ASSESSMENT OF BENTONITE CLAY PRETREATMENT OF PHARMACEUTICAL INDUSTRY WASTEWATER IN KENYA

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Assessment of Bentonite Clay Pretreatment of Pharmaceutical Industry Wastewater in Kenya

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DECLARATION

This thesis is my original work and has not been presented for a degree in any other university

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DEDICATION

Dedicated to my dear husband Emmanuel Muhuza and beloved children Kayleen and Kayson Muhuza.

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To Jehovah God be the glory and honor.

ABSTRACT

Serious negative effects on aquatic ecosystems and human health can result when raw or partially treated pharmaceutical effluent is disposed into the environment. Pharmaceutically Active Compounds (PhACs) can go through biological wastewater treatment plants unaltered and find their way into water bodies. Pharmaceutical effluent also contains a substantial amount of suspended solids and COD which need to be reduced to acceptable levels before disposal. This study characterized pharmaceutical effluent in Kenya and investigated the applicability of bentonite as a coagulant aid in its pretreatment. Wastewater samples had a COD range of 418.70- 195.63 mg/l, TOC 117.50- 99.47 mg/l, BOD 263.23- 85.23 mg/l, TSS 210.37- 74.33 mg/l and pH of 7.08-6.18. PhACs found in the samples included ciprofloxacin, sulfamethoxazole, ibuprofen, metronidazole and trimethoprim. Optimized coagulation using ferric sulfate at a dosage of 20 mg/l achieved maximum removal for TSS, turbidity, COD and TOC of 81.78%, 91.67%, 20.20% and 33.39% respectively and 83.88%, 91.70%, 25.25% and 41.63% with PAC at a dosage of 15 mg/l. Both coagulants achieved very little removal of PhACs. To investigate the effectiveness of bentonite, optimization of its dosage was carried out. Its optimum dosage was found to be 10 g/l, and this amount was mixed in the sample wastewater for 1 hour before coagulation was done. The maximum TSS, turbidity, COD and TOC removal by ferric sulfate together with bentonite was 96.82%, 98.81%, 30.30% and 54.20% respectively, and 96.96%, 98.21%, 48.48%, and 63.03% for PAC with bentonite. The use of bentonite reduced the optimal dosage of both ferric sulfate and PAC to 10 mg/l. This treatment resulted in complete removal of ciprofloxacin and ibuprofen. Maximum reduction of sulphamethoxazole, metronidazole and trimethoprim was 27.85%, 37.30% and 52 42% respectively. This study showed that pharmaceutical factories in Kenya fall under the formulation, drug mixing and preparation category, which produce effluent of low strength. Each factory had different treatment procedures but all included coagulation/ flocculation, using either aluminium or iron salts. Other methods of treatment employed in these factories included activated carbon filtration, ozonation, dissolved air floatation and activated sludge. The existing treatment systems needed improvement due to challenges of high chemical usage, poor floc formation and settling and high operational and maintenance costs. Bentonite pretreatment proved to be effective as it produced better quality effluent with improved removal of PhACs and reduced amount of coagulants used in comparison to optimized coagulation without bentonite. It is recommended that, with the addition of bentonite dosing equipment, pharmaceutical factories in Kenya should incorporate bentonite pretreatment into coagulation process to improve its efficiency. About 240 kilograms of bentonite would be required to treat 24,000 liters of pharmaceutical wastewater. During application, optimization of bentonite dosage should be carefully done to avoid excesses that could cause problems with coagulant dosing and formation of large volumes of sludge.

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$Al_2 O_3$	Aluminium Oxide
API	Active Pharmaceutical Ingredients
BOD	Biochemical Oxygen Demand
Ca O	Calcium Oxide
COD	Chemical Oxygen Demand
COMESA	Common Market for Eastern and Southern Africa
DO	Dissolved Oxygen
EPZA	Export Processing Zones Authority
FAS	Ferrous Ammonium Sulfate
$Fe_2 (SO_4)_3$	Ferric Sulfate/ Iron (III) Sulfate
$Fe_2 O_3$	Ferric Oxide/ Iron (III) Oxide
HPLC	High Performance Liquid Chromatography
IC	Inorganic Carbon
INECE	International Network for Environmental Compliance and Enforcement

K_2 O	Potassium Oxide
KAM	Kenya Association of Manufacturers
LOI	Loss on Ignition
Mg O	Magnesium oxide
Na_2 O	Sodium Oxide
NTU	Nephelometric Turbidity Units
PAC	Poly Aluminium Chloride
PhACs	Pharmaceutically Active Compounds
Si O_2	Silicon dioxide
TC	Total Carbon
TDSP	Total Dissolved Solid Particles
TOC	Total Organic Carbon
TS	Total Solids
TSS	Total Suspended Solids
WWTP	Wastewater Treatment Plants

CHAPTER ONE

INTRODUCTION

1.1 Background

The pharmaceutical industry manufactures biological products, medicinal drugs, botanical products, as well as other commodities. Pharmaceutical drugs are developed with the intention of having a beneficial biological effect on the organism to which they are administered. However, many such drugs pass into the environment by one route or another as the parent compound or as active metabolites, and are referred to as pharmaceutically active compounds (PhACs). The presence of PhACs in the environment is a growing concern because of their toxicity, bio-accumulating tendency, and threat to human life and the environment (Ibigbami et al., 2016).

PhACs can enter into the environment in numerous scattered points, but the main sources of contamination are pharmaceutical production plants and hospital effluents (Deegan et al., 2011). The growth of pharmaceutical plants accelerated by the enormous demands of life-saving products and manufacture of new products has exacerbated the wastewater treatment problems resulting from this industry (Gupta et al., 2006). Kenya is currently the largest producer of pharmaceutical products in the Common Market for Eastern and Southern Africa (COMESA) region, supplying about 50 per cent of the region's market.

Out of the region's estimated 50 recognized pharmaceutical manufacturers, 30 are based in Kenya (EPZA, 2005). This has resulted in an increase in the volume and variety of industrial wastewater produced and consequently the negative effects in the eco-system and human life.

Many pharmaceutical substances are, by nature, biologically active and hydrophilic so as to allow the human body to take them up easily. They are also persistent in order to avoid degradation before they have a curing effect (Radjenovic et al., 2007). Coupled with the relatively high throughput of convectional waste water treatment plants (WWTP) the levels of many pharmaceutically active compounds (PhACs) in the wastewater are barely reduced through the WWTP and are detected in the effluents. The presence of PhACs in surface, drinking, and wastewaters is well documented in literature (Otieno, 2011; Radjenovic et al., 2007). Although present at low concentrations in the environment, pharmaceuticals can have adverse effects on humans and aquatic organisms. These effects are chronic rather than acutely toxic, and depend on exposure (bioavailability), susceptibility to the compound in question, and the degradability of the compound (Deegan et al., 2011; Radjenovic et al., 2007). To ensure compliance with discharge requirements, upgrading of existing wastewater-treatment facilities and implementation of new technologies is envisaged as necessary next step in improvement of wastewater treatment. Therefore, there is an urgent need to develop efficient and economical methods of handling these wastewaters (Shi, 2009).

In addition to the problems associated with PhACs, another factor to consider in the pre-treatment of pharmaceutical effluent is the substantial amounts of organic pollutants trapped in suspended solids. High amounts of organic pollutants in suspended wastewater solids result in undesirable environmental effects due to microbial growth, deposition of sludge blanket, possible toxicity and turbidity in receiving bodies (Armenante, 2006; Kavitha et al., 2012). Usually, pharmaceutical wastewaters have a high COD concentration and relatively low BOD_5, meaning that the wastewater has a poor biodegradability. Reduction of these organic pollutants to permissible concentrations is necessary for the protection of ground and surface water, and human and environmental safety (Shi, 2009). Coagulation treatment of wastewater has been used to reduce the loading in terms of total suspended solids (TSS) and turbidity, though it has a low capability for reducing COD. This method involves the addition of a chemical reagent to wastewater to enmesh or combine with non-settleable colloidal solids and slow-settling suspended solids to produce a rapid-settling floc (Ean, 2008).

Presently, many techniques such as ozonation, Fenton process, membrane systems and activated carbon adsorption are being used for the removal of pharmaceutical compounds from wastewater (Elmolla & Chaudhuri, 2008; Merih, 2003; Soderberg, 2008). Adsorption technique is an economical process especially using low cost adsorbents. Many investigators have evaluated natural clays as low-cost adsorbents due to their adsorption properties. These have been found to be effective in the adsorption of acidic

dyes from textile industry effluent, arsenic from contaminated wastewater and the adsorption of organic matter from municipal wastewater, among others (Sanghi & Bhattacharya, 2003; Zahra et al., 2009; Zohra et al., 2014).

Bentonite a natural clay which can be used in treatment of wastewater. It is readily present in different parts of the country including Athi river basin, Timau, Meru and Namanga, though these local deposits have not been fully exploited (Mutisya and Maranga, 2012; Mutisya et al., 2013). It is composed of inorganic minerals and other proprietary compounds which adsorb a wide variety of contaminants, and encapsulates suspended solids, many organic compounds and toxicants. Bentonite when mixed in water disperses into colloidal particles providing a large surface area per unit weight of clay, but unlike other materials which possess a large surface area, the surface of bentonite has oxygen atoms which promote reactivity with other compounds and some organic materials (Clem & Doehler, 1963). Thus, bentonite particles can act as adsorbents for organic pollutants as well as add weight to slow settling flocs during the process of chemical coagulation.

This study therefore investigated the use of bentonite clay as a coagulant aid in the pretreatment of pharmaceutical industry wastewater. The pre-treatment aimed at improving the removal of PhACs, COD, TOC, and suspended solids while at the same time aiding in floc formation, reduce settling time and chemical usage, thus the overall efficiency of the treatment process. The wastewater used in this study was obtained from

formulation, drug mixing and preparation plants in Kenya that produce tablets, capsules, syrups, ointments and powders. The choice of the category of pharmaceutical plants on which the study was based on was dictated by the fact that formulation and drug mixing plants are the dominant pharmaceutical plants in the country. This is because the country has minimal raw materials for pharmaceutical products and relies on imported sources. The industry imports over 95% of the raw materials (EPZA, 2005)

1.2 Kenya's Pharmaceutical Industry

Pharmaceutical companies in Kenya include local manufacturing companies, and large multi-national corporations, subsidiaries or joint ventures. Most are located within Nairobi and its environs. The products produced under this sector include medical equipment and medicinal drugs in form of tablets, syrups, capsules, and injectables among others. The country exports its pharmaceutical products to Tanzania, Uganda, DRC, Rwanda, Burundi, the Comoros, Ethiopia and Malawi among other destinations. The number of companies engaged in manufacturing and distribution of pharmaceutical products in Kenya continues to expand, driven by the government's effort to promote local and foreign investment in the sector (EPZA, 2005).

The bulk of locally manufactured preparations are non-sterile, over- the-counter products, such as antibiotics, analgesics, or bronchial spasm relaxants, and there is little variation of the type of products from one company to another (EPZA, 2005; UNIDO, 2010). Table

1.1 shows some of the leading pharmaceutical manufacturing companies in Kenya. These companies fall under the formulation, drug mixing and preparation plant category of pharmaceutical industries. They mainly use raw materials such as sugar, corn syrup, lactose, gelatin, calcium, talc, alcohol, glycerin and aspirin which result in substantial amounts of organic pollutants (Gupta et al., 2006).

Table 1.1: Leading pharmaceutical manufacturing companies in Kenya

Company name	Location
Alpha Medical Manufacturers	Nairobi
Aventis Pasteur SA East Africa	Nairobi
Bayer East Africa Limited	Nairobi
Beta Healthcare (Shelys Pharmaceuticals)	Nairobi
Cosmos Limited	Nairobi
Dawa Pharmaceuticals Limited	Nairobi
Didy Pharmaceutical	Nairobi
Diversey Lever	Nairobi
Eli-Lilly (Suisse) SA	Nairobi
Elys Chemical Industries Ltd	Nairobi
Glaxo SmithKline	Nairobi
High Chem East Africa Ltd	Nairobi
Ivee Aqua EPZ Limited	Athi River
Mac's Pharmaceutical Ltd	Nairobi
Manhar Brothers (Kenya) Ltd	Nairobi
Novartis Rhone Poulenic Ltd	Nairobi
Novelty Manufacturers Ltd	Nairobi
Pfizer Corp (Agency)	Nairobi
Pharmaceutical Manufacturing Co (K) Ltd	Nairobi
Pharmaceutical Products Limited	Nairobi
Phillips Pharmaceuticals Limited	Nairobi
Regal Pharmaceutical Ltd	Nairobi
Universal Pharmaceutical Limited	Nairobi

Source: EPZA, 2005

1.3 Problem statement

The steady growth of the pharmaceutical industry in Kenya has resulted in an increase in industrial discharges which poses a problem in waste management. There is increasing concern that PhACs in the environment, even in trace amounts will progressively have a negative impact on aquatic organisms and humans, especially when different pathogenic bacteria develop tolerance to anti-microbial drugs (Basnyat, 2010). A wide variety of these compounds have been detected in different water samples from rivers, groundwater and drinking water sources and studies have shown that these pollutants are toxic even at low concentrations (Deegan et al., 2011; Elmolla & Chaudhuri, 2008; Otieno, 2011). Convectional biological WWTPs are designed to remove carbon, nitrogen and phosphorous, however, PhACs often go through the normal treatment plant unaltered. A study conducted on a pharmaceutical plant in Kenya that used chemical coagulation followed by activated sludge process showed that the treated effluent quality was not always up to the required standard mainly because PhACs were toxic to the bacteria in the activated sludge. In addition to this, there was also a high residual concentration of the pharmaceuticals in the treated effluent (Suominen, 2013). Another study by *Otieno* (2011) revealed that Kenyan rivers are heavily contaminated by PhACs, with antibiotics being the most common class of pharmaceuticals detected. Thus there is need for proper pretreatment of pharmaceutical effluent to minimize contamination and ecosystem disruptions. Towards the removal of PhACs from the wastewater, a lot of the research

carried out has been based on advanced oxidation processes like ozonation (Deegan et al., 2011; Merih, 2003) and Fenton treatment (Elmolla & Chaudhuri, 2008; San et al., 2003), activated carbon treatment (Deegan et al., 2011), modified biological treatment systems (Soderberg, 2008; Zheng et al., 2010) and membrane treatment like ultra-filtration and nano-filtration (Deegan et al., 2011). The setup, operation and maintenance of such treatment methods are quite sophisticated and costly, and therefore less appropriate for application in Kenya, thus there is a need for more affordable technologies.

1.4 Objectives

1.4.1 General objective

To investigate the use of bentonite clay as a coagulant aid in the pre-treatment of pharmaceutical industry wastewater

1.4.2 Specific objectives

1. To investigate and evaluate the methods currently used for treating pharmaceutical wastewater in Kenya and their limitations.
2. To characterize the general and specific quality of pharmaceutical wastewater.
3. To optimize the coagulation/ flocculation processes in a typical pharmaceutical wastewater pretreatment.

4. To investigate the applicability of bentonite for pretreatment of typical pharmaceutical wastewater in Kenya.

1.5 Justification

The monitoring of PhACs released from pharmaceutical production plants is not routine and it has been estimated that half of the pharmaceutical effluent produced worldwide is released without any treatment. The other half will pose a challenge to successful treatment using biological systems due to their relatively high levels of organic pollutants trapped in suspended solids, and the insufficient removal of PhACs (Chelliapan & Golar, 2011; Deegan et al., 2011). The available alternative methods for removal of PhACs from pharmaceutical plant effluent such as ozonation, Fenton process and activated carbon adsorption, are not only expensive but some also require special equipment and maintenance. Due to its structural properties, chemical stability and high specific area, bentonite has the potential for providing an adsorption medium for PhACs present in pharmaceutical wastewater and at the same time act as a coagulant aid by adding density to slow settling flocs thus improving the removal of COD, TOC and TSS in the effluent. The need for coagulant aids is because the effective application of chemical coagulation is often hindered by factors such as poor floc formation and long settling time which result in poor quality of the treated effluent. In addition to this, there is a need to reduce the amounts of chemicals used as these result in an increase in operational costs. Inorganic

polymers may be used as coagulant aids, though their application in industries is limited due to the costs involved, thus the need for a more affordable option. An additional advantage of the use of bentonite in wastewater treatment is that it has been shown to improve the quality of the sludge produced (Bourliva et al., 2010). This application of bentonite will also encourage exploitation of the readily available deposits in the country, which according to a research by Nyang et al. (2013), on physical and chemical properties of locally available bentonite showed that there is no difference in these properties compared to bentonite from Wyoming, in the United States of America, which is one of the top producers of bentonite in the world.

1.6 Scope

There are five major categories of pharmaceutical plants, namely;

i. fermentation plants,
ii. synthesized organic chemicals plants,
iii. fermentation/synthesized organic chemicals plants,
iv. biological production plants,
v. drug mixing, formulation, and preparation plants.

These vary depending on the processes involved in the manufacturing of pharmaceutical products. This study was limited to the fifth category, that is drug mixing, formulation and preparation plants which mainly produce tablets, capsules, solutions, etc.

The geographical scope of the study covered Nairobi city. This however can be taken as a representative of the pharmaceutical industry in Kenya because according to the list of manufacturing companies in Kenya, from Kenya's pharmaceutical industry, 2005, all the factories are located in Nairobi apart from Ivee Aqua EPZ Limited, which is in Athi River (EPZA, 2005).

1.7 Limitations

Different pharmaceutical industries produce different products leading to wastewater with varying characteristics. Therefore, the wastewater used in this study may not accurately represent wastewater produced by different pharmaceutical plants. In addition to this, the fact that most pharmaceutical companies in the country are drug mixing and formulation plants limited this study to that category. Another limitation faced when conducting this study was the difficulty in collecting data and information from some factories due to restrictions in access.

CHAPTER TWO

LITERATURE REVIEW

The pharmaceutical industry has been flourishing over the years as the world‘s population grows and new diseases emerge. It employs various processes and a wide variety of raw materials to produce an array of final products. As a result, a number of waste streams with different characteristics and volume are generated, which vary with plant, time, and even season, in order to fulfill the demands of some specific drugs (Gupta et al., 2006). For this reason, it is difficult to describe a “typical” pharmaceutical effluent. This effluent can be said to be organic in nature due to the use of organic substances such as gelatin, corn syrup, glycerin and aspirin in the manufacturing process (Shi, 2009). Pharmaceutical effluent may contain compounds with complex molecules which have different physical-chemical and biological properties and functionalities, which are developed and used because of their specific biological activity (Otieno, 2011). This makes the effluent one of the major complex and toxic industrial wastes that can cause serious environmental problems especially to aquatic life.

2.1 Categories of pharmaceutical industries

Based on the processes involved in manufacturing, pharmaceutical industries can be subdivided into the following five major subcategories (Gupta et al., 2006):

i. Fermentation plants.

ii. Synthesized organic chemicals plants.

iii. Fermentation/synthesized organic chemicals plants (generally moderate to large plants).

iv. Biological production plants (production of vaccines–antitoxins).

v. Drug mixing, formulation, and preparation plants (tablets, capsules, solutions, etc.).

Each category has roughly similar waste disposal problems, and treatment methods. The first category which is fermentation plants employ microorganism to convert organic material into relatively simple substances. During their lifespan, these microorganisms build a wide range of different molecules required for viability, adaptation, defense etc. These molecules could potentially serve as a drug's Active Pharmaceutical Ingredient (API). This process is mostly used in the production of antibiotics and vitamins. In contrast, the second category, synthesized organic chemical plants produce medicinal chemicals by organic synthesis processes whereby organic chemicals are used as raw materials and one or more chemical reactions are followed by a series of purifying operations (INECE, 2015). The third category of pharmaceutical industries is made up of a combination of fermentation/synthesized organic chemicals plants. Biological

production plants, which is the fourth category, produce vaccines and antitoxins through extraction of organic chemicals from vegetative material or animal tissue. The fifth category comprises drug mixing, formulation, and preparation plants, which produce pharmaceutical preparations in a final form such as tablets, capsules, ointments, and so on (Gupta et al., 2006).

The process of pharmaceutical production can be divided into three main stages. The first stage is research and development. This stage is defined by bench-scale activities or operations aimed at discovering or enhancing reliable manufacturing processes of drugs and bulk manufacturing to produce large volumes of drug ingredients. The second stage is the bulk drug manufacturing which involves the production of active pharmaceutical ingredients through process such as fermentation, extraction and chemical synthesis. The third stage involves compounding and formulation of pharmaceutical products (Basnyat, 2010). These three stages are illustrated in Figure 2.1.

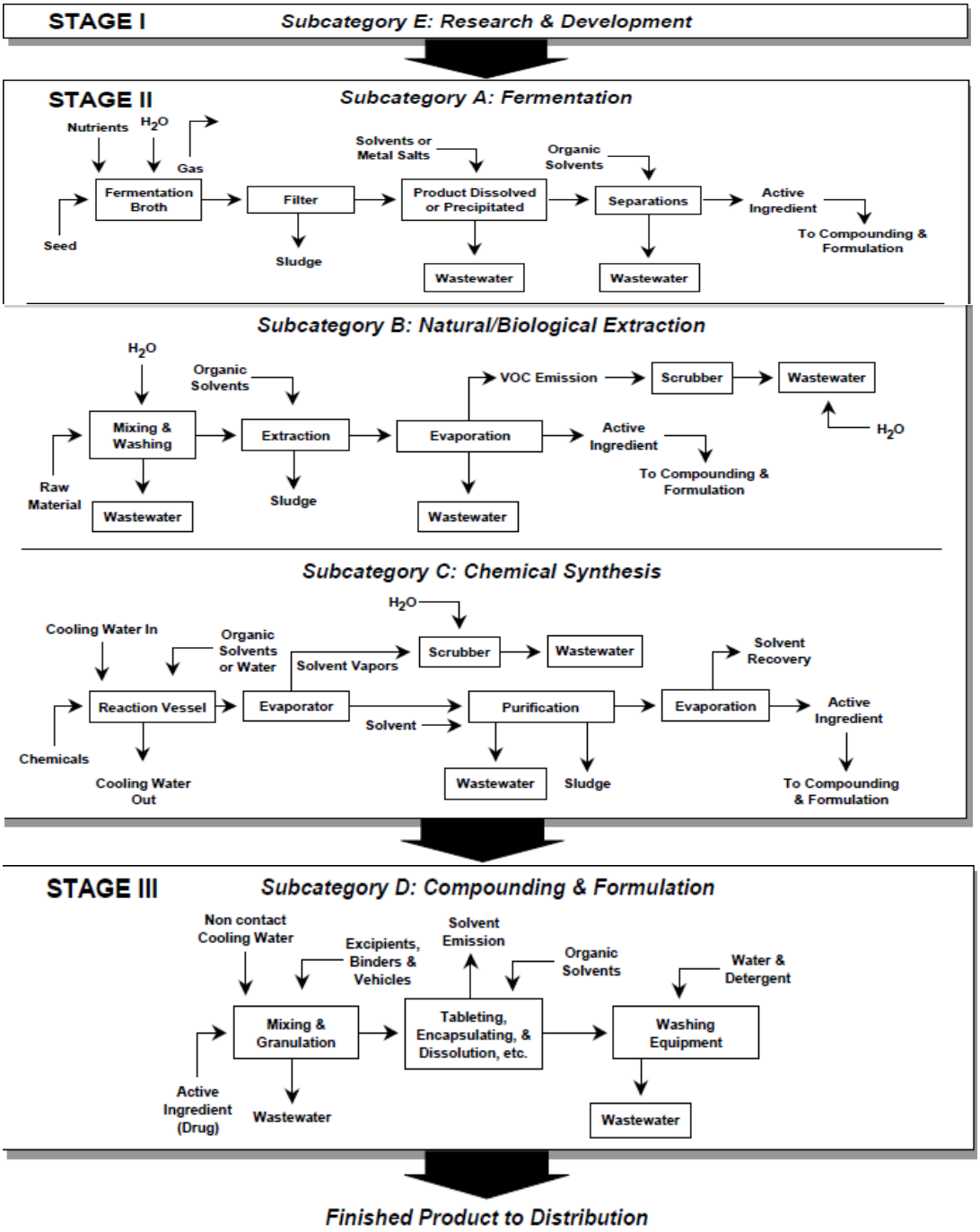


Figure 2.1: The three stages of pharmaceutical production (Basnyat, 2010)

2.2 Characteristics of pharmaceutical wastewater

In pharmaceutical industries wastewater is mainly generated through washing activities of equipment. Other sources of wastewater include spent liquors from fermentation processes (e.g. antibiotics and vitamins), chemical waste and condenser waste from evaporation. (Armenante, 2006; Kavitha et al., 2012). The wastewater produced from each of the five categories of pharmaceutical industries have roughly similar characteristics which are as a result of the similarity of products and production processes. Fermentation plants generally produce extremely strong and highly organic wastes with BOD values ranging from 5000 mg/l to 20,000mg/l. Synthetic organic chemical plants produce wastes which are strong, difficult to treat, and frequently inhibitory to biological systems, that have average TOC, COD and BOD values of 2109 mg/l, 4377 mg/l and 2221 mg/l respectively. The production of antitoxins and vaccines by biological plants generates wastewater containing very high BOD, COD and Total Solids (TS) with average values of 14,200 mg/l, 21,200 mg/l and 20,000 mg/l respectively. This wastewater is highly toxic, and has strong odor. The waste load from drug formulating plants is relatively low compared to the other categories. BOD and TSS values for drug formulating plants range between 750- 2000 mg/l and 200- 400 mg/l respectively (Gupta et al., 2006).

