

Bench-Scale Study of Chemically Enhanced Primary Treatment in Brazil

by

Irene W. Yu

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Signature of the Author _____
Department of Civil and Environmental Engineering
May 5, 2000

Certified by _____
Dr. Donald Harleman
Ford Professor Emeritus of Civil and Environmental Engineering
Thesis Supervisor

Certified by _____
Susan Murcott
Research Affiliate
Thesis Co-Supervisor

Accepted by _____
Daniele Veneziano
Chairman, Departmental Committee on Graduate Studies

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Irene W. Yu

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Abstract

MIT has been involved with bench-scale analyses of chemically enhanced primary treatment (CEPT) at several wastewater treatment plants in Brazil. The five plants studied were Pinheiros and Ipiranga in Sao Paulo, ETIG in Rio de Janeiro, and Tatui and Riviera de Sao Lourenço, smaller communities in the state of Sao Paulo, Brazil. CEPT is especially beneficial in countries, such as Brazil, because of the savings in cost and space, due to higher solids, organic matter, and nutrient removals. Each of these bench-scale analyses tested a wide variety of coagulants and flocculants to optimize the dosing system for possible full-scale CEPT implementation.

Despite differences in each of the plants, similarities did arise in the optimal chemical regime and polymer usage. Jar tests at all five plants resulted in FeCl_3 achieving the best COD and TSS removals. An optimal dosage of 50 mg/L FeCl_3 with no polymer achieved approximately 65-85 % COD removal and 90-100 % TSS removal. The jar tests also revealed that a combination of a metal salt and an anionic polymer of high molecular weight and high charge achieved the best removals. An optimal dosage of 50 mg/L metal salt with 0.5 mg/L anionic polymer yielded, on average, a 20 % increase in COD removal from that achieved with a metal salt alone, without the addition of polymer.

Thesis Supervisor: Dr. Donald Harleman

Title: Ford Professor Emeritus of Civil and Environmental Engineering

Thesis Co-Supervisor: Susan Murcott

Title: MIT Research Affiliate

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Chapter 1 - Introduction

This project involves several optimization studies of chemically enhanced primary treatment (CEPT) in Brazil. It is based on the collective effort of several Massachusetts of Technology (MIT) faculty and students, and help from some Brazilian private companies and government agencies. All of the CEPT testing conducted by MIT at various plants, including Pinheiros and Ipiranga in the city of Sao Paulo, ETIG in Rio de Janeiro, and a Tatui plant in the state of Sao Paulo, were completed within the last eight years. The most recent addition to these plants was one in Riviera de Sao Lourenço, located along the Atlantic Coast between Sao Paulo and Rio de Janeiro. Figure 1-1 shows Brazil and its major cities.



Figure 1-1 Map of Brazil

With funding from the John R. Freeman Fund of the Boston Society of Civil Engineers (BSCE) and the guidance of Professor Donald Harleman and Susan Murcott, both very experienced with CEPT, an MIT group of four students traveled to Riviera in January

2000 to conduct bench-scale, full-scale, modeling, and biosolids analyses. This paper focuses mainly on the bench-scale portion of these studies.

CEPT is a wastewater treatment technology that employs low dosages of metal salts and polymers to increase suspended solids and other pollutant removal via coagulation, precipitation, and settling. The metal salts serve to coagulate and/or precipitate the colloidal particles in the wastewater while the polymer helps to form larger flocs to speed up the settling time. This, together with the decreased organic loading following the CEPT process, reduces of both the primary and secondary units. Another advantage of CEPT is the higher nutrient removal capabilities at low cost due to its single stage process. Higher removal rates yield higher loading capabilities, and better efficiencies, as shown in Table 1-1.

Table 1-1 CEPT vs. Conventional Primary Treatment

	CEPT	Conventional Primary
Total Suspended Solids (TSS)	75-85 %	60 %
Biochemical Oxygen Demand (BOD ₅)	55-65 %	30 %
Phosphorus (P)	55-85 %	30 %
Nitrogen (N)	30 %	30 %

Chemicals for wastewater treatment have been used for more than one hundred years.¹ In the past, their usage was discouraged because lime was used and produced high quantities of sludge. More recently, chemical treatment has been used for regulating phosphorus levels in the water. The latest technological advancements in polymers, to be used as a

flocculant to the ferric salts, has both lowered the overall coagulant dosage levels and bettered the removal rates of TSS, BOD, and P.²

In Brazil, bench-scale analyses, involving jar tests, were performed to optimize chemical dosages at each Brazilian plant. All of the plants were either being retrofitted with CEPT or running laboratory tests to consider the use of CEPT. The plants in the cities of Sao Paulo and Rio de Janeiro were large plants, addressing the needs of these megacities year round, whereas the plants in Tatui and Riviera are on a much smaller scale. The plant at Riviera differs from the one in Tatui in their use of CEPT to improve the system's ability to handle large population fluctuations.

The subsequent chapters will cover the use of CEPT at each of these plants in Brazil. Chapter 2 will briefly discuss the importance of coagulation and flocculation in CEPT. Chapter 3 covers all of the materials and methods used for bench-scale analyses. Chapters 4 through 8 will provide detailed information about the individual bench-scale studies performed at Ipiranga, Pinheiros, ETIG, Tatui, and Riviera, respectively. Chapter 9 will compare the results from these five studies. Lastly, chapter 10 will draw some major conclusions regarding bench-scale analyses in Brazil.

¹ Culp, 1967, p.61.

² Morrissey et al., 1992, p.1.

Chapter 2 - Coagulation and Flocculation

2.1 Introduction

Water and wastewater treatment can occur by physical, chemical, and/or biological methods. Coagulation and flocculation are two concepts essential to chemical treatment methods. Coagulation can be defined as the conglomeration of small particles by neutralization of the natural particle charge to form larger particles. Flocculation, on the other hand, involves the transport of these particles. It can be defined as the aggregation of these particles to form larger groups. These groups of particles are called “flocs”, which then settle by gravity. Before delving into the mechanisms behind these two processes, the importance of colloids must first be emphasized.

2.2 Colloids

Conventional sedimentation is based on particle settling due to gravitational forces. This form of water and wastewater treatment removes particles greater than 40 microns in size. Of the particles that remain and are slow in settling, the vast majority of them are considered colloids, which are less than 1 micron in size. Figure 2-1 shows the range of particle sizes removed by different treatment processes. Note that the range of particle sizes covered by coagulation and flocculation is from 0.1 to 10 microns.

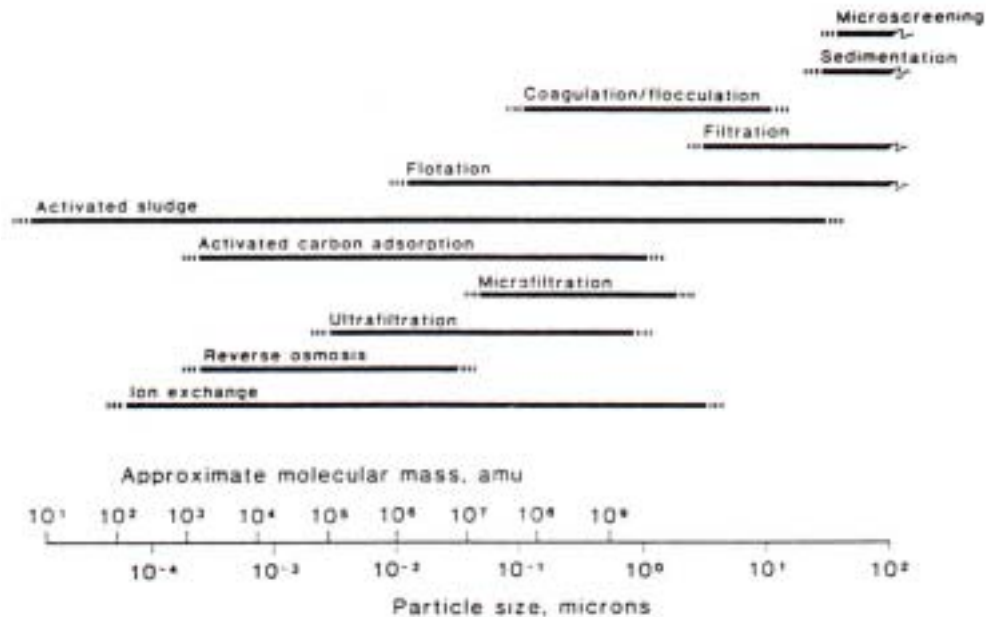


Figure 2-1 Size Distribution of Removed Particles by Various Treatment Processes³

Colloids can exist in three forms: solid, liquid, or gaseous. Because of their small size, colloids have a large surface area with respect to their volume. Therefore, the surface phenomena of colloids are important and relevant to both coagulation and flocculation.

In colloids, both electrostatic repulsion and hydration are important characteristics. Colloids in wastewater are stable particles due to their surface charge. Therefore, they do not aggregate on their own because of electrostatic repulsion. Coagulation comes into play by destabilizing these particles. The stability of colloids can also be attributed to their hydrophilic tendencies. Their affinity for water makes them very difficult to remove from the wastewater. To remedy this situation, a coagulant in the form of a metallic salt can be added to remove these hydrophilic colloids.

2.3 Coagulation

The coagulation of water and wastewater has been practiced since ancient times because of the existence of many naturally occurring coagulants. Coagulation cannot only be thought of as the conglomeration of particles, but as particle destabilization. Because of the stability and charged nature of colloids, they are unable to aggregate on their own, making coagulation necessary. Coagulation usually involves the addition of a metal salt. Typical metal salts that are used include aluminum sulfate (alum), ferrous chloride, ferric chloride, ferrous sulfate, ferric sulfate, lime, polyaluminum chloride (PAC), etc. The advantages and disadvantages of using certain metal salts will be discussed in section 3.3. More recently, seawater has been considered for coagulation usage by some coastal cities utilizing CEPT. Research has been conducted on this topic and the addition of seawater has been shown effective in removing algae from oxidation pond effluents.⁴ The reactions responsible for this algae removal yield the formation and precipitation of two metal compounds: CaCO_3 and $\text{Mg}(\text{OH})_2$.

The ability of a metal salt to coagulate pertains to its size and charge. According to the Schultze-Hardy rule, there is more than one order of magnitude increase in the effectiveness of an ion as its charge increases by one.⁵ The multivalent characteristics of these metal salts make them strongly attracted to the charged colloids. This attraction plus the insolubility of metal salts ensures their efficient removal.

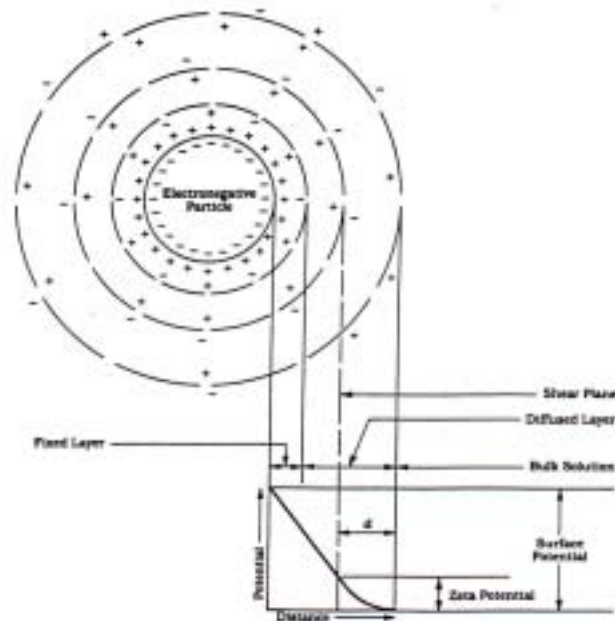
³ Levin et al., 1987, p.809.

⁴ Ayoub et al., 1986, p. 1265.

⁵ Droste, 1997, p. 384.

The destabilization process can be broken down into three smaller processes: sweep coagulation, charge neutralization, and interparticle bridging. In sweep coagulation, the selected metal salt is dosed to the wastewater. This dosage causes the precipitation of a metal hydroxide to occur. Precipitation is an important part of coagulation. This process involves the conversion of a soluble substance into a solid. In most cases, the addition of metal salts causes the precipitation of metals as hydroxides, such as $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$. These metal precipitates settle rapidly, carrying along with them the smaller colloidal particles. This sweeping effect traps other particles and foreign ions into the precipitate lattice, causing sweep coagulation.

The second process involved in coagulation is charge neutralization, where positively charged coagulants are introduced into the wastewater. In general, wastewater has a net negative charge due to the high organic nature and the adsorption of anions onto their surface. Each colloidal particle has a diffuse electrical double layer surrounding it. This double layer is a result of the colloids charged nature. Therefore, a colloid is surrounded by ions with an opposite charge, yielding a zero net electrical charge and electroneutrality. For two colloids to interact, the two diffuse layers must be compressed. This compression is a function of the cationic coagulants. They reduce the thickness of these double layers, reducing the surface potential and zeta potential. The zeta potential is the voltage difference between the bulk solution and the colloid. In other words, it is the charge of the colloid; therefore, it is partly responsible for the stability of the colloidal suspension. The higher the zeta potential, the higher the repulsive forces and the more stable the suspension is. All of these characteristics are shown in Figure 2-2.

Figure 2-2 Colloidal Layers⁶

Another result of charge neutralization is the increase in Van der Waals' forces. These are attractive cohesive forces between atoms and molecules, which differ from the forces in a chemical bond. An increase in these forces causes an increase in the particles' affinity for one another. As a result, the particles begin to stick together. The positively charged coagulants then adsorb onto the particle surfaces, increasing the overall particle size and settling velocity. For charge neutralization to occur, new compounds are created in the form of metal hydrolysis monomers such as $\text{Fe}(\text{OH})^+$ and $\text{Al}(\text{OH})^+$. These products materialize within microseconds, followed by the formation of small products such as $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$. These appear within a second after the metal salts come in contact with the colloidal particles. All of this is achieved through rapid mixing,

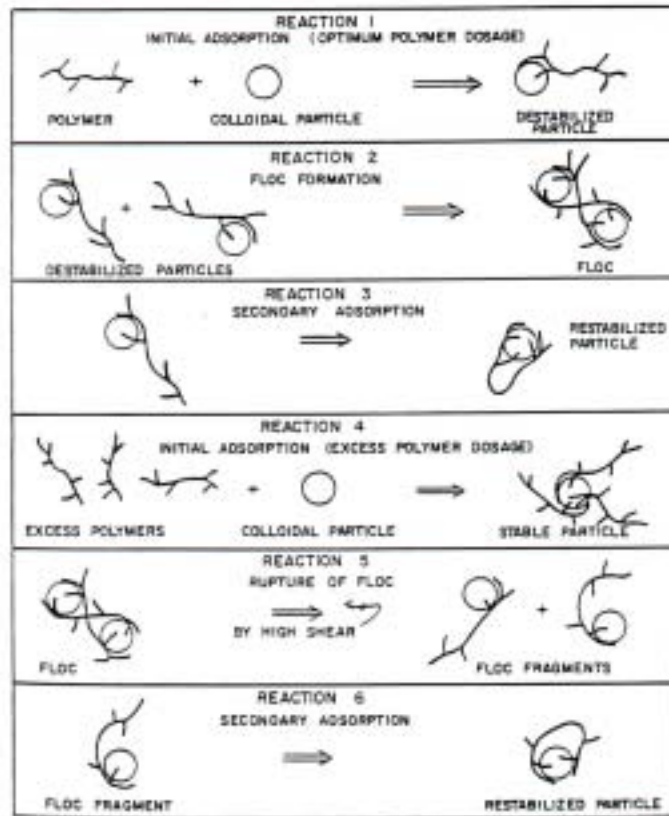
⁶ Reynolds and Richards, 1996.

causing collisions to occur between the colloidal particles and the hydrolysis and precipitation products.

