IMPROVEMENT OF ALUM & PACL COAGULANTS FOR THE TREATMENT OF PULP AND PAPER MILL WASTEWATER

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ABSTRACT

The wastewater arising from pulp and paper mills is highly polluted and has to be treated before discharged into rivers. Coagulation –flocculation process is a widely used water and wastewater treatment method. This method is used in pulp and paper mills to remove the suspended solids in the wastewater produced from the production processes. This study is aimed to provide a clear understanding of the effects of pH, settling time, and coagulant dosage towards the removal of pollutants in the wastewater. Also, it is aimed to improve the removal of pollutants by adding Fenugreek mucilage. The experiments were done using jar tests. Settling times were set to 30, 60, 90, and 120 minutes. The pH values were adjusted to 3, 6, and 9. Aluminium Sulphate (Alum), Polyaluminium Chloride (PACl) and Fenugreek mucilage dosages were manipulated at the values 50, 100, 500, 1000, 1500, and 2000 mg/L. The treated wastewater samples were tested for BOD, turbidity, and COD. The results showed the optimum pH for the research was 6, the optimum settling time was 30 minutes, and the optimum dosages of alum, PACl, and Fenugreek mucilage were 1000, 500, and 500 mg/L respectively. Through the research, it was deduced that Fenugreek mucilage improves pollutant removal when used with alum or PACl.

ABSTRAK

Air sisa yang dihasilkan dari kilang pemprosesan kertas mengandungi bahan pencemar yang tinggi dan mesti dirawat sebelum dilepaskan ke sungai. Coagulasi dan flokulasi adalah salah satu kaedah yang luas digunakan untuk merawat air sisa dari industri tersebut. Kaedah rawatan ini digunakan untuk mengurangkan jumlah bahan pencemar di dalam air sisa yang dihasilkan melalui proses pembuatan dalam kilang kertas. Kajian ini bertujuan untuk memberi gambaran yang lebih jelas mengenai kesan pH, masa pemendapan, dan dos kimia terhadap pemisahan bahan pencemar dalam air sisa tersebut. Selain itu, kajian ini adalah bertujuan untuk mengenalpasti keberkesanan bendalir halba terhadap pemisahan bahan pencemar dalam air sisa tersebut. Eksperimen dijalankan dengan menggunakan 'jar test'. Masa pemendapan telah ditentusah dengan nilai 30, 60, 90, dan 120 minit, dan nilai pH 3, 6, dan 9. Dos kimia yang dimanipulasi adalah 50, 100, 500, 1000, 1500, dan 2000 mg/L. Ujian BOD, kekeruhan, dan COD dijalankan terhadap air yang dirawat, dan keberkesanannya ditentukan. Menurut keputusan yang diperolehi, pH yang paling sesuai adalah 6, masa pemendapan adalah 30 minit, dan dos paling sesuai alum, PACl dan bendalir halba adalah 1000, 500, dan 500 mg/L masing-masing. Melalui kajian ini, adalah disimpulkan bahawa bendalir halba dapat mengurangkan jumlah bahan pencemar dalam air sisa yang dikaji.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

1.1 Background Study

In the field of water and waste water treatment, coagulation and flocculation process have been receiving great attention from the past century. Due to the vast widespread applications in industry, many researches and experiments have been done to study to enhance these processes. Flocculant aids which increases the rate of coagulation and flocculation is being studied on deeply. Coagulation process was found in the year 1881, and coagulation-flocculation process as a whole efficient method was introduced in 1972 [5,6].

1.1.1 Pulp and paper mill and its wastewater

Pulp and paper are manufactured from raw materials containing cellulose fibers, generally wood, recycled paper, and agricultural residues. In developing countries, about 60% of cellulose fibers originate from nonwood raw materials such as bagasse (sugar cane fibers), cereal straw, bamboo, reeds, esparto grass, jute, flax, and sisal. The main steps in pulp and paper manufacturing are raw material preparation, such as wood debarking and chip making; pulp manufacturing; pulp bleaching; paper manufacturing; and fiber recycling. Pulp mills and paper mills may exist separately or as integrated operations.