Generally, the main pollutants of concern in pharmaceutical wastewater streams from all categories of pharmaceutical plants are BOD, COD, TSS, ammonia and pH. Other chemical compounds may also be present including, but not limited to, solvents (e.g. methanol, ethanol, acetone, isopropanol, and methyl-ethyl ketone), organic acids (e.g. acetic acid, formic acid), organic halides, inorganic acids, ammonia, cyanide, toluene, and pharmaceutically active compounds (PhACs). These pollutants affect the biodegradability of this wastewater and some of them may be toxic to microorganisms.

Research on pharmaceutical effluent in Kenya has mainly focused on the removal of PhACs and their effect on biological treatment systems. Basnyat (2010) investigated the toxicity of these compounds on an activated sludge treatment system using the Oxygen Uptake Rate method and 11 of the compounds tested were found to be toxic to the system at various concentrations. A study by Suominen (2013) monitoring the effluent quality parameters of COD, BOD, TSS, total nitrogen and phosphorous found the particular factory under study had difficulty meeting the local requirement for discharge of TSS, BOD and PhACs (Suominen, 2013).

2.3 Pretreatment of pharmaceutical wastewater

Physical and chemical pretreatment methods are used with the intention of improving the quality of pharmaceutical wastewater to make it more suitable for disposal or biological treatment. These processes may include screening, sedimentation, floatation, air-

stripping, pH adjustment, flow equalization, coagulation/flocculation and filtration. The wastewater generated from pharmaceutical industry varies greatly in pH and are either alkaline or acidic. They thus require pH adjustment before biological treatment. The pH of the wastewater is adjusted by adding acid or alkali, depending on the specific requirements (Gupta et al., 2006). The flow of wastewater from a pharmaceutical factory can be intermittent and fluctuating depending on the production pattern (Chang & Chang, 2008). Due to this, equalization and extensive holding are important in order to avoid shock loading or under-loading which could result in operational problems especially in biological treatment plants. It has been shown that equalization tanks have been successful in controlling shock loading on further treatment units. The capacity and retention time of these tanks varies in each case and is dependent upon the variability in volume and composition of the wastewater (Gupta et al., 2006; Imran, 2005). Air stripping is a partial treatment used for the removal of volatile organics in pharmaceutical wastewater. A study by Gupta et al. (2006) reported a COD removal efficiency of up to 30-45% using air stripping.

2.3.1 Coagulation/ flocculation pretreatment

Coagulation/flocculation is a commonly used process in water and wastewater treatment. In this process, chemical coagulants are added to wastewater in order to destabilize the colloidal materials and cause the small particles to agglomerate into larger settleable

flocs. Besides metal salts, high molecular weight polymers or polyelectrolytes are also applied to produce a rapid settling floc (Ean, 2008; Ives & Jahn, 2001). Flocculation is the gentle agitation or slow stirring to aggregate the destabilized particles and form a rapid settling floc. The floc is subsequently removed by sedimentation or filtration.

Colloidal matter have particle size ranging from one millimicron to one micron (0.001 to 1 μm), while the suspended particles are generally larger than 1 μm. Colloidal particles are too small to be settled by gravity or filtered through common filtration media (Ravina & Moramarco, 1993). Colloids have an extremely large specific surface area with an electrostatic charge relative to the surrounding water. Since the attraction body forces between particles are considerably less than the repelling forces of the electrical charge, Bownian motion keeps the particles in suspension. The behavior of colloids is strongly influenced by their electrokinetic charge, which is important in maintaining dispersion and stability. The overall stability of a colloidal particle is controlled by double-layer repulsion forces and van der Waals forces of attraction (Ean, 2008).

The metal coagulants commonly used in water and wastewater treatment can be classified into two categories; those based on aluminium and those based on iron. The aluminium coagulants include aluminium sulfate, aluminium chloride, sodium aluminate and polyaluminium chloride. Iron coagulants include ferric sulfate, ferrous sulfate, ferric chloride and polyferric sulfate. The wide use of these coagulants is mainly due to their

effectiveness, relatively low cost, ease of handling and availability. However, their best performance and cost-effectiveness can only be achieved during the optimum conditions of coagulation and flocculation process. Hydrated lime (calcium hydroxide) and magnesium carbonate have also been used as coagulants. A significant advantage of iron salts over aluminium is the broader pH range for good coagulation. Thus, in the treatment of colored waters where color removal is best obtained at low pH, iron salts may be preferred as coagulants. Iron salts should also be considered for coagulation at high pH, since ferric hydroxide is highly insoluble in contrast to aluminium salts, which form soluble aluminate ions at high pH (Ives & Jahn, 2001). Sodium aluminate is mostly used for coagulation at medium pH. Synthetic organic poly-electrolytes have become available as coagulants but are generally not economical and are not readily available.

For good coagulation the optimal dose of coagulant should be fed into the water and quickly and properly mixed with it. It is important not to overdose the coagulants because a complete charge reversal and re-stabilization of colloid complex can occur. The optimal dose will vary depending upon the nature of the raw water and its overall composition. It is not possible to compute the optimal coagulant dose for a particular wastewater; therefore jar tests are carried out to determine the dosage empirically. Some of the drawbacks of conventional coagulation treatment of wastewater are high operating costs from the use of chemical substances, effectiveness which is highly dependent on pH, and complications in sludge disposal whereby its long term effects on human health are not

well understood. Therefore, attempts have been made to reduce these challenges by adding low cost natural substances to the coagulation process (Aygun & Yilmaz, 2010; Ugonabo et al., 2012b). These substances also promote the formation of denser, faster settling floc which in turn help to reduce treatment time, thus improving on the treatment efficiency.

Electro-coagulation is an alternative method to classic chemical coagulation. An advantage of this method is that it is capable of reducing the need for chemicals due to the fact that the electrodes provide the coagulant. In addition to this, it can reduce waste production from wastewater treatment and also reduce the time necessary for treatment. When applying this method, the electrodes performs a similar function as the coagulant, neutralizing the charge of the particulates, thereby allowing them to agglomerate and settle at the bottom of the tank. It has been found to have high removal efficiencies of color, COD and BOD. However, this method requires special equipment and is more expensive compared to chemical coagulation, though it is relatively cheaper compared to some pretreatments such as ultraviolet and ozone (Butler et al., 2011).

Carballa et al. (1999) investigated the use of coagulation and flocculation in the removal of pharmaceuticals and personal care products from municipal wastewater. From the study it was found that these processes were only effective for some of the pharmaceutical compounds and their removal was not dependent on the coagulant dose or temperature.

Saleem (2007) conducted a physicochemical study of pharmaceutical wastewater using alum, ferric chloride and ferrous sulfate as coagulants. These were not very efficient as they required a high dosage for the removal of color, TSS, BOD, COD and turbidity. Among these coagulants, alum was found to be the more effective, reducing the TSS, BOD, COD and turbidity by 76.6%, 34.8%, 48.6%, and 69.2% respectively. The removal of phenols and color from this wastewater required the use of activated carbon (Saleem, 2007). Another study on chemical coagulation of pharmaceutical wastewater used lime, ferric chloride and alum with average doses of 240 mg/l, 182 mg/l and 300 mg/l respectively. Similarly in this case, better removal values for TSS, BOD and COD were achieved when alum was used. However, ferric chloride aided by lime was recommended due to the quality of sludge produced which was more stable and settled easily compared to sludge produced from alum (Taleb et al., 2012).

Research has been done on the use of alternative natural coagulants in the pretreatment of pharmaceutical effluent. One example is the use of *corchorus olitorus,* which is an edible seed found abundantly in Western Nigeria. Extract of the seed was used at varying dosage and effluent pH to reduce the level of turbidity of the wastewater. This resulted in turbidity removal of 83.19% (Ugonabo, Menkiti, & Onukwuli, 2012a). A second example of the use of natural coagulants is the study done on snail shell derived coagulant. This system achieved a maximum turbidity removal of 90.82% measured in terms of TDSP (Ugonabo et al., 2012b).

2.3.1.1 Mechanisms of coagulation

During coagulation/flocculation, particle destabilization can be achieved through four mechanisms:

i. double layer compression

ii. charge neutralization

iii. colloid entrapment

iv. inter-particle bridging

Double layer compression and charge neutralization are considered to be coagulation, while enmeshment and bridging are classified as flocculation (Ean, 2008).

Double layer compression occurs when counterions is added as coagulant. Surrounding the negatively charged colloidal particle is an inner fixed layer and outer diffused layer of counterions. The concentration of counterions is highest at the particle surface and decreases to that of the bulk solution at the outer boundary of the diffused layer. This results in a lowering or elimination of the repulsive energy barrier. Destabilization of particles by counterions causes the diffused layer to compress around the particles. It is important to realize that this just compresses the colloid's sphere of influence and does not necessarily reduce its charge. High concentration of electrolyte in solution results in high concentrations of counterions in the diffused layer. Compression of the diffused

layer decreases the electrostatic repulsive forces between the similar colloidal particles and the zeta potential is mitigated. Thus, the attractive forces (van der Waals forces) can dominate to bind particles together (Ean, 2008). In general, double layer compression is not a practical coagulation technique for water treatment but it can have application in industrial wastewater treatment if waste streams with divalent or trivalent counter- ions happen to be available (Ravina & Moramarco, 1993)

Charge neutralization occurs when a charged particle is destabilized by coagulant ions. Inorganic coagulants (such as alum) and cationic polymers often work through charge neutralization. As the coagulant dissociates in water, hydrolysis reactions produce positively charged metal hydroxide ions that are adsorbed to the surface of the negative particles. The charge on the colloidal particle (zeta potential), is reduced to a level where the colloids are destabilized. A stoichiometric relationship exists between the coagulant and the particles under condition of charge neutralization. Charge neutralization is easily monitored and controlled using zeta potential (Ean, 2008). This is important because overdosing can reverse the charge on the colloid, and re-disperse it as a positive colloid, resulting in a poorly flocculated system. The detrimental effect of overdosing is especially noticeable with very low molecular weight cationic polymers that are ineffective at bridging (Ravina & Moramarco, 1993).

Colloid entrapment is sometimes referred to as sweep coagulation. It involves adding relatively large doses of coagulants, usually aluminum or iron salts which precipitate as hydrous metal oxides. The amount of coagulant used is far in excess of the amount needed to neutralize the charge on the colloid. Some charge neutralization may occur but most of the colloids are literally swept from the bulk of the water by becoming enmeshed in the settling hydrous oxide floc (Ravina & Moramarco, 1993).

Inter-particle bridging occurs when a coagulant forms threads or fibers which attach to several colloids, capturing and binding them together (Ravina & Moramarco, 1993). When a polymer with high molecular weight comes into contact with a colloidal particle, some of the reactive groups in the polymer adsorb at the particle surface and leave other portions of the molecule extending into the solution. A second particle can become attracted, which forms a particle-polymer-particle aggregate, with the polymer serving as a bridge (Ean, 2008). Inorganic primary coagulants and organic polyelectrolytes both have the capability of bridging. Higher molecular weights mean longer molecules and more effective bridging. Bridging is often used in conjunction with charge neutralization to grow fast settling and shear resistant flocs. For instance, alum or a low molecular weight cationic polymer is first added under rapid mixing conditions to lower the charge and allow microflocs to form. Then a slight amount of high molecular weight polymer, often an anionic, can be added to bridge between the microflocs. The fact that the bridging

polymer is negatively charged is not significant because the small colloids have already been captured as micro-flocs (Ravina & Moramarco, 1993).

2.4 Options for removal of PhACs from pharmaceutical wastewater

The pretreatment methods discussed under subheading 2.3 are not sufficient for removal of PhACs. A study by Suominen (2013) carried out in Kenya noted that in developing countries, the release of these compounds in pharmaceutical effluent is tolerated because their removal would require significant investment. In recent years, however, there has been increasing concern about the presence and fate of PhACs in water and wastewater, which are not completely removed through conventional wastewater treatment methods. These have been associated with environmental problems such as the feminization of male fish, renal failure of vultures and microbial resistance to antibiotics.

Pharmaceutical compounds can enter into the environment through sources such as hospitals, human excretion or landfills. However, a major source of these compounds is the pharmaceutical manufacturing industry. In order to remove these compounds from pharmaceutical effluent it is necessary to use other complementary methods of treatment such as membrane filtration, advanced oxidation processes and activated carbon adsorption together with the conventional treatment methods (Deegan et al., 2011). The choice of a treatment method is influenced by factors such as the type of pollutant to be removed, the availability of space and equipment, variations in the volume of wastewater

produced and the concentrations of the pollutants. Each of these methods of treatment has some limitations in its application. Although there are studies based in Kenya on treatment of pharmaceutical effluent, there is little information on what treatment procedures the factories are actually carrying out and their efficiency. Therefore, the first objective of this study is meant to carry out an investigation on the treatment procedures employed by the pharmaceutical factories in Kenya in order to fill this gap.

2.4.1 Membrane filtration

Membrane filtration includes microfiltration, ultrafiltration, nanofiltration, reverse osmosis, and membrane bioreactors. There is limited research on the use of these methods in removal of PhACs and the studies done are mainly for wastewater recycling plants or the treatment of groundwater (Deegan et al., 2011; Snyder et al., 2006). Reverse osmosis in different configurations showed efficient removal of antibiotics, lipid regulators, hormones and oral contraceptives, antiepileptics and analgesics (Snyder et al., 2006). An investigation on removal of a range of pharmaceuticals using nanofiltration and reverse osmosis on a drinking water treatment plant showed up to 85% reduction of all the compounds (Radjenovic et al., 2007). Microfiltration and ultrafiltration are unsuitable for removal of micro pollutants because the pore sizes are larger and may allow the micro pollutants to pass through. A major disadvantage of nanofiltration and reverse osmosis is that they are pressure driven and require a significant amount of energy. In addition to

this, the disposal of the sludge which could contain the pollutant in a more concentrated form remains a challenge (Deegan et al., 2011; Snyder et al., 2006).

2.4.2 Advanced oxidation processes

Advanced oxidation processes are based on the production of free hydroxyl radical which facilitate the conversion of pollutants to less harmful and more biodegradable compounds. A chemical agent such as hydrogen peroxide, ozone, transition metals and metal oxides are required for the process. In addition, an energy source such as ultraviolet-visible radiation, electric current, gamma-radiation and ultrasound is required (Deegan et al., 2011). Examples of advanced oxidation processes are ozonation and Fenton reactions. Significant research on ozone treatment of pharmaceutical wastewater has been focused on the removal of antibiotics or to enhance biodegradability and efficiency of subsequent treatment. A disadvantage of this treatment method is that the production of ozone is an energy intensive process which results in high costs (Deegan et al., 2011; Merih, 2003; Ying et al., 2009).

Fenton reactions, (reactions of hydrogen peroxide in the presence of iron to generate hydroxyl ions), has also been used for COD removal and to degrade pharmaceutical compounds present in the wastewater (Hussain et al., 2011; San et al., 2003). San et al. (2003) reported a maximum COD removal of 56.4% in the treatment of pharmaceutical wastewater using the Fenton reactions with hydrogen peroxide and ferrous ion

concentrations of 3 molar and 0.3 molar respectively. The optimum pH for Fenton reactions is between 2 and 4 which necessitate pH adjustment most of the time. It has been shown that the rate of degradation of pollutants increases with an increase in the concentration of hydrogen peroxide and ferrous ions. However, an increase in the hydrogen peroxide concentration past an optimum point results in a violent reaction followed by a quick boiling of the sample (San et al., 2003). One of the shortfalls of Fenton oxidation is that it is highly dependent on the aqueous solution pH and the concentration of hydrogen peroxide and ferric/ ferrous ions. The reactions in this process could also be inhibited by the presence of substances like sulfate or bromide ions which form complex iron ions (Stasinakis, 2008). In addition to this, hydrogen peroxide is toxic to some micro-organisms and an excess use of it prior to a biological treatment could lead to a deterioration of efficiency of the system. The disposal of the iron sludge produced required careful consideration in order to avoid detrimental effects to the environment (Deegan et al., 2011).

2.4.3 Activated carbon adsorption

Adsorption is a mass transfer process which involves the accumulation of substances at the interface of two phases. The adsorption process is affected by factors such as surface area, nature and initial concentration of adsorbate, solution pH, temperature, interfering substances, and nature and dose of adsorbent. Activated carbon is a commonly used adsorbent in wastewater treatment and is prepared from different materials like coal,

coconut shells and wood (Grassi et al., 2012). It is normally applied in powder form or in granular form in packed bed filters. A study conducted by Snyder et al. (2006) on the removal of estrogen which was present in trace concentration showed that both powdered and granular activated carbon were effective in removing more that 90% of the estrogen. Another study by Deegan et al. (2011) showed that there was more than 90% removal of 19 PhACs with the use of powdered activated carbon. However, powdered activated carbon poses a difficulty when it comes to separation of the carbon from water, which can be done either using sedimentation or membrane filtration. In activated carbon treatment, dissolved organic compounds, surfactants and humic acids compete with binding sites and block pores within the activated carbon structure, hence it is only suitable for pretreated effluent with low organic loading (Yanping & John, 2005). In addition to this disadvantage, the regeneration and disposal of activated carbon need careful consideration to avoid negative environmental impacts (Snyder et al., 2006). Economic constraints may limit the use of activated carbon adsorption of pharmaceutical effluent (Gupta et al., 2006).

2.5 Bentonite clay

Bentonite is a type of clay mineral that consists mostly of montmorillonite. In addition to montmorillonite, it also contains a small portion of other mineral matter like quartz, feldspar, organic matter, gypsum, pyrite or volcanic ash. Bentonite is usually formed from

the weathering of volcanic ash, most often in the presence of water. The bentonite industry initially began in Wyoming and South Dakota, in the United States of America, in 1898. The early uses of bentonite included consuming it for medicinal purposes, applying it to the skin, as a lubricant for squeaky wagon wheels, as soap and as a sealant for log cabin roofing. According to the United States Geological Survey, the largest producer of bentonite clay today is the United States of America, followed by Greece and Turkey (Mutisya and Maranga, 2012). Locally, bentonite clay deposits can be found in areas such as Athi River (Isinya), Timau (Lewa), Meru and Namanga (Amboseli), as shown in Figure 2.2.

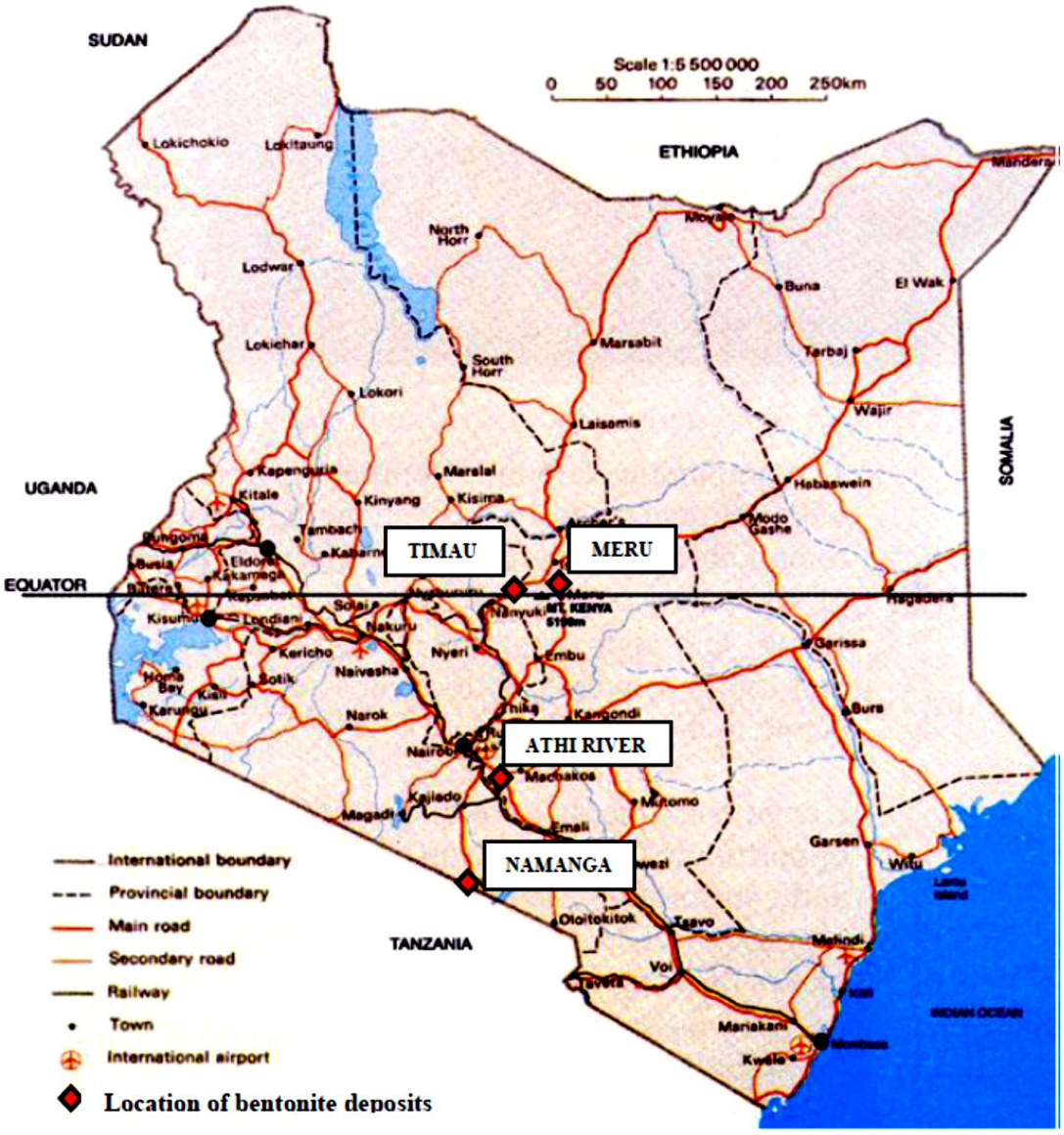


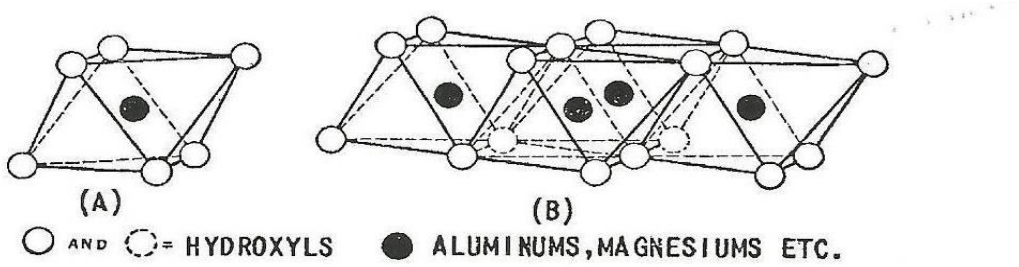
Figure 2.2: Geographical representation of bentonite deposits in Kenya

As early as 1952, bentonite from Athi river was mined intermittently for use as foundry sand bonding (Kennedy, 1990). Today, bentonite clay has a wide variety of applications

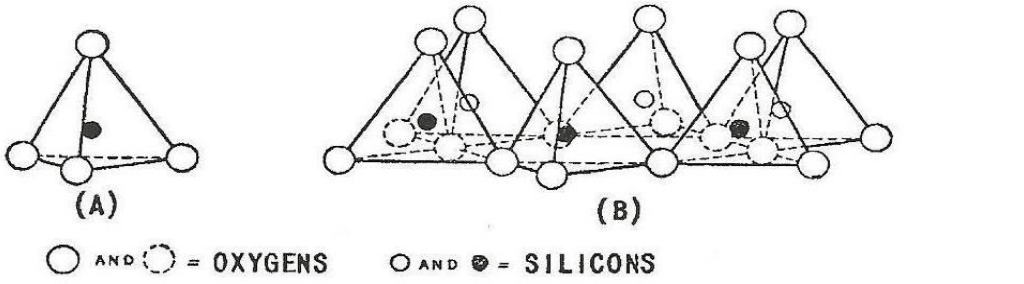
like palletizing iron ores, in foundry and ceramics, drilling mud, as a desiccant, as a pesticide carrier, in clarifying oils and fats and in the pharmaceutical, paint and cosmetic industry (Onal, 2006). In Kenya, bentonite clay is mainly used for drilling purposes and this includes geothermal and oil wells drilling. These applications rely mainly on bentonite imported from China and India, which is available in powder form packaged in 25 kilograms bags (Weramwanja et al., 2015). A study by Mutisya et al. (2013) showed that although both local mining and importation contribute to the bentonite used in Kenya, the former accounts for only 32.51% while the latter takes the larger share of 67.49%. The demand for the local and imported bentonite has been on the rise and several studies have been conducted to promote the exploitation of the local deposits so as to cut on importation costs, create employment opportunities and conserve foreign exchange (Mutisya and Maranga, 2012; Mutisya et al., 2013; Weramwanja et al., 2015). There are different types of bentonite clays, depending on the dominant element present in them such as potassium, sodium, calcium or aluminium. For industrial purposes, sodium and calcium bentonite are most commonly used. Bentonite deposits normally occur in lenses which are a few feet deep. These are strip mined by removing the overburden to expose the bentonite. After mining, the bentonite is stockpiled and dried. After this, it is separated according to particle sizes or ground to powder then packed. Many of the industrial applications of bentonite rely on its ability to absorb large amounts of water and other liquids into its structure which gives its swelling and adhesive properties. Application of

bentonite in wastewater treatment is mainly due to its ability to disperse into colloidal particles providing a large surface area per unit weight of clay. Bentonite particles can act as adsorbents for organic pollutants as well as add weight to slow settling flocs during the process of chemical coagulation. Polymers have been used as aids to improve the process of coagulation but clay minerals can provide a more affordable alternative (Aygun & Yilmaz, 2010). Even though research has been done on the use of bentonite in wastewater treatment, there are no detailed studies on using bentonite in coagulation process for pretreatment of pharmaceutical wastewater in Kenya.

