysis products for organic ligands. At too low pH values, the protons are the dominant ions (compared to metal ions) to interact with organic ligands. In this case, poor removal occurs due to the fact that some organic acids formed are not precipitated. Secondly, there is also a competition between hydroxide ions (OH^-) and organic anions over adsorption sites on metal hydrolysis products. As pH is increased, the coagulating metal species become less positively-charged and, consequently, are less attracted to organic anions *(Ching et al. 1994)*, which leads to negligible coagulation rates.

An optimum pH range should be determined when coagulants are being used to treat wastewater. Lowering the pH from alkaline to near neutral levels typically affects the coagulation positively in terms of turbidity, color, suspended solids, and COD reduction. Also, the addition of metals (from the coagulants) decreases the pH due to the formation of metal hydroxide precipitates (as a result of the hydrolysis of coagulant) *(Renault et al. 2009)*. The lignin in pulp and paper wastewater is found to precipitate by lowering the pH to about 3 with a suitable mineral acid *(Rohella et al. 1996)*.

Aluminum-based coagulants such as alum, aluminum chloride, aluminum nitrate, and polyaluminum chloride are widely used in wastewater treatment. It is believed that free Al^{3+} is first hydrated when aluminum salts are added to aqueous solutions releasing hydrogen ions *(Dorea 2009; Stephenson and Sheldon 1996)*. These hydrogen ion can depress the pH and, consequently, monomeric and polymeric hydrolyzed aluminum species such as $Al(OH)^{+}$, $Al(OH)^{2+}$, $Al_2(OH)_2^{4+}$, $Al_3(OH)_4^{5+}$, $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$ *(Lin et al. 2008)*, and solid precipitates such as $Al(OH)_3$) are formed (*Rebhun and Lurie, 1993*).

Generally, the nature of hydrolysis species formed upon adding the conventional metal coagulants (such as aluminum and ferric sulfates or chloride) to water and their consequent performance depends not only on pH but also on the coagulant concentration, and the temperature and the nature of the solution *(Bratby 2008)*, which makes the analysis more complex. As a result, pre-hydrolyzed coagulants of aluminum (such as polyaluminum chloride) and iron (such as polyferric sulfate or in general, pre-hydrolyzed inorganic coagulants) are found to be more effective due to the fact that the formation of their hydrolysis products (species) is controlled during the preparation process *(Renault* *et al. 2009)*. In other words, the hydrolysis reactions are directed more toward the formation of desired metal species that are more effective in the coagulation.

Among the advantages of pre-polymerized inorganic polymers are that they are efficient over wide ranges of pH and temperature, are less sensitive to low temperatures, lower dosages are required compared to conventional coagulants, and lower metal residuals in the solution are produced. Basicity ratio (r) is defined as the molar ratio of hydroxide ions bound per mole of metal ions ($[OH^-]/[Al]$). Consequently, pre-hydrolyzed inorganic coagulants with higher basicity ratios depress the pH less than those with lower values (due to the consumption of less alkalinity).

Relative basicity is a value expressed as a percentage referring to the molar ratio of negative to positive charges of the coagulant *(Bratby 2008)*. The required flocculation time to remove turbidity is decreased as alum or polyaluminum chloride (PACl) compounds with higher basicity ratios are used.

It was shown that polyaluminum chloride compounds with relative basicity of 65% resulted in the best removal of turbidity *(Gillberg et al. 1994)*. The polymeric portion of PACl is found to be responsible for the charge neutralization of the particles in water *(Lin et al. 2008; Wang and Hsu 1994)*.Furthermore, research *(Matsumi et al. 1998)* has proved that the charge neutralization mechanism induced by PACl, compared to the enmeshment mechanism of alum, leads to faster aggregation of particles, which produces more compact and sheer-resistant flocs *(McCurdy et al. 2004)*.

It is found that PACl-based chemicals are more effective coagulants than alum at low temperatures and also produce less sludge *(Wang et al. 2009)*. In other words, alum performance is hindered at low temperatures (less than 5 °C) (*Dorea 2009; Morris and*

Knocke 1984; Van Benschoten et al. 1994). Furthermore, polyaluminum chloride coagulants result in lower changes in pH during coagulation (since they are partially neutralized during the preparation processes) and obviate the need to adjust the pH after treatment *(Renault et al. 2009)*. *Gregory and Dupont (2001)* showed that polyaluminum chloride, in comparison with alum, produces larger and stronger flocs that also settle faster. Minimum solubility of aluminum lies in the pH range of 6.0-7.0. As a result, optimum turbidity reduction using alum occurs within pH range of about 6.0-7.5 *(Berube et al. 2007; Dorea 2009)*. Flocs formed by alum in cold water are found to be mechanically weak. Moreover high concentrations of sulfate ions (SO_4^{2-}) are introduced into the water using alum, which raise the level of total dissolved solids and may lead to downstream treatment problems. On the other hand, as opposed to aluminum salts, ferric chloride coagulants do not contribute to Aluminum Residual (AR) in the finished water. However, regarding the disadvantages, liquid ferric chloride is an acidic, corrosive, and dark brown solution, which necessitates special handling procedures *(Stephenson and Sheldon 1996)*. In cases when coagulation-flocculation treated wastewater is reused by pulp and paper industry, residual aluminum in the filtrate (filtered supernatant from coagulation treatment) can consume peroxide in the bleaching step and, thus, have a negative effect *(Leiviskä 2009)*. To prevent this, very low aluminum dosages should be applied when performing coagulation so that the resulting residual aluminum concentration in the filtrate is at most 20 mg/L *(Terelius et al. 1999)*.

The residual concentration of metal (e.g. aluminum and iron) in the supernatant is pH dependent and should be determined for each metal salt and solution type *(Lindquist, 2003)*. *Beulker and Jekel (1993)* found that an aluminum salt was the most effective coagulant of pulp and paper wastewater (using oxygen and chlorine for bleaching of the pulp compared to lime and magnesium hydroxide).

Stephenson and Duff (1993) investigated the addition of iron, aluminum and calcium chloride alone and in combination with each other in a full-factorial experiment. Little evidence of any improvement due to combining coagulants was observed. The result was believed to be due to the existence of similar mechanisms of removal by iron and aluminum (*Almemark and Ekengren 1989; Stephenson and Duff 1993*). On the other hand, in the same work done by *Stephenson and Duff 1993,* it was found that changing the wastewater pH from 1.5 to 12.5 proved ineffective to precipitate a significant fraction of organics from the bulk liquor. However, the solubility of precipitated solids resulting from metal coagulation was highly dependent on pH. The precipitate formed under acidic conditions was shown to return to colloidal phase upon neutralization. Generally, ferric chloride coagulants are readily dissolved and are more effective over a broader pH range compared to alum (4-12 compared to 4.5-8) and produce stronger and heavier flocs. High coagulant dosages are believed to increase the coagulation rate by two mechanisms: 1) by increasing the concentration of metal hydroxide precipitate which results in an increase in aggregation rate, and 2) by enmeshing particles by sweep coagulation *(Ching et al. 1994).*

For aluminum salts, at acidic pH levels, the monomeric aluminum species are believed to be the dominant factor responsible for charge-neutralization and precipitation *(Hundt and O'Melia 1998)*. However, increasing the hydroxyl ion concentration results in the formation of polymeric species dominantly, which leads to the removal of particles by adsorption *(Stephenson and Duff 1995). Licsko (1993)* reported two pH optima for coagulation using aluminum salts. In the pH range of 6.0 to 6.5, the highest removal of colloidal particle was observed. However, in the pH range of 5.3 to 5.7, soluble organic compounds were found to be removed most efficiently.

Garg et al. (2010) reported the results of coagulation of pulp and paper diluted black liquor using alum, aluminum sulfate and ammonium, and acid precipitation (using sulfuric acid 10% by weight) at 95 °C, atmospheric pressure, and pH of 8.0. Each of the coagulants was tested at 5000 mg/L. After the addition of coagulants, pH of the wastewater was reduced to 4.50-5.0. All aluminum-based coagulants mentioned exhibited the same COD reduction of 61% (initial COD of 7000 mg/L). It was shown that increasing the temperature (from 25 to 95 °C) did not improve COD removal. However, the settling characteristic of sludge was observed to improve at higher temperatures. They stated that dosages of 5000 and 2000 mg/L resulted in 90% and 85% color removal respectively at pH of 5 and 25 °C. However, the authors have not mentioned the initial color measurement of the wastewater (sufficed to state that the wastewater was dark brown). They have finally concluded that the capability of the coagulant to reduce COD and color strongly depends on the pH: At an optimum pH of 5, by using commercial alum, the maximum COD and color removal of 63% and 90% was achieved respectively. They believe that the COD removal was mainly achieved due to the separation of lignin from the wastewater.