Manufactured pulp is used as a source of cellulose for fiber manufacture and for conversion into paper or cardboard. The finished pulp may be dried for shipment (market pulp) or may be used to manufacture paper on site (in an “integrated” mill). Paper and cardboard are

made from pulp by deposition of fibers and fillers from a fluid suspension onto a moving forming device that also removes water from the pulp. The water remaining in the wet web is removed by pressing and then by drying, on a series of hollow-heated cylinders (for example, calender rolls). Chemical additives are added to impart specific properties to paper, and pigments may be added for colour [11]. The significant environmental impacts of the manufacture of pulp and paper result from the pulping and bleaching processes. In some processes, sulfur compounds and nitrogen oxides are emitted to the air, and chlorinated and organic compounds, nutrients, and metals are discharged to the wastewaters. The wastewater of this industry has significant effects to the environment, and is aesthetically unpleasant. The BOD/COD ratios are high. The total dissolved and suspended solids are not according to environmental standards as well [8].

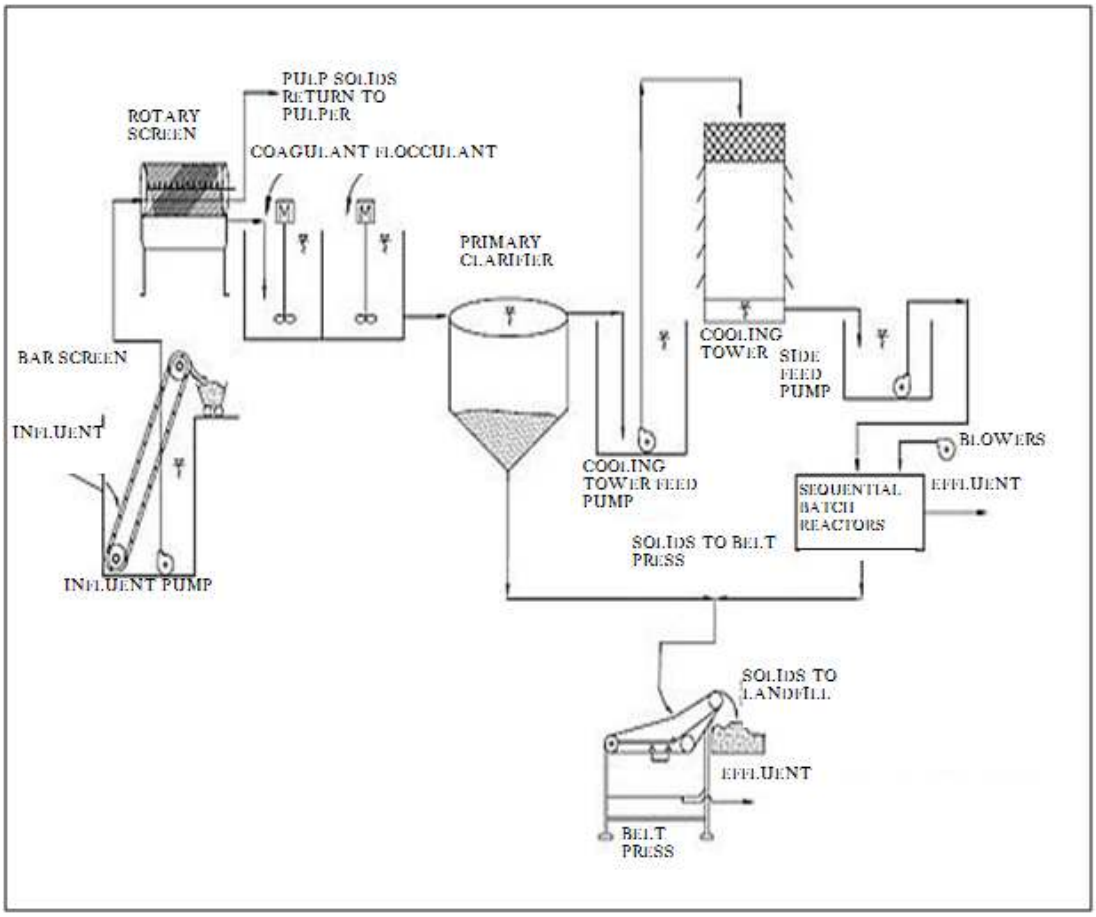

Figure 1.1: Traditional paper mill waste water treatment process [9].

1.1.2 Pulp and paper mill wastewater treatment

The effluent wastewater from pulp and paper mills contains some toxic materials. The amount of dissolved and suspended solids is also in large quantities. Hence, to provide effluent water which meets environmental quality standards, this wastewater has to be treated first before being discharged to surface water. There are three main categories of wastewater treatment widely used in paper mills. They are physical methods, chemical methods, and biological methods of wastewater treatment.