In the treatment of wastewater using chemical coagulation, different types of coagulants and flocculants at varying dosages can be used to effectively reduce the toxic loading. However, a major concern in these processes is the cost of the chemicals and the effect of the sediments produced on the environment, especially when these sediments contain high levels of toxic matter (Abdelaal, 2004). Clay based treatment products can be used to offer a relatively lower cost option for the removal of contaminants from industrial wastewater. The structure of bentonite is made up of two basic building blocks, the aluminium octahedral sheet and the silica tetrahedral sheet, as shown in Figure 2.3. One unit of montmorillonite consists of two silica tetrahedral sheets between which is an aluminium octahedral sheet (Clem & Doehler, 1963). This structure is illustrated in Figure 2.4.



Diagrammatic sketch showing (A) single octahedral unit, and (B) portion of an octahedral sheet structure.



Diagrammatic sketch showing (A) single silica tetrahedron, and (B) portion of a silica tetrahedral sheet structure.

Figure 2.3: Structures of alumina and silica sheets (Clem & Doehler, 1963)

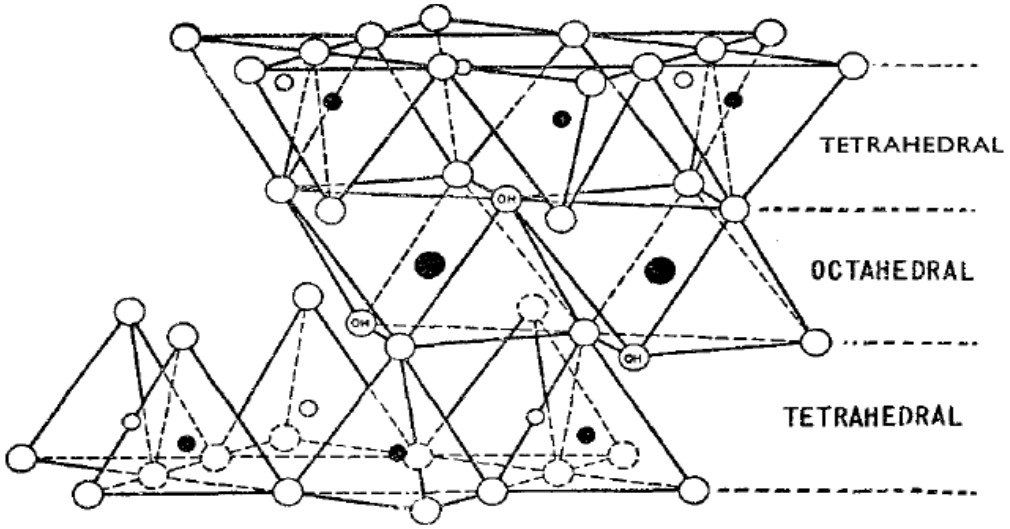


Figure 2.4: Structure of montmorillonite (Clem & Doehler, 1963)

The physical and chemical properties of clays can be modified by various processes and chemicals. Examples of these include acid activation, ion exchange, heating and hydrothermal treatments (Onal, 2006). Magnetic modifications of clay, in which bentonite was coated with iron, has also been carried out to study the removal of heavy metals from wastewater (Mockovčiaková & Orolínová, 2009).

The application of bentonite clay in the treatment of wastewater may be explained by the fact that the bentonite crystals are negatively charged because of ionic substitutions at various sites within their structure, thus exchangeable cations can be adsorbed on their surface. The bentonite particles may also work as nuclei for the adsorption of organic compounds from wastewater. In addition to this, the use of bentonite during the coagulation/flocculation process increases the opportunity for particle collusion resulting in rapid formation of settleable flocs. Previously reported data shows that once contaminants are microencapsulated and surrounded by a barrier of bentonite particles, it becomes non-reactive to external leaching (Abdelaal, 2004).

In a study conducted on mine wastewaters and oily wastewaters, Abdelaal (2004) used bentonite clay combined with chemical coagulants and cationic and anionic high molecular weight polymers as flocculants. For the mine wastewater, optimum results were obtained using a bentonite dosage of 0.1 g/l with 14 mg/l cationic polymer *Zetag32*. This yielded a 77% removal of COD and a 96% removal of suspended solids from the

mine wastewater. For the oily wastewater, the maximum percentage of COD and suspended solids removal was 99%. These results were obtained at a bentonite dosage of 2g/l in the presence of 4mg/l *Zetag32* polymer (Abdelaal, 2004).

Bentonite clay has also been used in the treatment of municipal wastewater to improve the coagulation and flocculation process (Bourliva et al., 2010). In this study, the addition of bentonite clay to the coagulation process made no significant difference in the removal of TSS. However, a COD removal of 80% was obtained using bentonite as opposed to the 66% obtained using coagulants only. Other pollutants such as nitrogen, phosphorous and heavy metals were also removed in the experiments.

Many studies have been carried out on the application of bentonite in the adsorption of heavy metals from wastewater. An example of this is the research carried out by Saad (2010) on the adsorption of metal ions (Cu, Co, Zn, Pb, As, Cd, and Cr) from industrial wastewater. He compared the results of using the bentonite and that of using roasted date pits. For both of these natural adsorbents, the minimum removal efficiency for the metal ions was found to be 97%. In another study bentonite clay was used for the removal of arsenic in wastewater through batch adsorption processes. The bentonite proved effective as 95% removal of arsenic was observed (Zahra et al., 2009).

Sanghi and Bhattacharya (2003) conducted a study for the adsorption-coagulation decolorisation of textile dye solutions using bentonite clay and compared the results to

those of using powdered activated carbon as adsorbents. The removal of dyes from the textile manufacturing effluent poses a major problem as these dyes are not removed by conventional wastewater treatment processes. This is because the dyes are fairly stable to light, heat and they resist biodegradation due to their complex molecular structure. Bentonite clay proved effective for the removal of the dyes though it remained suspended in solution for a long time. The addition of a small dose of polyaluminium chloride coagulant enhanced dye removal and produced a sludge that settled quickly. In addition to this, it has been shown that addition of clay minerals during coagulation had a positive effect on the dewaterability of the sludge in treating pulp-and-paper industry wastewaters (Aygun & Yilmaz, 2010)

An example of the use of modified bentonite clay is by Lizhong et al. (1996), who studied the removal of organic pollutants from wastewater using organobentonites which were synthesized through cation exchange. It was observed that the organic compounds removal using the organobentonites was up to 8 times more compared to the raw/unmodified bentonite.

Previous research on the application of bentonite in the treatment of wastewater has concentrated on effluent containing a high amount of heavy metals (e.g. from the mining industry), municipal wastewater and effluent with heavy color (e.g. from textile industry). This study seeks to examine the effect of bentonite clay on the pretreatment of

pharmaceutical industry wastewater. There is fairly limited research on locally available alternatives to the conventional treatment of pharmaceutical industry wastewater as compared to other industries. Most of the studies on pharmaceutical effluent have focused on advanced oxidation processes (Benatti et al., 2012; Elmolla & Chaudhuri, 2008; Merih, 2003; Pohja, 2011).

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Investigation of pharmaceutical wastewater treatment in Kenya

An investigation was carried out to determine the types of pharmaceutical factories most common in the country, the amount of wastewater they produce daily, the pretreatment processes they carry out and the challenges they face in handling the effluent. A desk study was done as well as visits to several factories, which were selected through simple random sampling. Information was collected through observation of the manufacturing processes and treatment facilities in the factories as well as interviews and questionnaires given to technical personnel in charge of effluent treatment plants in the factories. A sample questionnaire is provided in Appendix 1.This information served as a basis for the alternative treatment option proposed in this study and helped determine how this alternative can be incorporated into the already existing systems.

3.2 Wastewater sampling and characterization

For this study, raw wastewater was obtained from three pharmaceutical plants in Kenya, herein referred to as ‘Factory A’, ‘Factory B’ and ‘Factory C’ in order to protect their confidentiality. The selection of these factories was based on those which were

cooperative in providing information and giving access to their facilities for data collection.

The wastewater from each factory was collected using composite samples which were made up of three grab samples that were collected at an interval of two days so as to account for variations in production processes in the factories within a week. The sampling of the effluent was done at the end of the production process and before any treatment procedures were carried out on it. The samples were collected in five liter plastic containers, which had been previously prepared by scrubbing with a brush and laboratory detergent, then rinsed three times with tap water. This was followed by rinsing with distilled water, after which they were allowed to air dry.

During sample collection, nitrile gloves and lab coats were used as protective gear. Following the collection of the samples, the containers were sealed and labeled with an identifying number, the date, time and the location of collection. They were placed in a sample cooler with ice before being transported to the laboratory where analysis was carried out. In the laboratory, the samples were refrigerated at a temperature of between 4 and 8 degrees Celsius. During preparation for analysis, the samples were thoroughly mixed so as to produce a homogeneous sample. Analysis was carried out for TOC, COD, BOD, pH, TSS, turbidity and PhACs. The detailed procedures for the measurement of these parameters is discussed under sub-heading 3.3 (Analytical methods).

3.3 Analytical methods

The parameters that were monitored included pH, turbidity, Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD) and Total Organic Carbon (TOC). A High Performance Liquid Chromatography (HPLC) analysis was also carried out to determine the specific pharmaceutical compounds present in the wastewater.

pH measurement

The pH of a wastewater sample is an important parameter in the coagulation process because it affects the type of ions produced by the chemical coagulants. Very low pH may not allow coagulation to take place, while very high pH can cause the coagulated particles to re-disperse. The pH also affects the size and density of the floc formed. Measurement of pH was done on the effluent, before any treatment procedures were carried out and it was also monitored during the processes of optimization of the chemical coagulation process and optimization of bentonite pre-treatment. The pH of the sample water was measured with a WTW pH-meter which was calibrated with two buffer solutions (pH 7.00 and pH 4.00) before use. Measurements were taken by placing the electrode of the pH meter into the sample and allowing the readings to stabilize. The electrode of the pH meter was carefully rinsed with deionized water whenever it was taken from one sample to another, so as to avoid cross-contamination.

COD analysis

Chemical oxygen demand (COD) is the amount of oxygen required for the chemical oxidation of organic matter in water, as determined using a strong oxidant, such as potassium dichromate or permanganate. COD measurement was important in this study because it helped determine the amount of organic matter which was removed from the effluent through the removal of suspended and colloidal matter by the coagulation process and bentonite pre-treatment. COD measurement was done in the laboratory on the raw wastewater and also after every treatment process.

Determination of COD was done using the closed reflux titrimetric method. 10.0 ml of the samples, together with one blank were put in well cleaned digestion tubes. Following this, 6.0 ml of 0.0167 molar potassium dichromate solution was added into the digestion tubes. 14.0 ml of sulfuric acid reagent was then carefully run down the walls of the tube after which the tubes were tightly capped and slowly inverted several times for complete mixing so as to prevent local heating of the vessel bottom which could result in an explosive reaction. The digestion tubes were then placed in a block digester as shown in Figure 3.1 and heated at 105^{o}C for 2 hours. They were allowed to cool to room temperature and placed in a tube rack. Thereafter, the contents were transferred into a conical flask and 2 drops of ferroin indicator were added and this was titrated with 0.10 molar ferrous ammonium sulfate (FAS) to a sharp color change from blue-green to

reddish brown. The blank was likewise titrated. The COD value was calculated using equation 3.1.

$$COD\ (mg\ O_2/l) = \frac{(A-B)\times M\ \times 8000}{Ml\ sample} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3.1)$$

Where;

A – ml of FAS used for blank

B – ml of FAS used for sample

M – Molarity of FAS

Figure 3.1: COD samples in block digester

BOD analysis

BOD is a measure of dissolved oxygen present in a water sample that is needed by aerobic biological organisms in order to break down organic material in the water at a certain temperature over a specific period of time. The BOD value is most commonly expressed in milligrams of oxygen consumed per liter of sample during 5 days of incubation at 20 °C. In this study, BOD measurement was carried out in order to characterize the pharmaceutical effluent as well as to monitor the impact of the pretreatment that was later done on the samples. This measurement was taken on the raw samples as well as samples treated by coagulation and bentonite clay. BOD measurement was carried out in the laboratory by diluting different volumes of the wastewater with aerated distilled water in which BOD nutrients (phosphate buffer, magnesium sulfate solution, calcium chloride solution and ferric chloride solution) had been added. The samples were seeded using sludge obtained from a biological treatment plant. Figure 3.2 shows the aeration of the seed water and the dilution water that was used for BOD analysis. In the analysis of BOD, DO of each of the samples was measured before they were transferred into BOD bottles and incubated at 20 ^{o}C for 5 days. The DO was then measured after the 5 days incubation. The sample BOD was calculated using equation 3.2.

$$BOD_5\ (mg/l) = \frac{(D_0 - D_5) - (B_0 - B_5)f}{P} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3.2)$$

Where;

D_0 - Dissolved oxygen of the diluted sample immediately after preparation (mg/l)

D_5 - Dissolved oxygen of the diluted sample 5 days after incubation at 20 ^oC (mg/l)

B_0 - Dissolved Oxygen of diluted seed sample after preparation (mg/l)

B_5-Dissolved oxygen of diluted seed sample 5 days after incubation at 20 ^oC (mg/l)

f – Ratio of percentage seed in diluted sample to percentage seed in seed control

P- Decimal volumetric fraction of sample used

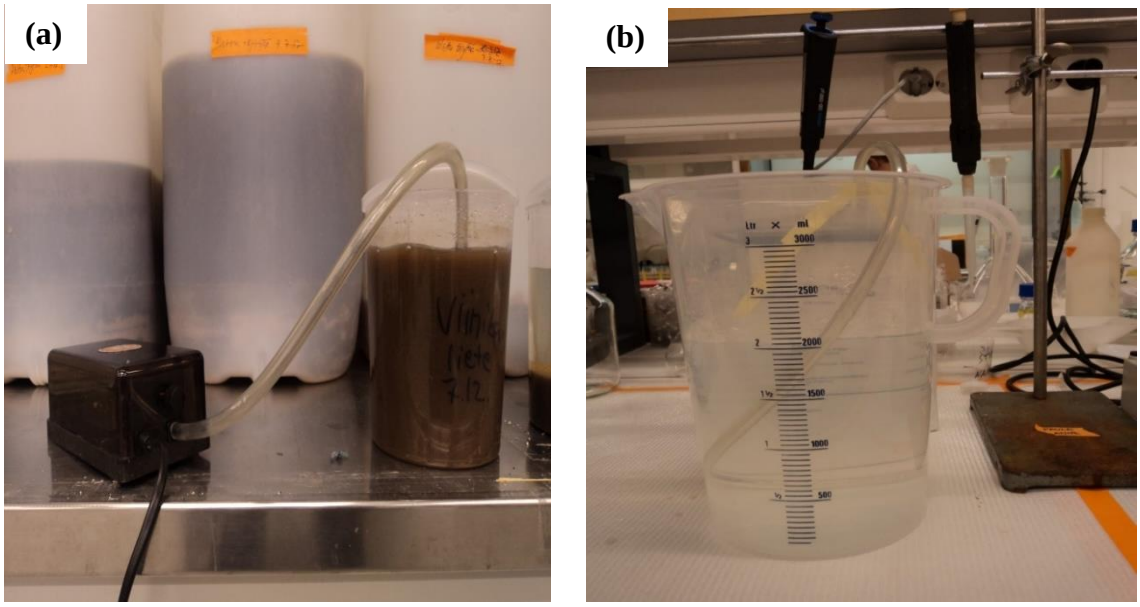


Figure 3.2: Aeration of (a) seed water (b) dilution water for BOD analysis

TOC analysis

Total organic carbon (TOC) is a measure of the carbon content of dissolved and organic matter present in the water. TOC measurements exclude inorganic carbon in the sample, which is composed of carbonates, bicarbonates and carbon dioxide. Unlike COD and BOD measurements, TOC does not measure other elements such as nitrogen and hydrogen which are organically bound and can contribute to the oxygen demand. TOC measurements provided fast and accurate results. The samples were put in TOC vials which were then placed in a Shimadzu TOC-5000 carbon analyzer, as shown in Figure 3.3. Total carbon (TC) is analyzed by injecting a sample into the combustion tube (+680 °C) filled with oxidation catalyst. Synthetic air is used as a carrier gas. The carbon

compounds are decomposed to carbon dioxide gas, which flows with the carrier gas to infrared gas analyzer where the carbon dioxide is detected. In the inorganic carbon (IC) analysis the sample is injected into an IC vessel where it is acidified. IC component of the sample is decomposed to carbon dioxide and detected by infrared gas analyzer. Total organic carbon (TOC) is obtained by subtracting inorganic carbon (IC) from the analyzed total carbon (TC).

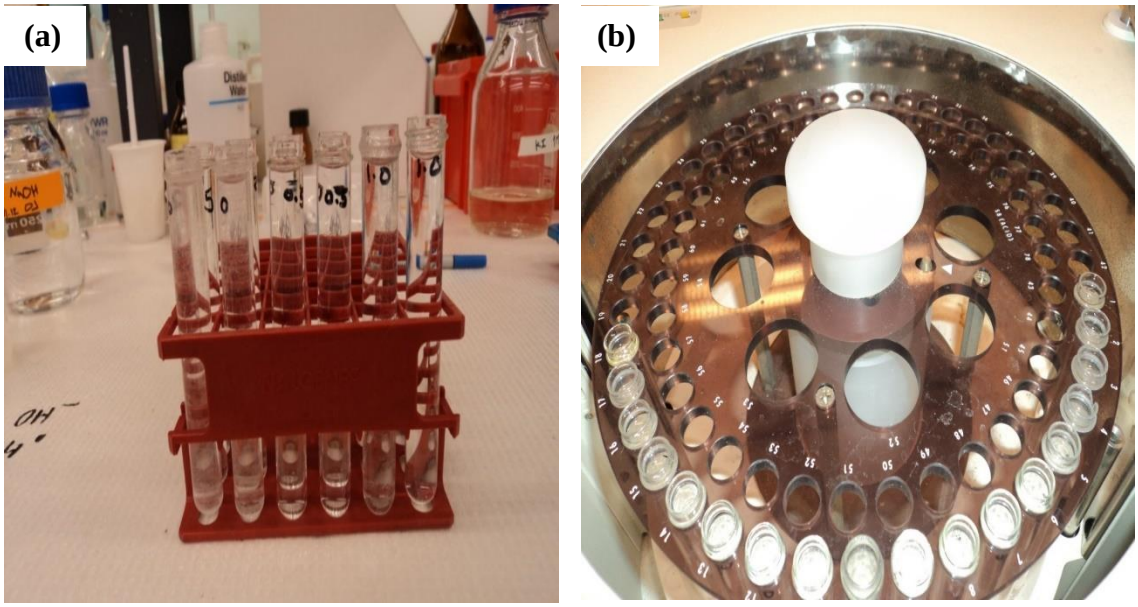


Figure 3.3: TOC samples (a) placed in TOC vials (b) in the Shimadzu TOC-5000 carbon analyzer

HPLC analysis

High performance liquid chromatography (HPLC) is a method which is widely used for analyzing organic and inorganic compounds. In this study, HPLC analysis was done to detect and determine the concentration of pharmaceutical compounds present in the samples. Analysis was carried out on raw effluent as well as effluent treated with chemical coagulants and coagulants in combination with bentonite clay. This method is convenient because it is capable of detecting several compounds at the same time. The equipment used was a Hewlett Packard 1100 –series HPLC.

The HPLC system was calibrated for eight pharmaceuticals which are produced by the companies and expected to be in the wastewater, namely; ciprofloxacin, clotrimazole, diclofenac, sulfamethoxazole, paracetamol, ibuprofen, trimethoprim and metronidazole. This helped to determine the retention time for each of pharmaceutical compounds. For the calibration, 0.1 g of the pure form of each of the pharmaceuticals was dissolved in 100 ml mixture of acetone and distilled water to form a solution with a concentration of 1 mg/ml. from this stock solution, six calibration solutions were prepared in vials. During the HPLC analysis, distilled water was used as blanks.

In HPLC, a small amount of sample (10 – 20 µl) is injected to the liquid phase (mobile phase or eluent) using injector. Liquid phase travels evenly in narrow capillaries with the help of pump into the column. The column is packed with stationary phase which consists

of small particles. These particles divide the sample into its components which stays in the particles for different time. At each turn, components come out from the column and into the detector which signals a peak into the chromatogram. The samples were filtered through a 0.20 µm filter to the HPLC vials before the analysis. Figure 3.4 shows the samples placed in HPLC vials and sealed before being placed in the analyzer.