Ahmad et al. (2008) used alum and polyaluminum chloride (PACl) alone (as coagulants) and in combination with cationic polyacrylamide (C-PAM) and anionic polyacrylamide (A-PAM) on wastewater collected from equalization tank of a paper mill to remove turbidity, TSS and COD. The authors performed jar tests using pre-adjusted pH's of 5, 6, 7, 8, 9, and 10 and alum dosages of 50, 100, 200, 500, 1000, and 1500 mg/L for each pH. Samples were rapid mixed for 2 minutes at 200 rpm followed by slow mixing for 15 minutes at 40 rpm. It was concluded that decreasing the pH from basic to near neutral levels had a strong positive effect on turbidity, TSS, and COD reduction and found an optimum pH range of 5.0 to 6.5 and an optimum alum dosage of 1000 mg/L, which resulted in 99.8%, 99.4%, and 91% removal of turbidity, TSS, and COD respectively. The same pH and dosage combinations using PACl were tested. However, the effects of coagulant dosage and pH on turbidity reduction were not significant. Yet, the turbidity reduction started to drop at pH of 10. The highest and lowest turbidity reduction of 99.9% and 99.3% were observed. The optimum PACl dosage and pH were observed to be 500 mg/L and 6.0 respectively. The authors concluded that the effect of increasing the PACl dosage was minor on removal efficiency of TSS and COD. However, pH was a factor with significant effect on TSS and COD removal in the 8 to 10 range. The reduction in turbidity, TSS, and COD was not significantly affected by changing the flocculent dosages (from 1.0 to 6.0 mg/L at constant coagulant dosage of 500 mg/L alum and 200 mg/L PACl and constant pH of 6.0). The effect of flocculent addition on turbidity, TSS, and COD removal was also tested by keeping the flocculent dosage (C-PAM and A-PAM) and pH constant at 1 mg/L and 6.0 respectively. The coagulant dosage was increased from 50 to 2000 mg/L. It was observed that the addition of flocculent had a significant effect at lower dosages of coagulant of 50, 100, and 200 mg/L: the reduction efficiency of turbidity was improved from 80 to 96% for the alum dosage of 50 mg/L (using C-PAM). PACl also showed the same trend although the effect was not observed to be as great as in the case of alum. Finally it was concluded that the effect of increasing PAM's dosage did not have a significant effect on alum and PACl coagulation to remove turbidity, TSS, and COD. Also, C-PAM showed better performance than A-PAM when coupled with alum or PACl in the treatment of pulp and paper wastewater. Overall, alum (1000 mg/L) in combination with C-PAM was shown to be the best alternative among those tested in this study.

Bagasse fly ash (BFA) is a waste produced in sugar industries and can be converted into an inexpensive and effective absorbent composed of SiO_2, Al_2O_3, CaO, Fe_2O_3, and MgO *(Gupta and Ali 2000). Srivastava et al. (2005)* studied the efficacy of polyaluminum chloride (PACl) and BFA in removing color and COD of pulp and paper wastewater. BFA – characterized by large-sized fibrous particles – can be used to remove COD and color of pulp and paper wastewater. In comparison to other coagulant, PACl treatment requires smaller dosages which results in generation of less sludge. Activated carbon is one of the most commonly used absorbents. However, from an economical point of view, researchers have been interested in finding more cost-effective absorbents including bagasse fly ash (which is a good adsorbent of organics).The general formula of PACl is shown to be $[Al_2(OH)_nCl_{6-n}]_m$ with n=2-5 and m=4-10. It has been observed that as pH decreases, the removal of COD and color increased. However, the removal does not improve significantly below pH of 3. Thus, optimum pH to remove lignin in this study was found to be 3. Jar tests were conducted to compare the efficacy of PACl, ferrous sulfate ($FeSO_4.7H_2O$), and alum ($Al_2(SO_4)_3.18H_2O$) at pH of 3 to remove COD and color. Using the similar dosages of coagulants, PACl showed highest removal. Flocs generated from PACl coagulation are denser than water. PACl, having multivalent aluminum ions, neutralizes the colloidal particle charges and the hydrolyzed aluminum flocs enmesh the colloids. As a result, the removal is mainly due to charge neutralization and adsorption.The authors showed that PACl dosage should be more than 2000 ppm to achieve more than 80% COD and 90% color removal. BFA is shown to have large surface area of about 168 m^2/g mainly comprised of pore surface area with average pore diameter of 23.97 Å. Lignin precipitation is shown to enhance in acidic solution in the presence of multivalent cations *(Lindström 1980; Marton 1964)*. BFA with multivalent cations in its structure is believed to accelerate the coagulation of lignin. On the other hand, large surface area of BFA is expected to increase the removal of soluble COD and color by adsorption mechanism. *Srivastava et al. (2005)* showed that increasing the BFA dosage increases COD removal and color up to a certain point. At that point, increasing the dosage of BFA does not affect the removal significantly. An efficient absorbent is characterized by rapid uptake of components and establishing the equilibrium in a short period of time. It has been shown that the removal rate using BFA is very fast during the initial 10-60 minutes and no significant change in removal occurs beyond that time range. One explanation is based on the fact that after a certain point in time, pore spaces are occupied to a degree that any further adsorption is inhibited by the repulsion forces between the existing occupants and the free components in solution. The authors found that coagulation followed by adsorption using BFA in a two-stage treatment will work better to remove COD and color and found pH of 3 to be the optimum pH to treat their samples of pulp and paper wastewater. Optimum dosage of polyaluminum chloride was found to be 3000 ppm.

Ghoreishi and Haghighi (2007) studied the efficacy of sodium borohydride ($NaBH_4$) to change the structure of chromophores existing in pulp and paper wastewater having 1500 color units by hydrogenation of the double bonds at ambient temperature and pressure. As the authors argued, sodium borohydrate reactions can be carried out in water and $NaBH_4$ seemed to be the proper reducing agent since the color-causing chromophores are dissolved in water. They showed that color removal reaction using 200 ppm sodium borohydride at pH of 7.8 was of first order, with an initial color of 1500 color units, and resulted in 97% color removal for the specified sample. Consequently, they concluded the color removal reaction using $NaBH_4$ was of first-order. However, the conclusion can be false due to the fact that different dosages of $NaBH_4$ might produce different results. The other dosages were not tested to see if it would still be a first-order reaction. The hydrogenation test using pure hydrogen at 200, 500 and 1400 psig at 25 °C, 136 °C, and 275 °C respectively lead to 58%, 69%, and 99% color removal accordingly. One disadvantage of using $NaBH_4$ is this study was the release of boron into the wastewater. The authors have argued that 15% of the total effluent is responsible for 90% of the wastewater color in this case. Consequently, after treating the 15% of the total effluent with sodiumborohydride and diluting the mentioned volume with the 85% that is only 10% responsible for the color would not have a boron concentration detrimental to the environment.

Some metal ions including Fe^{2+} have special oxygen transfer properties. Iron (II) sulfate is usually used as the ferrous ion source. Ferrous ion (which acts as a catalyst) reaction with hydrogen peroxide, called Fenton reaction, is pH dependent *(Kremer 2003; Lin and Peng 1995)* and can generate highly reactive hydroxyl ions (OH.) according to the following reaction *(Ashraf 2006)*:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\cdot$$

Consequently, the ferric ion (Fe^{3+}) generated in the reaction reacts with hydrogen peroxide to regenerate ferrous ion (Fe^{2+}):

$$Fe^{3+} + H_2O_2 \rightarrow Fe(OOH)^{2+} + H^+$$

$$Fe(OOH)^{2+} \rightarrow Fe^{2+} + HO_2^{\cdot}$$

As the reaction shows, hydrogen ions are produced in the Fenton reaction.

At $pH < 1$, the Fenton Reaction is limited to the oxidation of ferrous ions by hydrogen peroxide:

$$2\ Fe^{2+} + H_2O_2 \rightarrow 2\ Fe^{3+} + 2\ OH^-$$

It has been shown that the generation of O_2 decreases as the pH is lowered. However, above $pH = 1$, when an excess of hydrogen peroxide is present, the following reaction also occurs *(Kremer 2003)*:

$$2\ H_2O_2 \rightarrow O_2 + 2\ H_2O$$

High pH values have been shown to be unfavorable for oxidation of organic compounds by Fenton's Reagent *(Hassan and Hawkyard 2002; Hsueh et al. 2005)*. *Catalkaya and Karagi (2007)* studied advanced oxidation effect on color, TOC, and AOX removal by using Fenton's reagent. First, it was found that Fe^{2+} concentration of 2.5 mM works best when used alone. Consequently, they used a constant concentration of 2.5 mM Fe^{2+} using different dosages of hydrogen peroxide, and it was shown that the Fenton's reagent using 2.5 mM Fe^{2+}/50 mM H_2O_2 resulted in the highest color, TOC, and AOX removals (85%, 88%, and 89% respectively) at pH of 5 within 30 minutes. Consequently, they have concluded that the optimum molar ratio of H_2O_2 is 20 accordingly. However, this conclusion can be questionable due to the fact that only one concentration of Fe^{2+} was tested versus different hydrogen peroxide dosages. As a result, other possible combinations were ignored and the result cannot be generalized in the absence of more statistically supportive results.

Boardman et al. (1992) studied the efficacy of foam separation to remove color from pulp and paper wastewater with 2,280 PCU using cationic surfactants. Their findings suggested that EHDABr (Ethylhexadecyldimethylammoniumbromide) – with the molecular formula of $CH_3(CH_2)_{15}NBr$ can coagulate lignin due to its positive charge and form stable foams. The study suggested that the performance of EHDABr was not enhanced significantly to remove color by changes in pH from 3 to 9. The authors found that coagulation and settling of the wastewater at a dosage of 100 mg/L EHDABr worked best and resulted in about 77% color removal. The color removal efficiency did not improve by increasing the dosage up to 250 mg/L. Furthermore, they showed that 200 mg/L EHDABr and five minute detention time using continuous foam separation by 1500 cm^3/min air flow resulted in 90% color removal.