The last process involved in coagulation is interparticle bridging. Bridging comes into effect when the surface charge of the particle nears zero. This process is accomplished via medium to high molecular weight polymers and their ability to gather and hold flocs that are already charge-neutralized. Bridges are formed between two particles that repel one another. This network of bridges and coagulated particles is called a floc. Figure 2-3 depicts the six reactions behind interparticle bridging. The formation of this floc is important for the next process for discussion, flocculation.

2.4 Flocculation

Flocculation, or the transport of particles, is important in bringing destabilized particles together and causing collisions to occur. In the treatment of wastewater, flocculation is an important treatment step and serves two major purposes. First, it serves to remove suspended solids in the wastewater and second, it serves to remove dissolved organic and inorganic substances by precipitation and adsorption. Flocculation is often accomplished via slow and gentle mixing, versus the rapid mixing necessary for coagulation so particles can be kept in suspension with enough time for collisions to occur.

Figure 2-3 Schematic of Interparticle Bridging⁷

The aggregated particles formed during coagulation form even larger particles, which settle according to Stokes Law.

$$\omega_s = \frac{d_p^2 g (\rho_p - \rho_l)}{18 \mu_l} \quad \text{Equation (1)}$$

Where ω_s = Stokes terminal velocity of particle

d_p = Diameter of the particle

μ_l = Dynamic viscosity of the liquid

ρ_l = Density of the liquid

ρ_p = Density of the particle

g = Acceleration due to gravity

There are three mechanisms that drive these collisions: Brownian motion (perikinetic flocculation), shear force (orthokinetic flocculation), and differential sedimentation (a special case of orthokinetic flocculation). Brownian motion is caused by the thermal energy of the fluid. Based on the assumption that all of these particles are uniform, this motion is especially important for collisions between particles of less than 0.1 μm in size. The second mechanism, shear forces, is caused by the movement of fluid due to mixing. Unlike Brownian motion, shear forces are important for the collisions between particles greater than 1.0 μm in size. The last mechanism driving these collisions is differential settling or sedimentation by gravitational forces. This mechanism involves the rapid settling of particles, taking with them particles of smaller size and slower settling velocities.

⁷ O'Melia, 1970.

2.5 Conclusion

Coagulation and flocculation are two key concepts that are necessary in understanding how bench-scale analyses work. Figure 2-4 is a schematic that summarizes the important mechanisms behind these two processes.

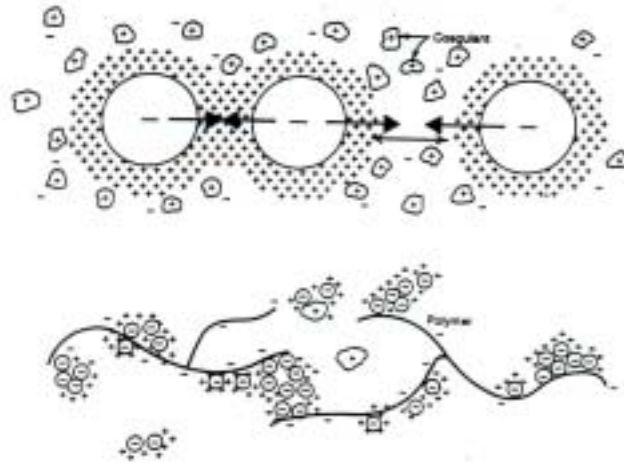


Figure 2-4 Summary of Coagulation and Flocculation

The top figure depicts the compression of the colloidal double diffuse layer via the addition of chemical coagulants. The bottom picture depicts the agglomeration with a metal salt and polymer resulting from both coagulation and flocculation.⁸

⁸ Hammer & Hammer, 1992.

Chapter 3 - Overview of Bench-Scale Analysis

3.1 Purpose

For many wastewater treatment plants, especially those using chemical coagulants, bench-scale testing serves as a quick and economical procedure that can provide information leading to possible full-scale operational improvement. In many cases, bench-scale tests offer more flexibility than setting up pilot plant studies, although pilot plant and full-scale studies are often run along with the bench-scale studies. Typically, bench-scale testing involves jar tests, which are conducted on the premises in a laboratory setting with all of the necessary equipment and supplies. The time-scale for jar testing can range from days to weeks, depending on the objectives. The standard purposes of jar tests are to determine the proper primary coagulant dosage and optimize the removal of TSS, BOD/COD, and phosphate (PO_4^{3-}). Other purposes include:

- To determine the optimum coagulant pH
- To evaluate the mixing duration and intensity
- To evaluate the optimum flocculant dosages
- To evaluate the effects of sludge recycle and concentrations necessary for sludge recycle
- To predict the design criteria for in-plant settling such as overflow rate⁹

These techniques, and many others, have been used in correlating jar test and plant operations data in many treatment plants. Growing confidence in the use of bench-scale testing is a significant result of wide applications, such as will be described in this thesis.

⁹ Hudson et al., 1981, p.218.

3.2 Materials and Setup

Many pieces of equipment and chemicals are necessary in preparation for jar tests. Also, a full understanding of the proper procedures in making up the chemical stock and feed solutions and appropriate mixing regimes are important. To perform these tests, the following items are necessary:

- Flocculator
- Sampling bucket
- Rope
- Personal protective equipment (gloves and lab coat)
- Large stirring stick
- 25+ gallon container (i.e. large plastic garbage can)
- Beakers, bottles, glassware
- 1, 5, and 10 ml pipettes or syringes
- Various coagulants and flocculants
- Stopwatch
- Blender

MIT research and testing has found that Phipps & Bird flocculators are generally preferred over other apparatuses. In previous experiments, a conventional Phipps & Bird jar apparatus, a modified jar apparatus and a continuous flow reactor (CFR) were tested using various coagulants and polymers to determine if any one apparatus was better. The results indicated that conventional jar tests were preferred over a modified jar apparatus due to ease-of-use. The conventional flocculator was preferred over the CFR because of higher TSS removals and the higher runs of samples. Therefore, the conventional Phipps

& Bird square jars, as shown in Figure 3-1, has been found to be an excellent flocculator for CEPT studies.¹⁰



Figure 3-1 Phipps & Bird Flocculators

Phipps & Bird flocculators come with either four or six paddles. The Phipps & Bird B-Ker jars hold 2 L of water. They have a tap that allows samples decanting from below the water surface. These jars are usually made of attached sheets of acrylic plastic, which have several advantages over the use of glass beakers or containers:

1. The plastic jars are less fragile.
2. The square shape provides better mixing than the conventional cylindrical beakers.
3. The rotational velocity stops quickly when stirring ceases.
4. No siphon or pipette is needed for sampling; therefore, the sample is retrieved without disturbing the settling water.
5. The walls are less heat-conductive than glass walls.¹¹

¹⁰ Murcott and Harleman, 2000.

¹¹ Hudson, 1981, p.219-220.

3.3 Coagulants

Numerous metal salts were examined as part of the bench-scale studies in Brazil. Metal salts are manufactured by replacing hydrogen atoms on acids with metal atoms or electropositive radicals. When these salts are added to water, they dissociate into ions. Their function is to enhance the coagulation of suspended solids in the wastewater. Therefore, immediately after adding the metal salt, the wastewater will undergo a period of intense mixing to form larger flocs. For bench-scale studies, these metal salts are individually chosen and tested for each plant based on the success of previous applications, availability, and economics. Some widely used coagulants are:

- Alum $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$
- Aluminum chloride AlCl_3
- Polyaluminum chloride PAC
- Ferric chloride FeCl_3
- Ferrous chloride FeCl_2
- Ferric sulfate $\text{Fe}_2(\text{SO}_4)_3$
- Ferrous sulfate FeSO_4
- Lime $\text{Ca}(\text{OH})_2$

Alum is a frequently used coagulant in potable water treatment due to its cost and ease of handling. But alum performance can easily be affected by several factors such as concentration, pH, temperature, colloidal nature, size of turbidity particles, and mixing rate.¹² AlCl_3 and PAC are both more effective than alum for precipitating out of organic acids in wastewater. The downside to both of these chemicals is that they are both more

¹² Kawamura, 1976, p.328.

difficult to handle and have higher costs. The most recent finding is the possible association of aluminum with Alzheimer's disease. The use of aluminum salts would increase the level of aluminum in the effluent water.¹³ The effective use of ferric and ferrous salts depends on the nature of the wastewater. In some cases, these salts produce little to no floc when organic nitrogenous, textile, or fermentation wastes are present.¹⁴ Ferrous salts are somewhat cheaper than ferric salts because ferric salts can be derived from ferrous salts via oxidation or from the waste products of steel and chemical mills. Overall, iron salts have the disadvantage of being aggressively corrosive.¹⁵ Lime can also be regarded as a coagulant, especially if the water contains Mg ions, resulting in the precipitation of $Mg(OH)_2$.¹⁶ One benefit of lime usage is the increase in pH of the wastewater, providing some disinfection. One drawback is the high volume of sludge that is subsequently generated.

3.4 Flocculants

Polymers or polyelectrolytes are different from metal salts in that they serve as coagulant aids. They consist of long chain organic molecules that have ionized sites for ions to attach. The polymerization, or combination of several monomers, single units, forms one of these polymers. Aside from their complexity, polymers are effective in small dosages, non-toxic in polymeric form, and relatively easy to handle. The application of polymers has become more standard because they serve many beneficial purposes:

¹³ Droste, 1997, p.386.

¹⁴ Rudolfs, 1996, p.1052.

¹⁵ Kawamura, 1976, p.328.

- To reduce the amount of sludge generated by the treatment process;
- To improve the sludge-dewatering process;
- To ease sludge digestion by microorganisms;
- To reduce the need for additional alkalinity for final pH control;
- To minimize chemical residuals in treated waters.¹⁷

Polymers are either natural or synthetic. Natural polymers, such as starch or gelatin, have been in existence for a long time; only recently have scientists invented synthetic polymers. Polymers can be categorized by charge, molecular weight, form, and charge density, as shown in Figure 3-2. Charge density is defined as the measure of the concentration of electric charges along a polymer chain and has the units of charge density in mole %.

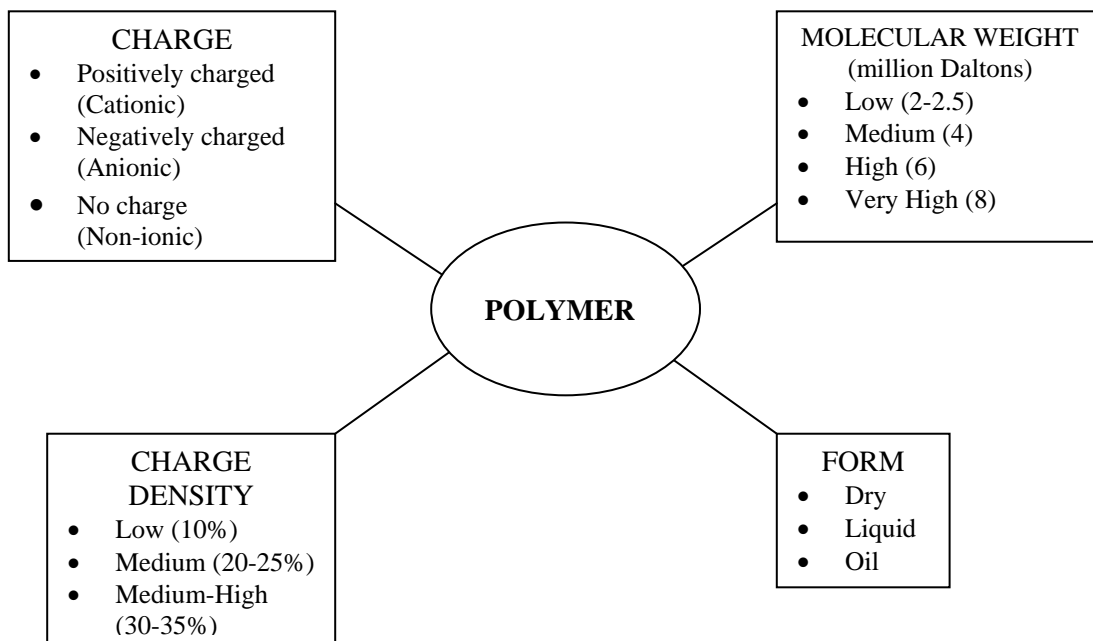


Figure 3-2 Classification of Polymers

¹⁶ Sontheimer, H. 195.

¹⁷ Kawamura, 1976, p.329.

3.5 Methods and Procedure

The practice of conducting jar tests has evolved through many years of experience. After getting all of the equipment and chemicals together, it is necessary to formulate the methodology and to establish certain parameters. First, it is important to determine an appropriate mixing regime (i.e. mixing intensity, mixing times, and settling/detention time). Second, an appropriate sampling scheme is necessary. Third, the chemicals are prepared with proper make-up procedure and/or dilutions to achieve correct percent solutions. Fourth, series of jar tests are run and samples are extracted for analysis. Fifth, the samples are analyzed both qualitatively (visually) and quantitatively (water quality analysis). Finally, after all of the jar tests are completed, the data is thoroughly evaluated.

3.6 Sedimentation Theory

To devise a mixing regime that mimics full-scale, the jar, as seen in Figure 3-3, is viewed as a scaled down version of a primary sedimentation tank, as seen in Figure 3-4.

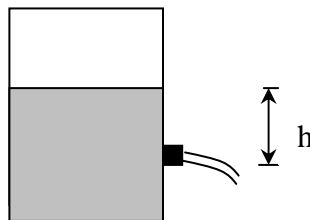


Figure 3-3 Jar Schematic

This perspective yields the calculation for an overflow rate based on given dimensions and flow rates. The overflow rate is thus related to the detention time.