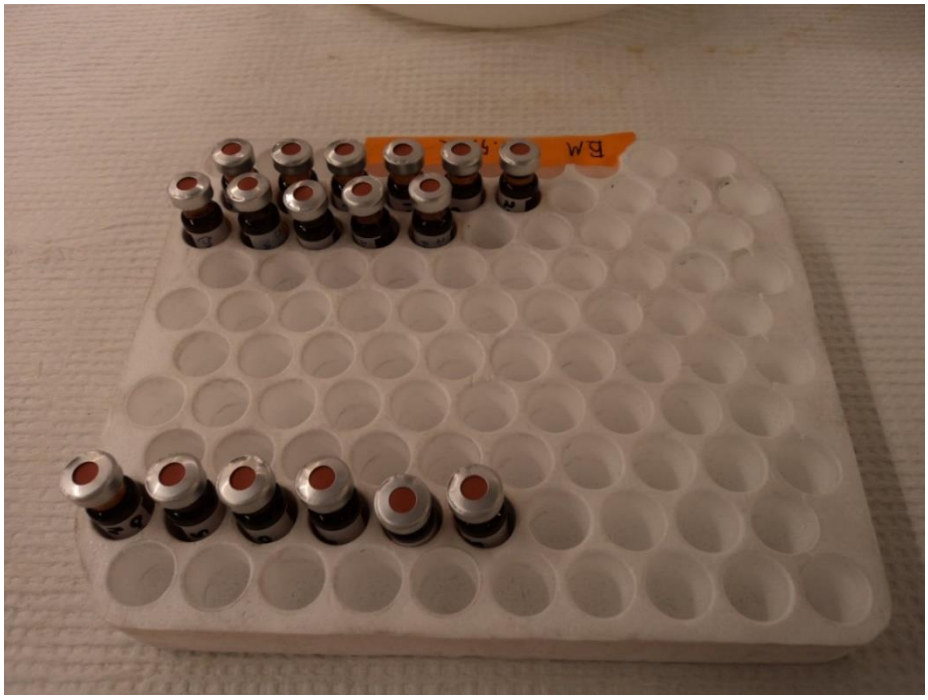


Figure 3.4: Samples in HPLC vials ready for analysis

Turbidity measurement

Turbidity is an expression of the optical property that causes light to be scattered and absorbed rather that transmitted with no change in direction though the sample. Its occurrence in water is caused by suspended and colloidal matter such as clay, silt, organic and inorganic matter or microscopic organisms (Ean, 2008). Turbidity was measured using a TR-3 turbidi-meter which produces readings on a liquid crystal display in Nephelometric Turbidity Units (NTU), as shown in Figure 3.5. The turbidity meter was calibrated with 20 NTU and 100 NTU standard solutions, after which the samples were put in vials and placed in the meter for analysis.

Figure 3.5: Turbidity measurement using a TR-3 turbidi-meter

Total suspended solids measurement

Total suspended solids (TSS) include all particles suspended in water which will not pass through a filter. This is a combination of settleable and non-settleable solids. To measure the TSS of the effluent, a well-mixed sample was filtered through a weighed standard glass-fiber filter and the residue retained on the filter was dried to a constant weight at 103 ºC to 105°C. The increase in weight of the filter represented the total suspended solids and was calculated using equation 3.3.

$$mg/TSS/L = \frac{(A-B)\times 1000}{Sample\ volume\ (ml)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3.3)$$

A - Weight of filter + dried residue, mg

B - Weight of filter, mg.

3.4 Optimization of coagulation/ flocculation pretreatment

To determine the optimum operating conditions for the coagulation/ flocculation pretreatment, jar test experiments were carried out. The performance of a coagulation process may be affected by factors such as type of chemical used, chemical dosage, pH, wastewater constituents, mixing speeds for fast and slow mixing and temperature, among others (Ean, 2008). In this study, the type and dosage of the coagulants used, as well as the pH were investigated. The jar test apparatus consisted of a set of six jars with a gang

stirrer which allowed the jars to be controlled simultaneously. The process of coagulation was carried out using two chemicals; ferric sulfate and polyaluminium chloride (PAC).

The pharmaceutical wastewater samples were collected from equalization tanks at the end of production of various pharmaceutical products, using the procedure outlined under sub-heading 3.2. The optimum coagulant dosage for each of the chemicals was determined by varying the amount from 5 mg/l to 40 mg/l at the natural pH of the samples. After adding the coagulants to the wastewater, rapid mixing at 200 rpm was done for two minutes. This was to ensure that the chemicals were evenly distributed throughout the wastewater and to create conditions favorable for the formation of micro-floc particles. This was followed by slow mixing at 40 rpm for 20 minutes to allow for flocculation to take place. The treated effluent was allowed to settle for 30 minutes after which it was collected and analyzed for TOC, COD, BOD, TSS, turbidity and pharmaceutical compounds using the procedures outlined under sub-heading 3.3 (Analytical methods). The best coagulation pH was determined by using each coagulant at its optimum dosage and varying the pH between 2 and 9. The pH was adjusted using 0.25 molar sulfuric acid and 0.25 molar sodium hydroxide solution. The process of coagulation and flocculation was repeated after which the treated samples were collected for analysis. The procedure for this coagulation pretreatment is illustrated in Figure 3.6. The performance of the two

coagulants, ferric sulfate and PAC were compared in order to find out which of the two was more effective.

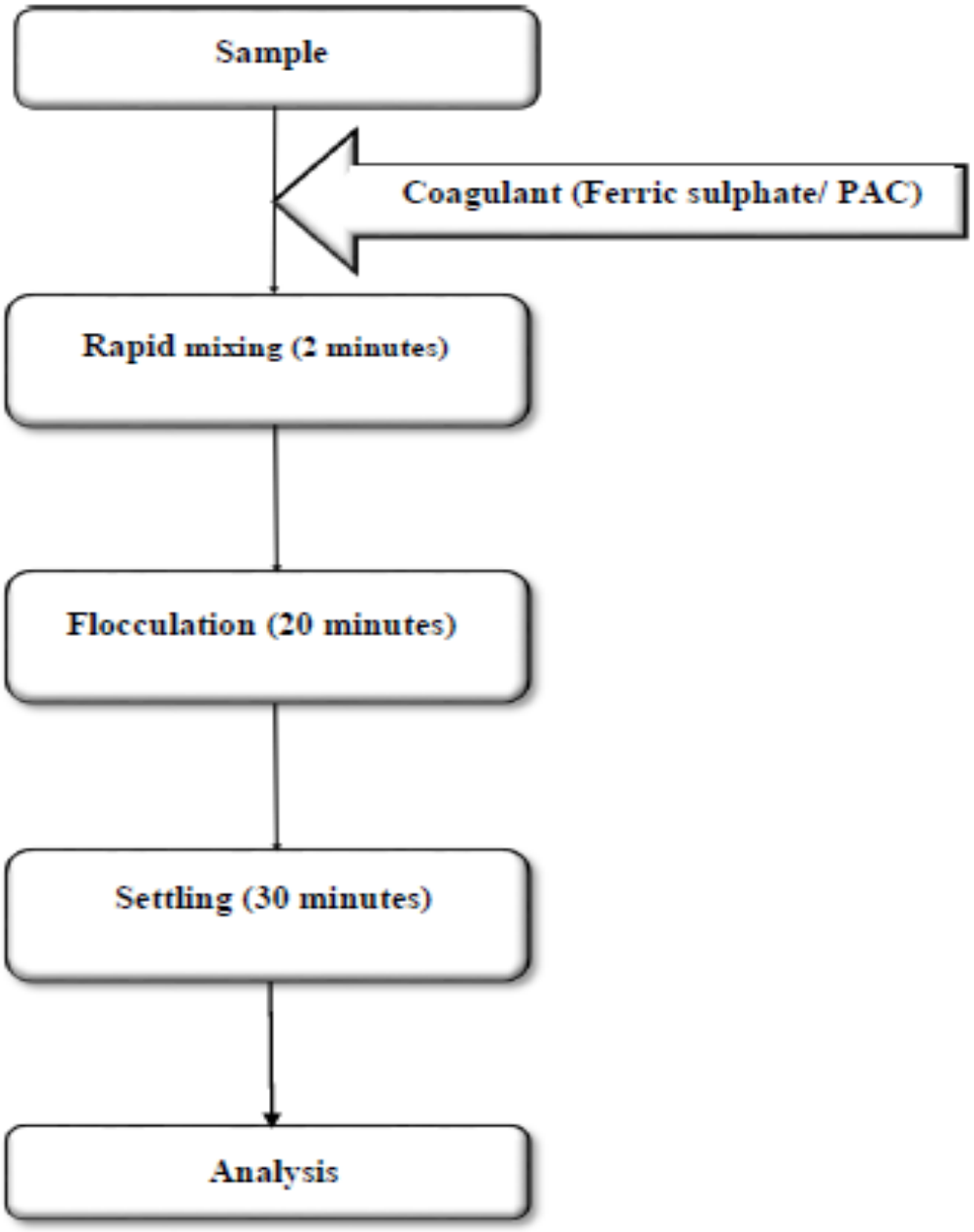


Figure 3.6: Steps of the treatment process using chemical coagulants (only) without bentonite clay pre-treatment

3.5 Optimization of bentonite dosage and its use in pretreatment of effluent

The optimization of bentonite dosage and its application in the pretreatment of the effluent was carried out in the second set of experiments. Varying amounts of the clay was added to the sample water and mixed at 200 rpm for 60 minutes. The purpose of this step was to allow for adsorption or any reaction between the pollutants and the bentonite to take place. The rapid mixing at 200 rpm was done in order to avoid settling of the bentonite and ensure maximum contact between its particles and any organic pollutants. The contact time of 60 minutes was chosen based on a review of previous studies on adsorption carried out at different time intervals that showed that this treatment process attained an equilibrium at one hour (Abu-Safa et al., 2012; Saad, 2010; Soderberg, 2008). After this, coagulation/flocculation treatment was carried out using Ferric sulfate and PAC at their optimum dosages and pH respectively as determined under subheading 3.4 (Optimization of coagulation/ flocculation pretreatment). The coagulants were rapidly mixed into the samples at 200 rpm for two minutes, which was followed by slow mixing at 40 rpm for 20 minutes to allow for formation of flocs. The samples were then left undisturbed for 30 minutes for settling to take place and then collected and analyzed as outlined in subheading 3.3 (Analytical methods).

From this procedure, an optimum amount of bentonite for the treatment of the samples was determined. This bentonite dosage was used in experimentation with chemical

dosage being varied from 5 mg/l to 40 mg/l. Likewise, the bentonite was rapidly mixed in the samples at 200 rpm for 60 minutes before the coagulants were added. The treatment process for this second setup is illustrated in Figure 3.7. In order to determine the effect of the clay in the pretreatment, the results from the first set of experiments which used chemical coagulants only was compared to those of the second set in which the bentonite clay was added to the coagulation process.

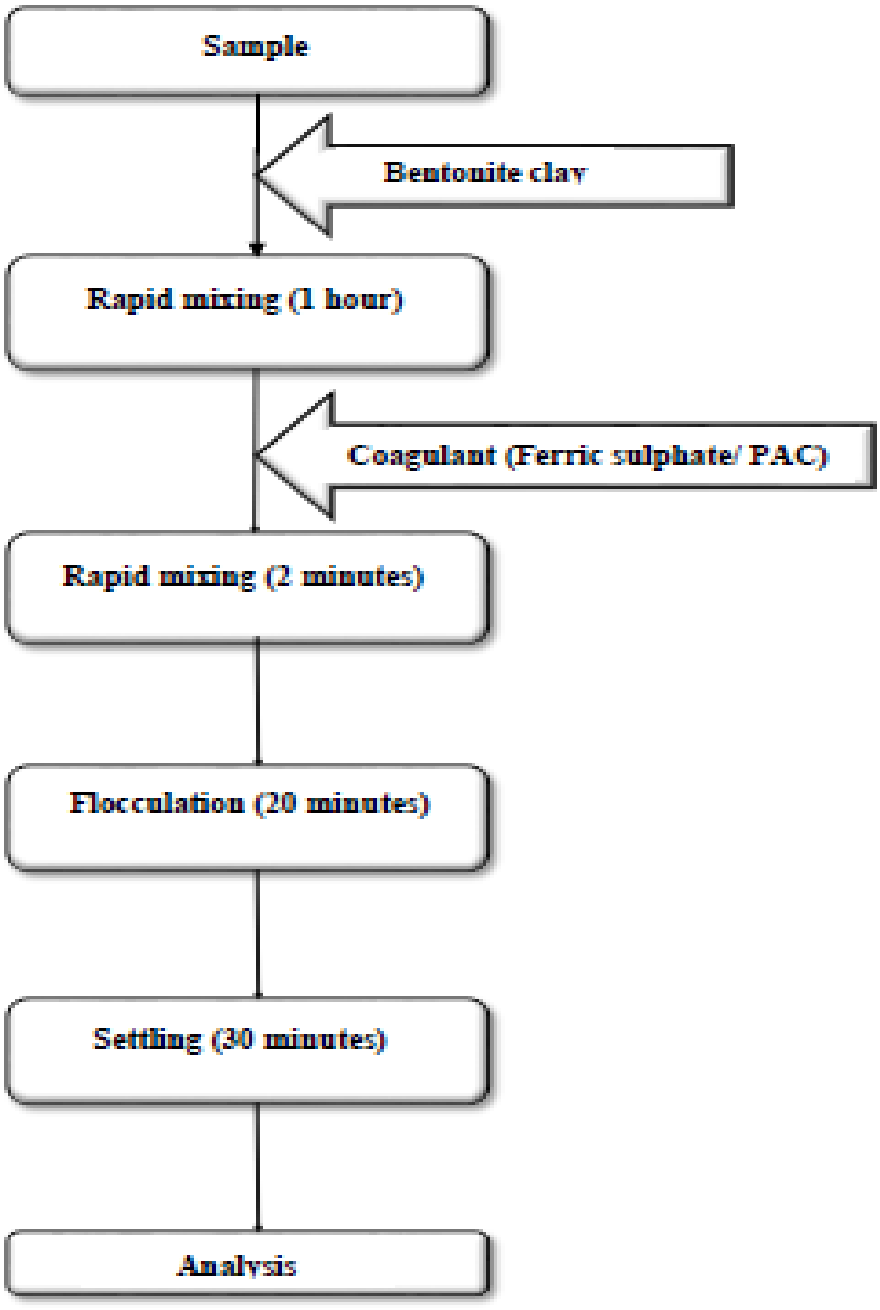


Figure 3.7: Steps of the treatment process using chemical coagulants together with bentonite clay pretreatment

CHAPTER FOUR

MANAGEMENT OF PHARMACEUTICAL WASTEWATER IN KENYA

4.1 Wastewater generation

Pharmaceutical plants in Kenya have little variation in the range of products and formulations. Most of the leading firms all fall under the formulation, drug mixing and preparation plant category that are involved in compounding and packaging medicines, repacking formulated drugs and processing bulk drugs into doses using predominantly imported active ingredients and excipients. These factories are mainly involved in the production of syrups, suspensions and tablets. However, it was noted that the large multinational corporations in Kenya are mainly involved in distribution of pharmaceutical products which are manufactured elsewhere.

The companies involved in production release an average of 2000- 6000 litres of process wastewater per day, mainly from washing of drug formulation and mixing equipment. The production of creams, suspensions and syrups contributes to about 43% of the wastewater while the processes of granulation and coating of medicinal products contributes about 28% each. All the sampled factories carried out pre-treatment of the

wastewater before disposing it or taking it for biological treatment either on site or in the public wastewater treatment plants.

4.2 Characterization of pharmaceutical effluent

The characteristics of the raw wastewater, which was sampled at the end of the production process from three factories, were determined from analysis and are presented in Appendix II. The range of values for the measured parameters are shown in Table 4.1.

Table 4.1: Characteristics of pharmaceutical industry wastewater

Measured parameter	Range value
pH	6.18 - 7.08
TSS (mg/l)	74.33 – 210.37
Turbidity (NTU)	63 - 127
COD (mg/l)	195.63 – 418.70
TOC (mg/l)	99.47 – 117.50
BOD (mg/l)	85.23 – 263.23

The pH of the samples ranged from 6.18- 7.08. This was neither too high nor too low. Extremes of pH in wastewater are generally not acceptable because they result in problems in wastewater treatment systems (Kavitha et al., 2012). TSS and turbidity of the samples wastewater ranged between 74.33- 210.37 mg/l and 63- 127 NTU

respectively. COD ranged between 195.63- 418.70 mg/l, while the range of TOC was 99.47-117.50 mg/l. The BOD range was between 85.23- 263.23 mg/l.

The variations in the concentration and composition of the samples could be attributed to varying production processes that may have been carried out. The effluent is of low strength compared to those reported by other researchers in different countries (Herumurti & Petronas, 2008; Isa et al., 2010; Kavitha et al., 2012). According to a study carried out by Herumurti and Petronas (2008) on low strength pharmaceutical wastewater the COD ranged between 460- 526 mg/l, BOD was between 299-386 mg/l and TSS was between 15-50 mg/l. Study by Isa et al. (2010) used pharmaceutical wastewater with a COD range of 300- 2000 mg/l, and TSS of between 32-45 mg/l. The TSS values in the present study were higher compared to those observed in the above mentioned studies, but still fall within the range of low strength pharmaceutical effluent as described by Gupta et al. (2006), who gave the TSS range as 200-400 mg/l. This variation could be a result of use of different raw materials such as cocoa, talc, calcium or gelatin which are required for some formulations. High strength pharmaceutical effluent can have COD values as high as 7280 mg/l, BOD of 4132 mg/l and TSS of up to 4300 mg/l as reported in the study conducted by Kavitha et al. (2012).

The results from the characterization of the samples was within the expected range because the wastewater was from drug mixing and formulation plants which produce

wastewater with a relatively lower waste load compared to other categories of pharmaceutical industries (Gupta et al., 2006). This study focused on this particular type of wastewater because majority of pharmaceutical manufacturing plants in Kenya fall under the drug mixing and formulation category, whereby they use various raw materials, some of which are imported, to prepare drugs in the final form of syrups, tablets, capsules, creams etc. (EPZA, 2005).

4.3 Pre-treatment methods

Data collected from the pharmaceutical factories under study showed that each of the factories had its own unique processes of handling effluent. However, despite the variation in processes, all of them carried out coagulation and flocculation as an initial step in the pre-treatment of the wastewater mainly to remove suspended solids and reduce COD. The most commonly used coagulant is aluminium sulfate, ferric sulfate and ferric chloride, mainly because of their availability and relatively low cost.

In Factory A, process water is collected in three equalization tanks each with a capacity of 25,000 liters. From these equalization tanks, the effluent flows into a coagulation tank, shown in Figure 4.1, where aluminium sulfate is added as a coagulant. In order to enhance the formation and settling of flocs, a polymer known as Rapid Floc is added during the flocculation process. After the coagulation/ flocculation step, the effluent flows into an aerated balancing tank where it mixes with sanitary wastewater from the factory that has

passed through a fine screen. The wastewater then passes through a biological treatment by the activated sludge process. After the treatment, the effluent is allowed to infiltrate into the ground though soak pits. This factory undertakes the biological treatment because it is not connected to a municipal wastewater system due to its location. The problems encountered in the treatment of effluent in this factory includes high residual TSS, BOD and PhACs. A possible reason for this is that the PhACs present in the effluent could be toxic to bacteria and thus interfere with the activated sludge process. In addition to this, they experienced very poor floc formation and when they tried to remedy the situation by introducing the polymer it resulted in high increases in cost because the polymer was imported from South Africa.

Figure 4.1: Coagulation tank for pre-treatment of pharmaceutical wastewater

In Factory B, wastewater from an equalization tank flows into the coagulation treatment tank where ferric chloride is used for coagulation/ flocculation. In this step, sulfuric acid and sodium hydroxide are used to adjust the pH. After the removal of suspended solids, the effluent is passed through an activated charcoal filter to remove residual color and PhACs, following which the effluent is released into the municipal wastewater system. The main problems encountered in effluent treatment in this factory is controlling the high doses of chemical coagulants used and the relatively short service life of the activated charcoal filters, which may at times interfere with the effectiveness of the treatment system.

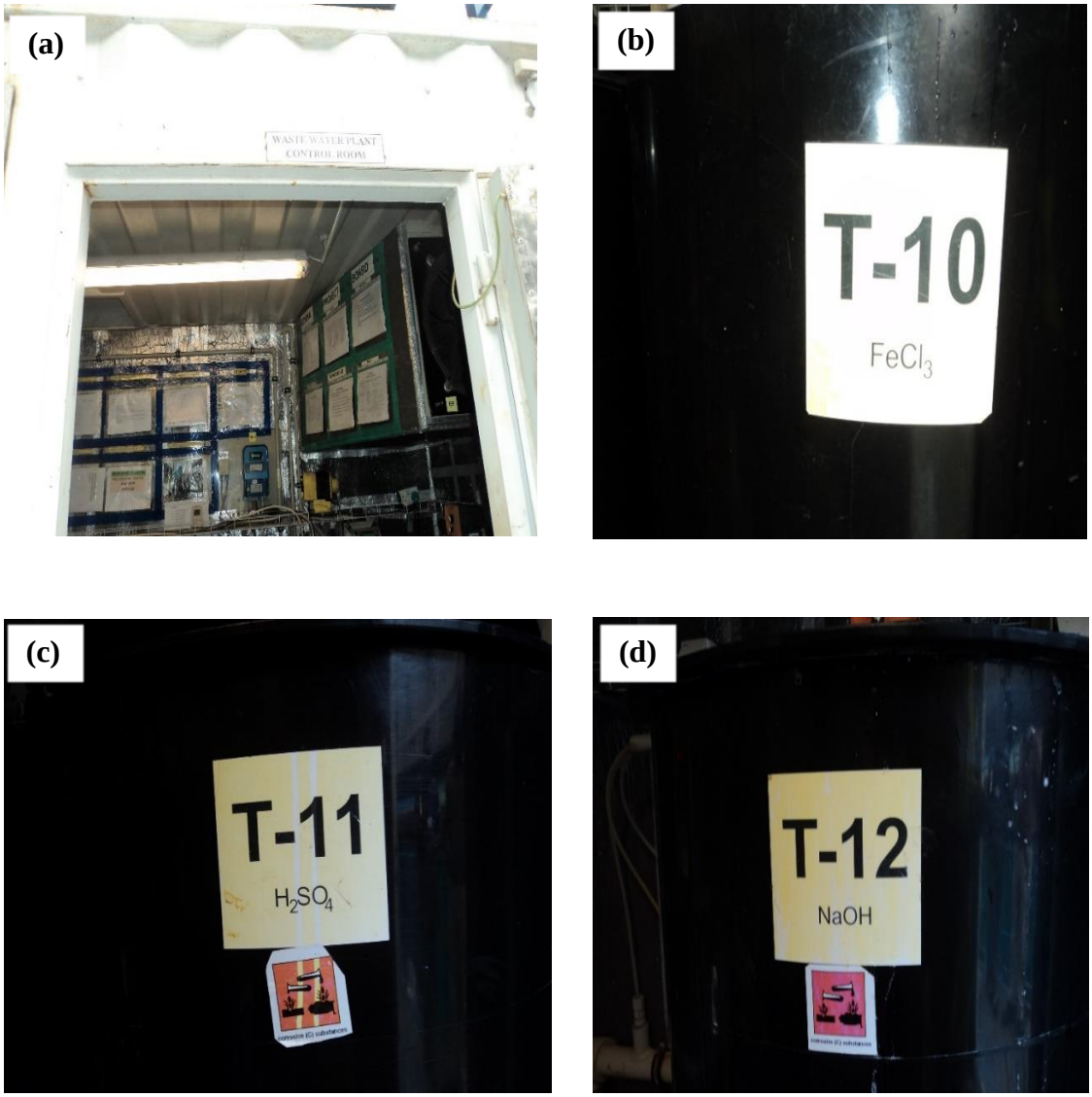


Figure 4.2: Some of the equipment for wastewater treatment (a) wastewater treatment control room (b) dosing equipment for ferric chloride coagulant (c) dosing equipment for sulfuric acid used for pH adjustment (d) dosing equipment for sodium hydroxide used for pH neutralization

In Factory C, effluent is collected in four equalization tanks. From there, it flows into the first treatment tank which has a capacity of 24,000 liters and as it does so it passes through a screen bar and blowers which aerate it. In this treatment tank, aluminium sulfate is added as a coagulant as well as a polyelectrolyte that enhances the flocculation process for removal of suspended and colloidal matter, using the chemical dosing equipment shown in Figure 4.3. This is followed by ozonation, where an ozonator converts oxygen from an oxygen concentrator into ozone using an electric discharge field. Figure 4.4 shows the equipment used in ozone production. The ozone produced oxidizes organic matter and other pollutants present in the effluent. The effluent goes through two dissolved air floatation tanks where floatable matter is removed. Finally the effluent is passed through an activated carbon filter system, shown in Figure 4.5, where residual organic matter is removed before being released into the municipal sewerage system. A press filter, shown in Figure 4.6, is used for sludge dewatering. The main challenges encountered in this facility are reducing the high chemical dosages used, high operation and maintenance costs of the equipment and production of large volumes of sludge.