Ganjidoust et al. (1997) and *Tong et al. (1999)* compared the effectiveness of several coagulants including chitosan (horseradish peroxide), aluminum sulfate ($Al_2(SO_4)_3$), two synthetic cationic polymers, namely hexamethylene diamine epichlorohydrine polycondensate (HE) and polyethyleneimine (PEI), and PAC (polyacrylamide) to remove AOX (Adsorbable Organic Halides), TOC (Total Organic Carbon), and color and showed that chitosan worked the best in coagulating the kraft mill black liquor. However, poor sludge settling characteristic was observed using chitosan

(Leiviskä 2009; Pokhrel and Viraraghavan 2004). Chitin is a natural polymer (polysaccharide) and the major component of the shells of crustaceans and insects. Chitosan, a derivative of chitin, is a biodegradable compound, partially soluble in dilute mineral acids, and has low toxicity. The protonation of amino groups in chitosan brings about positive charges in the polymer molecule making it capable of coagulating negatively-charged colloidal particles. Alum resulted in the same color removal compared to HE, PEI. Furthermore, HE and PEI (cationic polymers) were observed to bear better removal of TOC and color compared to PAM (nonionic polymer) *(Leiviskä 2009)*. *Tasumi et al. (1994*) also drew the same conclusion that cationic polymers worked better compared to nonionic ones. HE and PEI are examples of polyelectrolytes, which are linear macromolecular chains having a large number (on the order of polymerization degree) of charged or chargeable groups when dissolved in a certain polar solvent (generally water).

In addition, *Garcia-Heras* and *Forster (1989)* reported 99% color removal of a eucalyptus kraft pulp bleaching effluent using ferric chloride ($FeCl_3$). However, poor settling velocity and a high sludge volume production were observed. *Chou et al. (1998)* showed that using polyaluminum chloride (PACl) and dimethyl diallyl ammonium chloride (a cationic polyelectrolyte) as coagulant and flocculent respectively, results in a higher solid-removal efficiency of pulp wastewater (due to production of better flocs) compared to using PACl alone. *Lombardo et al. (1997)* reported a substantial improvement in floc settling characteristics when bentonite or organic flocculents were used in conjunction with ferric chloride or polyaluminum salts. *Rohella et al. (2001)* reported better removal of turbidity, COD, and color using polyelectrolytes compared to an aluminum salt. *Wong et al. (2006)* found that PAM (polyacrylamide) used alone worked effectively to remove turbidity, TSS, and COD from pulp and paper wastewater. Cationic polyacrylamide having a very high molecular weight with low charge density performed the best.

Ahmad et al. (2008) suggested that reduction of turbidity, TSS (total suspended solids), and COD were enhanced when polyacrylamide (PAM) was also used in conjunction with aluminum salt and polyaluminum chloride in the treatment of pulp and paper mill wastewater. Furthermore, cationic PAM was found to produce less sludge compared to anionic PAM.

Mohan and Karthikeyan (1997) investigated the uptake of lignin and tannin from an aqueous solution (prepared in the lab) by activated charcoal of geometric mean size of 70 μm and reported the sorption reaction to be of a first order, where chemosorptive, monolayer, and irreversible uptake of lignin and tannin occurs on a rather homogeneous surface of activated charcoal. The reaction mixture was composed of 50 mL solution with tannin/lignin concentration of 50 mg/L and 200 mg/L activated charcoal. The initial rate of color removal was shown to be rapid (63% within 20 minutes) and reached an equilibrium value of about 74% (from minute 60 to 600 (total percent removal and time). As a result, a contact time of one hour was found to be sufficient for the sorptive uptake of color. Furthermore, the authors reported that the amount of color removal was increased significantly for both tannin and lignin as the pH was lowered from 11 to 2. Ferrate (FeO_4^{2-}) is a supercharged molecule containing iron in the plus 6 oxidation state. Ferrate is extremely powerful and can provide more than one type of pollutant removal (oxidation, coagulation, and disinfection). Ferrate can be used to treat industrial wastewater that is difficult to treat (e.g., process wastewater from cellulose production). *White and Franklin (1998)* used sodium ferrate as a reagent for drinking water treatment. The chemical was used as a flocculent to remove color and manganese from a water source. *Jiang and Wang (2003)* evaluated the use of potassium ferrate (K_2FeO_4) as a chemical coagulant. They demonstrated that potassium ferrate performed better than ferric sulfate in treating waters containing humic and fulvic acids. Potassium ferrate was effective in reducing dissolved organic carbon levels and in lowering the trihalomethane formation potential (THMFP) by providing enhanced coagulation. *Wang et al. (2008)* investigated the ability of ferrate in conjunction with UV radiation to remove COD and color from printing and dyeing wastewater. The experimental results indicated that 77.5% COD and 76.6% color removal could be achieved at pH 5 with 77 mg/L^{-1} ferrate. Using the same ferrate dosage at a pH of 3 provided COD and color removal of 69% and 87.5%, respectively.

3. Materials and methods

3.1 Pulp and paper wastewater samples

Samples for study in this work were taken from a specialty pulp mill in the State of Tennessee. The samples were stored at 4 °C in 25-Liter Nalgene containers. Before performing each test, the sample was allowed to reach room temperature (23° C on average). The sample container was shaken before each test to mix any sediment that settled over time to the bottom of container and was, subsequently, used to perform the analysis.

3.2 Analysis

Laboratory experimentation is essential to establish the optimum criteria such as pH and coagulant dosage for coagulation of a wastewater. Two procedures are usually practiced in this type of analysis: jar test and zeta potential measurement.

Jar tests were performed on the samples in this work using *Phipps and Bird PB-700 Jartester*. Untreated raw wastewater sample was analyzed in each jar test performed. In this work, the main focus was to utilize the least amount of chemicals while not compromising the purpose of the study.

The samples in this study were not diluted and the following analyses were performed in each jar test in the following order.

- pH:

  Raw sample pH was determined using Orion *920A+ pH Meter*. The meter was calibrated using three standard buffer solutions with pH of 4, 7, and 10.

- Total alkalinity:

The total alkalinities of the samples were determined by potentiometric titration with sulfuric acid standard solution to end-point pH of 4.5. For the raw wastewater alkalinity measurement, 1 liter of raw sample and a 10N sulfuric acid solution prepared from *Fisher Scientific Certified A.C.S Plus Sulfuric Acid* were used. The samples were titrated against the acid solution and the pH was monitored continuously using the pH meter until the pH of 4.5 was reached, which is the titration endpoint for industrial or complex wastewaters. In this case, an indicator could not be used due to the fact that the pulp and paper samples were colored thus making it essentially impossible to notice the color change of indicator (if used). The alkalinity was calculated according to the following formula and reported as mg/L $CaCO_3$ *(Standard Methods for Examination of Water and Wastewater 2008):*

$$Alkalinity,\ \frac{mg}{L}CaCO_3 = \frac{\left(mL\ of\ \ acid\ \ used\right)\times\left(acid\ \ normality,\ \ \frac{equivalent}{L}\right)\times\left(50\frac{g\ \ CaCO_3}{equivalent}\right)\times\left(1000\frac{mg}{g}\right)}{mL\ of\ \ sample}$$

The justification to choose 10N acid solution and one liter of sample to perform the analysis for the raw wastewater was to minimize the increase in volume of the sample due to the addition of acid solution.

- Jar test:

  Before performing the jar test, the pH of each jar was adjusted to the desired level using sulfuric acid. Jars each containing 1000 mL of sample with adjusted pH were used to perform the jar test. The desired amounts of coagulant/coagulant aid were added to each jar followed by 3 minutes of rapid mixing at 175 rpm. In the next stage, the desired amounts of flocculent were added to each jar followed by 15 minutes of slow-mixing at 30 rpm. Sizes of the flocs were recorded during the slow-mixing phase. Consequently, the mixing was stopped and the flocs formed (if any) were allowed to settle and 15-minute-settleabilities and 30-minute-settleabilities were recorded.

- Color:

  The supernatants of the jars were extracted, filtered and used to measure the true color using a *DR/2400 Hach Spectrophotometer, Method 8025 Platinum Cobalt 5-500 units, Program 125 Color 465 nm*. Generally, color may be measured in terms of “apparent” or “true” color. The apparent color originates from both dissolved and suspended materials while the true color is merely due to the existence of dissolved materials in the solution. True color was determined in this work by filtering the treated samples (supernatants from the jar tests) prior to color measurement. In cases when the reading was beyond the range of the method, the solutions were diluted so that the color reading would fall in the range of the method. Efforts were made to minimize the dilution factor to reduce the potential error associated with the dilution process. Triplicate readings were performed for each measurement and the average value was reported.