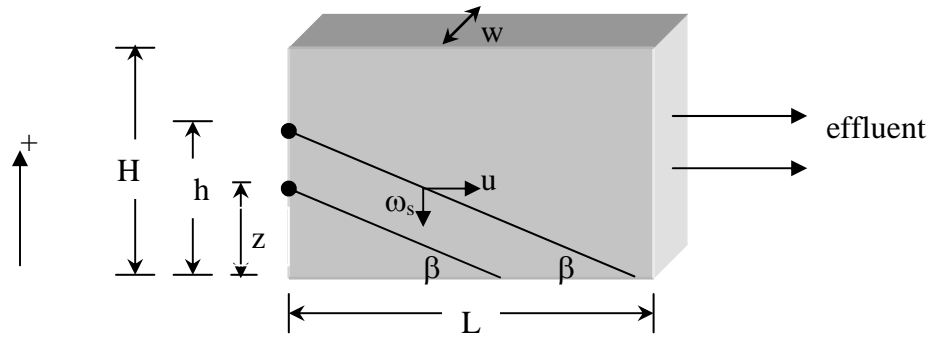


Figure 3-4 Simple Sedimentation Tank Theory

This theory makes the assumption that there is no turbulence and that all the particles of the same size entering between $z = 0$ and $z = h$ are removed. Hence,

$$\begin{aligned} \% \text{removal} &= \frac{h}{H} & h &= \frac{\omega_s L}{u} \\ \tan \beta &= \frac{\omega_s}{u} = \frac{h}{L} & \% \text{removal} &= \frac{\omega_s L}{uH} \end{aligned}$$

The flow rate through the tank is $Q = Hwu$

$$H = \frac{Q}{wu}$$

$$\% \text{removal} = \frac{\omega_s Lwu}{Qu} = \frac{\omega_s L}{Q}$$

The surface area of the tank is $A_s = wL$

$$\% \text{removal} = \frac{\omega_s}{Q/A_s}$$

The surface overflow rate (OFR) is

$$OFR = \frac{Q}{A_s}$$

A relationship in settling times can be established between jar tests and continuous flow tanks because of the observation that the settling time in jar tests, t_j , is equivalent to the residence time in the tank, t_r .

Thus, Q can be re-written as:
$$Q = \frac{LwH}{t_r} = OFR \times A_s$$

If h_j is the settling depth in the jar test:
$$OFR = \frac{H}{t_r} = \frac{h_j}{t_j}$$

Therefore, a jar test with $h_j = 4 \text{ in.} = 0.1 \text{ m}$ and $t_j = 5 \text{ minutes} = 0.0034 \text{ days}$ yielding a $SOR = 30 \text{ m/d}$, which is normal for conventional primary treatment. CEPT can be simulated in a jar test with a settling time $t_j = 1.5 \text{ minutes} = 0.001 \text{ days}$, yielding an OFR of 100 m/d . This higher overflow rate demonstrates the impact of CEPT on settling times and overall efficiency.

3.7 Sampling

Fresh wastewater samples should be mixed thoroughly using a long stick or rod, as shown in Figure 3-5. The volume of wastewater needed depends solely on the amount of testing planned. After mixing, 1 or 2 liters of raw wastewater, depending on the intending tests, are poured into each of the jars. Approximately 100 ml of the well-mixed raw wastewater should also be placed into a labeled beaker, which will be blended and analyzed for TSS, COD, and other parameters to be used for later comparison.



Figure 3-5 Mixing of Wastewater

3.8 Preparation of Chemicals

The choice of which coagulants and polymers to test depend mainly on the specific goals and objectives of jar tests. Typically, research is done beforehand to determine which of the coagulants and polymers may be best suited for that type of wastewater or that location, etc. For a series of jar tests, it is best to run all of the coagulants being considered, each one separately in doses of 0-100 mg/L, in increments of 10 mg/L. The choice to use a flocculant depends on these results. If polymer is necessary, jar tests should be run with an average dosage of coagulant and varying polymer doses of 0-0.5 mg/L, in increments of 0.1 mg/L. Polymers of different charge and molecular weight should be tested to determine which works best with the coagulant to produce the best flocculation. With each series of jar tests, it is good practice to always have a “zero chemical” jar, that simulates conventional primary treatment.

In general, coagulant and polymer solutions are prepared as 0.1 or 1 % solutions from either a dry product or a liquid product. Due to the high relative humidity in Brazil, solutions should be prepared often, as specified by the manufacturer, to ensure adequate freshness. Also, tap water is usually used to prepare the solutions because tap water, not distilled water, is what would be used in full-scale applications.

A good example of preparing a solution from a dry product is when preparing GAC anionic and cationic polymer solutions. Once prepared, these anionic solutions stay fresh for about a month. To make a 100 ml of a 0.1 % solution, the following steps need to be followed:

1. Measure out 1 gram of polymer.
2. Wet the polymer with a couple drops of alcohol. This addition will improve the solubility of the polymer in the water.
3. Add 100 ml of tap water to the polymer to make a 1 % solution.
4. Mix this solution thoroughly. Using a hand-held blender for 5 seconds works best.
5. Take 10 ml of the solution in step 3 and add 90 ml of tap water to make a 0.1 % solution.

To prepare solutions using a liquid stock, several important pieces of information are necessary about the coagulant or polymer, such as the specific gravity and the percent solids. This information is usually available on the chemical data sheets provided by the manufacturer. The following equations are used to make the appropriate dilution:

$$\text{Concentration of stock solution} = C_1 \text{ (mg/L)}$$

$$\text{Concentration of solution after dilution} = C_2 \text{ (mg/L)}$$

$$\text{Volume of stock solution} = V_1 \text{ (L)}$$

$$\text{Volume of solution after dilution} = V_2 \text{ (L)}$$

$$C_1 \times V_1 = C_2 \times V_2$$

$$V_1 = (\text{desired percent of solution} / \% \text{ solids}) \times (V_2 / \text{specific gravity}) \quad \text{Equation (2)}$$

A good example of preparing a solution from a liquid stock is when preparing some of the metal salts. Unlike polymers, these metal salt solutions should be prepared daily because they tend to degrade much faster at room temperature. To make 200 ml of a 1 % solution of Varennes FeCl_3 , the following series of steps is required:

1. Perform the calculation using equation 2 to determine the amount of stock solution is necessary to make the final solution.

$$V_1 = \frac{0.01}{0.396} \times \frac{200\text{ml}}{1.434} = 3.5 \text{ ml FeCl}_3$$

2. Fill the rest up with tap water to make up the 200 ml solution.
3. Mix thoroughly.

3.9 Mixing Regime

Now, jar tests can be performed using a typical mixing regime, as shown in Table 3-1.

Table 3-1 Standard Mixing Procedure for Jar Tests

Step	Mixing Time (min)	Mixing Speed (rpm)
Coagulant addition with rapid mixing	0.5	100
Polymer addition with rapid mixing	0.5	100
Medium mixing	2.5	70
Slow mixing	2.5	30
Settling	5	0

3.10 Visual Test

When performing jar tests, it is good practice to jot down visual observations such as:

- Rate of floc formation;
- Floc size;
- Overall settling time;
- Amount of floating suspended solids;
- Color and clarity of supernatant.

The determination of floc size is a subjective, qualitative evaluation. The chart in Appendix A is often used in classifying the size. The placement of this chart close the flocculator is helpful.

3.11 Total Suspended Solids (TSS) Test

The methods used to determine TSS removal percentages are outlined below. This is a modified version of the TSS procedure outlined in Standard Methods. A 47-mm diameter Whitman glass fiber filter, or other comparable filter, is used to filter the supernatant. Also, filtration apparatuses vary, using either a magnetic seal or a metal clamped seal. The TSS procedure is as follows:

1. Weigh dried filter in metal tin.
2. Place filter with the rough side up in the filtration apparatus.
3. Wet the filter with distilled water and turn on the vacuum.
4. Using a graduated cylinder, pour 25 or 50 ml of the blended supernatant, depending on the amount of TSS in the sample. The sample sizes vary because of the differences in TSS concentration among the samples. Typically, raw and zero chemical supernatants have high solids concentrations; therefore, 25 ml samples are used. All others are run at 50 ml.
5. Wash the graduated cylinder and cup with at least three successive 10 ml portions of distilled water.
6. Continue suction for 3 minutes after filtration to remove as much water as possible.
7. Turn off the vacuum and discard the unnecessary filtrate.

8. Place the filter back into the metal tin and put the samples into the oven at 103 to 105°C for 1 hour.
9. Cool in a dessicator and weigh.

TSS and TSS % removal can be calculated using the following equations:

$$\text{TSS (mg/L)} = \frac{(\text{weight of filter + tin after filtration}) - (\text{weight of filter + tin before filtration}) \text{ (mg)}}{\text{volume of sample added (L)}}$$

$$\text{TSS \% Removal} = \frac{TSS_{\text{sample}}}{TSS_{\text{raw}}} \times 100\%$$

3.12 Chemical Oxygen Demand (COD) Test

Testing for COD provides a good measure of the oxygen required to chemically oxidize organic matter in a wastewater sample. One widely used method for measuring COD is Hach's U.S. EPA approved Dichromate COD Method. This method introduces a silver compound catalyst that promotes the oxidation of resistant organic compounds in the wastewater. Mercuric sulfate, which needs to be properly disposed of after usage, is also present in the reagent to reduce the interference caused by the oxidation of chloride ions by dichromate.¹⁸

COD tests are preferred over BOD₅ tests for several reasons. First, the BOD₅ test is not stoichiometrically valid. In other words, five days is an arbitrary period that is set, which does not necessarily correspond to the period where all of the organics in the wastewater are consumed. Second, the COD test can produce results within several hours, whereas the BOD₅ test takes five days. Third, with the BOD₅ test, there is often interference

¹⁸ Hach Company, 2000.

caused by nitrification. Last of all, the BOD₅ test requires strict laboratory conditions of maintaining a constant temperature of 20°C, which would be difficult in Brazil. Despite these advantages of COD over BOD₅, several states in Brazil, including Sao Paulo, maintain regulations that specify a BOD₅ limit and not a COD limit.

The methods to determine percent COD removals are outlined below:

1. Pipette 2 ml of the blended wastewater sample into the Hach COD vials, already containing 3 ml of COD reagent, yielding a total volume of 5 ml in each vial.
2. Cap the vial and shake vigorously. Avoid touching the glass portion of the vial due to exothermic reaction. Use kemwipes or paper towels to prevent transmitting oils from your hands to the glass vials.
3. Keep the samples away from sunlight prior to cooking.
4. Make a “blank” by pipetting 2 ml of distilled water into a Hach COD vial with 3 ml of reagent.
5. Cook the samples, including the blank, in the Hach COD reactor, as shown in Figure 3-6, for 2 hours at 150°C.
6. Let the samples cool down to room temperature.
7. Zero the Hach spectrophotometer using the blank sample.
8. Place each of the cooked samples in the Hach spectrophotometer and record the COD readings.
9. Properly dispose of the chemicals contained within each vial.

COD % Removal can be calculated using the following equation:

$$\text{COD \% Removal} = \frac{\text{COD}_{\text{sample}}}{\text{COD}_{\text{raw}}} \times 100\%$$



Figure 3-6 Sample Cooking in Hach COD Reactor

Chapter 4 - Review of Pinheiros WWTP¹⁹

4.1 Background

Pinheiros was constructed in the mid-1970s as a conventional primary treatment plant. It was supplied by two pumping stations that fed water from various districts of Sao Paulo. Pinheiros consists of two influent pumping stations, sand removal, a primary clarifier, anaerobic digesters, centrifuges, and processors with thickening to handle the generated sludge, as shown in Figure 4-1.

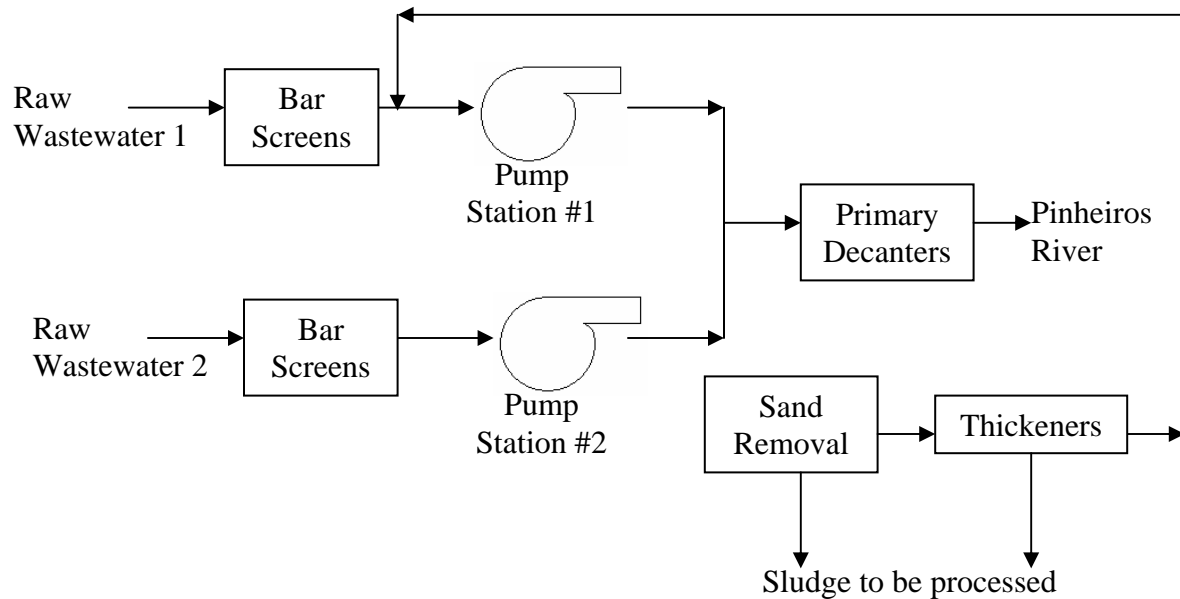


Figure 4-1 General Schematic of Pinheiros Prior to CEPT Upgrade

Originally, the plant was planned for closing with flow redirection to Barueri but for CEPT testing, Pinheiros was kept in operation. The wastewater entering the treatment plant consists of about 70 % municipal waste and 30 % industrial waste. Based on wastewater sampling during 1993-1995, the average flow entering the plant was 1.3 m³/s

¹⁹ Harleman and Murcott, 1995.

with an influent TSS reading of 162 mg/L, BOD reading of 211 mg/L, and COD reading of 378 mg/L.

4.2 Bench-scale Analysis

The bench-scale analysis performed at Pinheiros focused mainly on the removals of BOD, COD, and TSS. Jar testing equipment was provided by both FSFM and SABESP, and was set up in laboratory facilities onsite. A Phipps & Bird 6-paddle flocculator with 2-L jars was used to test a variety of chemicals and polymers.

4.3 Chemicals

A wide variety of coagulants and polymers were tested. Tables 4-1 and 4-2 show the metal salts and polymers that were tested.