Figure 4.3: Chemical dosing system for coagulation/ flocculation process

Figure 4.4: Equipment used for ozonation treatment of pharmaceutical effluent

Figure 4.5: An activated carbon filtration system

Figure 4.6: A press filter used for sludge dewatering

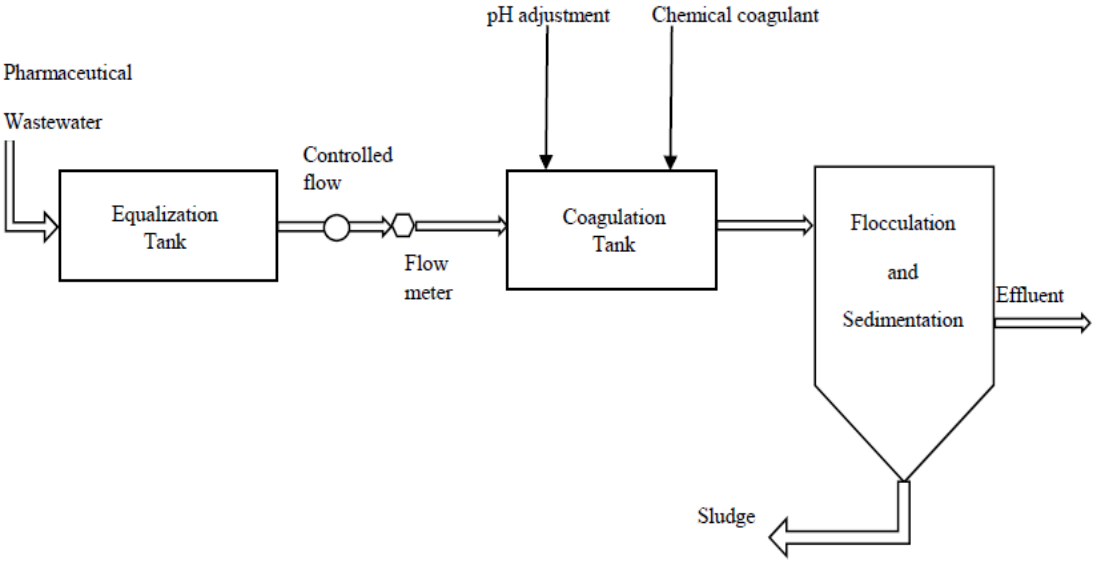


Figure 4.7: Typical coagulation/ flocculation treatment process for pharmacuetical effluent

Figure 4.7 illustrates the typical process employed for pretreatment of pharmaceutical wastewater using chemical coagulation. Wastewater is first collected into equalization tanks, which vary in number and size from one factory to another. The purpose of these tanks is to control fluctuations in wastewater quality and quantity in order to provide optimum conditions for pretreatment. From the equalization tank, the wastewater flows to the coagulation tank. Here, adjustments in pH are made when necessary either using sulfuric acid or sodium hydroxide. It is in the coagulation tank that chemical coagulants are added and rapidly mixed to facilitate their dispersion into the wastewater. The wastewater then flows into the flocculation tank where slow mixing takes place to allow

formation of floc, which are then allowed to settle at the bottom of the tank and later released as sludge from the bottom of the tank. However, the exact setup and equipment used may vary from one factory to another as observed in the three examples considered.

The main problems they face with the coagulation pretreatment is poor floc formation, long settling time and a need to reduce the amount of chemical coagulants used so as to reduce costs incurred. These are common drawbacks of the coagulation and flocculation process hence the introduction of polymers, which are meant to enhance the efficiency of treatment. Figure 4.8 shows the improvement of floc formation and settlement with the use of Rapid Floc polymer (visual comparison of the first jar from the left and the third jar from the left). However, the use of polymers has proved to be inefficient cost wise, thus showing the need for a cheaper alternative. There is also a need to remove or at least reduce the concentration of pharmaceutical compounds from the effluent before disposal. Methods such as ozonation, Fenton oxidation and activated carbon adsorption meant for removal of these compounds involve high maintenance and operational costs, hence the need for a cheaper alternative. It is for these reasons that this study investigated the application of bentonite clay pre-treatment of pharmaceutical effluent, which if effective may cut down on the subsequent polishing processes currently employed in some plants.

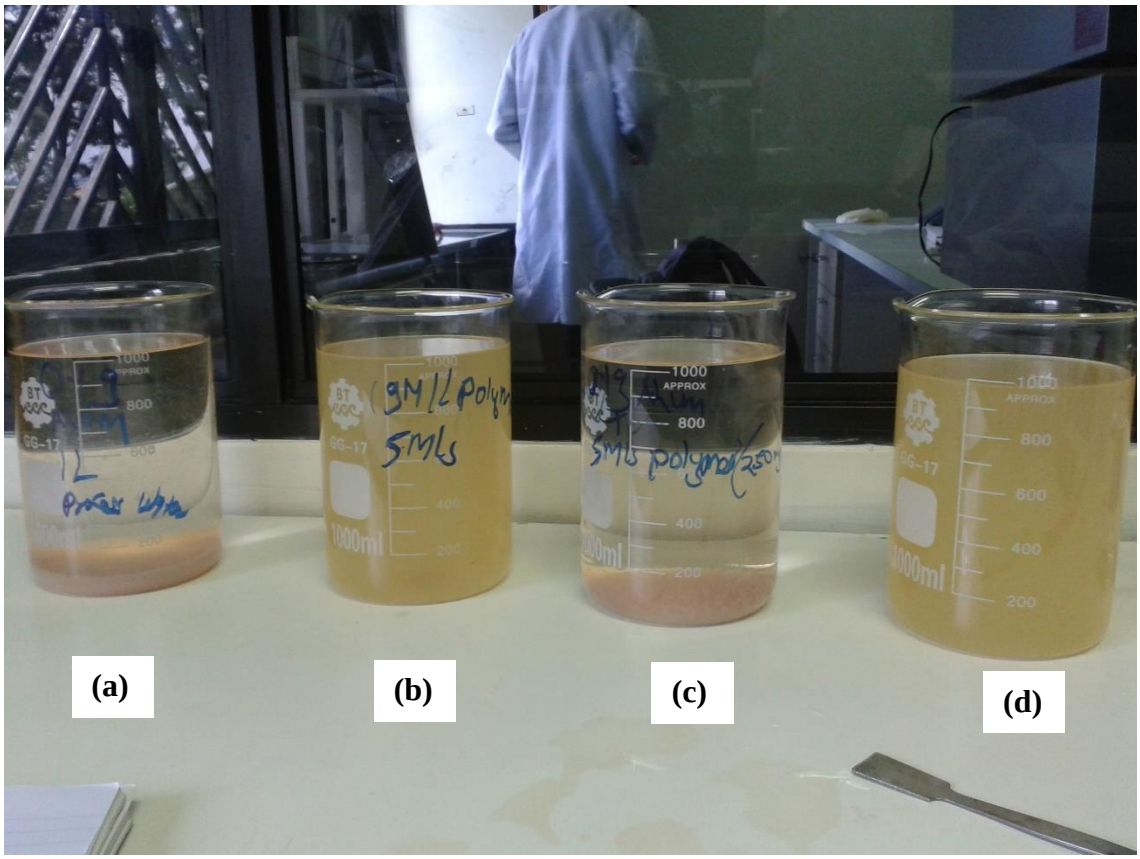


Figure 4.8: Comparison of the effect of polymers on coagulation/ flocculation treatment of pharmaceutical effluent. (a) treatment with aluminium sulfate only (b) treatment with Rapid floc polymer only (c) treatment with aluminium sulfate and Rapid floc polymer (d) raw effluent

4.4 Pharmaceutical wastewater management summary

An investigation into methods of treating pharmaceutical effluent in Kenya showed that they resulted in an average of 35% to 58% removal of COD and 79% to 86% removal of TSS. There was weak floc formation in most cases which resulted in poor settling.

Removal of BOD was low, ranging between 8% and 22%. This however was not a cause for concern because the initial concentration of the BOD was also low in all the cases under study. Apart from the factory that carried out ozonation treatment, removal of pharmaceutical compounds was minimal, thus showing a great need for improvement in this area. This was especially so with the factory which discharged its effluent though soak pits because it had a challenge meeting the NEMA standard of 0.05 mg/l of PhACs in effluent discharged into the environment. However, the presence of pharmaceutical compounds in treated effluent should not only be of concern to the plants that discharge into the environment but also to those that release into municipal sewers because research has shown that these compounds are not being treated in these WWTPs and are finding their way into streams and ground water resources (Beckel et al., 2011).

Table 4.2 shows a summary of the treatment plant surveyed and the efficiency of the different treatment systems they employed. Factory A employed coagulation together with activated sludge treatment and achieved removal of TSS, COD, BOD and PhACs of 79%, 42%, 22% and 21% respectively. The main disadvantage of this system was poor floc formation and poor quality of the treated effluent. The use of polymers to improve on the formation of flocs resulted in increased operational costs. Factory B used coagulation/ flocculation treatment followed by activated charcoal filtration which achieved an average percentage removal for TSS, COD, BOD and PhACs of 84%, 38%, 8% and 46% respectively. This system faced a challenge of high usage of chemicals and

high maintenance costs. Factory C, which proved to be the most efficient in parameter removal, used a combination of coagulation, dissolved air floatation, ozonation and activated carbon filtration and achieved an average removal for TSS, COD, BOD and PhACs of 86%, 58%, 17% and 74% respectively. However, this system was expensive to operate and maintain.

Table 4.2: Pharmacutical plants surveyed and their treatment systems

	TREATMENT SYSTEM EMPLOYED	PARAMETER REMOVAL (%)	CHALLENGES FACED
A.	Flow equalization Coagulation/ flocculation Activated Sludge treatment	TSS: 79 COD: 42 BOD: 22 PhACs: ≈21	i. Poor floc formation ii. Increased cost due to use of polymers iii. Poor quality of treated effluent
B.	Flow equalization Coagulation/ flocculation Activated charcoal filtration	TSS: 84 COD: 38 BOD: 8 PhACs: ≈46	i. High doses of chemical used ii. Short service life of activated carbon filters iii. High operation and maintenance costs
C.	Flow equalization Coagulation/ flocculation Ozonation Dissolved air floatation Activated carbon filtration	TSS: 86 COD: 58 BOD: 17 PhACs: ≈74	i. High chemical dosage ii. High volume of sludge produced iii. High operation and maintenance cost of equipment

CHAPTER FIVE

OPTIMIZATION OF COAGULATION/ FLOCCULATION PROCESSES FOR PHARMACEUTICAL WASTEWATER TREATMENT

In coagulation/ flocculation treatment, the determination of optimum conditions of operation is important because each coagulant has a specific range at which maximum removal is achieved. The variables of importance include the coagulant dosage and the pH. These variables are important because if adjusted into the optimum range, coagulation treatment may provide good organic pollutants removal (Sahu & Chaudhari, 2013). The results obtained from optimization tests are presented in Appendix III.

5.1 Determination of the optimum coagulant dosage

Determination of the optimum coagulant dosage is important in coagulation/ flocculation treatment because each coagulant has its optimum dosage range and the insufficient or excessive dosing of coagulants will result in poor treatment efficiency. This investigation was undertaken for ferric sulfate and PAC coagulants. The amount of coagulant was varied in jar tests at the samples' natural pH, while keeping other conditions such as mixing rate and time constant. The efficiency was determined by observing the removal rates for TSS, turbidity, COD and TOC. The percentage removal for these parameters by ferric sulfate and PAC are represented in Figure 5.1 and Figure 5.2 respectively.

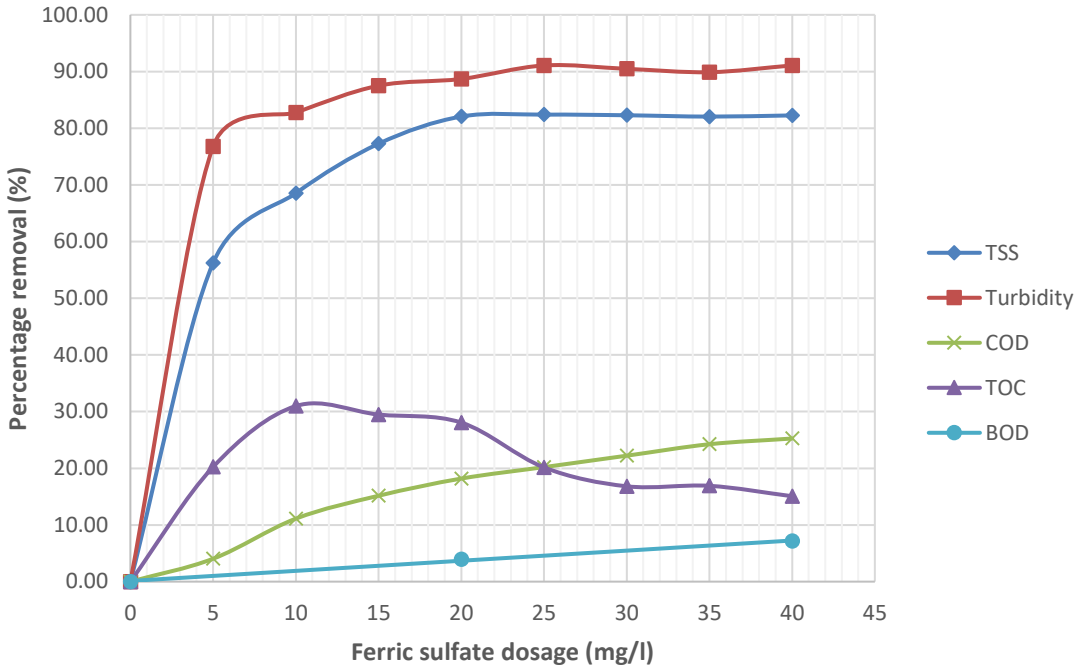


Figure 5.1: Effect of Ferric sulfate dosage on percentage removal of TSS, Turbidity, COD, TOC and BOD

The initial concentration of the observed parameters of the sample wastewater were 96 mg/l of TSS, 84 NTU of turbidity, 396 mg/l of COD, 120.1 mg/l of TOC and 273.2 mg/l of BOD. Figure 5.1 shows that as the ferric sulfate dosage increased, the percentage removal of these parameters also increased. TSS and turbidity removal was the most significant, attaining a maximum removal percentage of 91.07% and 82.39% at a dosage of 25 mg/l of ferric sulfate. A further increase in the coagulant dosage did not produce a major difference in the percentage removal of these two parameters. A study carried out by Saleem (2007) on coagulation pre-treatment of pharmaceutical wastewater using

ferrous sulfate, ferric chloride and alum showed that higher doses of coagulant did not result in significant improvement of the TSS and turbidity reduction and he attributed this to the inorganic nature of suspended solids in the wastewater.

The percentage removal of COD increased steadily as the coagulant dosage was increased from 5 mg/l to 40 mg/l, with the maximum removal being 25.25%. However, when considering percentage removal of TOC, there was a peak of 30.97% at a dosage of 10 mg/l, after which there was a decline in the removal as the dosage was increased. The BOD removal was very low at only 3.92% as the initial value was only reduced to 262.5 mg/l. This was expected because coagulation / flocculation process is not meant for BOD removal, as this is best achieved through biological treatment processes.

From these results, it is evident that the removal efficiencies for TSS, turbidity, COD, TOC and BOD differs greatly, however, a general trend as shown in Figure 5.1 is that as the dosage is increased the percentage removal of these parameters increases up to a certain optimum point. This trend shows that some of the parameters may be related. For instance, turbidity could be associated with suspended solids in the wastewater. Likewise, some organic compounds could be trapped in the suspended and colloidal matter such that their removal through the coagulation/ flocculation process resulted in small reduction of COD and TOC (Chaudhari et al., 2010; Ean, 2008)

In coagulation/ flocculation treatment, the main parameters of concern are TSS and turbidity, thus these were given priority in determination of the optimum coagulant dosage. Based on this, the dosage of 20 mg/l of ferric sulfate was picked as the optimum, where the residual TSS and turbidity was 17.23 mg/l and 9.5 NTU respectively, which translates to a removal of 82.06% and 88.7%. Even though the dosage of 25 mg/l yielded the maximum removal of TSS and turbidity, the value of 20 mg/l was chosen as the optimum because the difference between these two doses is insignificant at only 0.33% and 2.38% for the two parameters. This was done so as to avoid excessive dosing of the coagulant which reduces treatment costs and minimizes negative effects on the environment. In addition to this, there was significant drop in the value of TOC from 20 mg/l to 25 mg/l which make the latter unsuitable as an optimum point. At a dosage of 20 mg/l, the residual COD and TOC was 32.4 mg/l and 86.4 mg/l respectively, which are equivalent to a removal percentage of 18.18% and 28.06%.

The equilibrium chemistry of Fe (III) in water has been explained by considering:

- Five monomers; Fe^{3+}, $Fe(OH)^{2+}$, $Fe(OH)_2^{\bullet}$, $Fe(OH)_3$ (molecule) and $Fe(OH)_4^{\bullet}$
- A dimer and a trimer; $Fe_2(OH)_2^{4+}$, and $Fe_3(OH)_4^{5+}$
- A solid precipitate; $Fe(OH)_3$

In addition to this, there exists a range of dissolved polymeric species that have a medium and high molecular mass, during hydrolysis process, prior to the formation of precipitates.

Different hydrolysis products can cause different treatment performances (Jiang & Graham, 1998).

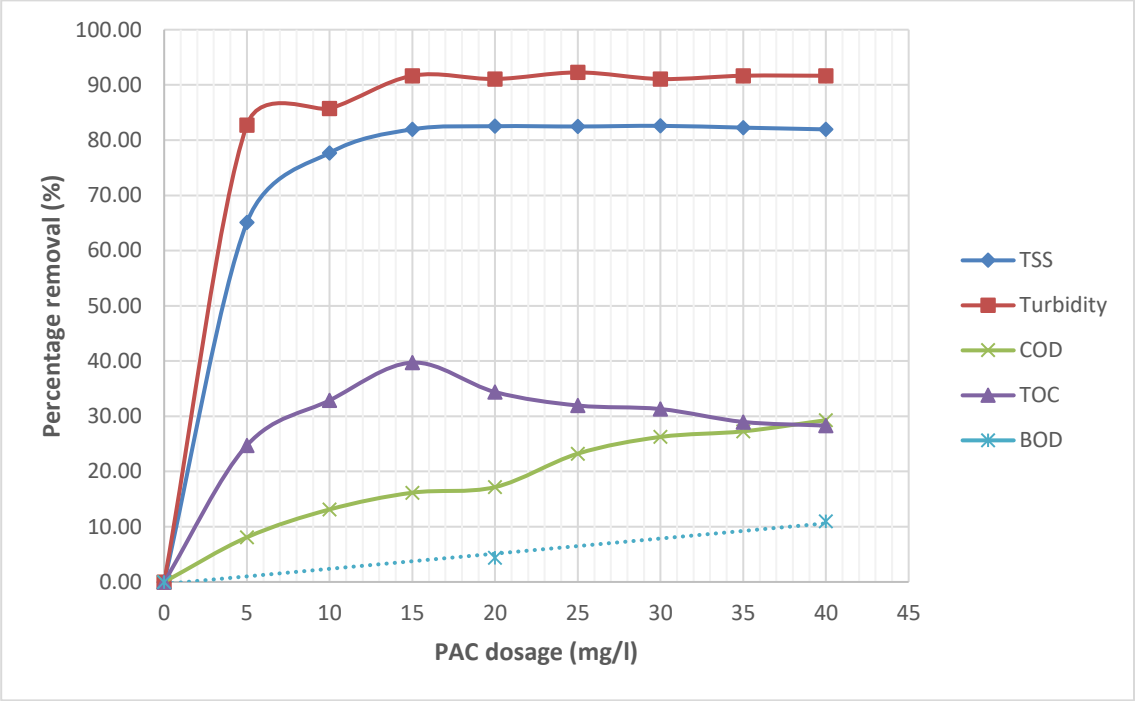


Figure 5.2: Effect of PAC coagulant dosage on percentage removal of TSS, Turbidity, COD, TOC and BOD

Figure 5.2 shows the effect of PAC dosage on the removal efficiencies of TSS, turbidity, COD, TOC and BOD. From the graph, it can be seen that there was sharp rise in the percentage removal of TSS and turbidity to 65.08% and 82.74% respectively at a coagulant dosage of 5 mg/l. A further increase in the dosage resulted in smaller increases in the percentage removal of the two parameters. The maximum removal for TSS was 82.59% at a dosage of 30 mg/l while that of turbidity was 92.26% at a dosage of 25 mg/l.

The percentage removal of COD had small increases gradually as the dosage was increased from 5 mg/l to 40 mg/l and achieved a maximum removal of 28.31%. The removal of TOC increased gradually to a maximum of 39.72% at a dosage of 15 mg/l, after which a further increase in the dosage resulted in a drop of percentage removal. The maximum BOD removal at a dosage of 40 mg/l was 10.5%.

The optimum dosage for PAC was chosen as 15 mg/l, which resulted in a TSS of 17.32 mg/l, turbidity of 8 NTU, COD of 33.2 mg/l, TOC of 72.4 mg/l and BOD of 261.2 mg/l. These values translate to a percentage removal of 82.0%, 91.7%, 16.16%, 39.72% and 4.39% respectively. The dosage of 15 mg/l of PAC was picked as the optimum because beyond this point, the quality of the treated samples did not show an improvement significant enough to warrant the increased amount of coagulant used.

PAC was originally produced as a result of efforts to improve the efficiency of the coagulation process, through partial polymerization of aluminium solutions. PAC is similar to alum, which is the most widely used aluminium salt in the treatment of wastewater, but contains high charge polymeric aluminum species as well as the monomer. An Al_{13} with the formula $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$ has been shown to dominate the species (Sahu & Chaudhari, 2013). Thus, better performance by PAC could be attributed to the presence of pre-formed polymeric species that have a high cationic

charge and medium to high molecular weight, which are able to persist long enough to enhance the rate of colloid charge neutralization (Jiang & Graham, 1998).

5.2 Determination of the optimum pH

The effect of pH on the percentage removal of TSS, turbidity, TOC and COD for ferric sulfate and PAC coagulants at their previously determined optimum dosages is shown in Figure 5.3 and Figure 5.4 respectively. There is an interrelationship between pH and the type of metal hydroxide formed and this in turn determines the charge on the hydrous oxide complex. The pH also affects the solubility of the metal ions. Thus, a drop in pH can result in high solubility of the metal ions, thereby affecting the efficiency of the treatment.

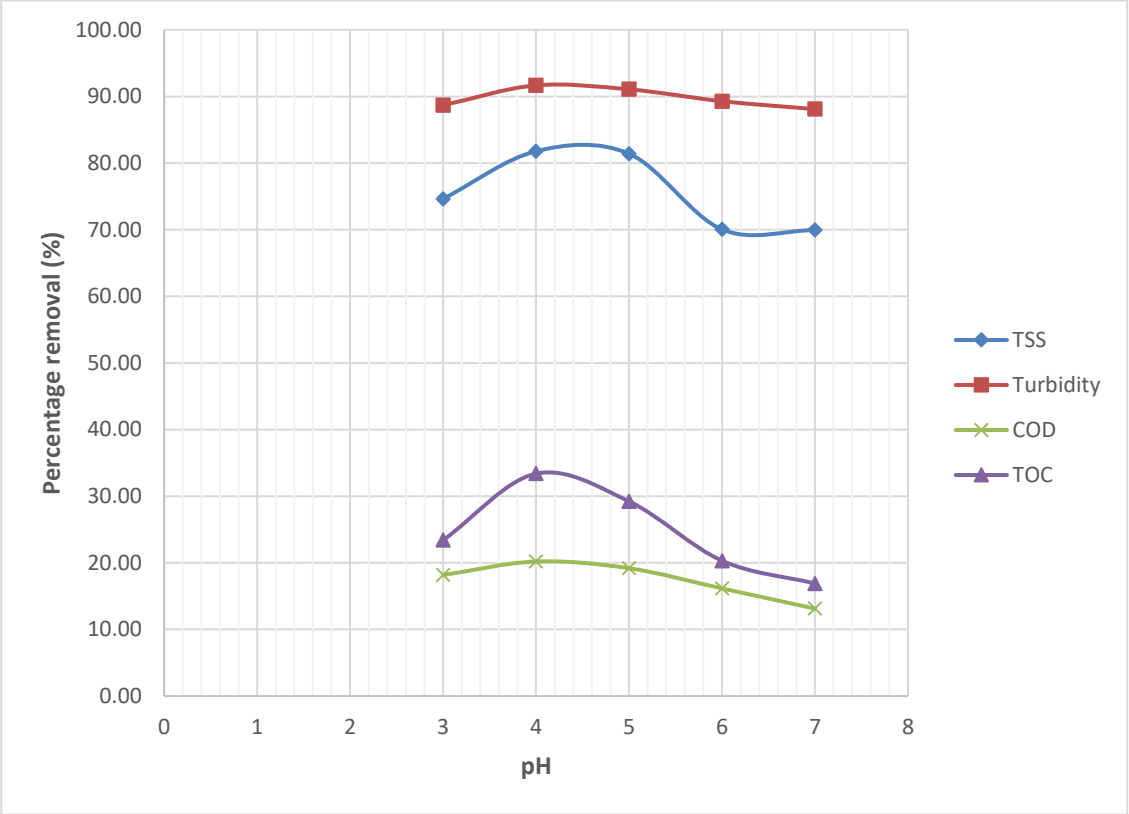


Figure 5.3: Effect of pH on percentage of TSS, turbidity, COD and TOC removal for ferric sulfate

For this study the pH range of 3-8 was chosen, and for ferric sulfate a constant coagulant dosage of 20 mg/l which had previously been determined as the optimum was used. With the use of ferric sulfate, the maximum percentage removal of TSS, which was 81.78% to 81.41%, was achieved between pH 4.0- 5.0. At this optimum point, percentage removal for turbidity was 91.67% to 91.07%, COD was 20.20% to 19.19% and TOC was 33.39% to 29.23%. After this point, a further raise in the pH value resulted in reduced percentage removal of TSS, COD and TOC, but its effect on turbidity was slight. Treatment at a pH

higher than 7.0 resulted in solid particles that remained dispersed in the water and would not settle. The optimum pH range for ferric sulfate is fairly acidic and may not favor subsequent biological treatment without further pH adjustment.