- Solids:

  Total Suspended Solids (TSS) and Volatile Suspended Solids (VSS) of the supernatants as well as the raw wastewater were measured using *Whatman 934-AH Glass microfiber filters* with particle retention of 1.5 μm for each sample in triplicate according to Method 2540 D of Standard Methods for the Examination of Water and Wastewater 2005 Edition. The pads containing the supernatant solids were dried in the oven with a temperature of 105 °C for one hour, cooled in a desiccator for 15 minutes, and were weighed. For VSS measurement, the solids were also ignited at 550 °C for 15 minutes, cooled in the dessicator for 15 minutes and weighed again. Since the filter pad was almost clogged in a few seconds filtering the raw wastewater, only 10 mL of raw wastewater was filtered each time in order to reduce the filtration time knowing the fact that the effective particle retention size usually decreases as the filter becomes more clogged during the filtration process, which leads to retention of particles smaller than about 1.5 μm (that is not desired).

- Chemical Oxygen Demand:

  COD of each supernatant was measured using *DR/2400 Hach Spectrophotometer, Method 8000 3-15 mg/L, Program 439 COD LR* according to *Method 8000* described on the instrument manual. Two 0-150 mg/L COD digestion solution vials were used for each treated sample for COD measurement. A Hack COD Reactor was used to heat the vials for 2-hour digestion. Dilution factors of 20, 40, 50, and 100 were used depending on the test.

- BOD_5:

  Raw wastewater and the jar test supernatant BOD_5 values were determined each time according to Method 5210 of Standard Methods for Examination of Water and Wastewater (2005 Edition). DO was measured using *YSI 5100 Dissolved Oxygen Meter*. As a quality check measure, only the samples resulting in a minimum DO depletion of 2.0 mg/L and with at least 1.0 mg/L of residual DO were considered valid. Six replicates of each sample with two different concentrations were used. Six blank and six seed control solutions were also included in each BOD_5 test. The BOD was calculated according to the following formula *(Standard Methods for Examination of Water and Wastewater 2005):*

$$BOD_5,\ \frac{mg}{L} = \frac{(D_1 - D_2) - (S)V_s}{P}$$

Where:

D_1 = DO of diluted sample immediately after preparation, mg/L

D_2 = DO of diluted sample after 5 days incubation at 20 °C, mg/L

S = Oxygen uptake of seed, Δ DO per seed suspension volume added per bottle

V_s = Volume of seed in the test bottle, mL

P = Decimal volumetric fraction of sample used, where 1/P = dilution factor

3.3 Experimental design

In order to achieve color removal, a set of variables were systematically varied to determine a combination of variables at certain values which would yield the best results compared to others. The main purpose was to find a proper “combination” of treatments based on a systematic evaluation of a series of different variable values. Clearly, from the view point of limited resources, it is hardly possible to test all the possible combinations of a set of these variables. As a result, for each variable, the choice was limited to certain specified values to find the best choice among the selected options. Consequently, other possibilities were eliminated systematically to narrow the range of variable values. To do so, the main step was to determine the extreme ranges of variables beyond which the treatments were not effective (pH, coagulant/flocculent dosages, etc) in order to have a reasonable estimate of the ranges from which values should be chosen. In the next step, some specified values in the range were tested to narrow the choices as much as possible, which would fit the limited time and resources available the best, as all combinations of variables could not be tested.

Variables adjusted in the jar tests were as follows:

1. pH
2. Coagulant type
3. Coagulant dosage
4. Coagulant aid dosage
5. Flocculent dosage
6. Activated carbon dosage
7. Bentonite clay dosage
8. Temperature

Polyamine (PA) and polyacrylamide (PAM) were chosen as the coagulant aid and flocculent, respectively, in the beginning of the study. The general blueprint of the study consisted of the steps that follow. The results are reported in the Results and Discussion section.

3.3.1 Preliminary screening of primary coagulants

As the first step, pH of the raw wastewater was not adjusted. Initially, the performance quality of the coagulants was judged visually to observe the size of the flocs formed (if any). The following types were tested to determine the coagulant type(s) that were superior in performance to coagulate the raw wastewater.

1. Aluminum Chlorohydrate (ACH)
2. Polyaluminum Chloride (PACl)
3. Alum
4. Ferric Sulfate
5. Poly-DAMDAC
6. Epiamine
7. Aluminum Chloride (AC)
8. Sodium Aluminate

The types of coagulants with the most reasonable performance from preliminary test steps were chosen as the primary coagulants with which to work in this study. Floc sizes in this jar test were recorded as either x-large, large, medium, or small judged visually on a relative basis.

3.3.2 Detailed evaluation of the coagulants that were most effective in preliminary screening

At this step, the following variables were examined:

1. Primary coagulant dosage
2. Solution pH

3. Coagulant aid (polyamine) dosage
4. Flocculent (polyacrylamide) dosage

3.3.3 Evaluation of measures to enhance color removal

Finally, at this step, complementary tests were performed to determine whether or not the following variables could enhance the coagulation/flocculation process to achieve more color removal:

1. Bentonite clay dosage
2. Powdered Activated Carbon (PAC) dosage
3. Temperature

Table 3-1 depicts all the treatments performed in this work.

Table 3-1 Summary of the Treatments Performed in the Study

Step 1		**Preliminary screening of primary coagulants**
		Testing 8 chemicals: aluminum chlorohydrate (ACH), aluminum chloride (AC), alum, polyaluminum chloride, ferric sulfate, poly-DAMDAC, epiamine, sodium aluminate
Step 2		**Evaluation of pH and coagulant (ACH and AC) dosages**
	Test 1	[ACH]=1000 mg/L, [PA]=200 mg/L, [PAM]=5 mg/L, pH=4
		[ACH]=3000 mg/L, [PA]=200 mg/L, [PAM]=5 mg/L, pH=4
		[ACH]=1000 mg/L, [PA]=200 mg/L, [PAM]=5 mg/L, pH=7
		[ACH]=3000 mg/L, [PA]=200 mg/L, [PAM]=5 mg/L, pH=7
	Test 2	[AC]=1000 mg/L, [PA]=200 mg/L, [PAM]=5 mg/L, pH=4
		[AC]=3000 mg/L, [PA]=200 mg/L, [PAM]=5 mg/L, pH=4
		[AC]=1000 mg/L, [PA]=200 mg/L, [PAM]=5 mg/L, pH=7
		[AC]=3000 mg/L, [PA]=200 mg/L, [PAM]=5 mg/L, pH=7
		Further evaluation of ACH and AC dosage
	Test 3	[ACH]=500 mg/L, [PA]=200 mg/L, [PAM]=5 mg/L, pH=4
		[ACH]=750 mg/L, [PA]=200 mg/L, [PAM]=5 mg/L, pH=4
		[AC]=500 mg/L, [PA]=200 mg/L, [PAM]=5 mg/L, pH=4
		[AC]=750 mg/L, [PA]=200 mg/L, [PAM]=5 mg/L, pH=4
		Further evaluation of pH
	Test 4	[ACH]=500 mg/L, [PA]=200 mg/L, [PAM]=5 mg/L, pH=3
		[ACH]=500 mg/L, [PA]=200 mg/L, [PAM]=5 mg/L, pH=5
		[ACH]=500 mg/L, [PA]=200 mg/L, [PAM]=5 mg/L, pH=9.8
		[AC]=750 mg/L, [PA]=200 mg/L, [PAM]=5 mg/L, pH=3
		[AC]=750 mg/L, [PA]=200 mg/L, [PAM]=5 mg/L, pH=5
		[AC]=750 mg/L, [PA]=200 mg/L, [PAM]=5 mg/L, pH=9.8
		Evaluation of coagulant aid (PA) and flocculent (PAM) dosage
	Test 5	[ACH]=500 mg/L, [PA]=50 mg/L, [PAM]=2 mg/L, pH=3
		[ACH]=500 mg/L, [PA]=50 mg/L, [PAM]=4 mg/L, pH=3
		[ACH]=500 mg/L, [PA]=100 mg/L, [PAM]=2 mg/L, pH=3
		[ACH]=500 mg/L, [PA]=100 mg/L, [PAM]=4 mg/L, pH=3
		[ACH]=500 mg/L, [PA]=150 mg/L, [PAM]=2 mg/L, pH=3
		[ACH]=500 mg/L, [PA]=150 mg/L, [PAM]=4 mg/L, pH=3
	Test 6	[AC]=500 mg/L, [PA]=50 mg/L, [PAM]=2 mg/L, pH=3
		[AC]=500 mg/L, [PA]=50 mg/L, [PAM]=4 mg/L, pH=3
		[AC]=500 mg/L, [PA]=100 mg/L, [PAM]=2 mg/L, pH=3
		[AC]=500 mg/L, [PA]=100 mg/L, [PAM]=4 mg/L, pH=3
		[AC]=500 mg/L, [PA]=150 mg/L, [PAM]=2 mg/L, pH=3
		[AC]=500 mg/L, [PA]=150 mg/L, [PAM]=4 mg/L, pH=3