Table 4-1 Metal Salts Tested at Pinheiros

Chemical	Manufacturer	Form	% Solids	Specific Gravity
FeCl ₃	Eaglebrook	Liquid	30	1.38
FeCl ₃	Barueri			
Fe ₂ (SO ₄) ₃	Kemira (Ferrix-3)	Liquid	56	3.1
FeClSO ₄	Tibras/Sanchelor	Liquid	35	1.38
Alum	Guacu Industries Quimical	Liquid	50	1.32
Sodium aluminate	FSFM	Liquid	38	1.5
Lime	FSFM	Dry	100	

Table 4-2 Polymers Tested at Pinheiros

Manuf.	No.	Form	Charge	% Solids	Specific Gravity	M.W.	Charge Density
Nalco	7172	Emulsion	Anionic	33	1	High	Medium
Nalco	7174	Emulsion	Anionic	33	1	High	High
Nalco	7128	Emulsion	Cationic	33	1	High	Medium
Nalco	8105	Emulsion	Cationic	33	1.15	Medium	Medium
Nalco	8181	Emulsion	Non-ionic	33	1	Medium	
GAC	2540	Liquid	Anionic	0.75	1	Very High	High
GAC	120	Dry	Cationic	95		Normal	Medium
GAC	131	Dry	Cationic	95		Normal	Medium-High
GAC	140	Dry	Cationic	95		Normal	High
GAC	531	Dry	Cationic	95		High	Medium-High

4.4 Results

First, the zero chemical jars were looked at to evaluate the performance of the plant. Sampling occurred during the bench-scale analysis period in September 1995. The results showed considerable variability, which suggests that at this plant, uncovering a link between the jar tests and the full-scale performance would be complicated on account of the two distinct and variable flows. Therefore, separate jar tests were performed on each wastewater. BOD₅ tests, in addition to COD and TSS tests were performed at Pinheiros. This data was then compared to the state of Sao Paulo regulatory limit of < 60 mg/L BOD for river discharges.

4.5 Wastewater Stream 1

The ferric chlorides and anionic polymers fared the best with at Pinheiros. Therefore, FeCl_3 was tested in doses of 10-50 mg/L with polymer. Three anionic polymers were found to be the most effective: GAC #2540, Nalco #7172, and Nalco #7174. These combinations yielded BOD removals between 60-90 % with combinations of about 25-50 mg/L of ferric chloride and 0.3-0.5 mg/L of anionic polymer. With the use of chemicals, the average BOD concentration in the samples was less than the Sao Paulo limit of 60 mg/L. COD removals were measured using the same dosage range for FeCl_3 with 0.5 mg/L of #2540. This combination yielded 20-50 % more removal than the zero chemical jars. TSS removals were measured using the same dosage range for ferric chloride with 2 different polymers: #2540 and #7172. With 20-50 mg/L of ferric chloride and 0.3-0.5 mg/L of anionic polymer, the TSS removals ranged from 60-87 %.

4.6 Wastewater Stream 2

Again, ferric chlorides were tested with anionic polymers. Doses of 10-50 mg/L of ferric chloride with 0.5 mg/L of anion #2540 yielded matching BOD and COD results. The removal percentages ranged from 40-65 % as compared to removal percentages of 10-20 % in the zero chemical jars. The 10-20 % removal rates for the zero chemical jars were lower than what was typically expected at Pinheiros.

To measure TSS, 25 and 50 mg/L FeCl_3 with 0.3 mg/L of #2540 and #7174 were tested. The zero chemical jars yielded low TSS removals of 10-22 %. The lower dosage combination actually yielded a higher removal rate.

4.7 Both Wastewater Streams

A close examination of the two wastewater streams shows poorer coagulation performance in stream 2 than in stream 1. The main difference is that the flow of stream 1 is stronger than stream 2. Stream 2 has a sand gravity thickener overflow and centrate whereas in stream 1, there is no sand removal overflow or recycle flow. Stream 2 consists mainly of domestic, commercial and industrial waste but more importantly, it includes wastewater from Sao Paulo University.

Upon further testing of coagulants and polymers, FeClSO_4 and alum performed well, if not better than FeCl_3 . Results from comparison tests yielded an optimal dosage of 30 mg/L with the highest TSS removal rate achieved by FeClSO_4 of 95 %, and then alum of 65–70 %, and FeCl_3 of 60-65 %.

Several cationic polymers also performed very well and yielded equal or better results than FeCl_3 . Therefore, cationic polymers can be seriously considered as a substitute for metal salts as primary coagulants. The advantage to using cationic polymers is the good results achieved at low doses of 1-10 mg/L.

4.8 Settling Tests

Settling tests were conducted to optimize the design parameters for full-scale testing by looking at the surface-loading rate. TSS % removals were compared for three different surface loading rates of 2, 4, and 8 m/hr. The zero chemical jar yielded 65 % TSS for the typical overflow rate of 2 m/hr; with higher rates, this percent removal decreased to 50

%. Jars dosed with both coagulant and polymer yielded much better results. Regimes with 10-50 mg/L ferric chloride and 0.5 mg/L anionic polymer or cationic polymer and 10 mg/L bentonite yielded much higher percent TSS removals of 85-90%. This range corresponds to an overflow rate of 2 m/hr and with an increase in overflow rate, these numbers fall, but not as drastically as the zero chemical jars. Therefore, these results support the theory that CEPT produces good results with higher overflow rates.

4.9 Conclusion

From these bench scale tests, it is apparent that CEPT is successful in achieving higher percent removals for BOD, satisfying the Sao Paulo limit of 60 mg/L on BOD for river discharges. The optimal coagulant and polymer dosages were found to be 25 mg/L of a ferric salt and 0.3 mg/L of an anionic polymer. An equal and optimal chemical regime would be the use of 5 mg/L of cationic polymer. This dosing system would be difficult to apply to full-scale testing at Pinheiros because of the difference in the two wastewater streams, stream 1 being stronger than stream 2, and because of the discrepancies found in the zero chemical jars.

Chapter 5 - Review of Ipiranga WWTP²⁰

5.1 Background

E.T.E. Jesus Neto, also known as Ipiranga, has been in operation for over 70 years. Ipiranga was built as a conventional primary facility with activated sludge biological treatment. During these 70 years of operation, the growing population in Sao Paulo has overloaded the existing system. Therefore, the use of CEPT was considered for increasing the plant efficiency and capacity, and various bench and full-scale tests were conducted in March 1996. The upgrade consisted of the addition of FeCl_3 at the pump station, proportional to the flow and the number of pumps operating. The Ipiranga system prior to the CEPT upgrade test is shown in Figure 5-1.

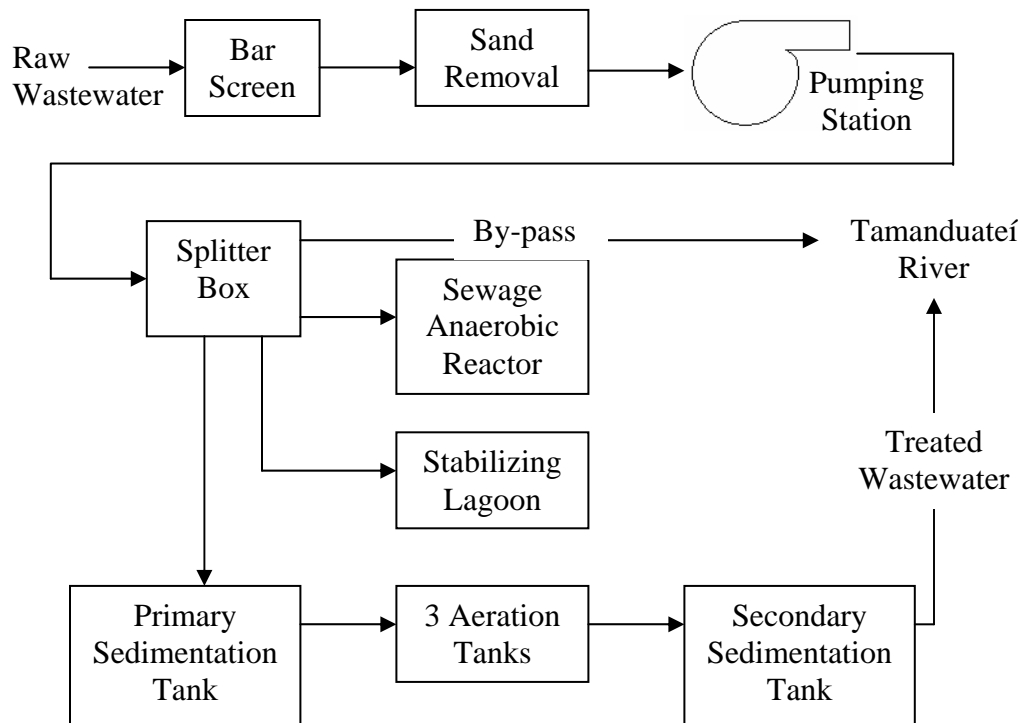


Figure 5-1 General Schematic of Ipiranga Prior to CEPT Upgrade

²⁰ Fundação Salim Farah Maluf and SABESP, 1996.

At Ipiranga, the typical flow rate to the primary settling tank is 25 L/s. This flow rate is produced by one of two pumps, and the flow can be doubled if both pumps are run at the same time. The general characteristics of the raw water entering the plant were, in 1996, on average 531 mg/L COD, 286 mg/L BOD, and 178 mg/L TSS.

5.2 Bench-scale Analysis

To test the feasibility of CEPT at Ipiranga, many jar tests were conducted in 1995 and 1996. Although, several parameters were looked at in the full-scale testing analysis (total, fixed, and volatile solids, total and soluble COD, total and soluble BOD, pH, and total PO_4^{3-}), only COD was measured for jar testing. Both SABESP, the environmental agency of Sao Paulo, and Fundação S. F. Maluf (FSFM), conducted bench-scale analyses on the Ipiranga wastewater.

5.3 Chemicals

Few chemicals were tested at Ipiranga. A liquid FeCl_3 solution, consisting of 40 % solids, was tested both with and without an anionic polymer. This FeCl_3 product was manufactured by the Brazilian chemical company, NHEEL, and provided by SABESP. Two anionic polymers were tested, both similar in charge and molecular weight. The first was an emulsion in water (E), and the second was soluble in water (S). The emulsion is the Nalco polymer #7174, manufactured in Brazil. The second polymer is the GAC polymer #60540, imported from the United States. Both of these chemicals were obtained from FSFM.

5.4 Results and Conclusion

Based on the few jar tests run, some conclusions can be made about what combination of FeCl_3 and polymer were most effective, and at what dosage. Jar tests were run without any chemical, 25 mg/L FeCl_3 and 50 mg/L FeCl_3 , with varying polymer dosages. Without chemicals, tests yielded a 12.5 % COD removal on average. Figure 5-2 shows the results of jar tests run with FeCl_3 and varying dosages of polymer of 0.25 or 0.5 mg/L. The resulting trend was an increase in COD removal with increased polymer dosage. Looking closely at the two polymers, the S polymer outperformed the E polymer in all instances.

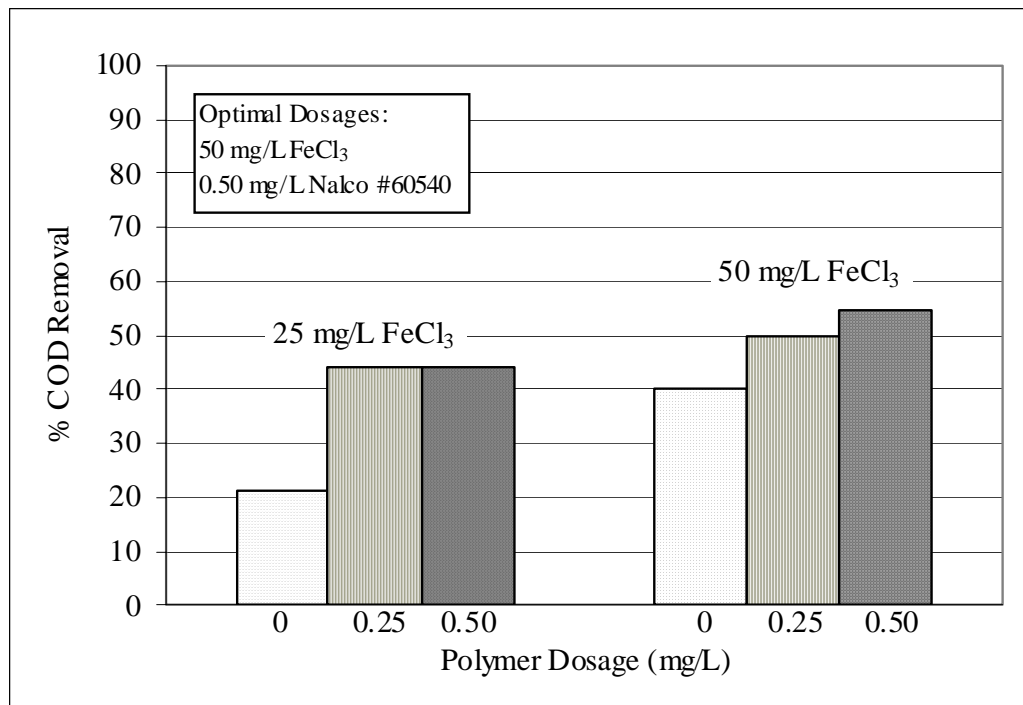


Figure 5-2 Primary Coagulant with Polymer COD Removal Performance at Ipiranga

Chapter 6 - Review of ETIG WWTP²¹

6.1 Background

Estação de Tratamento de Esgotos da Ilha do Governador (ETIG) is located in the state of Rio de Janeiro on Governor's Island in Guanabara Bay. It was selected as a good site for CEPT because of its highly polluted waters, containing high levels of coliforms, low levels of dissolved oxygen, and severe eutrophication problems. ETIG was built in 1980 as a conventional primary treatment plus secondary activated sludge facility. The basic design prior to full-scale CEPT demonstration testing is shown in Figure 6-1.

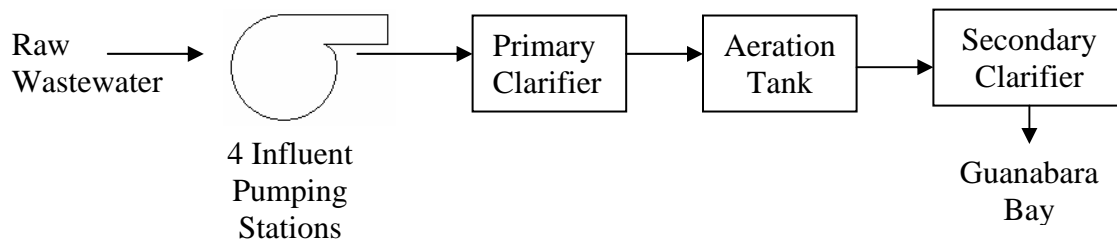


Figure 6-1 General Schematic of ETIG Prior to CEPT Upgrade

ETIG was originally designed for a flow of 230 L/s, but after the completion of additional construction in 1997, the average flow increased to 525 L/s with a maximum flow of 900 L/s. This corresponded to an average BOD loading of 11 Mg/day, which is slightly higher than in previous years. A picture of the ETIG chemical dosing scheme and sedimentation tank is shown in Figure 6-2.

Bi-weekly raw water samples were analyzed and recorded during the sampling period of 1994-1997. The average TSS of the influent was 262 mg/L. The TSS values throughout this period steadily increased from a minimum of 193 mg/L up to a maximum of 344

²¹ Harleman and Murcott, 1997.

mg/L. The average BOD of the influent was 235 mg/L, again with an increasing trend. The average COD of the influent was 486 mg/L and the average PO_4^{3-} of the influent was 47 mg/L. Fewer samples were analyzed for COD and PO_4^{3-} during this time period.