Pulp and paper mill wastewater contains a wide variety of solids. Effective removal of these solids may require a combination of unit operations such as screening. Operations to eliminate large pollutants in size, along with flow measurement are included in this process. Normally physical treatment methods in pulp and paper mill industry must be preceeded by chemical coagulation. Physical methods normally use naturally occurring forces, such as gravity forces to operate. Physical methods of wastewater treatment include sedimentation, flotation, and adsorption, as well as the use of physical barriers such as bar racks, screens, deep bed filters, and membranes.

Chemical treatment processes are the most important unit operations in wastewater treatment in pulp and paper mill industry. Chemical methods of wastewater treatment take advantage of two types of properties, which are the chemical characteristics of the pollutants and the chemical characteristics of the products of reaction between pollutants and treatment chemicals. An example of chemical treatment used in paper mills are oxidation by hydrogen peroxide. Hydrogen peroxide (H_2O_2) is a strong oxidant and its application in the treatment of various inorganic and organic pollutants is well established [10]. Hydrogen peroxide is normally used to remove chlorides in paper mill wastewater. Production of hydroxyl radicals attack the chlorine based pollutants in the wastewater and is oxidized.

Biological methods are important in removing organic pollutants in wastewater. Biological treatment of industrial wastewater is a process whereby organic substances are used as food by bacteria and other microorganisms. Biological treatment is divided into two main

categories, which are aerobic and anaerobic. An example of biological method used in paper mill industry is trickling filters.

1.1.2.1 Coagulation

Coagulation is the neutralization of the charges on colloidal matter. When choosing coagulants, several aspects need to be studied. Particle size, particle distribution, and particle-solvent interaction are some of the main aspects. Coagulants here mean insoluble particulate material and chemicals added to natural waters to enhance coagulation process [2]. Coagulation involves rapid mixing of the wastewater for a short period of time.

1.1.2.2 Mechanism of coagulation

The basic idea of coagulation is to reduce the surface charges of the particles. It employs a cationic metal as a coagulant agent that usually promotes water hydrolysis and the formation of hydrophobic hydroxide compounds with different charges, depending on the pH of the solution. It may also lead to the formation of polymeric compounds. The coagulant agents interact with colloidal materials by either charge neutralization or adsorption, leading to coagulation–flocculation. This process is usually followed by sedimentation [1]. Coagulation effectiveness and cost depend on coagulant type and concentration, solution pH, ionic strength, as well as both concentration and nature of the organic residues in effluent [3,4]. Figure 1.5 shows the mechanism of floc formation during coagulation.