Table 3-1 Continued Summary of the Treatments Performed in the Study

Step 3	**Evaluation of bentonite clay added before chemical treatment**	
	Test 7	[Clay]=0 g/L,[ACH]=500 mg/L, [PA]=150 mg/L, [PAM]=2 mg/L, pH=3
		[Clay]=0.5 g/L,[ACH]=500 mg/L, [PA]=150 mg/L, [PAM]=2 mg/L, pH=3
		[Clay]=1.0 g/L,[ACH]=500 mg/L, [PA]=150 mg/L, [PAM]=2 mg/L, pH=3
		[Clay]=2.0 g/L,[ACH]=500 mg/L, [PA]=150 mg/L, [PAM]=2 mg/L, pH=3
		[Clay]=5.0 g/L,[ACH]=500 mg/L, [PA]=150 mg/L, [PAM]=2 mg/L, pH=3
		[Clay]=10.0 g/L,[ACH]=500 mg/L, [PA]=150 mg/L, [PAM]=2 mg/L, pH=3
	Evaluation of powdered activated carbon added after chemical treatment	
	Test 8	[ACH]=500 mg/L, [PA]=150 mg/L, [PAM]=2 mg/L, pH=3; [PAC]=0.25 g/L
		[ACH]=500 mg/L, [PA]=150 mg/L, [PAM]=2 mg/L, pH=3; [PAC]=0.50 g/L
		[ACH]=500 mg/L, [PA]=150 mg/L, [PAM]=2 mg/L, pH=3; [PAC]=1.0 g/L
		[ACH]=500 mg/L, [PA]=150 mg/L, [PAM]=2 mg/L, pH=3; [PAC]=2.0 g/L
		[ACH]=500 mg/L, [PA]=150 mg/L, [PAM]=2 mg/L, pH=3; [PAC]=5.0 g/L
	Evaluation of powdered activated carbon alone	
	Test 9	[PAC]=0.5 g/L pH=3 No chemical treatment
		[PAC]=1.0 g/L pH=3 No chemical treatment
		[PAC]=2.0 g/L pH=3 No chemical treatment
		[PAC]=5.0 g/L pH=3 No chemical treatment
		[PAC]=10 g/L pH=3 No chemical treatment
		[PAC]=20 g/L pH=3 No chemical treatment
	Evaluation of temperature	
	Test 10	T=30 °C, [ACH]=500 mg/L, [PA]=150 mg/L, [PAM]=2 mg/L, pH=3
		T=40 °C, [ACH]=500 mg/L, [PA]=150 mg/L, [PAM]=2 mg/L, pH=3
		T=50 °C, [ACH]=500 mg/L, [PA]=150 mg/L, [PAM]=2 mg/L, pH=3
		T=60 °C, [ACH]=500 mg/L, [PA]=150 mg/L, [PAM]=2 mg/L, pH=3
		T=70 °C, [ACH]=500 mg/L, [PA]=150 mg/L, [PAM]=2 mg/L, pH=3
		T=80 °C, [ACH]=500 mg/L, [PA]=150 mg/L, [PAM]=2 mg/L, pH=3

4. Results and discussion

4.1 Wastewater characteristics

The pulp and paper wastewater in this study was a highly-colored, hazy, dark brown wastewater with an intense caustic odor. The characteristics of the wastewater are summarized in the table 4-1.

Table 4-1 Pulp and Paper Raw Wastewater Characteristics

Sample	Color, Pt.Co.	Alkalinity, mg/L $CaCO_3$	COD, mg/L	BOD_5, mg/L	TSS, mg/L	VSS, mg/L	FSS, mg/L
Raw	29,000	4,300	4,900	1,700	1,100	900	200

As suggested by solids measurements, approximately 82% of the suspended materials in the wastewater are volatile solids. Prior to performing the jar tests, pH of 1000 mL of raw wastewater sample was adjusted from 9.8 to the desired value using sulfuric acid with normality of 10. As sulfuric acid was added, rising bubbles were observed to form – which are believed to be CO_2 – within the solution, which created some foam on the top surface of the liquid. As pH was decreasing by adding sulfuric acid, bubble formation rate was observed to be maximum at pH 5, which made the solution look light brown as a result of having many gas bubbles inside. The foam resulting from rising bubbles was almost completely dissipated within 30 minutes. Formation of some floc was also observed when pH was adjusted from 9.8 (as is) to the lower pH. Figures 4-1 and 4-2 depict the titration and residual alkalinity curves of the raw wastewater respectively.

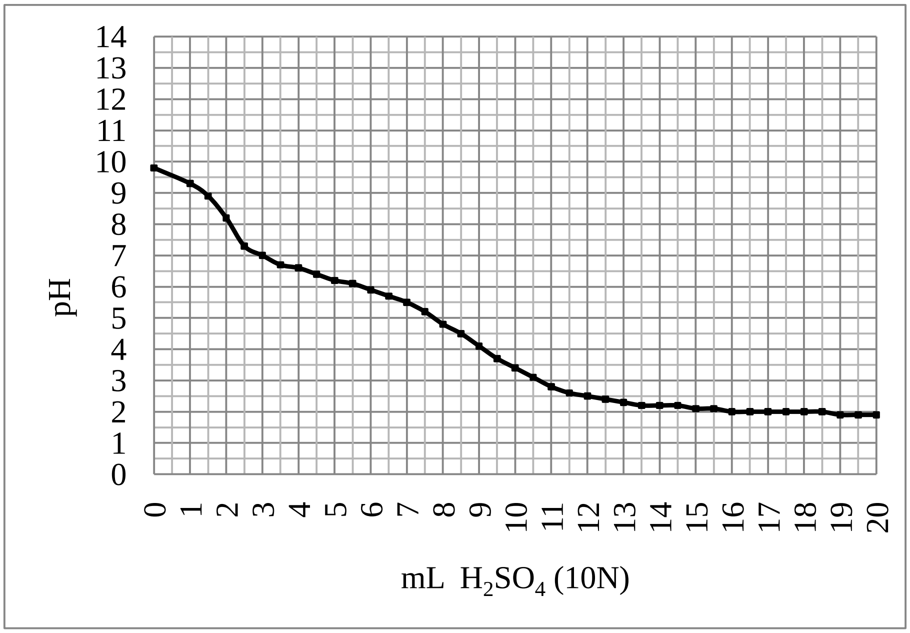

Figure 4-1 Potentiometric Titration Curve of Pulp and Paper Wastewater

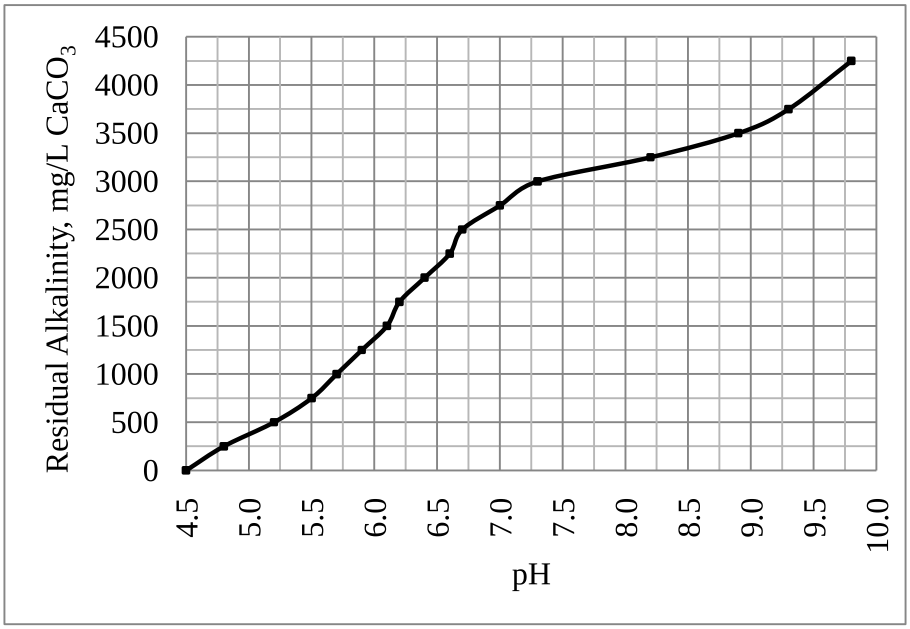

Figure 4-2 Pulp and Paper Wastewater Residual Alkalinity versus pH

4.2 Preliminary screening results

In order to perform the preliminary screening, eight coagulants were analyzed. Each coagulant was added to the wastewater in 500 mg/L increments to a total of 1500 mg/L until the highest floc size/quantity (if any) was observed. The sizes of the flocs were judged visually on a relative basis and classified as large, medium, or small. The results are shown in the table 4-2.

Table 4-2 Results of Coagulant Preliminary Screening

Coagulant Name	Floc Quantity	Floc Size
Aluminum Chlorohydrate (ACH)	Many	Large
Aluminum Chloride (AC)	Many	Large
Alum	Few	Medium
Polyaluminum Chloride (PACl)	Rare	Small
Ferric Sulfate	No Floc	-
Poly-DAMDAC	No Floc	-
Epiamine	No Floc	-
Sodium Aluminate	No Floc	-

Consequently, aluminum chlorohydrate (ACH) and aluminum chloride (AC) were chosen for the rest of the study. Also, polyamine (a cationic polymer) and polyacrylamide (an anionic polymer) were chosen as coagulant aid and flocculent at initial dosages of 200 and 5 mg/L, respectively. The dosage of coagulant aid and flocculent was varied in subsequent jar tests to determine the best conditions for color removal. Other coagulants and absorbents were evaluated as well.