The mechanisms of coagulation by ferric sulfate is mainly by charge neutralization and sweep coagulation. Charge neutralization occur at low pH (<6.5) and generally requires less coagulant dosage and produces a relatively lower amount of sludge. During charge neutralization, overdosing the coagulant could result in colloid restabilization. Sweep coagulation occurs near neutral pH and has better removal performance of trace impurities. Due to hydrolysis, Fe^{3+} ions do not exist in solution around pH 6-8 and therefore hydrolysis products are responsible for the destabilization of colloids. At the pH of the pharmaceutical wastewater of 6.62, the addition of the ferric sulfate resulted in rapid and uncontrolled hydrolysis and rapid precipitation. The nature of the coagulating species cannot be controlled in this case (Jiang & Graham, 1998).

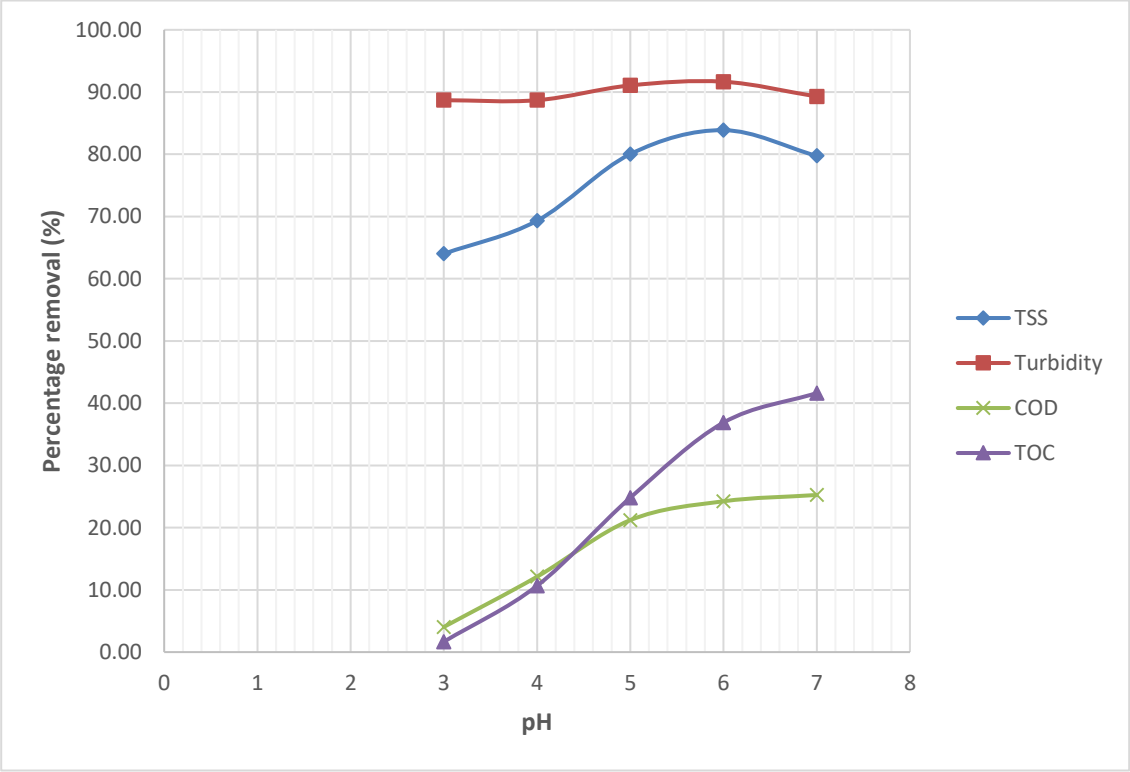


Figure 5.4: Effect of pH on the removal percentage of TSS, turbidity, COD and TOC for PAC

Figure 5.4 shows the percentage of TSS, turbidity, COD and TOC removal for PAC. These values were obtained for the pH range of 3- 8 at a constant coagulant dosage of 15 mg/l, which had been determined as the optimum dosage for the coagulant. Based on the percentage removal of TSS and turbidity, it is evident that PAC achieved the best results at a pH range of 5.0-6.5. This yielded a percentage removal of 79.74% to 83.88% for TSS, 89.29% to 91.70% for turbidity. At this pH range, the removal of COD ranged from 21.21% to 25.25%, while that of TOC ranged from 24.81% to 41.63%. A further increase

in pH resulted in a decline in removal of TSS, turbidity and COD, while treatment at pH values higher than 8.0 did not produce any settleable solids.

From these results, is clear that PAC resulted in better treatment efficiency compared to ferric sulfate. Previous research has proven PAC to be more efficient in lower dosages, in wider pH, temperature and colloids concentration ranges compared to un-polymerized metal coagulant (Sahu & Chaudhari, 2013). The experiments carried out corroborated the efficiency of PAC.

5.3 Summary of coagulation/ flocculation process of pharmaceutical wastewater

This chapter covered the optimization of coagulation treatment of pharmaceutical effluent using ferric sulfate and PAC. The optimum coagulant dosage for ferric sulfate was determined as 20 mg/l while that of PAC was 15 mg/l. At these dosages, the highest removal percentages of parameters under observation were obtained at pH 4.0- 5.0 for ferric sulfate and pH 5.0- 6.5 for PAC. The results for percentage removal of parameters at optimum conditions are as summarized in Table 5.1.

Table 5.1: Percentage of parameters removal at optimum conditions

	Ferric Sulfate	**PAC**
Optimum dosage	20 mg/l	15 mg/l
Optimum pH	4.0- 5.0	5.0- 6.5
TSS % removal	81.78	83.88
Turbidity % removal	91.67	91.70
COD % removal	20.20	25.25
TOC % removal	33.39	41.63

At optimum conditions, ferric sulfate achieved a maximum percentage removal for TSS, turbidity, COD and TOC of 81.78%, 91.67%, 20.20% and 33.39% respectively. Polyaluminium chloride had a maximum percentage removal TSS, turbidity, COD and TOC of 83.88%, 91.70%, 25.25% and 41.63% respectively. PAC proved to be more efficient compared to ferric sulfate as shown by the higher removal percentages for all the parameters, which it achieved at a lower coagulant dosage.

CHAPTER SIX

THE APPLICABILITY OF BENTONITE CLAY PRETREATMENT IN PHARMACEUTICAL WASTEWATER TREATMENT

In this study, bentonite clay was incorporated into the coagulation / flocculation treatment as a coagulant aid and at the same time taking advantage of it adsorptive properties to remove PhACs from pharmaceutical effluent. Results from treatment of the samples with bentonite clay together with ferric sulfate and PAC coagulants were compared to those of treatment using the coagulants only as discussed in Chapter 5.

6.1 Bentonite clay properties

Table 6.1: Chemical composition of bentonite

Oxide	CaO	MgO	K_2O	Na_2O	Al_2O_3	SiO_2	Fe_2O_3	LOI
Analysis	1.30%	2.70%	0.30%	2.43%	20.69%	69.56%	4.85%	4.80
Trace Minerals	Feldspar, Quartz, Calcite, Gypsum							

Source: American Colloid Company, 2001

Bentonites are generally classified depending on their dominant exchangeable interlayer cation, either sodium or calcium. Table 6.1 shows the chemical composition of the

bentonite clay used for this study. This table shows that the bentonite used was sodium bentonite because the sodium oxide was predominant with a percentage of 2.43% compared to that of Calcium oxide which was 1.30%. Sodium bentonite allows a large amount of water to be absorbed into the interlayer which results in a higher swelling capacity compared to calcium bentonite. Sodium bentonite has an exceptionally high surface area (one gram of bentonite produces a surface area of 750 m^2 when fully dispersed) due to its uniformly broad and flat platelets (CETCO, 2013; Clem & Doehler, 1963). These properties of sodium bentonite make it a good medium of adsorption and at the same time allows it to act as a coagulant aid by adding weight to slow settling flocs. The bentonite used had a specific gravity of 2.6 and was insoluble in water. It had a light brown color (tan) and a soft slippery texture. The pH of the bentonite was 8.5- 10.5 at 2% solids and it had a dry particle size of 74 microns. The chemical formula of the bentonite as provided by the manufacturer is as shown in Formula 6.1 (American Colloid Company, 2001).

Dioctahedral smectite, and expanding layer silicate:

$$(Na,Ca)_{0.33}(Al_{1.67}Mg_{0.33})Si_4O_{10}(OH)_2nH_2O$$ ……..Formula 6.1

Research has shown that many types of organic material are adsorbed by montmorillonite. This adsorption is mainly influenced by type and composition of the organic material, the organic concentration, pH and the presence or absence of water in the system (Clem & Doehler, 1963).

6.2 An evaluation of bentonite clay application in pharmaceutical wastewater pretreatment

The application of bentonite clay in the pretreatment of pharmaceutical wastewater began with determining the suitable amount of bentonite to be used in order to produce the most efficient treatment. This process of optimization of bentonite is discussed under subheading 6.2.1. The optimum bentonite dosage was then applied to samples which were treated with varying coagulant dosages of ferric sulfate and PAC to determine the effect of bentonite on the treatment efficiency as discussed in subheading 6.2.2.

6.2.1 Optimization of bentonite for wastewater pretreatment

The samples were treated with bentonite dosages varying from 2.5 g/l to 25 g/l. Table 6.2 shows how these dosages affected the pH of the samples. Following the addition of bentonite, coagulation/ flocculation was carried out at the optimum conditions of pH and coagulant dosage previously established for ferric sulfate and PAC. The data collected from these tests is presented in Appendix IV.

Table 6.2: The effect of varying bentonite dosages on sample pH

Bentonite dosage (g/l)	0.0	2.5	5.0	7.5	10.0	12.5	15.0	17.5	20.0
pH	6.61	8.83	9.98	10.01	10.23	10.28	10.38	10.25	10.41

Table 6.2 shows that the pH of the samples was raised with an increase of bentonite dosage. This was expected because the pH of bentonite was previously determined to be basic, ranging between 8.5 and 10.5 at 2% solids. The initial pH of the samples was 6.61 and it raised steadily with increase of bentonite to a maximum of 10.41.

The results for different parameter removal obtained after the coagulation/ flocculation procedures are represented in Figure 6.1 and Figure 6.2.

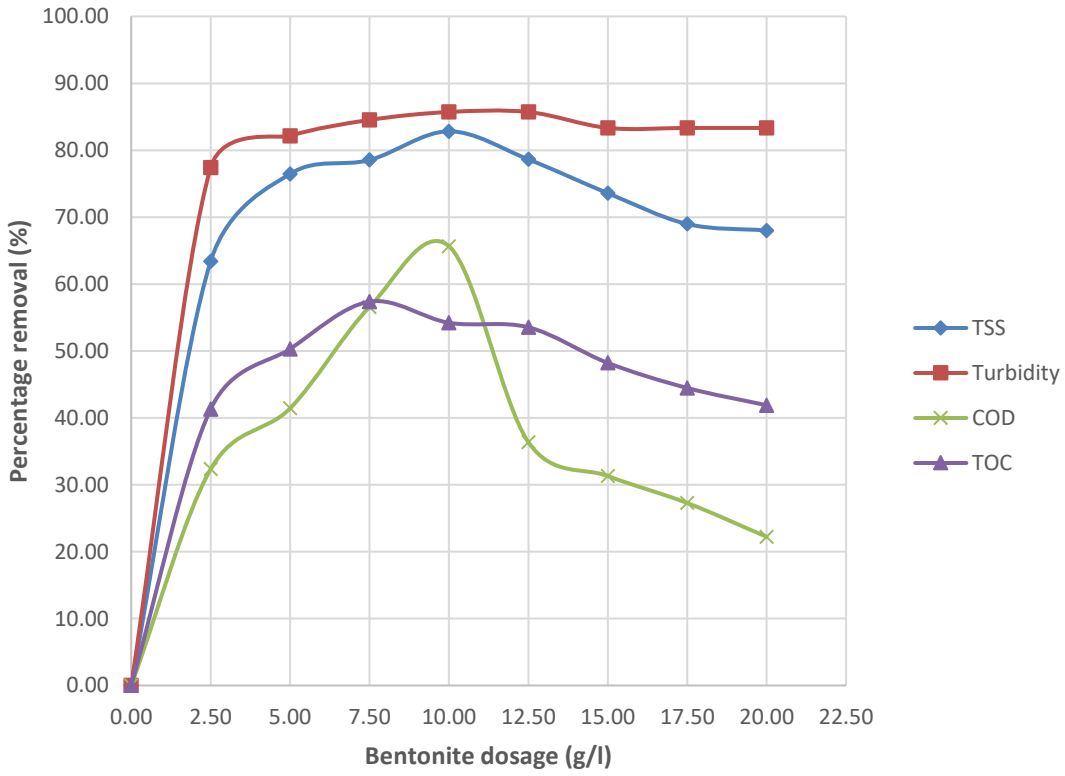


Figure 6.1: Effect of bentonite dosage on percentage parameter removal for ferric sulfate

Figure 6.1 represents results obtained after samples were pretreated with varying amounts of bentonite which was followed by coagulation with 20 mg/l of ferric sulfate at a pH of 4.0- 5.0. The percentage removal of TSS and turbidity increased greatly to 63.39% and 77.38% respectively, following the initial treatment with 2.50 g/l of bentonite. Higher doses of bentonite resulted in smaller increases in TSS and turbidity removal, achieving a maximum of 82.82% and 85.71% respectively at a dosage of 10.00 g/l. Bentonite dosages higher than 10.00 g/l resulted in a reduced percentage removal of TSS, COD and TOC. With these higher doses, the suspended solids in the samples did not agglomerate and required an increase in coagulant for complete flocculation to take place. Percentage removal of COD increased from 2.50 g/l to 10.00 g/l, with a peak of 65.66%. TOC had the highest percentage removal of 57.37% at a dosage of 7.50 g/l. Apart from TOC, all parameters of interest had their peak percentage removal at a bentonite dosage of 10.00 g/l, hence this was taken as the optimum for use with ferric sulfate.

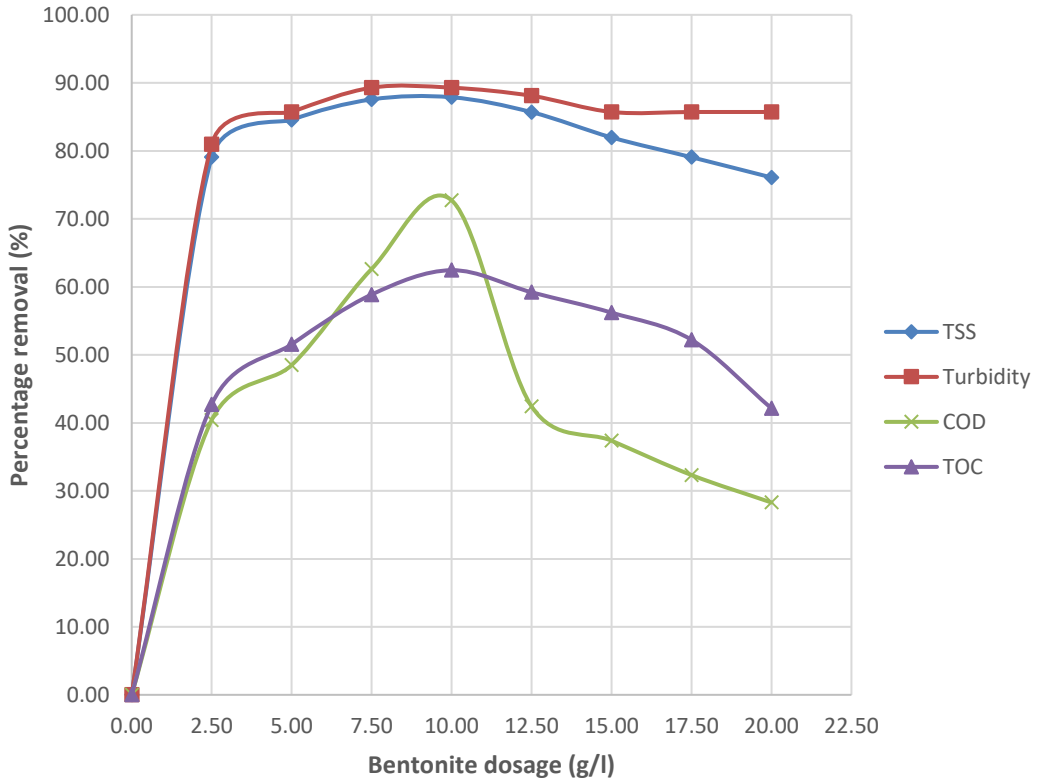


Figure 6.2: Effect of bentonite dosage on percentage parameter removal for PAC

From Figure 6.2 representing optimization of bentonite dosage using PAC, it was observed that treatment with the initial amount of 2.50 g/l resulted in a sharp increase in the percentage removal of TSS and turbidity to 79.07% and 80.95% respectively. A further increase in the bentonite dosage to 10.00 g/l resulted in smaller increases in the percentage removal of these two parameters, and attained a peak removal of 87.88% and 89.29% for TSS and turbidity respectively. This increase could be attributed to increased density of flocs formed and effective adsorption of organic matter to the increasing

surface area of the bentonite available (Bourliva et al., 2010). Bentonite dosages higher than 10.00 g/l caused a notable drop in the removal of TSS while the drop in turbidity removal was slight. This was because excess bentonite was left in suspension and needed addition coagulant to be removed. Percentage removal of COD had large increments from 2.50 g/l to 10 g/l, with a peak of 72.73%. Higher doses of bentonite caused a drastic drop in COD removal, with 28.28% as the lowest removal at a 20 g/l bentonite dosage. TOC had the highest percentage removal of 64.45% at a dosage of 10.00 g/l, after which there was a gradual drop in its removal with an increase of bentonite. From these trials, the amount of 10.00 g/l was similarly found to be the optimum dosage of bentonite for use with PAC as this was the point at which all parameters had a maximum removal percentage.

6.2.2 The effect of bentonite on the removal of typical parameters

Following the optimization of pH and bentonite dosage, the treatment assessment illustrated in Figure 3.7 was carried out using jar tests. This section discusses the results from this setup and compares it to that of treatment using chemical coagulants without pretreatment with bentonite, which is illustrated in Figure 3.6, so as to determine the advantages of using bentonite in pretreatment of pharmaceutical wastewater. The parameters assessed to measure the performance of bentonite pretreatment before coagulation with regard to ferric sulfate or PAC are TSS, turbidity, COD, TOC and BOD. Figure 6.3 shows the removal of parameters when ferric sulfate was used together with

bentonite clay pre-treatment, while Figure 6.4 compares these results with those obtained using ferric sulfate by only.

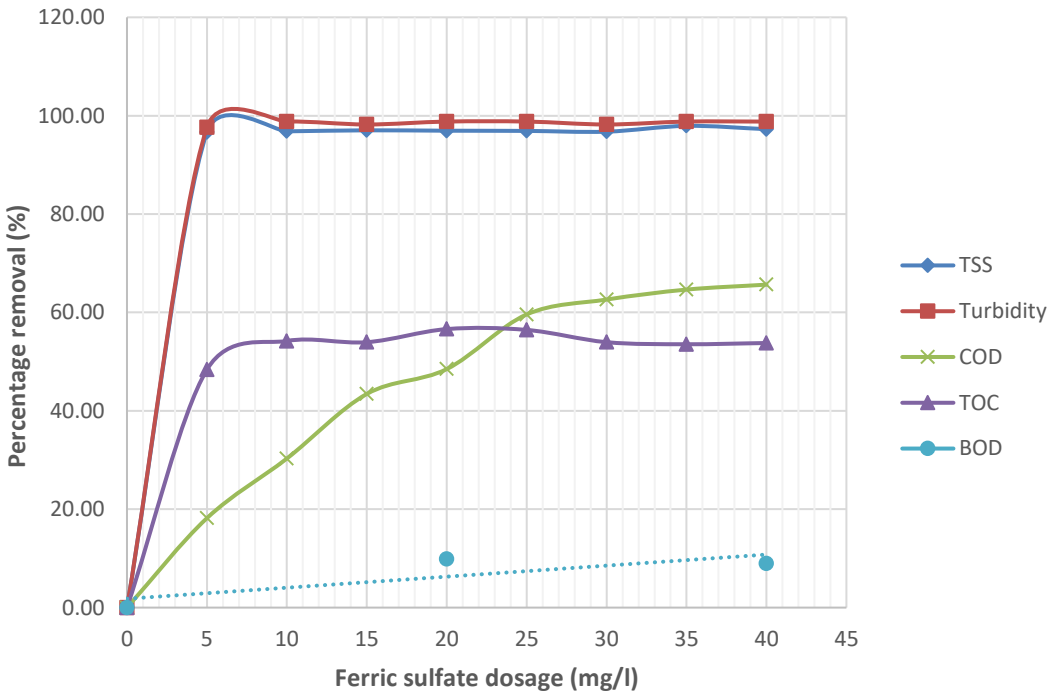


Figure 6.3: Percentage removal of TSS, turbidity, COD, TOC and BOD using ferric sulfate with bentonite clay pre-treatment

From Figure 6.3, an initial ferric sulfate dosage of 5 mg/l after the sample had been pretreated with 10.00 g/l of bentonite resulted in a TSS and turbidity removal of 96.67% and 97.62% respectively. A coagulant dosage of 10 mg/l increased these values to 96.82% and 98.81, after which subsequent increases in dosage produced fairly similar results in the percentage removal. The percentage removal of COD continued to rise gradually with

an increase in ferric sulfate dosage up to a maximum of 65.66% at 40 mg/l. TOC removal with the initial dosage of coagulant was 48.38%, which was followed by 54.08% at a dosage of 10 mg/l. Increases in the coagulant doses resulted in smaller increases in the percentage removal, until a maximum of 56.62% was achieved at 20 mg/l. BOD removal was very low with a dosage of 20 mg/l yielding a maximum of 9.88%. From this results, the optimum dosage for ferric sulfate was 10 mg/l, as this was the point at which TSS, turbidity and TOC had the highest removals. COD removal was not taken into account because of the high dosages of ferric sulfate required to remove only a small amount of COD. Likewise, BOD removal was not considered in determining the optimum dosage. This optimum dosage was a reduction by half from the 20 mg/l that was obtained previously by using the coagulant by itself. At this optimum point, the percentage removals for TSS, turbidity, COD, TOC and BOD was 96.82%, 98.81%, 30.30%, 54.20% and 4.00% respectively.