Figure 6-2 Chemical Dosing Area at ETIG

6.2 April 1997 Bench-Scale Analysis

Jar tests were conducted from April 10-18, 1997 and subsequently, in June – August 1997, PENHA wastewater was tested against the ETIG wastewater for comparison. Several removal rates were evaluated, including TSS, BOD, COD, and PO_4^{3-} . In addition to standard jar tests to determine optimal chemical type, dose, mixing time and mixing speed, settling tests were conducted to identify design parameters for full-scale testing.

Ecosystems Engineering provided the equipment which was set up in the laboratory onsite. Wastewater samples were collected every morning by staff or by Susan Murcott. Samples were obtained using a 10-L plastic bucket, extracting wastewater leaving the grit chamber before the Parshall flume, and then transferred to a large 50-L container. A Phipps & Bird 4-paddle flocculator with 2-L jars was used, in addition to a HACH DR/2000 spectrophotometer and COD reactor for analysis.

6.3 Chemicals

During the April 1997 bench-scale tests, several metal salts and polymers were tested, as listed in Tables 6-1 and 6-2.

Table 6-1 Metal Salts Tested at ETIG (April 1997)

Chemical	Manufacturer	Form	% Solids	Specific Gravity
FeCl ₃	Eaglebrook	Liquid	30 %	1.35
Fe ₂ (SO ₄) ₃	Kemwater Brazil S.A. (Ferrix-3)	Dry	--	--
FeClSO ₄	Kemwater Brazil S.A. (PIX-110)	Liquid	41 %	1.47
Alum	General Alum and Chemical (GAC)	Liquid	49.5 %	1.33
PAC	Kemwater (PAX-XL60s)	Dry	--	--

Table 6-2 Polymers Tested at ETIG (April 1997)

Manufacturer	No.	Form	M.W.	Charge
GAC	15	Dry	High	High
GAC	19	Dry	Very high	High
Kemwater	A305	Dry		

6.4 Mixing Regime

The mixing scheme used to compare the coagulation produced by these coagulants and flocculants was adapted from the plant design, as shown in Table 6-3.

Table 6-3 Jar Test Mixing Regime at ETIG (April 1997)

Step	Mixing Time (minutes)	Mixing Speed (rpm)
Coagulant addition with rapid mixing	0.1	150
Polymer addition with rapid mixing	0.5	100
Medium mixing	2.5	70
Slow mixing	2.5	30
Settling	5	0

This mixing regime has a higher mixing speed for coagulant addition than most standard mixing regimes used for bench-scale analysis on account of greater turbulence at the point of chemical addition in the full plant.

6.5 Jar Test Results

These results provide insight into both the performance of the full plant treatment and the optimization of the metal salt and polymer usage. The zero chemical jars simulate

conventional primary treatment and should be able to be compared with the full plant performance to determine the effectiveness and functionality of the plant. Typically, conventional primary treatment achieves TSS removal rates of 60 % and BOD and COD removal rates of about 30 %. Table 6-4 shows these removal rates in the zero chemical jars at ETIG as compared to the full-scale performance.

Table 6-4 Results of the Zero Chemical Jar Tests at ETIG (April 1997)

	TSS	BOD	COD	PO₄³⁻
Full plant primary treatment performance	42 %	19 %	27 %	1 %
Zero chemical jar	59 %	29 %	42 %	16 %

This data shows that at ETIG, the primary treatment plant performance was functioning below the efficiency expected of a functional conventional primary treatment plant.

The main goal of these tests was to determine which of the metal salts and polymers could achieve the best PO₄³⁻ removal, while also improving TSS, BOD, and COD removals. First, comparison tests were conducted over the entire range of metal salts, then with polymer added. FeCl₃ and Fe₂(SO₄)₃ were first tested with 25, 50, 75, and 100 mg/L and as expected, both chemicals had better COD, TSS, and PO₄³⁻ removals at higher doses. With a dose of 50 mg/L, FeCl₃ was compared with aluminum salts. FeCl₃ and PAC yielded the best COD and TSS removal in comparison to alum and Fe₂(SO₄)₃. These results are shown in Figures 6-3 and 6-4. Overall, FeCl₃ fared the best for PO₄³⁻ removal.

At ETIG, there is a greater improvement in COD removal from the higher dosage of 50 mg/L FeCl₃ with polymer compared to the same dosage of FeCl₃ without polymer. Therefore, the optimal dosing scheme is 50 mg/L of FeCl₃ and 0.5 mg/L of GAC #15. Some TSS measurements were taken and the use of polymer was found to have a smaller effect on TSS removal percentages, increasing from 92% without polymer to 93% with polymer.

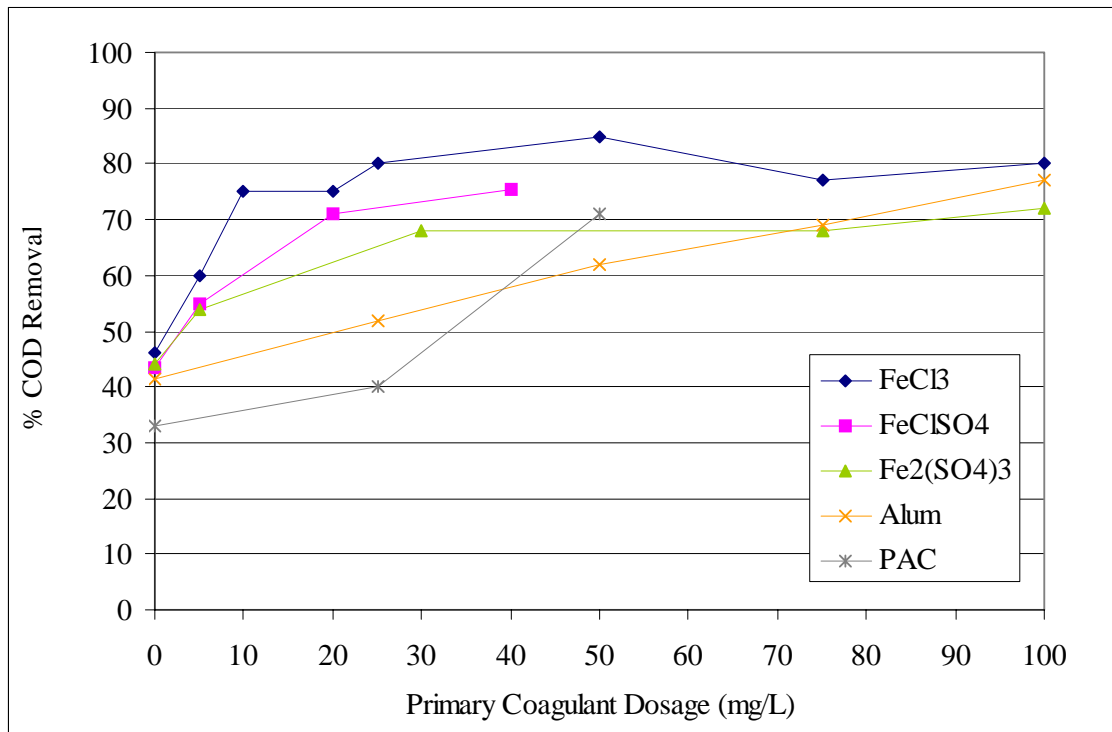


Figure 6-3 Primary Coagulant COD Removal Performance without Polymer at ETIG

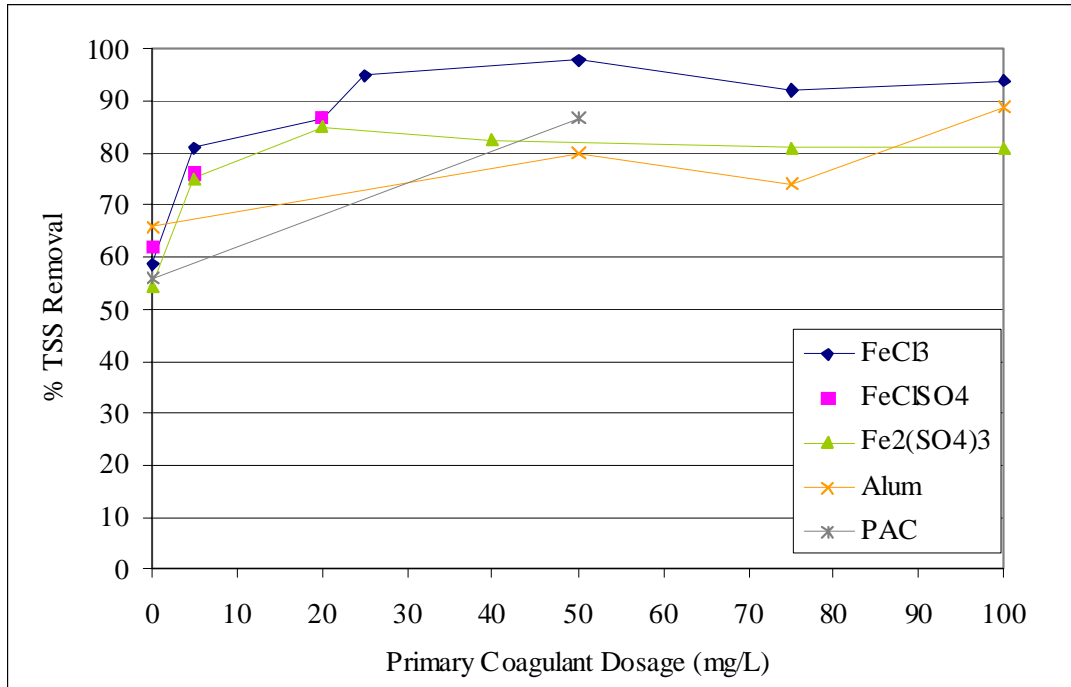


Figure 6-4 Primary Coagulant TSS Removal Performance without Polymer at ETIG

Next, the effect of polymer was tested with 50 mg/L of FeCl₃ and PAC, individually. Two of the three polymers tested were found optimal at Ipiranga. The ETIG results showed that the addition of polymer did not improve COD removals. GAC #15 yielded the best phosphate removals at a dosage of 0.5 mg/L, 88 % removal with 50 mg/L FeCl₃, and only 72 % removal with 50 mg/L of PAC. Therefore, the optimal chemical combination was found to be 50 mg/L of metal salt and 0.5 mg/L of GAC #15, as shown in Figure 6-5. Halving the coagulant dosage lowered the removals for both COD and PO₄³⁻.

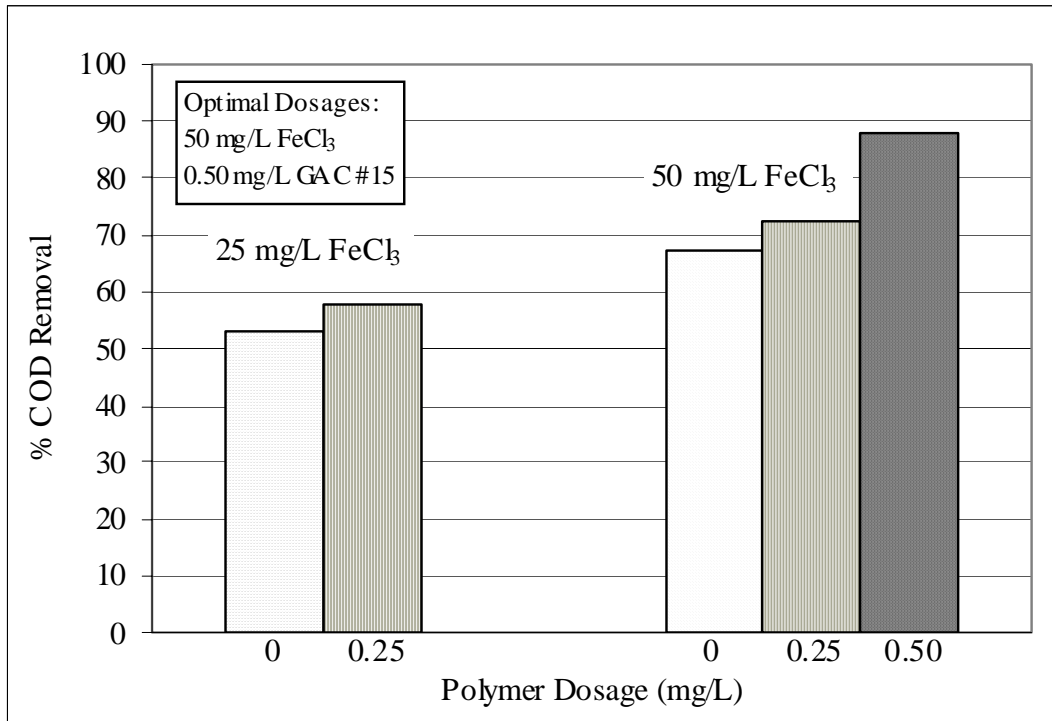


Figure 6-5 Primary Coagulant with Polymer COD Removal Performance at ETIG

6.6 Settling Test Results

A settling time of five minutes in the jar tests was correlated to a surface overflow rate of 1.8 m/hr at ETIG, as calculated by equations in Section 3.6. PAC and FeCl₃ were both tested with and without GAC #15. Without the polymer, both metal salts yielded poor settling due to poor coagulation; therefore, they required at least 2 minutes for settling. This settling rate equals an overflow rate of 4.5 m/hr at ETIG. With polymer, flocs settled much faster, within a minute or less. This settling rate translates to an overflow rate of approximately 9 m/hr at ETIG. Therefore, the use of polymer should allow for doubling of the higher overflow rate or possibly more, depending on optimal plant conditions.

6.7 June-August 1997 Bench-Scale Analysis

The purpose behind additional bench-scale testing was to confirm the April results and to test additional coagulants. This set of jar tests was performed with wastewater from PENHA, a nearby treatment plant, to determine similarities, if any, to ETIG. The additional coagulants tested during this period are shown in Table 6-5.

Table 6-5. Additional Metal Salts Tested at ETIG (June – August 1997)

Chemical	Manufacturer	Form	% Solids	Specific Gravity
FeCl ₃	Eaglebrook	Liquid	36 %	1.40
Alum	Cataguazes -- Minas Gerais, BR	Dry	--	--

Upon analysis of both wastewater samples, the ETIG and PENHA plants were found to have similar levels of TSS, BOD, COD, and PO₄³⁻. Therefore, jar tests run with PENHA wastewater could be compared to previous jar tests run with ETIG wastewater. These tests yielded the same conclusions, as did the April jar tests, in which FeCl₃ yielded the best removals at a dose of 20 mg/L. At slightly higher doses, FeCl₃ was indistinguishable from the other iron salts tested.

6.8 Conclusion

Based on the jar tests performed at ETIG, the most promising coagulant was FeCl_3 . Not only did it outperform other metal salts, it also had the lowest cost per ton. The only disadvantage to using FeCl_3 at that time, was its availability in Brazil. Today in Brazil, there are at least two local supplies of FeCl_3 , NHEEL and Guaçu. Better coagulation occurred when polymer was used, and according to the April 1997 tests, the best polymer in conjunction with FeCl_3 was the anionic polymer, GAC #15.