4.3 Detailed evaluation of ACH and AC performance

At this step, the following factors were evaluated for aluminum chlorohydrate and aluminum chloride:

- Coagulant dosage
- pH
- Coagulant aid dosage
- Flocculent dosage

The main factor to design the experiments in series was the amount of color removed. Other characteristics of treated wastewater such as alkalinity (if any), COD, solids, and BOD_5 were also determined and reported for each jar test. What follows describes the jar tests performed and the results obtained. For all the jar tests, 1000 mL of sample was used in each jar. In each jar test, the floc sizes were judged on a relative basis. However, finished water quality was the primary basis for gaging performance of the various treatments.

4.3.1 Initial evaluation of ACH; jar test 1

The purpose of this test, first, was to determine the effect of pH on the coagulation process using ACH; pH values of 4 and 7 were selected as the lower acidic and neutral conditions, respectively, to see which pH yielded the better results. The main purpose here was to determine a rough value of pH for effective color removal. Secondly, for each pH, two different dosages of 1000 and 3000 mg/L were chosen for ACH to see if the coagulation process was improved at the upper concentration extreme. Polyamine and polyacrylamide dosages were held constant at 200 and 5 mg/L, respectively, for all the samples. As the pH dropped from 9.8 to 4, some dark brownish floc formed. The results are summarized in the tables 4-3 and 4-4.

Table 4-3 Initial Conditions and Visual Results for Jar Test 1

Jar	pH	Coagulant, mg/L	Coagulant aid, mg/L	Flocculent, mg/L	Floc Size	15' Settleability, mL	30' Settleability, mL
1	4	ACH, 1000	PA, 200	PAM, 5	Large	150	200
2	4	ACH, 3000	PA, 200	PAM, 5	Medium	270	270
3	7	ACH, 1000	PA, 200	PAM, 5	Small	70	70
4	7	ACH, 3000	PA, 200	PAM, 5	Medium	200	200

Table 4-4 Jar Test 1 Supernatant Analytical Results

Jar	True Color, Pt.Co.	% Color Removal	Alkalinity, mg/L $CaCO_3$	COD, mg/L	BOD_5, mg/L	TSS, mg/L	VSS, mg/L	FSS, mg/L
Raw	29,000	-	4,300	4,900	1,700	1,100	920	180
1	3,300	89	0	3,290	850	160	130	30
2	2,200	92	0	3,150	1,100	40	25	15
3	17,000	41	2,490	4,750	1,200	1,400	1,200	200
4	8,200	72	2,400	3,550	1,100	1,000	780	240

As the data suggest, pH of 4 provided better color removal apparently. Also, increasing the coagulant dosage from 1000 mg/L to 3000 mg/L could enhance color removal from 89 to 92%. Although there was a statistically significant difference between the color measurements using 1000 and 3000 mg/L of ACH for treatment (p=0.0004), the difference in percent removal of color was very small (3%). Thus, in terms of practical significance, using an ACH dosage three times higher is not justified. Consequently, the dosage of 1000 mg/L was considered more cost-effective, which resulted in approximately 89% color removal, and was chosen for the next step.

4.3.2 Initial evaluation of AC; jar test 2

This jar test was aimed to study the performance of AC as the primary coagulant. All the factors were the same as those in the previous jar test except the coagulant type, which was AC instead of ACH. Tables 4-5 and 4-6 show the results of jar test 2.

Table 4-5 Initial Conditions and Visual Results for Jar Test 2

Jar	pH	Coagulant, mg/L	Coagulant aid, mg/L	Flocculent, mg/L	Floc Size	15' Settleability, mL	30' Settleability, mL
1	4	AC, 1000	PA, 200	PAM,5	Small	400	320
2	4	AC, 3000	PA, 200	PAM,5	Medium	330	300
3	7	AC, 1000	PA, 200	PAM,5	Medium	90	90
4	7	AC, 3000	PA, 200	PAM,5	Large	200	200

Table 4-6 Jar Test 2 Supernatant Analytical Results

Jar	True Color,	% Color Removal	Alkalinity, mg/L $CaCO_3$	COD, mg/L	BOD, mg/L	TSS, mg/L	VSS, mg/L	FSS, mg/L
Raw	29,000	-	4,300	4,900	1,700	1,100	900	200
1	3,100	89	0	3,210	790	50	35	15
2	3,400	88	0	3,080	1,000	40	30	10
3	16,000	45	2,400	4,500	940	1,440	1,100	340
4	6,400	78	2,400	3,300	780	1,060	770	280

As the data suggest, obviously, pH of 4 provided better color removal using AC also. Furthermore, increasing the coagulant dosage by a factor of 3 at this pH significantly decreased the color removal efficiency ($p=0.005$). Consequently, 1000 mg/L AC at pH of 4 was determined the most appropriate choice with the highest color percent removal of about 89%.

4.3.3 Evaluation of ACH dosage; jar test 3

The purpose of this jar test was to determine if decreasing the ACH or AC dosage from 1000 to 750 or 500 mg/L has a significant effect on color removal. Again, the dosages of Polyamine and the anionic flocculent were held constant at 200 and 5 mg/L respectively. The results of jar test 3 are summarized in tables 4-7 and 4-8.

Table 4-7 Initial Conditions and Visual Results for Jar Test 3

Jar	pH	Coagulant, mg/L	Coagulant aid, mg/L	Flocculent, mg/L	Floc Size	15' Settleability, mL	30' Settleability, mL
1	4	ACH, 500	PA, 200	PAM,5	Large	250	250
2	4	ACH, 750	PA, 200	PAM,5	Medium	250	250
3	4	AC, 500	PA, 200	PAM,5	Small	200	200
4	4	AC, 750	PA, 200	PAM,5	Large	250	250

Table 4-8 Jar Test 3 Supernatant Analytical Results

Jar	True Color,	% Color Removal	Alkalinity, mg/L $CaCO_3$	COD, mg/L	BOD, mg/L	TSS, mg/L	VSS, mg/L	FSS, mg/L
Raw	29,000	-	4,300	4,900	1,700	1,100	900	200
1	4,200	86	0	3550	1,300	64	44	20
2	2,900	90	0	3300	1,200	87	65	22
3	5,000	83	0	3850	1,300	610	530	80
4	2,900	90	0	3800	980	50	22	28

As the data suggest, dosage of 500 mg/L ACH resulted in about 86% color removal versus 90% achieved using 750 mg/L ACH. However, although the treatment showed statistically significance difference (p=0.02), 500 mg/L of ACH was preferred in order to use less chemicals for the treatment. Also, 500 mg/L AC resulted in about 83%

color removal versus 90% using 750 mg/L AC. In this case, since the difference in two treatments was noticeable (p=8.03E-05), AC dosage of 750 mg/L was chosen.

4.3.4 Evaluation of pH; jar test 4

As mentioned earlier, pH’s of 4 and 7 were considered the starting point for evaluating pH impacts. In jar test 1, a rough evaluation showed that coagulation process was enhanced at pH of 4, which is considered acidic. Consequently, the purpose of jar test 4 was to determine whether pH of 3 or 5 yields better color removal compared to pH of 4. Samples with unadjusted pH of 9.8 (as is) were also examined to be able to compare the effect of pH adjustment. Tables 4-9 and 4-10 show the results of jar test 4.

Table 4-9 Initial Conditions and Visual Results for Jar Test 4

Jar	pH	Coagulant, mg/L	Coagulant aid, mg/L	Flocculent, mg/L	Floc Size	15' Settleability, ml	30' Settleability, ml
1	3	ACH, 500	PA, 200	PAM,5	Large	175	175
2	5	ACH, 500	PA, 200	PAM,5	Medium	50	50
3	9.8	ACH, 500	PA, 200	PAM,5	X-small	50	50
4	3	AC, 750	PA, 200	PAM,5	Large	250	250
5	5	AC, 750	PA, 200	PAM,5	Medium	50	50
6	9.8	AC, 750	PA, 200	PAM,5	X-small	50	50

Table 4-10 Jar Test 4 Supernatant Analytical Results

Jar	True Color, Pt.Co.	% Color Removal	Alkalinity, mg/L $CaCO_3$	COD, mg/L	BOD, mg/L	TSS, mg/L	VSS, mg/L	FSS, mg/L
Raw	29,000	-	4,300	4,900	1,700	1,100	900	200
1	2,700	91	0	3,400	1,400	42	20	22
2	12,000	59	100	4,400	1,600	1,200	1,100	100
3	24,000	17	4,200	5,000	1,700	1,300	1,000	200
4	2,400	92	0	3,200	1,500	51	19	32
5	10,000	66	300	4,000	1,500	1,400	1,200	200
6	25,000	14	4,200	4,300	1,400	1,400	1,100	300

As the results suggest, decreasing the pH to 3 enhanced color removal for both ACH and AC to 91% and 92%, respectively. However, color removal was moderately effective at pH of 5. Consequently, pH of 3, in conjunction with ACH or AC dosage of 500 and 750 mg/L, respectively, were chosen for the next jar tests.