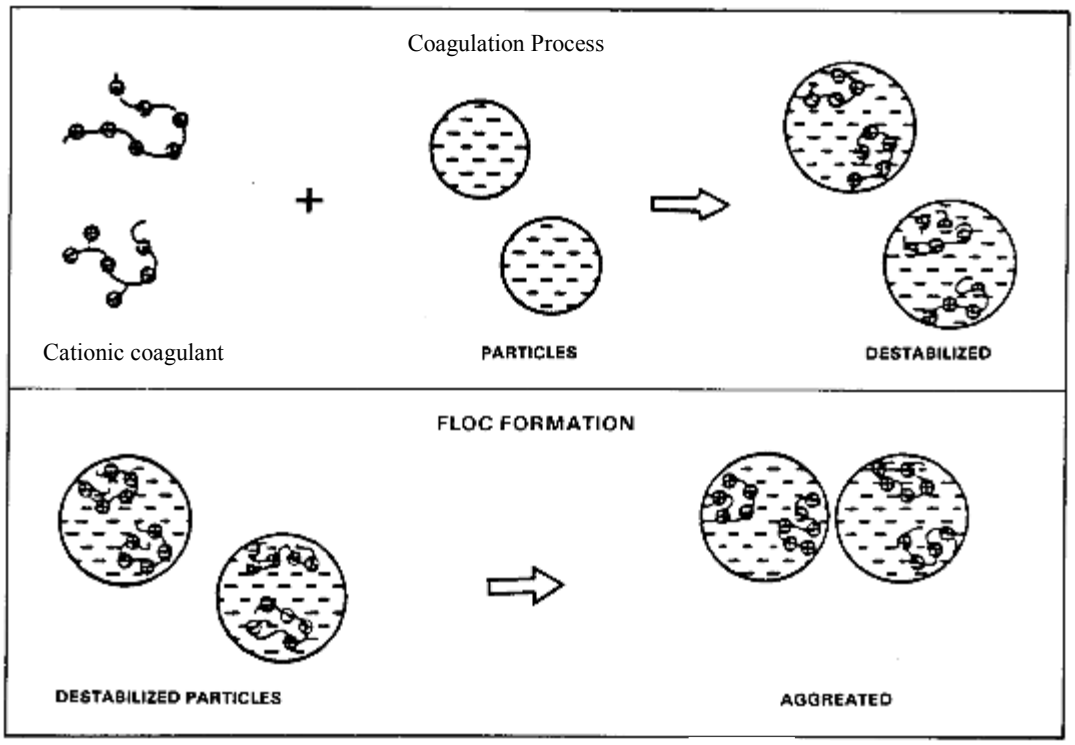

Figure 1.2: Floc formation process [7].

1.1.2.3 Flocculation

Flocculation relates to the aggregation of destabilized particles, where the surface charge of the particle has been reduced. Further addition of coagulants would form precipitation products, which are called flocs. This would be easier for the suspended solids to be removed by settling and sedimentation. The few criteria which have to be studied are (1) mixing intensity and destabilization method, (2) type and concentration of coagulant and flocculant aids, (3) selection of separation process, (4) mixing intensity and time for flocculation.

1.2 Problem Statement

The cellulose and paper industry employs large amounts of water [8], and produce equally large amounts of wastewater, which constitutes one of the major sources of aquatic pollution. The lignin and its derivatives contained in this residue may produce highly toxic and refractory compounds, some potentially mutagenic [9]. The largest volume of pollutants are produced in the cellulose pulp bleaching step, which generates several chlorinated compounds via chlorination, and others toxic organic compounds, including lignin-derived refractory ones. The wastewater from pulp and paper industry has high COD/BOD ratios, which is not suitable to be treated by biological treatment methods alone. Hence, coagulation and flocculation is applied to reduce this ratio to provide a more suitable COD/BOD ratio for biological treatment. This research gives a solution in removing lignin and other pollutants in pulp and paper mill waste water. The advantage of using natural flocculant aid is that it is biodegradable. Unlike conventional synthetic flocculant aid which need to be removed from the treated waste water effluent by further processing.

1.3 Objectives

The method proposed in this research decreases the amount of pollutants in pulp and paper mill wastewater. The importance of this study is to investigate the relationship between coagulant and flocculant aid dosage, pH, settling time, and the effectiveness of pollutant removal in the waste water.

The aim of this research is to investigate the improvement of Aluminium Sulphate (Alum) and Polyaluminium Chloride (PACl) performance using natural organic material in removing particles in pulp and paper waste water. The natural flocculant aid chosen for this research is Fenugreek mucilage.

1.4 Scope of Study

The experiments are done using jar test. Four groups of experiments are conducted as follows:

1. Treatment by alum only
2. Treatment by PACl only
3. Treatment by alum with Fenugreek mucilage
4. Treatment by PACl with Fenugreek mucilage

The pH value used in the experiment is within the range 3<pH<9. The dosages of alum, PACl and Fenugreek mucilage are manipulated using the values of 50, 100, 500, 1000, 1500, and 2000 mg/L. The efficiency in pollutant removal is determined by turbidity, BOD and COD percentage removal. Turbidity of the treated waste water is determined by turbiditimeter. The more wavelength of light passing through the sample means the removal of pollutant is more efficient. BOD is measured by means of dissolved oxygen. COD is measured using spectrophotometer.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Pulp and paper mill wastewater has high biochemical oxygen demand (BOD and chemical oxygen demand (COD), which affects the environment if discharged without treatment. The wastewater generated also contains toxic materials like lignin, chlorinated organics, and toxic fibres. There are a few categories of pulp and paper mill wastewater treatment, such as physicochemical treatment, biological treatment and integrated treatment processes. A new approach in the wastewater treatment should be developed to face more stringent environmental regulations of the effluent wastewater. Coagulation and flocculation is a chemical treatment method to remove suspended solids especially those formed by colloidal matters. This method is trial and error, since there are no exact parameters yet to be found. Coagulation and flocculation involves charge neutralization, floc formation and settling. This treatment method is affected by parameters such as pH, chemical aid dosage, temperature, and mixing intensity.