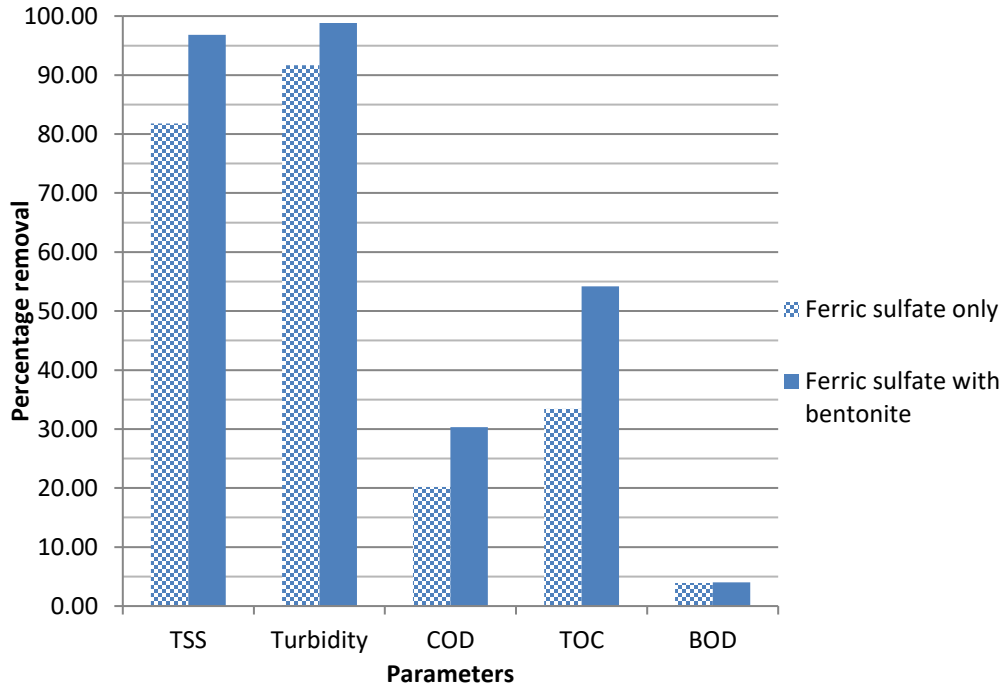


Figure 6.4: Effect of bentonite clay pre-treatment on removal of parameters using ferric sulfate coagulant

Figure 6.4 compares the removal percentages obtained from treatment using ferric sulfate with that from using ferric sulfate with bentonite clay pretreatment at their optimum points. This figure shows that there was an improvement in the percentage removal of TSS, turbidity, COD and TOC of 15.04%, 7.14%, 10.10% and 20.81% respectively. This improvement could be attributed to bentonite particles increasing the opportunity for particle collusion and joining small floc during the coagulation/ flocculation process thus improving the removal of suspended solids (Abdelaal, 2004). In addition to this, bentonite

particles act as nuclei for the adsorption of organic compounds from wastewater, resulting in a decrease in the amount of COD and TOC in the treated effluent.

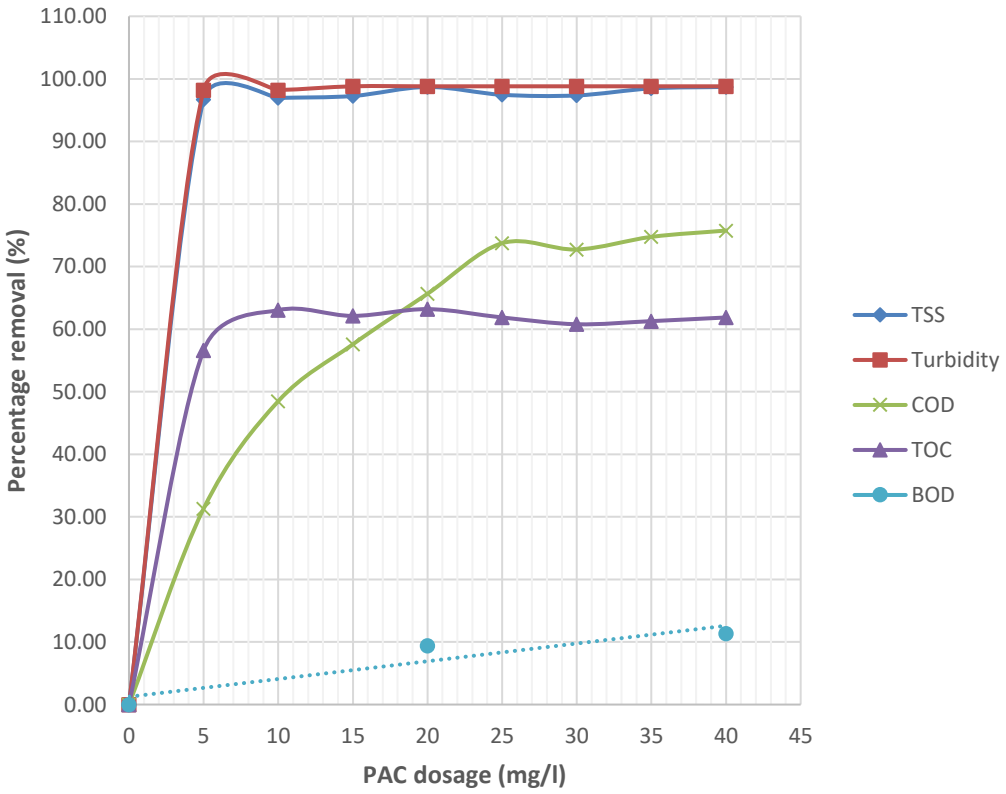


Figure 6.5: Percentage removal of TSS, turbidity, COD, TOC and BOD using PAC with bentonite clay pre-treatment

Figure 6.5 shows the percentage removal for the parameters with the use of PAC coagulant together with bentonite clay pre-treatment. PAC dosage of 10 mg/l was taken as the optimum for use with bentonite as it achieved the highest removals for TSS,

turbidity, and TOC which were 96.96%, 98.21% and 63.03% respectively. At this dosage COD and BOD removal were 48.48%, and 4.00% respectively. This optimum coagulant dosage was a reduction from that obtained from using PAC without bentonite pre-treatment, which was 15 mg/l. As was the case with ferric sulfate, increase in the coagulant dosage beyond the optimum point did not result in a significant change in the percentage removals for TSS, turbidity and TOC.

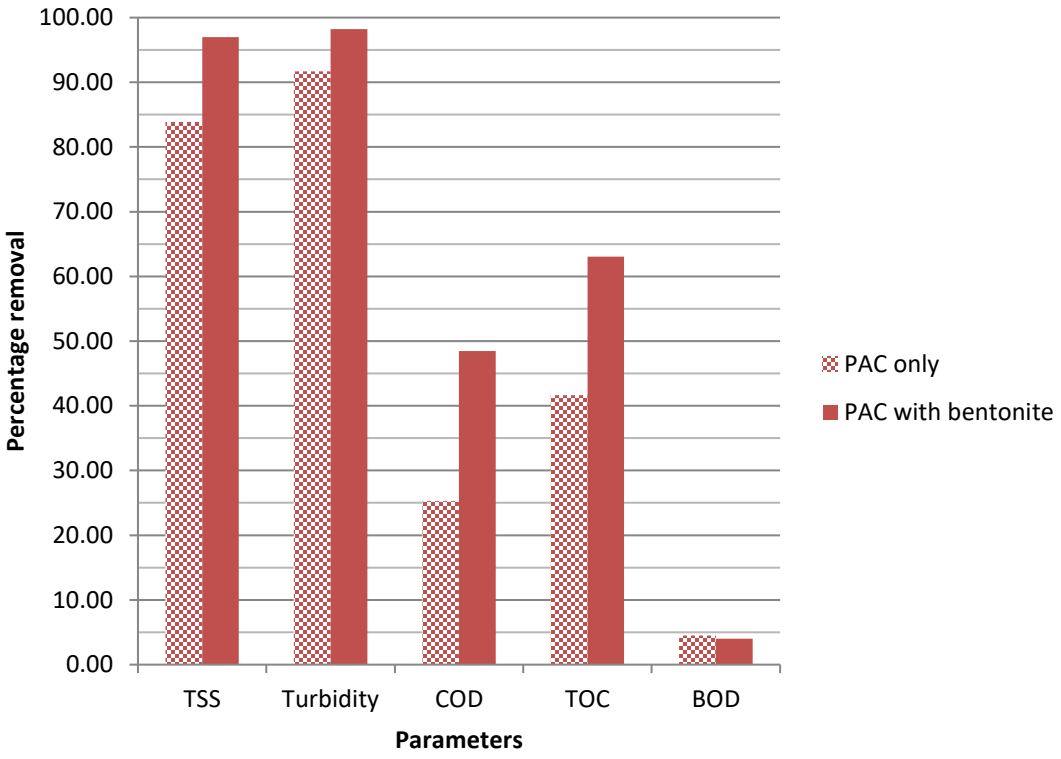


Figure 6.6: Effect of bentonite clay pre-treatment on removal of parameters using PAC

Figure 6.6 compares the maximum percentage removals obtained from coagulation/ flocculation treatment with PAC and that of PAC with bentonite clay pretreatment. Likewise there was an increase in the percentage removals in TSS, turbidity, COD and TOC by 13.08%, 6.51%, 23.23% and 21.40% respectively. The greater increase in the percentage removal of COD and TOC could be attributed to the effective adsorption of organic matter onto the large surface area of the clay. For all the experimental setups, the percentage removal of BOD was generally low, showing that these methods of treatment are not effective in BOD removal. Since this study is focusing on pre-treatment of pharmaceutical wastewater, it is therefore recommended that following the coagulation and bentonite treatment, the effluent should be taken to a biological treatment plant in order to reduce the BOD levels to the allowable limits for discharge.

The use of bentonite in the treatment process produced stronger flocs which settled faster compared to those produced from treatment without bentonite. This was because the bentonite particles added density and joined the small flocs together. However, the volume of the sludge produced from bentonite treatment was higher. Figure 6.7 shows the difference between the floc formation from treatment with and without bentonite clay after 30 minutes of settling.

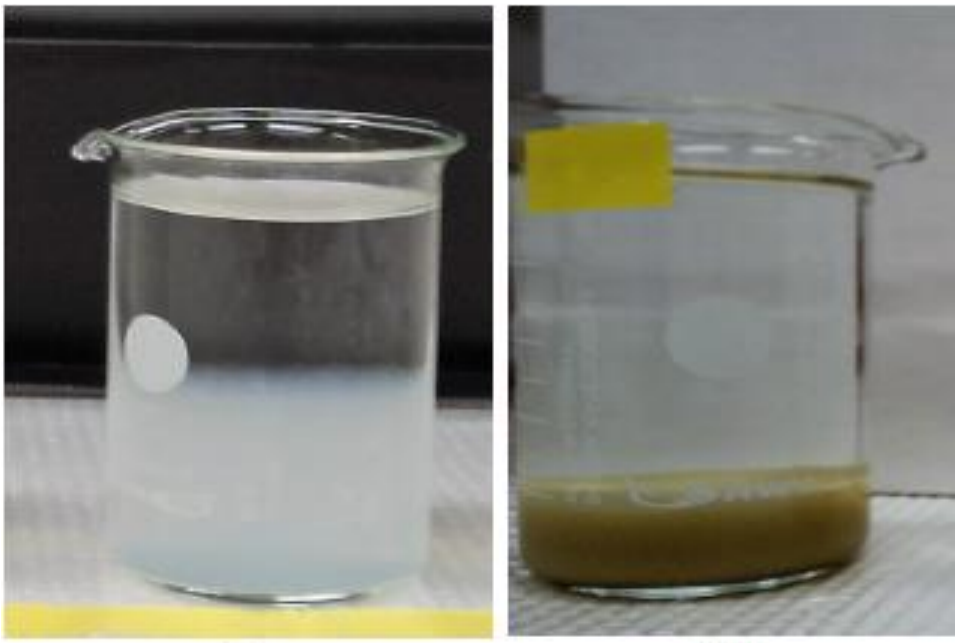


Figure 6.7: Floc formation from (a) treatment with PAC only (b) PAC with bentonite clay pre-treatment

6.2.3 The effect of bentonite on pharmaceutically active compounds

Calibration for the HPLC analysis was done using eight pharmaceutical compounds which were expected to be in the wastewater. Table 6.3 shows these pharmaceuticals and their retention times as determined during the calibration. Retention time is the time taken by a compound to pass through a chromatography column and is calculated as the time from injection of the compound into the column to the time it is detected. HPLC analysis of the sample wastewater showed that it contained ciprofloxacin, sulfamethoxazole, ibuprofen, metronidazole and trimethoprim. The molecular structure of these compounds is shown in Figure 6.8. HPLC analysis was likewise carried out on samples treated by chemical coagulation/ flocculation and by bentonite clay and the results are compared in Figure 6.9 and Figure 6.10.

Table 6.3: Retention times of pharmaceutical compounds used for calibration of the HPLC system

Pharmaceutical compound	Retention time (minutes)
Ciprofloxacin	4.801
Clotrimazole	0.417
Diclofenac	7.519
Sulfamethoxazole	5.395
Paracetamol	1.363
Ibuprofen	8.579
Trimethoprim	4.429
Metronidazole	7.021

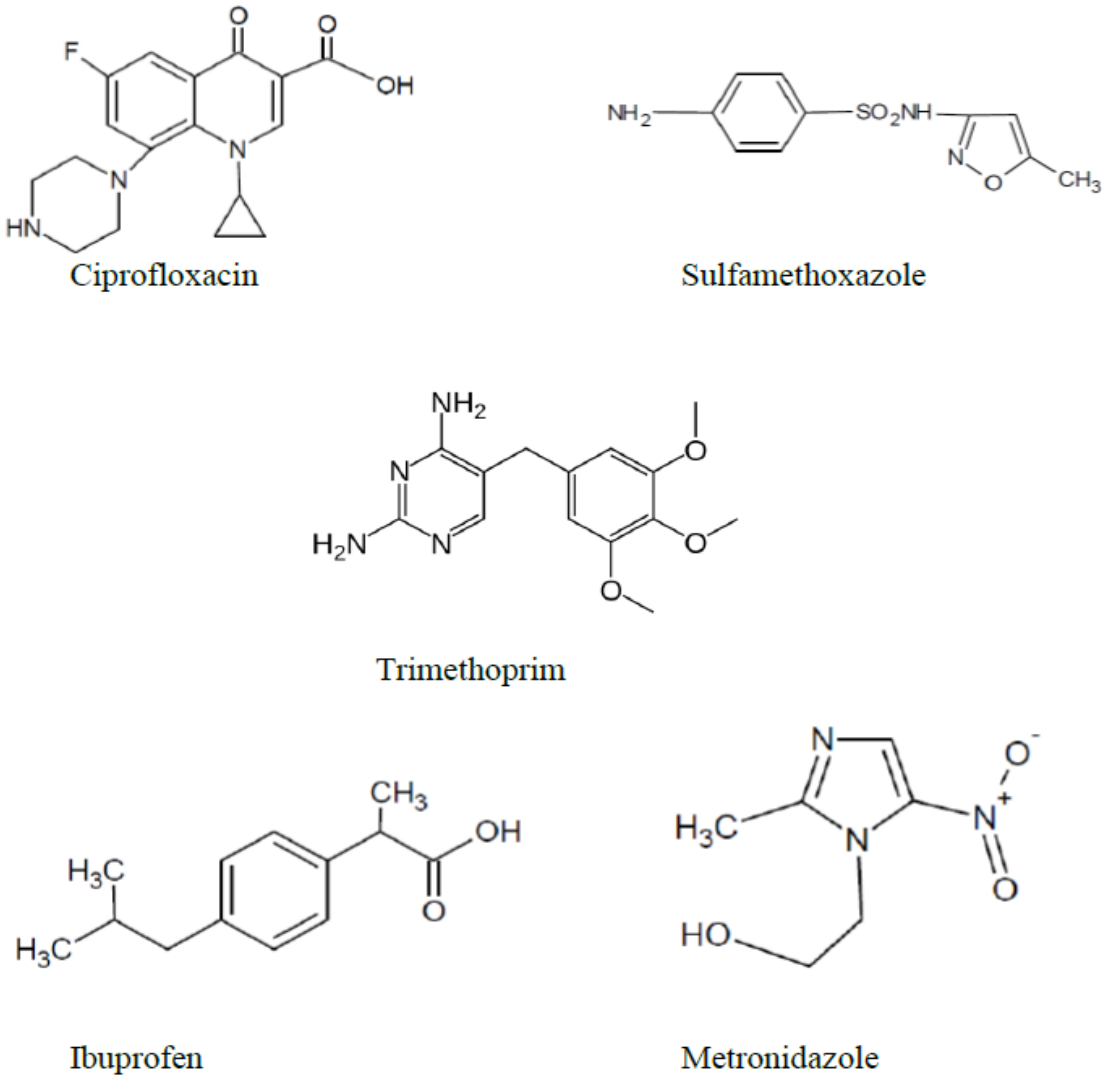


Figure 6.8: Molecular structures of ciprofloxacin, sulfamethoxazole, ibuprofen, metronidazole and trimethoprim (Otieno, 2011; Pohja, 2011)

Table 6.4: Concentration of PhACs in pharmaceutical wastewater sample

Pharmaceutical compound	Concentration (mg/l/)
Ciprofloxacin	14.98
Sulfamethoxazole	62.83
Ibuprofen	26.54
Metronidazole	29.92
Trimethoprim	208.30

Table 6.4 shows the concentration in mg/l of the PhACs which were present in the effluent. The highest concentration was of trimethoprim which was 208.30 mg/l. This compound is a synthetic antibiotic used to treat malaria, respiratory and urinary infections. It is sometimes used in combination with sulfamethoxazole to make it more effective because of the frequent development of its resistance (Medicinenet, 2015). Sulfamethoxazole, which is an anti-bacterial agent, had the second highest concentration of 62.83 mg/l. Metronidazole and Ibuprofen had a concentration of 29.92 mg/l and 26.54 mg/l respectively. Metronidazole is an antibiotic effective against anaerobic bacteria and some parasites which works by selectively blocking some of the functions within the bacteria cells and the parasites resulting in their death. Ibuprofen is a nonsteroidal anti-inflammatory drug used in the treatment of mild to moderate pain, fever and inflammation (Medicinenet, 2015). Ciprofloxacin, which is a quinolone antibiotic used to treat a variety of bacterial infections, had the lowest initial concentration of 14.98 mg/l.

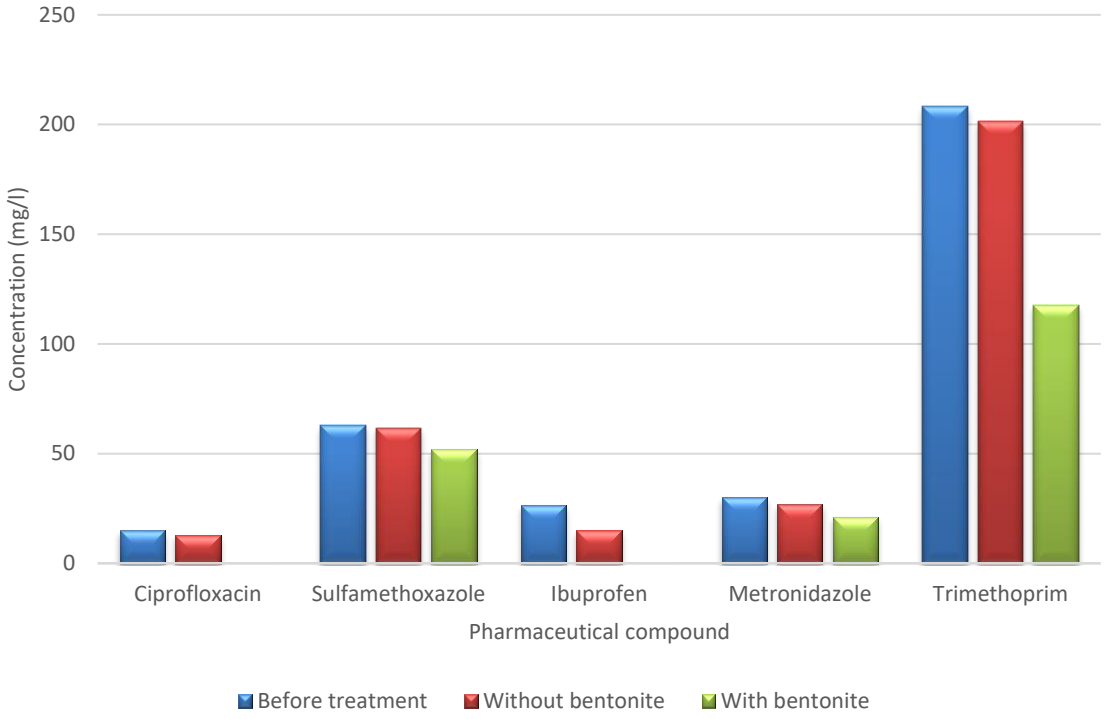


Figure 6.9: Removal of pharmaceutical compounds from wastewater using ferric sulfate coagulant.

As shown in Figure 6.9, treatment with ferric sulfate together with bentonite resulted in complete removal of ciprofloxacin and ibuprofen. Ciprofloxacin and ibuprofen had a percentage removal of 13.55% and 43.41% respectively when the coagulant was used without bentonite pretreatment. Sulfamethoxazole had a 1.77% reduction when the coagulant was used without bentonite and a 17.19% reduction with the use of bentonite. Metronidazole was reduced by 10.42% when the effluent was treated with ferric sulfate only and 29.31% when bentonite clay was used together with the coagulant.

Trimethoprim was reduced by 43.50% with the use of bentonite which was a significant improvement from the 3.26% reduction from use of ferric sulfate only.

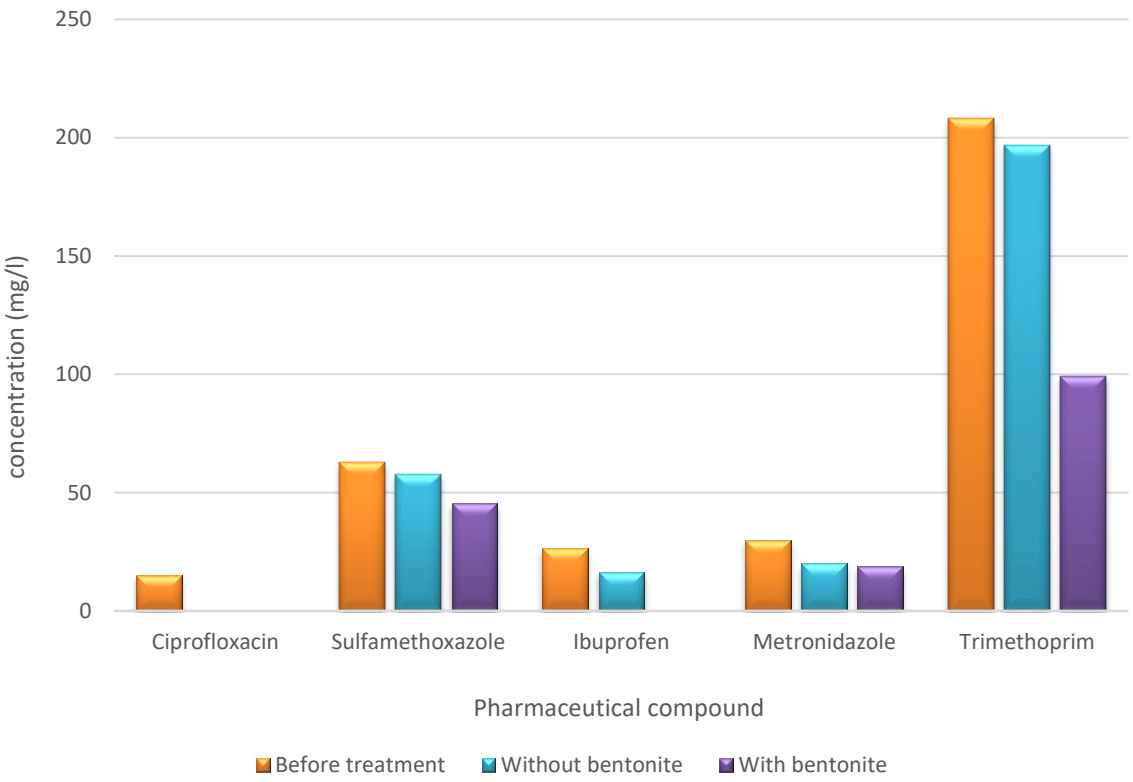


Figure 6.10: Removal of pharmaceutical compounds from wastewater using PAC coagulant.