Chapter 7 - Review of Tatui WWTP²²

7.1 Background

The wastewater treatment facility in Tatui, CEAGESP, was designed for a small city. Tatui is located in the state of Sao Paulo. With a growing population, the plant facilities have become overloaded and poorly maintained. The plant scheme consists of raw water entering an anaerobic lagoon, followed by a facultative lagoon, as shown in Figure 7-1.

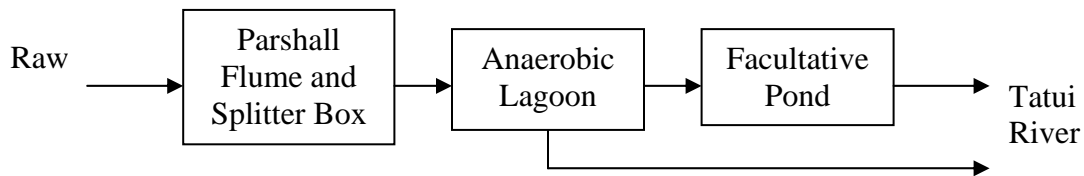


Figure 7-1 General Schematic of Tatui Plant Prior to CEPT Upgrade

The CEAGESP personnel recorded raw water characteristics. According to 1992 data, the inflow rate was 161 L/s, the average raw water influent BOD was 276 mg/L, and the influent TSS level was 200 mg/L. No influent COD was recorded.

It is easy to determine the efficiency of the system by looking closely at the COD removals in the two lagoons. From full-scale field sampling, both lagoons appear to be operating well below design specifications. Only about 35% COD removal was achieved in the anaerobic lagoon and 26 % removal in the facultative lagoon, both of which fall below the expected BOD₅ % removals.²³ This poor efficiency serves as the impetus for making system improvements.

²² Gotovac, 1999.

²³ Metcalf & Eddy, 1991.

7.2 Bench-scale Analysis

In January 1999, a group of MIT students conducted a field study of the CEAGESP facility. Their goals were to propose an upgraded design for the system to reduce the overload to the facility. Two alternatives were studied:

1. Construct a CEPT tank as a pre-treatment for the lagoon
2. Add coagulant chemicals directly at the inlet to the first lagoon

Jar tests were carried out from January 15-17 on the raw influent wastewater to predict the efficiency of a proposed CEPT design. Also looked at was the optimization of chemicals and their dosages.

7.3 Chemicals

The main chemical coagulants tested at Tatui were $\text{Fe}_2(\text{SO}_4)_3$ and FeCl_3 of various manufacturers in Brazil. Also, several aluminum salts were tested as requested by SABESP. Initial testing of aluminum salts showed poor removals, therefore no further analysis was taken. The coagulants tested at Tatui are shown in Table 7-1.

Table 7-1 Metal Salts Tested in Tatui

Chemical	Manufacturer	% Solids
FeCl_3	NHEEL – BR	38
FeCl_3	Eaglebrook Schereville, IN	40
FeCl_3	Liex	40
$\text{Fe}_2(\text{SO}_4)_3$	Sanchelor Sao Paulo, BR	40
$\text{Fe}_2(\text{SO}_4)_3$	Kemwater – BR	43

Lime was not considered for several reasons. First, lime generates a large amount of sludge and second, it has a tendency to form particles with high settling velocities. This formation can lead to clogging of the inlet pipes that direct the flow to the CEPT lagoons and basins.

The recycling of CEPT sludge as a coagulant was also considered. Several plants exist in France that engage in this practice. It is an attractive option due to the reduction in sludge output and cost.

Several polymers were tested to improve the settling of solids. Initial testing showed that anionic polymers performed better than non-ionic and cationic polymers; therefore, jar tests were only run with anionic polymers, listed in Table 7-2.

Table 7-2 Polymers Tested in Tatui

Manufacturer	Number	Form	M.W.	Charge
GAC	13	Dry	High	Low
GAC	15	Dry	High	High
GAC	17	Dry	Medium	Medium
GAC	19	Dry	Very High	High

Due to time and other supply constraints, only metal salts and polymers were tested, but no combinations.

7.4 Results

The three ferric chlorides ran very well in Tatui, as shown in Table 7-3.

Table 7-3 Jar Test Results of Ferric Chlorides in Tatui

Manuf.	COD % Removal	TSS % Removal	Optimal Dosage (mg/L)	Floc Size	Relative Cost
NHEEL – BR	57-68	84-96	40-50	Large	Inexpensive
Liex – BR	62-71	76-82	40-50	Small	Inexpensive
Eaglebrook Schereville, IN	60-72	92-96	40-50	Largest	Most expensive

Both NHEEL and Liex are attractive options because they are inexpensive and easily attainable in Brazil. NHEEL was chosen as the optimal coagulant over Liex and Eaglebrook because it achieved higher COD and TSS removals with an overall lower cost. Results from these series of jar tests are summarized in Figures 7-2 and 7-3.

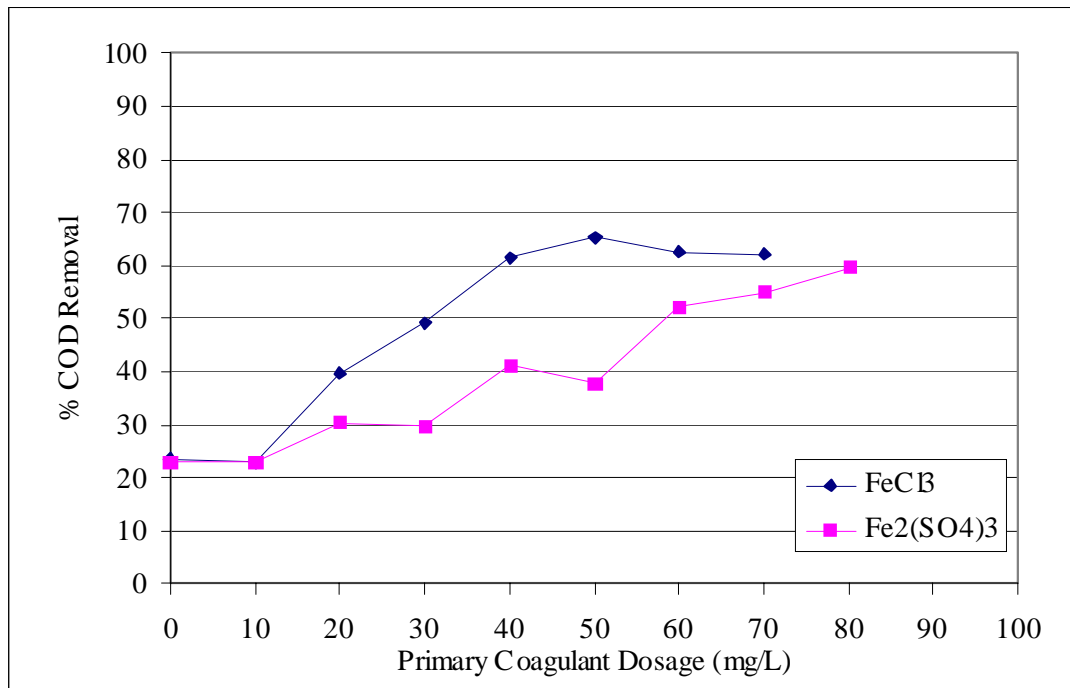


Figure 7-2 Primary Coagulant COD Removal Performance without Polymer in Tatui

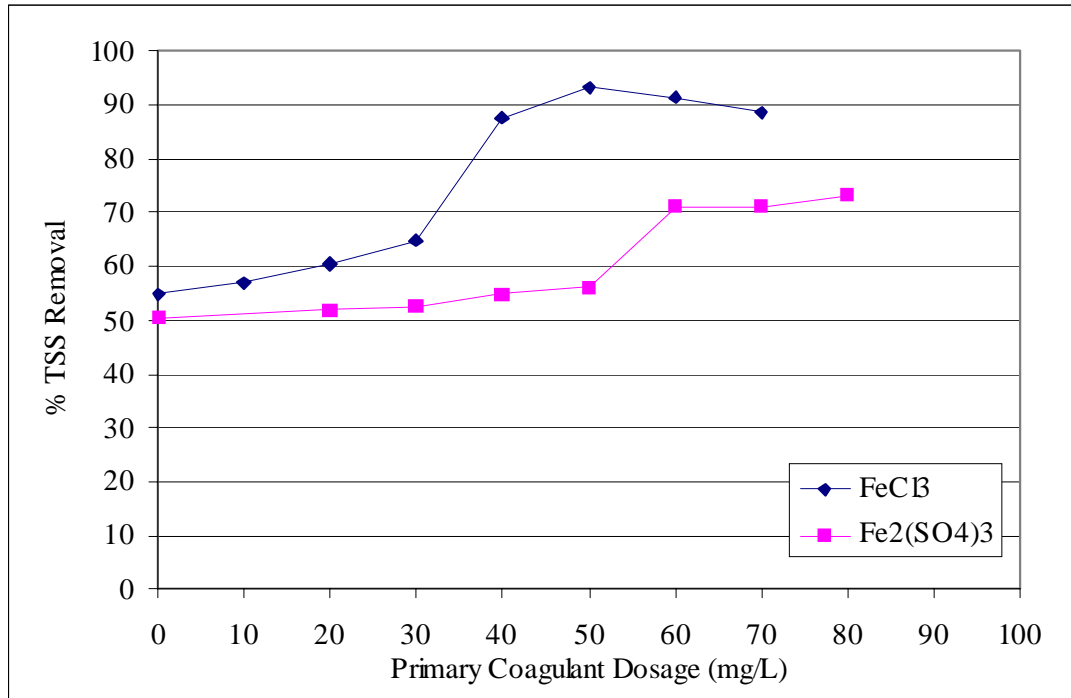


Figure 7-3 Primary Coagulant TSS Removal Performance without Polymer in Tatui

Next, a comparison was made between the optimal NHEEL FeCl₃ and the two ferric sulfates tested, Sanchelor and Kemwater. Table 7-4 shows the results from this comparison.

Table 7-4 Jar Test Results of Ferric Sulfates in Tatui

Manufacturer	COD % removal	TSS % removal	Optimal Dosage (mg/L)	Floc Formation
Sanchelor	38-67	64-94	40-60	
Kemwater	40	48	60	Poor

Kemwater performed the poorest of all coagulants tested. It yielded both poor floc formation and poor clarity of the supernatant. In spite of similarities in type and cost, Sanchelor Fe₂(SO₄)₃ performed better than Kemwater Fe₂(SO₄)₃, but not up to par with FeCl₃. The use of Sanchelor would require a higher dosage to achieve the same removal

as FeCl_3 . Therefore, a larger storage tank and pump would be needed, costing more money. The reason for these poorer removals may be due to the SO_4^{2-} portion of the compound. Because of dissociation, $\text{Fe}_2(\text{SO}_4)_3$ will release three SO_4^{2-} ions into the wastewater, yielding the formation of odorous H_2S .

Jar tests in Tatui also investigated the use of recycled sludge for improved settling. Sludge was collected on various occasions and tested under different conditions and different mixing regimes, as shown in Table 7-5.

Table 7-5 Mixing Regime for Chemical Sludge Recycle Jar Tests in Tatui

Step	Mixing Time (minutes)	Mixing Speed (rpm)
Rapid mixing	0.25	100
Sludge addition with slow mixing	2.5	30
Settling	5	0

This test with NHEEL-generated sludge displayed poor COD and TSS percent removals. A maximum of 27 % COD removal and 72 % TSS removal was achieved with a dosage of 60 mg/L. These mediocre removals can be attributed to the mixing regime. The slow mixing speed of 30 rpm was still turbulent enough to cause the flocs to break, yielding poor performance. To remedy this situation, more jar tests were run using a combination of both NHEEL and NHEEL-generated sludge. The mixing regime was altered, as shown in Table 7-6, to reduce the chance of floc breakup.

Table 7-6. Altered Mixing Regime for Chemical Sludge Recycle Jar Tests in Tatui

Step	Mixing Time (minutes)	Mixing Speed (rpm)
Rapid mixing	0.25	100
Coagulant addition with rapid mixing	0.5	100
Rapid mixing	2.5	70
Medium mixing	2.5	30
Sludge addition with slow mixing	2.5	15
Settling	5	0

These jar tests yielded better because of the addition of NHEEL to enhance coagulation and resolved the problem of floc break-up. Despite the appearance of better results, the jar tests did not reflect any better removals than before. From these jar tests, it was concluded that the recycling of chemical sludge would not be advantageous for CEAGESP.

Of the anionic polymers tested, GAC #17, of medium charge density and medium molecular weight, produced the best overall removals. GAC #13 has a low charge density of 10 % and a high molecular weight of 6 million Daltons. It performed the worst of the four polymers tested. GAC #19 with a high charge density of 40 % and a very high molecular weight of 8 million Daltons also performed poorly in comparison to GAC #15 and GAC #17. GAC #15 was similar to GAC #19 because of its high charge density of 40 % and high molecular weight of 6 million Daltons. It performed well, dramatically increasing the floc size and, therefore, decreasing the settling times. Overall, GAC #17 with a medium charge density of 20 % and a medium molecular weight of 4 million Daltons produced the best results and was chosen as the optimal polymer.

7.5 Conclusion

The MIT group did not have the opportunity to conduct comparison tests between Sanchelor and NHEEL with GAC #17 to determine the optimum coagulant-polymer combination and dosages. The group decided that a metal salt and polymer system would be too complex and expensive for Tatui. Therefore, it was their professional decision to propose a design for CEAGESP, which included the sole use of a NHEEL FeCl_3 and no polymer, based on the jar test results.

Chapter 8 - Review of Riviera WWTP

8.1 Background

Riviera de Sao Lourenço is a resort community along the Atlantic Coast located in the state of Sao Paulo. This planned community was designed and built by the Sobloco Construction company with the idea of maintaining the public's health and a pristine environment. Therefore, the city includes a modern municipal wastewater treatment system, as shown in Figure 8-1.

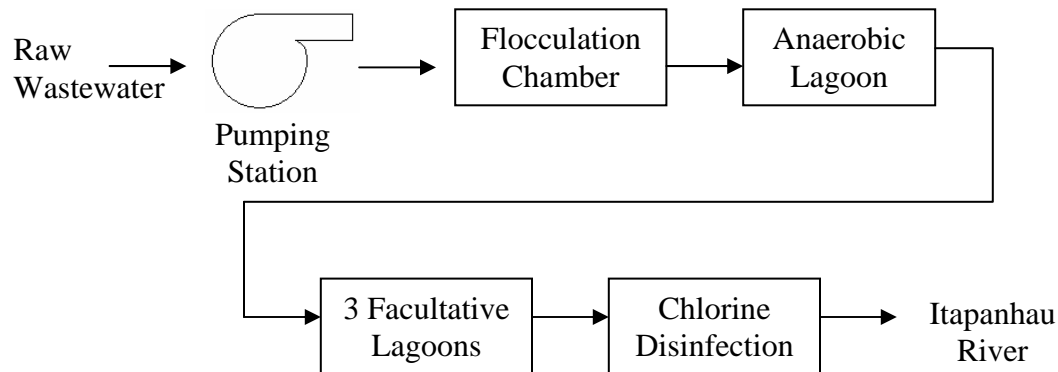


Figure 8-1 General Schematic of the Riviera Plant Prior to CEPT Upgrade

The main problem with the wastewater system is that during their summer season of December – February, Riviera experiences a large influx in population causing a major burden on their system. The current average daily flow of wastewater to the system is 23 L/s with a high of about 93 L/s during the summer season. A similar increase can be seen in the BOD loading with 300 kg/day during the off-season and up to 1,200 kg/day during the peak season. CEPT has been selected as an appropriate pre-treatment for improvement of the existing lagoon system. This upgrade is shown in Figure 8-2.