4.3.5 Determination of effective coagulant aid/flocculent dosage using ACH as the primary coagulant; jar test 5

The purpose of this jar test was to determine the dosage of coagulant aid (polyamine) that yields reasonable results among dosages of 50, 100, and 150 mg/L compared to 200 mg/L from previous jar tests. For each polyamine dosage, two different flocculent dosages of 2 and 4 mg/L were tested in order to observe the effect on flocculation and also to determine if a lower flocculent dosage would yield better results. For all the jars, pH was kept constant at 3 since this pH proved to be the best among the others tested. ACH at 500 mg/L was used as the primary coagulant. Tables 4-11 and 4-12 summarize the results of jar test 5.

Table 4-11 Initial Conditions and Visual Results for Jar Test 5

Jar	pH	Coagulant, mg/L	Coagulant aid, mg/L	Flocculent, mg/L	Floc Size	15' Settleability, mL	30' Settleability, mL
1	3	ACH, 500	PA, 50	PAM, 2	Medium	250	250
2	3	ACH, 500	PA, 50	PAM, 4	Large	200	200
3	3	ACH, 500	PA, 100	PAM, 2	Medium	400	300
4	3	ACH, 500	PA, 100	PAM, 4	Large	250	250
5	3	ACH, 500	PA, 150	PAM, 2	Medium	430	300
6	3	ACH, 500	PA, 150	PAM, 4	Large	250	250

Table 4-12 Jar Test 5 Supernatant Analytical Results

Jar	True Color,	% Color Removal	Alkalinity, mg/L $CaCO_3$	COD, mg/L	BOD, mg/L	TSS, mg/L	VSS, mg/L	FSS, mg/L
Raw	29,000	-	4,300	4,900	1,700	1,100	900	200
1	3,900	87	0	3,300	1,600	27	13	14
2	4,100	86	0	3,200	1,500	26	14	12
3	3,700	87	0	3,200	1,300	30	15	15
4	3,600	88	0	3,200	1,300	31	19	12
5	2,900	90	0	3,100	1,200	26	13	13
6	3,200	89	0	3,200	1,200	26	13	13

As the results suggest, 500 mg/L of ACH as the primary coagulant, 150 and 2 mg/L of coagulant aid and flocculent, respectively, provided to the highest color removal of approximately 90% and was, therefore, chosen for the next step.

4.3.6. Determination of effective coagulant aid/flocculent dosage using AC as the primary coagulant; jar test 6

The only distinction between this jar test and jar test 5 was that AC at 750 mg/L was used in jar test 6 (instead of 500 mg/L of ACH in jar test 5). Tables 4-13 and 4-14 show the results of jar test 6.

Table 4-13 Initial Conditions and Visual Results for Jar Test 6

Jar	pH	Coagulant, mg/L	Coagulant aid, mg/L	Flocculent, mg/L	Floc Size	15' Settleability, mL	30' Settleability, mL
1	3	AC, 750	PA, 50	PAM, 2	Very Small	340	290
2	3	AC, 750	PA, 50	PAM, 4	Small	290	250
3	3	AC, 750	PA, 100	PAM, 2	Very Small	300	260
4	3	AC, 750	PA, 100	PAM, 4	Large	250	250
5	3	AC, 750	PA, 150	PAM, 2	Very Small	310	290
6	3	AC, 750	PA, 150	PAM, 4	Large	250	240

Table 4-14 Jar Test 6 Supernatant Analytical Results

Jar	True Color,	% Color Removal	Alkalinity, mg/L $CaCO_3$	COD, mg/L	BOD, mg/L	TSS, mg/L	VSS, mg/L	FSS, mg/L
Raw	29,000	-	4,300	4,900	1,700	1,100	900	200
1	3,700	87	0	3,200	1,500	28	12	16
2	3,700	87	0	3,300	1,500	24	9	15
3	3,600	88	0	3,200	1,700	19	7	12
4	3,500	88	0	3,100	1,600	19	8	11
5	3,000	90	0	3,300	1,600	26	10	16
6	3,100	89	0	3,200	1,700	35	18	17

The measurements suggest that at 750 mg/L AC, 150 mg/L coagulant aid and 2 mg/L flocculent, respectively, 90% color removal was achieved. Furthermore, the results obtained from both jar tests 5 and 6 showed that the higher polyacrylamide dosage of 4 mg/L (compared to 2 mg/L) produced larger flocs.

At this point, reviewing the color removal results, the lesser dosage of 500 mg/L ACH was preferred over 750 mg/L AC since the amount of color removal was approximately the same in terms of percent removal (both 90%). Thus, 500 mg/L ACH, 150 mg/L polyamine, and 2 mg/L polyacrylamide were chosen to be used for the next step.

4.4. Evaluation of measures to enhance coagulation/color removal

This step was aimed to find additional measures to enhance the coagulation/color removal process. Consequently, the effect of following factors on the process was examined:

1. Bentonite clay
2. Powdered Activated Carbon (PAC)
3. Temperature

4.4.1 Evaluation of bentonite clay; jar test 7

The purpose of this jar test was to determine whether or not bentonite clay can improve the color removal process when used in combination with chemical treatment (coagulation). Clay was added first, rapid mixed for 2 minutes, and slow mixed for 15 minutes. Subsequently, chemical treatment was carried out using 500 mg/L ACH, 150 mg/L polyamine, and 2 mg/L polyacrylamide. It was believed that clay would adsorb color constituents and work in conjunction with the chemical treatment to enhance color removal. The main idea was to use clay as a cheaper initial physical-treatment material (compared to coagulants) to see if it could help reducing the dosage of chemicals needed in the next step. Results of jar test 7 are shown in tables 4-15 and 4-16.

Table 4-15 Initial Conditions and Visual Results for Jar Test 7

Jar	pH	Clay, g/L; Coagulant, mg/L	Coagulant aid, mg/L	Flocculent, mg/L	Floc Size	15' Settleability, mL	30' Settleability, mL
1	3	Clay, 0; ACH, 500	PA, 150	PAM, 2	Large	240	230
2	3	Clay, 0.5; ACH, 500	PA, 150	PAM, 2	Medium	240	230
3	3	Clay, 1.0; ACH, 500	PA, 150	PAM, 2	Medium	210	200
4	3	Clay, 2.0; ACH, 500	PA, 150	PAM, 2	Medium	190	180
5	3	Clay, 5.0; ACH, 500	PA, 150	PAM, 2	Medium	150	150
6	3	Clay, 10; ACH, 500	PA, 150	PAM, 2	Medium	150	140

Table 4-16 Jar Test 7 Supernatant Analytical Results

Jar	True Color, Pt.Co.	% Color Removal	Alkalinity, mg/L $CaCO_3$	COD, mg/L	BOD, mg/L	TSS, mg/L	VSS, mg/L	FSS, mg/L
Ra	29,000	-	4,300	4,900	1,700	1,100	900	200
1	3000	90	0	3,500	1,300	26	12	14
2	3100	89	0	3,400	1,400	17	5	12
3	3100	89	0	3,200	1,500	20	12	8
4	3000	90	0	3,300	1,400	20	4	16
5	2800	90	0	3,200	1,500	24	11	13
6	2300	92	0	3,200	1,700	41	14	27

As the results indicate, bentonite clay provided little to no increase in color removal except at the 10 g/L dosage. However, it was observed that clay could enhance the settling velocity of the flocs formed by chemical coagulation. Furthermore, high dosages of clay caused the settled sludge to become more compact. Obviously, although the 10 g/L bentonite clay dosage provided improvement in color removal, this high dosage was not seemed to be justified economically (in terms of the amount of material used/sludge produced).

4.4.2 Evaluation of powdered activated carbon (PAC) used in combination with ACH; jar test 8

This test was aimed to determine the efficiency of PAC when used in combination with ACH. First, coagulation/flocculation was performed using 500 mg/L ACH, 150 mg/L polyamine, and 2 mg/L polyacrylamide. In the next step, supernatants were removed and prescribed amounts of PAC were added to each. Subsequently, each sample was rapid mixed for 3 minutes followed 60 minutes of slow-mixing. Tables 4-17 and 4-18 show the results of jar test 8.

Table 4-17 Initial Conditions and Visual Results for Jar Test 8

Jar	pH	Coagulant, mg/L; PAC, g/L	Coagulant aid, mg/L	Flocculent, mg/L	Floc Size	15' Settleability, ml	30' Settleability, ml
1	3	ACH, 500; 0.25	PA, 150	PAM, 2	Medium	270	250
2	3	ACH, 500; 0.5	PA, 150	PAM, 2	Medium	260	250
3	3	ACH, 500; 1.0	PA, 150	PAM, 2	Medium	250	250
4	3	ACH, 500; 2.0	PA, 150	PAM, 2	Medium	260	250
5	3	ACH, 500; 5.0	PA, 150	PAM, 2	Medium	250	250

Table 4-18 Jar Test 8 Supernatant Analytical Results

Jar	True Color,	% Color Removal	Alkalinity, mg/L $CaCO_3$	COD, mg/L	BOD, mg/L	TSS, mg/L	VSS, mg/L	FSS, mg/L
Raw	29,000	-	4,300	4,900	1,700	1,100	900	200
1	2,900	90	0	2,100	1,900	16	10	7
2	2,800	90	0	2,200	1,900	25	14	11
3	3,400	88	0	2,000	1,800	39	24	15
4	2,600	91	0	1,600	1,700	95	71	24
5	1,400	95	0	1,400	1,600	330	250	80

As the data suggests, using 500 mg/L ACH, 150 mg/L polyamine, and 2.0 mg/L polyacrylamide in combination with 5.0 g/L PAC resulted in the highest color removal of about 95%. The other carbon dosages provided little to no improvement in color removal when compared to chemical treatment alone.