2.2 Treatment methods

Recently, a review done by Pokhrel and Viraraghavan [33] classified the treatment methods of pulp and paper mill wastewater into three major categories, physicochemical treatment, biological treatment and integrated treatment processes. All of the reported methods have their respective advantages, weaknesses and limitations.

ferric sulphate or polyaluminum chloride led to a significant increase in the settling speed. In the earlier work done by Stephenson and Duff [28], they found that the removal of total carbon, colour and turbidity of up to 88, 90 and 98%, respectively, were observed in the treatment of mechanical pulping effluent using ferric chloride, ferrous sulphate, aluminum chloride and aluminum sulphate. Aluminum and iron salts are widely used as coagulants in water and wastewater treatment and in some other applications.

Their mode of action is generally explained in terms of two distinct mechanisms: charge neutralization of negatively charged colloids by cationic hydrolysis products and incorporation of impurities in an amorphous hydroxide precipitate so-called sweep flocculation [29]. The relative importance of these mechanisms depends on factors such as pH and coagulant dosage. Natural polymers like chitosan and the coagulants like alum and lime for the removal of lignin (TOC and colour) from black liquor has been investigated by many research workers. Poly aluminium chloride has been used by many investigators in the treatment of oil–water emulsions, however, the use of PACl for the removal of soluble and colloidal organics from pulp and paper mill effluents has been scarcely studied [30]. PACl, which is an inorganic polymer, has been found to exhibit improved performance over other coagulants in terms of removal of colour, turbidity, and so on. PACl treatment requires smaller dosage leading to generation of smaller sludge volume than that obtained with other coagulants.

Studies also indicted that temperature may affect particle/floc formation more so for coagulants due to pH shifts with temperature. It may be concluded that there are some inherent differences between these coagulants in their hydrolysis, nucleation, growth, and aggregation in the ultimate formation of various hydrolyzed species. These important differences in speciation and structural composition may cause these coagulants to interact differently with various fractions of organic matter, which still needs to be carefully evaluated. To evaluate the effectiveness of these alternative coagulants both in particulate (i.e., measured as turbidity) and organic (i.e., measured as dissolved organic carbon (DOC)) removal, several approaches were undertaken; first by carefully characterizing these metal coagulants to determine their potential effectiveness, and then confirming their anticipated performance through jar testing with a representative source water.

2.4 Flocculation Theory & Mechanism

The advantage of polymeric flocculants is their ability to produce large, dense, compact and stronger flocs with good settling characteristic compared to those obtained by coagulation. It can also reduce the sludge volume. Furthermore, the polymer performance is less dependent on pH. There are no residual or metal ions added such as Al^{3+} and Fe^{3+}, and the alkalinity is maintained. The flocculation performance of flocculants primarily lies on the type of flocculant and its molecular weight, ionic nature and content, on the suspension content in the wastewater and the type of wastewater [15]. Flocculation also depends on mixing intensity. Too high mixing speed might cause the agglomerated particles to shear, which is sometime irreversible. Technological advancements in polymer chemistry have improved the flocculant technology to provide polyelectrolytes with greater purification efficiency. However, flocculation optimization practices in industry are still reliant, to a very large extent, performed on a trial and error basis due to the highly complex nature of the flocculation process and the large variety of polyelectrolyte available. A better understanding on how polymer molecular weight and charge density distribution affect the flocculation performance may lead to improved flocculant manufacturing processes and better choice of flocculants for the users in specific industrial application [15]. Figure 2.2 gives a better visual understanding of flocculation process.