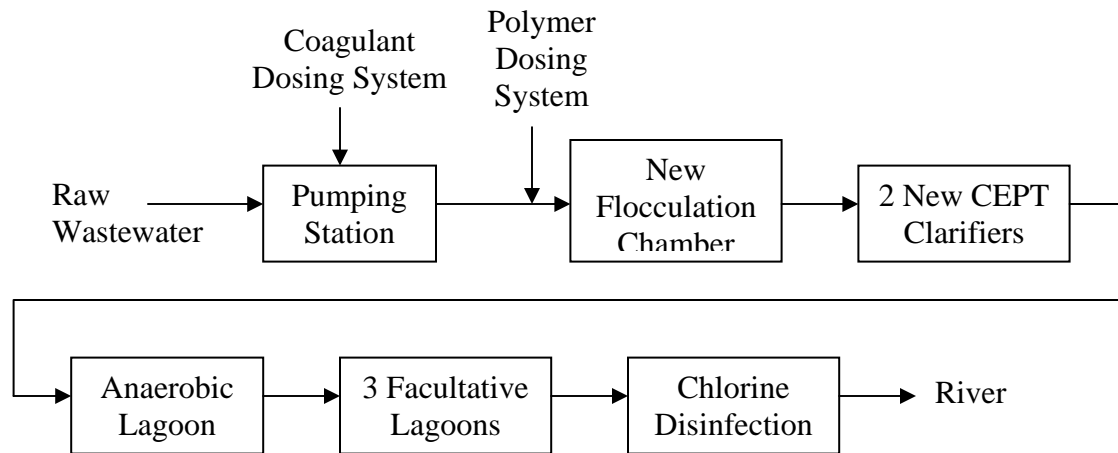


Figure 8-2 General Schematic of Riviera Plant After CEPT Upgrade

The treatment plant personnel record raw water characteristics, daily for COD and weekly for BOD. The average COD level is 415 mg/L and the average BOD level is 183 mg/L. TSS is not typically measured at Riviera, although some TSS measurements were recorded during the three-week period of the January 2000 MIT field study. The average raw water TSS concentration recorded during the bench-scale analysis was 206 mg/L. A full-scale pilot plant was constructed to work in January 2000. Unfortunately, during the visit, the system only ran for about 20 hours due to the sludge scraper failure. Figures 8-3 and 8-4 show the setup of the full-scale pilot plant.



Figure 8-3 Chemical Dosing System and Ultrasonic Flow Meter at Riviera



Figure 8-4 Flocculation and CEPT Tanks and Lagoon at Riviera

8.2 Parameters

Despite this full-scale test mishap, a group from MIT conducted several studies including a bench-scale study from January 6-20, 2000. Samples of wastewater from the nearby pumping station, prior to chemical dosing, were used for testing. During these two weeks, various parameters were looked at:

- Different coagulants, as shown in Table 8-1;
- Different anionic polymers, as shown in Table 8-2;
- Different combinations of coagulants and polymers;
- Different dosages: 0-100 mg/L of coagulant and 0-05 mg/L of polymer;
- Settling times.

Table 8-1 Metal Salts Tested in Riviera

Chemical	Manufacturer	Form	% Solids	Specific Gravity
Fe ₂ (SO ₄) ₃	Kemwater	Liquid	42 %	1.6
FeCl ₃	Varenes	Liquid	39.6 %	1.434
Fe ₂ (SO ₄) ₃	Eaglebrook	Liquid	8.2 %	11.64
FeCl ₃	Eaglebrook	Liquid	26.1 %	1.274
Alum	GAC	Liquid	49.5 %	1.332

Table 8-2 Polymers Tested in Riviera

Manufacturer	Form	Number	M.W.	Charge
Nalco	Liquid	4686		
GAC	Dry	13	High	Low
GAC	Dry	14	High	Medium
GAC	Dry	15	High	High
GAC	Dry	16	Medium	Low
GAC	Dry	17	Medium	Medium
GAC	Dry	18	Medium	High
GAC	Dry	19	Very high	High
Adesol	Liquid	W 301	High	High
Adesol	Liquid	W 302	High	Low

Jar tests were performed using the standard mixing regime outlined earlier.

8.3 Problems Encountered

These results were not as conclusive as the other bench-scale studies performed in Brazil. During the analysis, several problems were encountered, which may account for the variability in the data:

- ***High moisture interference***

Due to the summertime conditions in Brazil, the relative humidity in the laboratory greatly fluctuated. Usually, the humidity was within the range of 60-80%. This high moisture content may have caused discrepancies in TSS analysis.

- ***Blending of samples***

For homogeneity, all of the supernatant samples were blended prior to TSS or COD analysis. Blending was accomplished by use of a hand-held blender for 5-10 seconds.

This blending may have caused a contamination of previously blended samples by the constant reuse. Also, the blending of the samples caused a disruption in floc, which may have interfered in both the TSS and COD analysis. Nonetheless, blending of the samples prior to analysis is the procedure recommended by Standard Methods and a better practice needs to be developed for future analyses.

- ***Incorrect amount of COD digestion solution for 1/6-1/8 samples***

The first three days of testing and sampling served as a trial period where errors in the system were both discovered and fixed. The laboratory technicians incorrectly filled the sample vials with excess COD digestion solution. This oversight caused erroneous COD data during that time period.

- ***Spectrophotometer problems***

During the first week of sampling, a problem in the precision of spectrophotometer readings was discovered. Luckily, three spectrophotometers were on hand: Hach DR/2000, Hach DR/4000, and Hach DR/890. Standards were made to check the reliability of each of the instruments before continuing their usage.

Also, the MIT group had hoped to conduct several additional jar tests, which would have involved the following:

- Potable water sludge from the nearby plant as a coagulant aid to the metal salt
- Recycled CEPT sludge
- Addition of 3-5% sea water with the metal salt

Due to the lack of time, none of these extra jar tests were run but these areas would be of great interest in future studies.

8.4 Results and Conclusion

Aside from these problems, some conclusions can be made from the data collected. First, the use of a metal salt and polymer combination was found to be necessary at Riviera. When a coagulant was dosed alone, without a polymer, there was no visible floc formation and poor removal efficiencies. Second, FeCl_3 achieved better flocs and better TSS and COD removal percentages than $\text{Fe}_2(\text{SO}_4)_3$, as shown in Figures 8-5 and 8-6. Third, after an extensive study of $\text{Fe}_2(\text{SO}_4)_3$ and varying polymer types and dosages, there is improved flocculation and better floc formation with both a higher charge and higher molecular weight polymer. Results of these jar tests can be seen in Appendix B.

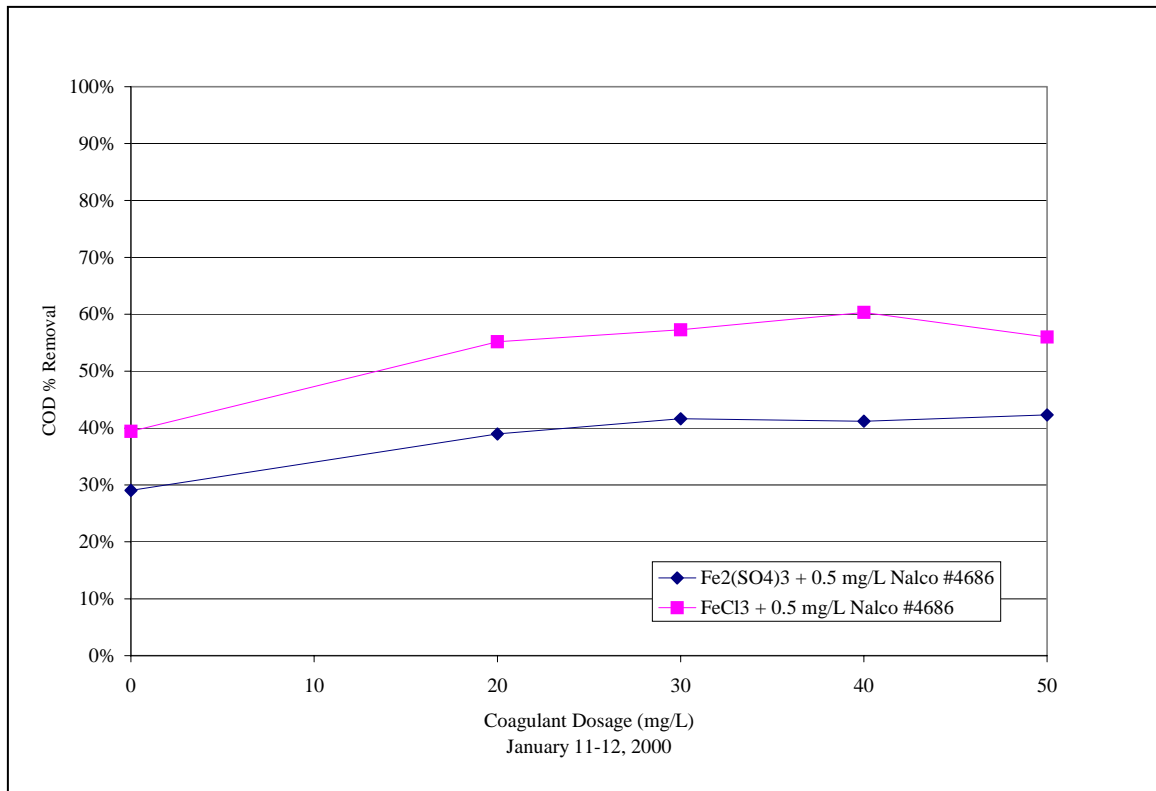


Figure 8-5 Graphical Comparison of COD % Removal for $\text{Fe}_2(\text{SO}_4)_3$ vs. FeCl_3

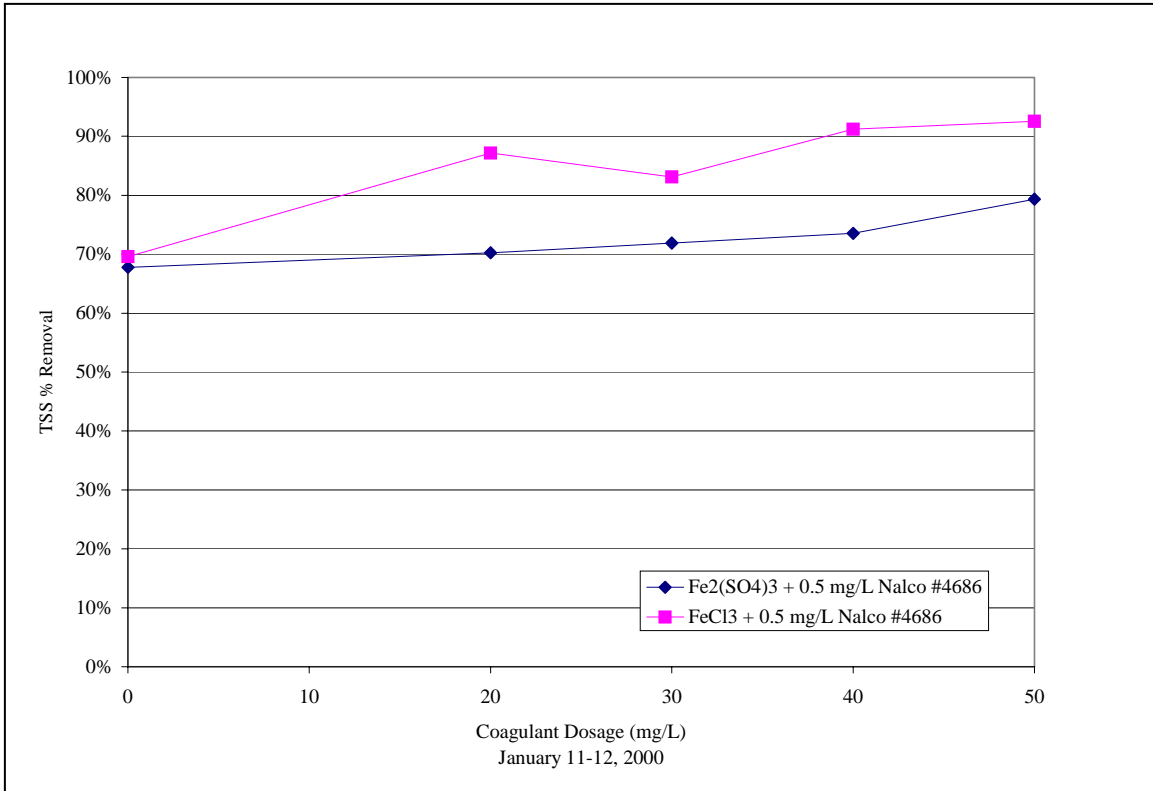


Figure 8-6 Graphical Comparison of TSS % Removal for Fe₂(SO₄)₃ vs. FeCl₃

Chapter 9 - Overall Comparison of Brazil Plants

9.1 Raw Water Characteristics

When trying to compare the bench-scale analyses of the five Brazil plants, it is important to first look at the general characteristics of the existing treatment plant. Each plant has a different layout, and is based on different design parameters. Each plant has a different flow rate and different raw influent characteristics, all of which contribute to the overall efficiency of the system. Table 9-1 shows the different inflow rates to each of the plants and Figure 9-1 shows the corresponding raw water characteristics.

Table 9-1 Average Inflow Rates of Brazil WWTPs

Plant	Flow Rate (L/s)
Pinheiros	1300
Ipiranga	25
ETIG	525
Tatui	161
Riviera	23

Note that Riviera's flow rate is the lowest. The numbers presented in Table 9-1 are average inflow rates, therefore, they do not reflect Riviera's higher flow rate of 93 L/s in its peak season.

Again, there is a large variability between plants for BOD, COD, and TSS. There is data missing for both Tatui and Riviera because at the Tatui plant, COD is not recorded and at the Riviera plant, TSS is not recorded. The average values for BOD, COD, and TSS, during the respective testing periods are shown in Table 9-2.