4.4.3 Evaluation of powdered activated carbon (PAC) when used alone; jar test 9

The purpose of this test was to determine the color removal efficiency of powdered activated carbon used alone (without addition of ACH, polyamine, and flocculent). PAC was added to the raw wastewater with adjusted pH of 3, rapidly mixed at 175 rpm for 3 minutes, slowly mixed at 35 rpm for 15 minutes, and was allowed to settle for 30 minutes. The supernatants were extracted subsequently for analysis. Jar test 9 results are shown in tables 4-19 and 4-20.

Table 4-19 Jar Test 9 Supernatant Analytical Results

Jar	pH	PAC, g/L	True Color, Pt.Co.	% Color Removal	Alkalinity, mg/L	COD, mg/L	BOD, mg/L	TSS, mg/L	VSS, mg/L	FSS, mg/L
Raw	9.8	-	29,000	-	4,300	4,900	1,700	1,100	900	200
1	3	0.5	4100	86	0	1,900	1,400	100	84	16
2	3	1.0	4100	86	0	1,700	1,500	68	57	12
3	3	2.0	3100	89	0	1,600	1,400	80	62	18
4	3	5.0	2900	90	0	1,000	1,200	200	157	43
5	3	10	500	98	0	670	1,000	400	320	80
6	3	20	200	99	0	560	850	230	170	60

As the color measurements suggest, color removal efficiency was enhanced with increasing PAC dosage. The highest color removal of about 99% was associated with using 20 g/L PAC. The lowest dosage of 0.5 g/L PAC led to about 86% color removal. To provide color removal that matches the chemical treatment alone (ACH, polyamine, and flocculent), A PAC dosage of 2.0 g/L would be necessary. This very high powdered activated carbon dosage likely cannot be justified because of its high cost.

4.4.4 Evaluation of temperature effect; jar test 10

The purpose of this test was to determine if increasing the wastewater temperature could enhance the coagulation/flocculation color removal efficiency. Wastewater pH was adjusted prior to heating. Consequently, samples were heated one at a time to the target temperatures slowly to prevent boiling (which could potentially change the composition of suspended solids. Jar test on each sample was performed immediately after heating. Tables 4-20 and 4-21 show the results of jar test 10.

Table 4-20 Initial Conditions and Visual Results for Jar Test 10

Jar	pH	T, °C	Coagulant, mg/L	Coagulant aid, mg/L	Flocculent, mg/L	Floc Size	15' Settleability, ml	30' Settleability, ml
1	3	30	ACH, 500	PA, 150	PAM, 2	Medium	200	200
2	3	40	ACH, 500	PA, 150	PAM, 2	Large	200	200
3	3	50	ACH, 500	PA, 150	PAM, 2	Small	200	200
4	3	60	ACH, 500	PA, 150	PAM, 2	X-Small	300	300
5	3	70	ACH, 500	PA, 150	PAM, 2	X-Small	300	300
6	3	80	ACH, 500	PA, 150	PAM, 2	X-Small	200	200

Table 4-21 Jar Test 10 Supernatant Analytical Results

Jar	True Color,	% Color Removal	Alkalinity, mg/L $CaCO_3$	COD, mg/L	BOD, mg/L	TSS, mg/L	VSS, mg/L	FSS, mg/L
Raw	29,000	-	4,300	4,900	1,700	1,100	900	200
1	3210	89	0	1,800	1,300	31	16	15
2	3329	89	0	1,800	1,200	39	20	19
3	3600	88	0	1,900	1,200	36	15	21
4	3680	87	0	1,800	1,200	40	21	19
5	3770	87	0	1,800	1,300	55	22	33
6	3940	86	0	1,900	1,300	51	32	19

As the data suggest, color removal efficiency was observed to decrease as the wastewater temperature was increased. The highest percent removal of approximately 89% was associated with temperature of 30 °C. It was also observed that the floc size was decreased at higher temperatures. However, increasing the temperature enhanced the settling velocity of the flocs. Because this particular pulp and paper industry wastewater has an elevated temperature, color removal in the actual process wastewater will be slightly adversely affected. Equalization and cooling of the process wastewater prior to chemical treatment may be justified.

4.5. Conclusion

This study was focused on finding a combination of factors such as coagulant, coagulant aid, and flocculent dosage as well as pH that worked most reasonably to remove color from a specialty pulp and paper mill wastewater. It was found that 500 mg/L aluminum chlorohydrate (ACH), 150 mg/L polyamine (PA), and 2 mg/L polyacrylamide (PAM), when wastewater pH was adjusted from 9.8 (as is) to 3.0, worked most reasonably among other options tested. This chemical treatment approach led to about 90% color removal from the raw process wastewater sample having approximately 29,000 Pt.Co. units.

The effect of pH was evaluated during the research effort. The pH of the specialty pulp and paper wastewater was adjusted to pH values of 4, 5, 7, and 9.8 (as is) prior to chemical coagulation and flocculation. Jar test results clearly indicated that better results were obtained at an initial pH of 3. Large amounts of acid will be necessary for neutralization prior to chemical coagulation and flocculation. This will add substantially to the treatment cost.

Of the various primary coagulants examined in this research, aluminum chlorohydrate at a dosage of 500 mg/L was very effective in color removal. Aluminum chloride also provided excellent color removal but an AC dosage of 750 mg/L was needed to match the results obtained with ACH. In each case, polyamine and polyacrylamide were needed to achieve excellent results. A polyamine dosage of 150 mg/L in conjunction with a polyacrylamide dosage of 2 mg/L seemed to provide outstanding color removal.

The addition of bentonite clay prior to chemical coagulation and flocculation provided marginal improvement in color removal, except at the very high bentonite clay dosage of 10 g/L. This high clay dosage does not seem warranted because of cost and increased sludge solids content. Moreover, a high clay dosage improved sludge compaction characteristics.

Use of powdered activated carbon (PAC) to treat the supernatant of the chemically coagulated and settled wastewater provided marginal improvement in color removal. A very high PAC dosage (5 g/L) was needed to incrementally increase color removal efficiency from 90% (chemical treatment only) to 95% (chemical treatment plus 5 g/L PAC).

Use of powdered activated carbon (PAC) alone also provided excellent color removal. However, very high PAC dosages were required. A PAC dosage of 2000 mg/L was needed to match the performance of chemical treatment alone. This high PAC dosage does not appear to be as cost-effective as chemical treatment alone.

Increasing the temperature of the process wastewater to 30 °C, 40 °C, 50 °C, 60 °C, 70 °C, and 80 °C prior to chemical coagulation and flocculation had a slightly negative effect on color removal. Since this specialty pulp and paper wastewater has a high temperature as it leaves the production process, equalization and cooling of the process wastewater prior to chemical treatment seems to be justified.

Another important conclusion is that large quantities of chemical sludge will be produced during chemical coagulation and flocculation. Based on results of this study, approximately 0.2 gallons of sludge will be produced for every gallon of process wastewater treated. This is a phenomenal amount of sludge that likely will required thickening, dewatering, and landfill disposal. The cost of this sludge treatment and disposal will be substantial.

Last but not least, there are limitations to the treatment approach provided in this work. First of all, there are high costs associated with the chemicals/materials to use. Secondly, due to production of large amounts of sludge, there would also be costs associated with proper handling the sludge. Furthermore, due to the release of residues into the water after chemical treatment, care should be taken when the chemically-treated wastewater is re-used in the pulp and paper mill process, as these residues might pose limitations to re-use applications.

4.6 Recommendations

The author poses the following ideas for the future research:

1. To test a broader range of natural/nature-friendly polymers/chemicals that can be used as coagulants/flocculants which would produce acceptable results both technically and economically to remove color and turbidity from this specialty pulp and paper wastewater.

2. To perform life cycle assessment of pulp and paper wastewater color removal (using chemical coagulation treatment) to define the limits beyond which the disadvantages of chemical treatment (such as sludge production, metal residuals, etc.) outweigh the benefits achieved from a holistic point of view.

As public awareness regarding the fate of chemicals used in different processes is increased, the question posed is whether using the chemicals is beneficial from a holistic point of view. Life Cycle Assessment (LCA) is a useful tool in this respect to determine the universal environmental impacts of a function due to its fundamental holistic philosophy *(Olsen et al. 2001)* rather than the benefits achieved instantaneously. In other words, in spite of the fact that short-term benefits – such as color removal of pulp and paper wastewater – can be achieved using certain chemicals, from a different perspective, these chemicals can leave residuals (for instance, aluminum residuals using alum for coagulation) behind in the water, which can be of concern in a broader view of environmental impacts. The same logic can be applied to the issue regarding handling of the waste sludge left from the chemical treatment of pulp and paper wastewater. Such issues have resulted in the popularity of new treatment methods using “green” or “eco-friendly” technologies to treat wastewater.

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