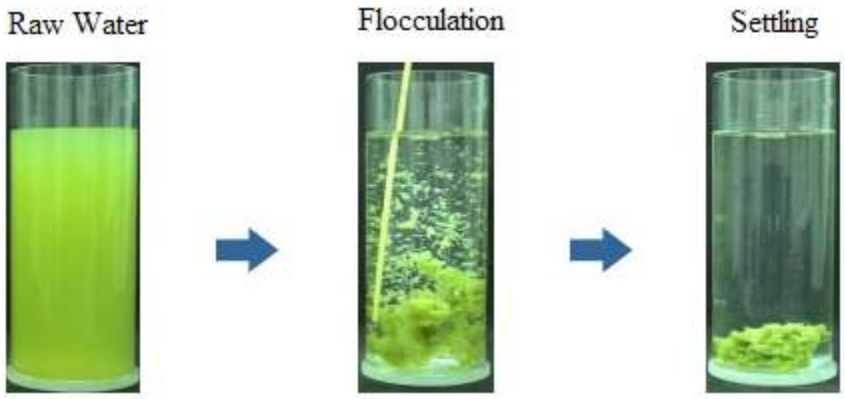

Figure 2.2: Flocculation

2.5 Coagulant & Flocculant Aid

Conventional coagulants are basically salts of a strong acid (e.g., HCl or H_2SO_4) and a weak base ($Al(OH)_3$ or $Fe(OH)_3$); thus they are a mixture of a cation (from a base) and an anion (from an acid) [31]. However, alternative coagulants are specially prepared and may include additional anions as additives (i.e., anions such as sulfate) and may have differences in mechanisms by which conventional and alternative coagulants may interact in particulate and organic removal. However, the removal mechanisms of alternative coagulants are still to this date not clearly understood. Past studies have clearly shown some of the advantages and disadvantages of the alternative coagulants. Past research compared the hydrolytic reaction of alum with laboratory prepared PACl and noted that they form different solid phases. PACl tends to exist as a cluster of small spheres (<25mm) and/or chain-like structures, whereas alum flocs are usually fluffy, porous structures (ranging from 25 to 100mm). Due to their structure, polymeric species cause lesser turbidity in suspension than alum. Prehydrolyzed aluminum polymers have also been found to be less sensitive to temperature variation than alum.

Recently, the use of synthetic polyelectrolytes as flocculants for suspended solids removal in wastewater treatment has grown rapidly. Acrylamide is a crystalline and relatively stable monomer which is soluble in water and many organic solvents. Acrylamide is a polyfunctional molecule that contains a vinylic carbon–carbon double bond and an amide group. The electron deficient double bond of acrylamide is susceptible to a wide range of chemical reactions including nucleophilic additions, Diels–Alder and free radical reactions. The flocculations of the suspended particles occur via the double bond. Polyacrylamide (PAM) is a commonly used polymeric flocculant because it is possible to synthesize polyacrylamides (PAMs) with various functionalities (positive, neutral or negative charge) which can be used to produce a good settling performance at relatively low cost [15].

Another flocculant aid used is snail shell. Snail shell is being proposed as a low-cost material to remediate basic dye, malachite green (MG), bearing water in the present studies. Mollusks make up the phylumMollusca. Gastropoda (snails and slugs), a class under the phylum Mollusca, are asymmetrical and have only one shell or, as in slugs, are shell-less. Snails belong

to the class Gastropoda and the African land snail is classified as *Achatina achatina*. The snail shell has got the same basic construction as other Mollusk shells. It consists of three layers. The Hypostracum, is the innermost layer, followed by the Ostracum, as the basically shell-building layer and the Periostracum as the outermost layer. Basically, the snail shell consists of mainly $CaCO_3$, as well as various organic compounds. The Hypostracum is a form of Aragonite, a type of $CaCO_3$. The Ostracum is built by several layers of prism-shaped $CaCO_3$ crystals with embedded proteid molecules. The Periostracum, the outermost shell layer, is not made of $CaCO_3$, but of an organic material called Conchin, amixture of organic compounds, mostly of proteids. Conchin not onlymakes the outer shell layer, but also embedded between the $CaCO_3$ crystals of deeper layers. The use of calcium-richmaterials in thewater industry has been studied and reported by different researchers. Traditionally, limestone is used as a coagulant aid (an adsorbent-weighting agent) in the treatment of low-turbid water. In addition, it provides alkalinity to its adsorbent-weighting action.

The use of limestone (calcite) and other calcium-rich materials (e.g. sludge from fullers earth production, blast furnace slag, fly ash etc.) has been reported as coagulant aid in the treatments of petroleum refining wastewater and phosphate removal from aqua med

CHAPTER 3

METHODOLOGY

3.1 Introduction

In this chapter, a detailed experiment outline will be presented which includes materials to be used, description of experimental procedure and analysis methods.

This research aim is to investigate the improvement of alum and PACl performance using natural Fenugreek mucilage in removing pollutants in pulp and paper mill waste water. The method to achieve this aim is by chemical wastewater treatment method, which is coagulation-flocculation method. Bench scale experiments were done by using jar tests. The percent removal of turbidity, BOD and COD were analyzed.

Four sets of experiments were run:

1. Treatment by alum only
2. Treatment by PACl only
3. Treatment by alum with Fenugreek mucilage
4. Treatment by PACl with Fenugreek mucilage