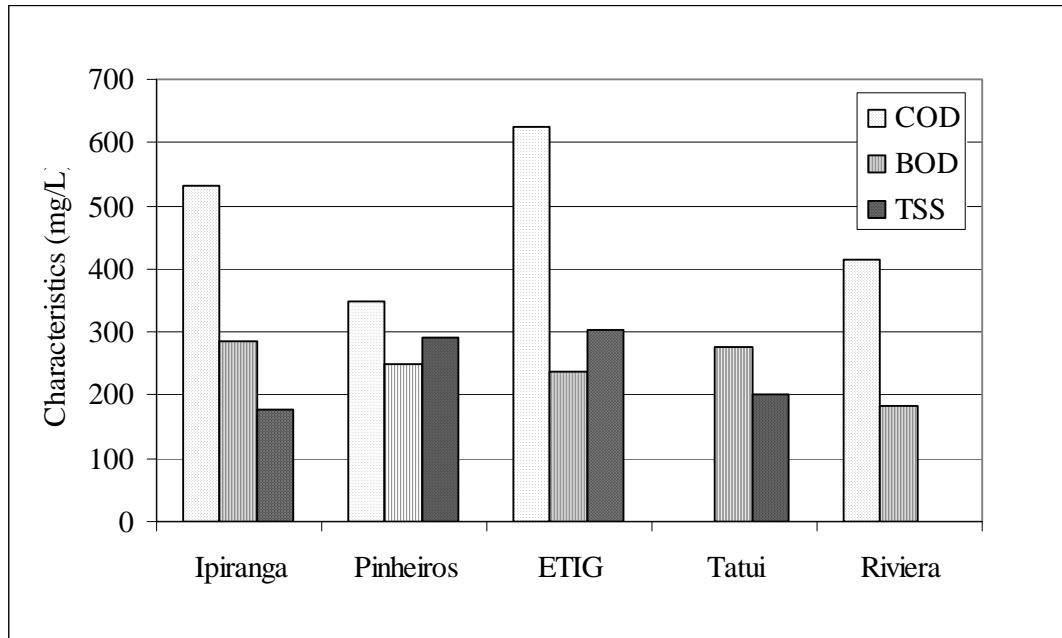


Figure 9-1 Raw Water Characteristics of Brazil WWTPs

Table 9-2 Average BOD, COD, and TSS Values of Brazil WWTPs

Plant	BOD (mg/L)	COD (mg/L)	TSS (mg/L)
Pinheiros	162	211	378
Ipiranga	178	286	531
ETIG	262	235	486
Tatui	200	276	--
Riviera	--	183	415

9.2 Optimal Chemical Combinations

Despite these differences in plant characteristics, a comparison of the optimal coagulants and polymers for each of the plants finds more similarities than differences. Table 9-3 shows the optimal combination and dosages of chemicals for each of the five plants.

Table 9-3 Optimal Chemical Combinations and Dosages for Brazil WWTPs

Plant	Optimal Coagulant	Optimal Coagulant Dose (mg/L)	Optimal Polymer	Optimal Polymer Dose (mg/L)	% COD Removal	% TSS Removal
Pinheiros	FeClSO ₄	25	Nalco #2540	0.3	60 %	90 %
Ipiranga	FeCl ₃	50	GAC #60540	0.5	55 %	--
ETIG	FeCl ₃	50	GAC #15	0.5	87 %	97 %
Tatui	FeCl ₃	50	None	--	65 %	93 %
Riviera	FeCl ₃	40	Nalco #4686	0.5	60 %	92 %

Almost every plant found FeCl₃ to be the optimal primary coagulant, producing the highest removals of COD and TSS. Pinheiros was one of a few plants to test FeClSO₄, and there, the next best coagulant was found to be FeCl₃. Notice that there is a high variability in COD removal percentages, whereas TSS removal percentages consistently range from 90-97 %. Figures 9-2 and 9-3 show how FeCl₃ fared at various plants in Brazil. Only ETIG, Ipiranga, and Tatui are displayed in these two figures because no jar tests were run without polymer at Pinheiros and the jar tests from Riviera yielded poor results.

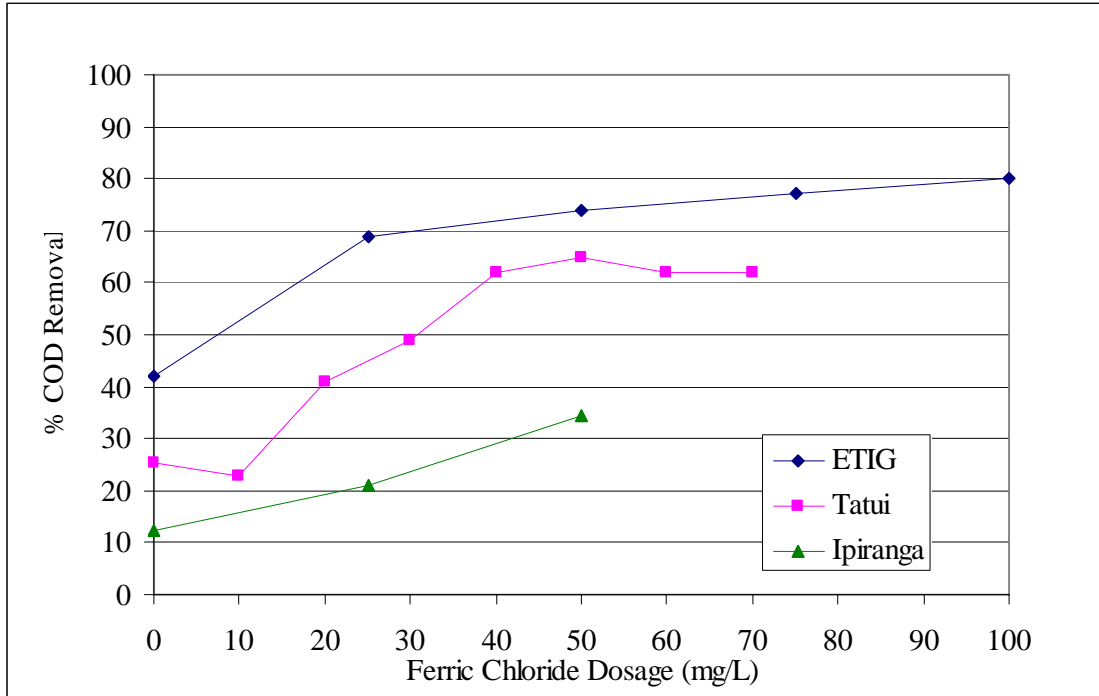


Figure 9-2 COD Removal Percentages with Only FeCl₃

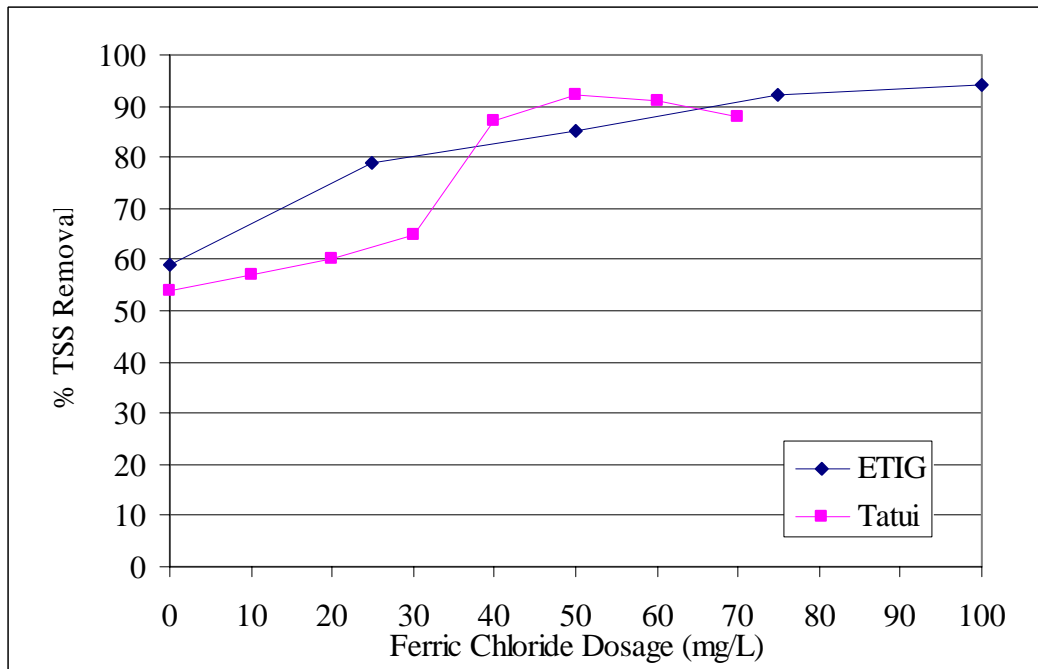


Figure 9-3 TSS Removal Percentages with Only FeCl₃

9.3 Polymer Usage

All but one plant chose to use a polymer to enhance flocculation. These polymers were all anionic and of high molecular weight and high charge. With the addition of anionic polymer, both COD and TSS percent removals improved and lowered dosages of coagulant were used.

9.4 Conclusion

Overall, FeCl_3 acts as the best coagulant for wastewater treatment plants in Brazil as shown by jar test results from each of the five plants tested. The use of only a coagulant and no polymer produces better removal efficiencies than no chemicals at all, and even better removal efficiencies are achieved with the addition of an anionic polymer of high molecular weight and high charge.

Chapter 10 - Conclusion

The performance of bench-scale analyses in the form of jar tests is both beneficial and economical in determining if the implementation of CEPT, for an upgrade or for a design of a new system, is suitable. In developing countries like Brazil, jar tests as a precursor to pilot or full plant tests or implementation are even more advantageous because they save money, space, time, and better optimize the chemical types and dosages for a full-scale test.

There are numerous coagulants and flocculants known to work well for CEPT, but optimizing the chemical type, dose, and possible combinations of these chemicals for a plant is the main goal of jar tests. The cost and availability of the chemicals should also be taken under consideration. A mixing scheme of rapid, medium, and slow mixing followed by settling that closely simulates the full-scale plant is used. A total of three sets of analyses are performed: visual, COD, and TSS tests. The removal percentages of COD and TSS especially, but also depending on objectives of PO_4^{3-} prove the latter two prove the efficiency of chemical usage and can be compared to no chemical usage to determine if there is improvement. Jar tests can also be used to prove the significance or insignificance of polymer usage.

All five plants function under different operating conditions, different inflow rates, and service different municipalities and industries. Therefore, each of their raw water characteristics is very different from one another. But, a similarity does lie in the optimal chemical regime. Jar tests found FeCl_3 to yield the highest or next to highest removal

percentages of COD and TSS. A dosage of 50 mg/L FeCl_3 with no polymer achieved approximately 65-85 % COD removal and 90-100 % TSS removal. Only at Pinheiros, jar tests showed FeClSO_4 to yield slightly higher removals than FeCl_3 . Another agreement was the necessity of polymer in their dosing scheme. Only at Tatui was no polymer recommended. The optimal polymers for each of the other four plants were all anionic and of high molecular weight and charge. An optimal dosage of 50 mg/L metal salt with 0.5 mg/L anionic polymer yielded, on average, a 20 % increase in COD removal from that achieved without the addition of polymer.

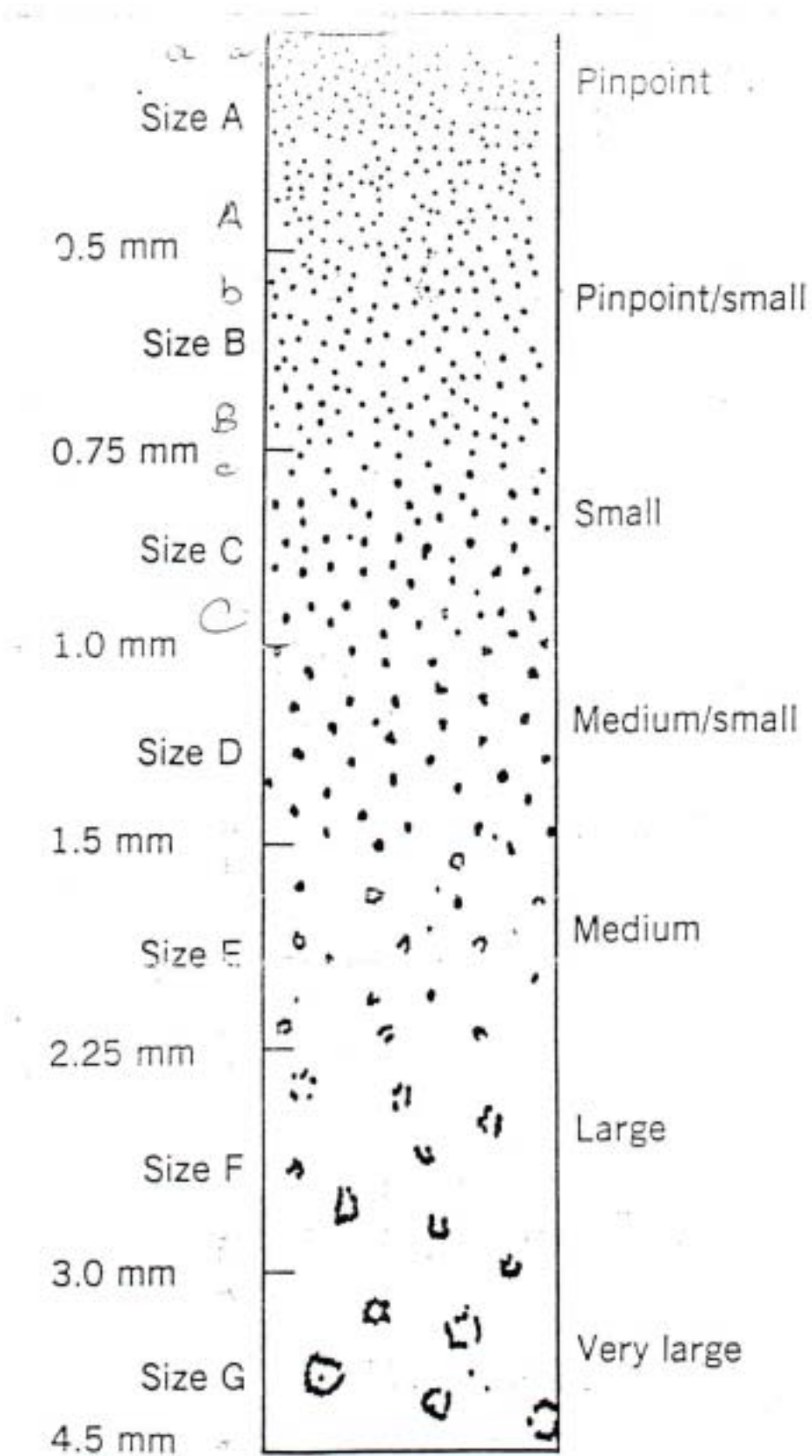
Bench-scale tests provide a good idea of what may work on a larger scale. However, there are always complications when applying these to full-scale, which no one expects. Nonetheless, bench-scale studies in Brazil, and anywhere else in the world, are an important and economical first step in the optimization process of CEPT and its implementation in wastewater treatment plants.

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Appendix A - Visual Test Sheet



Appendix B - Polymer Jar Test Results in Riviera