As shown in Figure 6.10, treatment with bentonite clay resulted in complete removal of ciprofloxacin and ibuprofen. It was noted that ciprofloxacin was also eliminated from the wastewater by chemical coagulation only, without the use of bentonite. This implies that the ciprofloxacin present in the wastewater was in an insoluble form as suspended or colloidal matter. This result is supported by a study carried out on flocculation of

pharmaceutical wastewater which showed that 64.4% of the ciprofloxacin present in the wastewater was removed by the process of chemical coagulation (Pohja, 2011). Sulfamethoxazole and metronidazole had a maximum removal of 27.85% and 37.30% respectively after treatment with bentonite clay. Although there was some reduction in these two compounds, it was not clear whether it was statistically significant. Therefore, an analysis of variance on the two conditions (treatment with bentonite and treatment without bentonite) was carried out on sulfamethoxazole and metronidazole using excel spreadsheets and the results are presented in Table 6.5.

Table 6.5: Analysis of variance for removal of sulfamethoxazole and metronidazole

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
Sulfamethoxazole	3	165.95	55.31667	81.150533
Metronidazole	3	68.71	22.90333	37.328433
Before treatment	2	92.75	46.375	541.53405
Without bentonite	2	76.55	38.275	761.67045
With bentonite	2	65.36	32.68	320.045

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	1575.936	1	1575.936	66.617145	0.014681	18.512821
Columns	189.6447	2	94.82235	4.0082803	0.199669	19
Error	47.31323	2	23.65662			
Total	1812.894	5				

For this analysis, an Alpha value of 0.05 was used, and as seen from the table, the ‘P value’ of 0.1997 was larger than the alpha value indicating that there was no statistically significant difference between treatment with bentonite clay and treatment with coagulants only for these two compounds. This can further be shown by comparing the ‘F value’, which is the test statistic to ‘F critical’, which is the critical value for the statistic. In this case the ‘F value’ of 4.0083 is less than the ‘F critical’, 19.000 showing that there was no significant change. These results imply that although there was some reduction in the concentration of these two compounds, the difference of coagulation and treatment with bentonite clay was not significant. Trimethoprim had the highest initial concentration of 208.3 mg/l and was reduced by 52.42% after treatment with bentonite clay.

Treatment of the wastewater with chemical coagulants only, without the use of bentonite resulted in very little removal of pharmaceutical compounds, other than ciprofloxacin. This is because many pharmaceutical compounds are polar and have less tendency to sorb onto surfaces due to their low octanol-water partition coefficients (Basnyat, 2010). The option of using chemical coagulants only is therefore effective in the removal of insoluble, suspended and colloidal pharmaceutical compounds. The reduction of dissolved pharmaceuticals during the coagulation/ flocculation procedure could be due to adsorption of these onto the flocculated aggregates thus providing a mechanism of removal (Carballa et al., 1999).

The improved removal of pharmaceutical compounds with the use of bentonite clay can be attributed to the adsorption of these compounds onto the surface of the bentonite. This is supported by studies which show that pharmaceuticals and personal care products can be removed from the water environment depending on their ability to interact with naturally occurring clays, among other things (Carballa et al., 1999). The adsorption of organic material onto bentonite is similar to that of water, onto basal surfaces increasing the c-axis. Bentonite adsorbs water on its basal surfaces and this pries adjacent flakes apart resulting in an overall increase in its volume. This swelling is evident in an increase of the c-axis (the axis perpendicular to the plane of movement of the mineral strata) dimension of the clay (Clem & Doehler, 1963). This is shown in figure 6.11.

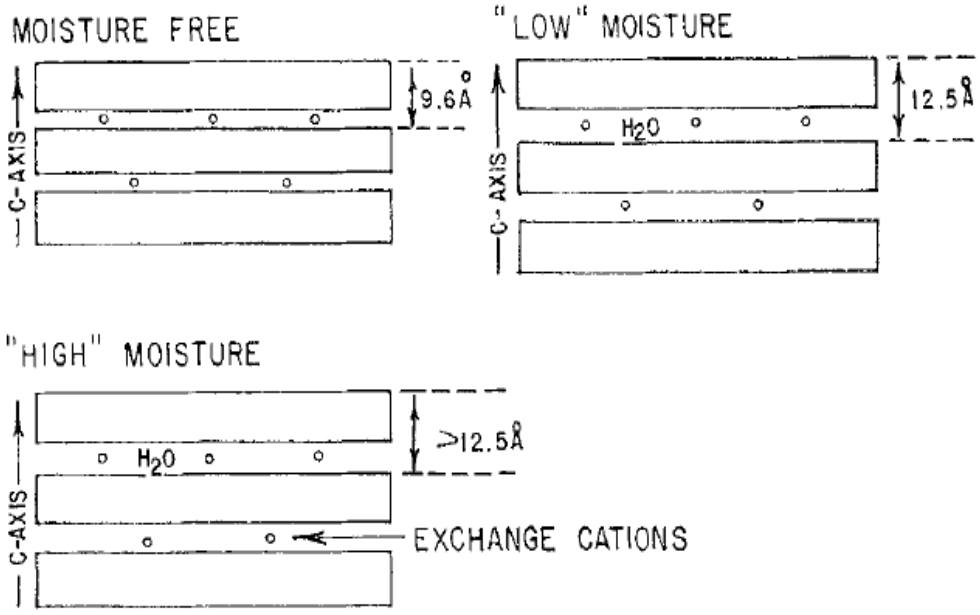


Figure 6.11: Sketch showing the swelling action of bentonite with increasing moisture content (Source: Clem & Doehler, 1963)

Previously reported data shows that once contaminants are microencapsulated and surrounded by a barrier of bentonite particles, it becomes non-reactive to external leaching (Abdelaal, 2004). This is important for safe handling and disposal of the sludge. These findings are important because the presence of pharmaceutical compounds in the environment has been a cause of great concern. For example, when antibiotics find their way into water bodies, they lead to mutation of bacteria into strains that are resistant to widely available antibiotics paving way to infections that are difficult to cure (Deegan et al., 2011; Otieno, 2011).

6.3 Summary of application of bentonite clay pretreatment in pharmaceutical wastewater

This study has shown that the use of bentonite clay in the coagulation pretreatment system improved the removal of COD and pharmaceutical compounds and also resulted in better formation and settling of floc as shown in Figure 6.7 . The advantage of the proposed pretreatment system is that it does not require major changes to the typical existing coagulation/ flocculation treatment systems illustrated in Figure 4.7, because all it needs is equipment used for bentonite dosing.

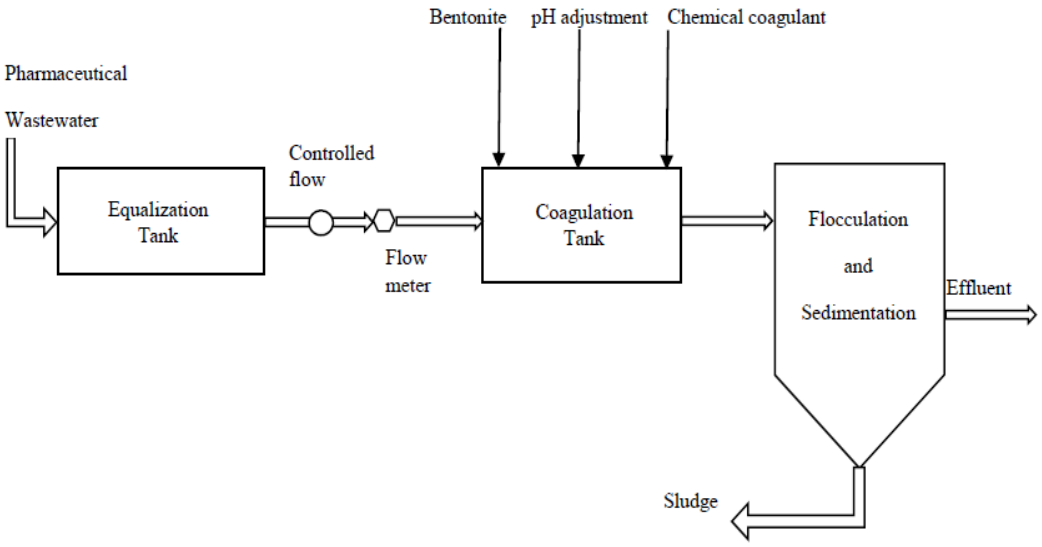


Figure 6.12: Proposed pharmaceutical wastewater pretreatment process using bentonite clay and chemical coagulation

As illustrated in Figure 6.12, the bentonite which is available in powder form can be added to the wastewater in the coagulation tank and mixed into the wastewater using the same mechanism used for rapid mixing during coagulation. After allowing the bentonite adequate time to react with any organic pollutants in the wastewater, the coagulation and flocculation process can then be carried out as usual.

Bentonite clay can be dispersed into the treatment tank manually with a measuring scoop, for smaller pharmaceutical plants, or continuously with a dry feed system (Aygun & Yilmaz, 2010). The major advantage of the dry feeder compared to feeding the bentonite as a slurry through a wet feeder is that it is more compact and less costly and it is able to

handle the bentonite delivered to the feeder in bulk (Nalco Chemical Company, 2009). Figure 6.13 shows some examples of dry feeders that could be used in dosing the bentonite.

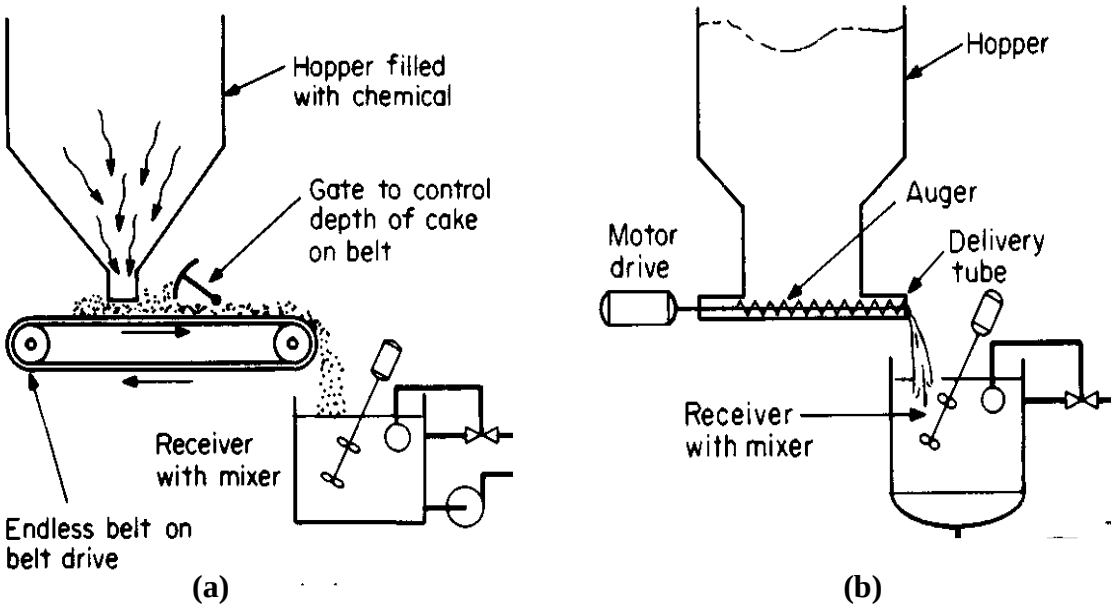


Figure 6.13: Examples of dry feeders (a) Feeder with a gate to control depth of bentonite. (b) Feeder with auger to deliver bentonite through tube. Source (Nalco Chemical Company, 2009)

Figure 6.13 (a) shows a feeder with an endless belt that has a gate to control the bentonite dosage rate. This rate could be adjusted by varying the speed of the belt drive or by varying the height of the control gate. The second example, Figure 6.13 (b), shows a feeder which uses an auger to deliver the bentonite through a tube. The rate of dosing in

this case is adjusted by varying the number of auger revolutions per minute (Nalco Chemical Company, 2009).

Table 6.6 and Table 6.7 show the summaries of multiple regression analysis correlating the bentonite dosages to the characteristics of wastewater in order to predict the amount of bentonite required for different types of pharmaceutical effluent. The data used for the regression analysis is presented in Appendix VI.

Table 6.6: Multiple regression analysis of bentonite dosage with four variables

Regression Statistics								
Multiple R	0.9592							
R Square	0.9201							
Adjusted R Square	0.8135							
Standard Error	1.2590							
Observations	8							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	4	54.7446	13.6861	8.6340	0.0538			
Residual	3	4.7554	1.5851					
Total	7	59.5						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-34.6674	19.3393	-1.7926	0.1709	-96.2136	26.8789	-96.2136	26.8789
TSS	0.1257	0.0325	3.8612	0.0307	0.0221	0.2292	0.0221	0.2292
COD	0.0591	0.0269	2.1968	0.1155	-0.0265	0.1447	-0.0265	0.1447
Turbidity	0.0259	0.0713	0.3628	0.7408	-0.2012	0.2529	-0.2012	0.2529
TOC	0.0409	0.0401	1.0207	0.3825	-0.0866	0.1684	-0.0866	0.1684

Table 6.6 shows the predictive analysis for bentonite dosage as the dependent variable using TSS, COD, turbidity and TOC as independent variables. The *'R square'* value of

0.9201 implies that these independent variables affected the outcome of the bentonite dosage by 92.01%. The value of '*Significance F'* was 0.0538, which was almost equal to 0.05 for a 95% confidence level meaning that the model was statistically significant. An inspection of the predictive values (*p-value*) of the independent variables was carried out in order to eliminate values that were 0.15 or higher since this meant that those values were not significant in prediction of the outcome. Going by this, turbidity and TOC, which had a '*p value'* of 0.7408 and 0.3825 respectively, were eliminated as independent variables since they did not significantly affect the bentonite dosage.

Table 6.7: Multiple regression analysis of bentonite dosage with two variables

Regression Statistics								
Multiple R	0.9445							
R Square	0.8922							
Adjusted R Square	0.8490							
Standard Error	1.1328							
Observations	8							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	2	53.0841	26.5420	20.6845	0.0038			
Residual	5	6.4159	1.2832					
Total	7	59.5						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	-24.2178	9.3902	-2.5791	0.0495	-48.3561	0.0796	48.3561	0.0796
TSS	0.1180	0.0284	4.1503	0.0089	0.0449	0.1910	0.0449	0.1910
COD	0.0516	0.0173	2.9852	0.0306	0.0072	0.0960	0.0072	0.0960

The regression analysis was carried out again, this time with TSS and COD as the only independent variables as shown in Table 6.7. The implications of these two variables on the outcome of the bentonite dosage reduced to 89.22% as indicated by the *'R square'* value. The value of '*Significance F'* reduced to 0.0038, which was well below 0.05 for a 95% confidence level. The predictive value of TSS and COD reduced from 0.0307 to 0.0089 and 0.1155 to 0.0306 respectively, showing an increase of their significance on the bentonite dosage. This analysis gave an intercept value of -24.2178, which was the constant for the resulting linear equation, with 0.1180 as the TSS coefficient and 0.0516 as the COD coefficient. These yielded equation 6.1 for the prediction of bentonite dosage.

$$Bentonite\ dosage\ \ (g/l) = -24.2178 + 0.1180(TSS) + 0.0516(COD) \quad \ldots\ldots (6.1)$$

To validate this equation, a sample with a TSS of 96.00 mg/l and a COD of 396.00 mg/l was used. The optimum bentonite dosage for this sample had previously been determined through laboratory testing to be 10 mg/l. Application of the predictive equation for bentonite dosing (Equation 6.1) for this sample is shown below.

$$Bentonite\ dosage\ \ (g/l) = -24.2178 + 0.1180(96.00) + 0.0516(396.00)$$

$$Bentonite\ dosage = 7.5\ g/l$$

The optimum bentonite dosage given by the equation was 7.5 g/l, which was slightly smaller than that obtained through laboratory testing. This variation could be attributed

to factors other than TSS and COD, which were not factored into the equation as indicated by the 'R square' value of the analysis. This implies that there may be a need to conduct trials within the factory to determine the optimum bentonite dosage before upscaling this pretreatment method to cater for other conditions specific to each factory.

The pharmaceutical factories reviewed in this study produced an average of 2000- 6000 liters of wastewater per day. This wastewater was stored in equalization tanks before being conveyed to treatment tanks in batches of approximately 24,000 liters. From the laboratory studies conducted, it was established that the optimal dosage of bentonite for pretreatment of this pharmaceutical effluent was 10 g/l. Assuming that this dosage is directly proportional to the amount of wastewater being treated, these values could be used to estimate the quantity of bentonite required (feed rate) for pretreatment in a factory setting.

$$Feed\ rate\ (kg/hr) = wastewater\ flow\ rate\ (l)\ x\ bentonite\ dosage(g/l) x\ 0.001$$

$$Feed\ rate\ (kg/hr) = 24{,}000\ x\ 10\ x\ 0.001$$

$$Feed\ rate = 240\ kgs/hr$$

The above calculation shows that 240kgs of bentonite will be required for pretreatment of 24,000 l of pharmaceutical effluent in one treatment session. The actual feeder output can be determined from the operating range of settings determined by the manufacturer.

The approximate volume of storage facilities required for the bentonite can be estimated using its specific gravity which was indicated in subheading 6.1 (Bentonite clay properties) as 2.6.

$$Volume\ of\ bentonite\ m^3 = \frac{mass\ of bentonite\ (kg)}{specific\ gravity\ x\ 1000}$$

$$Volume\ of\ bentonite\ m^3 = \frac{240}{2.6\ x\ 1000}$$

$$Volume\ of\ bentonite = 0.092\ m^3$$

Assuming that the maximum amount of wastewater produced per day is 6000 *l*

Total amount of wastewater produced in one week = (6000 *l* × 7 days) = 42,000 *l*

Amount of wastewater treated in one session is 24,000 *l*

Number of treatment sessions per week = $\frac{42000}{24000} = 1.75 \approx 2$

Volume of bentonite required for one month treatment = (0.092 m^3 × 8 *sessions per month)* = 0.736 m^3

Therefore, the hopper holding the bentonite could be designed with a capacity of approximately 0.8 cubic meters to cater for pretreatment for a period of one month.

The problems encountered by pharmaceutical plants in Kenya using coagulation treatment include high chemical usage, poor floc formation and poor settling. In addition to this, there is little removal of PhACs which pose a serious threat to the environment. Methods of treatment like ozonation and activated carbon filtration involve high operational and maintenance costs. This study has shown that application of bentonite clay pretreatment reduced the coagulant dosage required and resulted in formation of stronger floc which settled out readily. Bentonite also reduced the concentration of PhACs and other parameters in the effluent, thus improving its overall quality.

CHAPTER SEVEN

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

The purpose of this study was to investigate the use of bentonite clay in pretreatment of pharmaceutical industry wastewater, using ferric sulfate and PAC coagulants. From the research carried out:

- The pharmaceutical manufacturing factories in this study all fall under the formulation and drug mixing category and employ coagulation/ flocculation process to their wastewater as one of the pretreatment steps. Other forms of pretreatment include activated carbon filtration, ozonation, dissolved air floatation and activated sludge treatment.
- The pH of the samples collected ranged from 6.18-7.08 while COD, TOC and BOD ranged between 195.63 – 418.70 mg/l, 99.47 – 117.50 mg/l and 85.23 – 263.23 mg/l respectively. Based on previous studies on pharmaceutical effluent and available literature, the wastewater produced from Kenyan pharmaceutical factories is of low strength and the variations in its concentration and composition is due to variations in production processes.

- The existing pretreatment systems resulted in removal ranges of 79%- 86% for TSS, 38%- 58% for COD, 8%- 22% for BOD and 21%- 74% for PhACs. The main challenges faced by these systems are high usage of chemicals, high operation and maintenance costs and poor floc formation and settling in coagulation process. These findings show that there is a need to improve on the pretreatment systems especially with regard to removal of PhACs, which pose a serious threat to the environment.
- The optimum operation conditions for ferric sulfate was a pH of 4.0- 5.0 and a dosing of 20 mg/l, while that of PAC was pH of 5.0- 6.5 and a dosing of 15 mg/l. Ferric sulfate achieved maximum removal for TSS, turbidity, COD and TOC of 81.78%, 91.67%, 20.20% and 33.39% respectively while PAC had a maximum removal of 83.88%, 91.70%, 25.25% and 41.63% respectively. Thus, PAC is a more efficient coagulant for pharmaceutical effluent because it resulted in better quality effluent at a lower dosage as compared to ferric sulfate.
- Application of bentonite clay pretreatment increased the removal rates of TSS, turbidity, COD and TOC by 15.04%, 7.14%, 10.10% and 20.81% respectively for ferric sulfate and 13.08%, 6.51%, 23.23% and 21.40% respectively for PAC. The optimum dosage for ferric sulfate reduced by 50% while that of PAC reduced by 33%. Bentonite clay pretreatment is an effective method of improving the quality

of pharmaceutical effluent and should be incorporated into the coagulation process to reduce chemical usage.

- The wastewater under study was found to contain five pharmaceutical compounds namely; ciprofloxacin, sulfamethoxazole, ibuprofen, metronidazole and trimethoprim at a concentration of 14.98 mg/l, 62.83 mg/l, 26.54 mg/l, 29.92 mg/l and 208.30 mg/l respectively. The removal of these compounds was higher with the use of bentonite clay compared to using chemical coagulants only, further indicating the benefits of bentonite clay in the pretreatment of pharmaceutical wastewater.

7.2 Recommendations

To achieve the best results in the application of this pre-treatment to a particular situation, optimization of bentonite dosage should be carefully done because it was noted that an excess of bentonite required a higher dosage of coagulants for proper flocculation and settling to take place. In addition to this, high amounts of bentonite resulted in larger volumes of sludge which could result in disposal problems.

To further improve the knowledge in this field, it is recommended that further research should focus on:

i. The influence that different mineral compositions of bentonite have on its pre-treatment performance. This should be done through a comparison of the performance of bentonite clays from different sources in the pre-treatment of pharmaceutical effluent.

ii. The options available for modification of bentonite to make it more effective in the pre-treatment. The main aim of these modifications would be to increase bentonite's capacity as an adsorbent for PhACs.

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APPENDICES

Appendix I: Sample questionnaire

MSc Research: Assessment of Bentonite Clay Pretreatment of Pharmaceutical Industry Wastewater in Kenya

QUESTIONNAIRE- TREATMENT OF PHARMACEUTICAL WASTEWATER IN KENYA

1. Under which category does the pharmaceutical factory fall?
   - ☐ Fermentation plants.
   - ☐ Synthesized organic chemicals plants.
   - ☐ Fermentation/synthesized organic chemicals plants.
   - ☐ Biological production plants (production of vaccines–antitoxins).
   - ☐ Drug mixing, formulation, and preparation plants (tablets, capsules, solutions, etc.).
2. Approximately how many litres of wastewater does the factory produce per day?

   _____

   _____
3. Which water quality parameters do you consider in monitoring the wastewater?

   _____

   _____

_____

_____

4. Briefly describe the treatment process carried out on your wastewater.

_____

_____

_____

_____

_____

_____

_____

5. What are the approximate percentage removal of the parameters mentioned in Q 3 from the pre-treatment process?

_____

_____

_____

_____

_____

_____

6. How do you dispose of the effluent?

_____

_____

_____

_____

_____

7. What challenges do you face in the pre-treatment and handling of the wastewater?

_____

_____

_____

_____

_____

_____

☺ THANK YOU FOR YOUR CO-OPERATION ☺

Appendix II: Characterization of pharmaceutical wastewater

Parameter	Factory A				Factory B				Factory C			
	Sample 1	Sample 2	Sample 3	**Average**	Sample 1	Sample 2	Sample 3	**Average**	Sample 1	Sample 2	Sample 3	**Average**
Total Organic Carbon (TOC) mg l^{-1}	120.1	96.7	133.4	**116.73**	133.7	116	102.8	**117.50**	98.6	109.0	90.8	**99.47**
Chemical Oxygen Demand (COD) mg l^{-1}	396.0	388.6	406.4	**397.00**	423.2	402.4	430.5	**418.70**	191	211.7	184.2	**195.63**
Biochemical Oxygen Demand (BOD) mg l^{-1}	273.2	265.9	250.6	**263.23**	238.0	202.9	197.2	**212.70**	50.7	85.4	119.6	**85.23**
pH	6.62	6.2	7.24	**6.69**	7.53	7.01	6.55	**7.03**	7.69	6.53	7.02	**7.08**
Total Suspended Solids (TSS) mg l^{-1}	96.0	87.5	97.5	**93.67**	61.5	84.0	77.5	**74.33**	230.0	174.6	226.5	**210.37**
Turbidity (NTU)	84	97	75	**85.33**	72	69	63	**68.00**	129	118	134	**127.00**

Appendix III: Optimization of coagulation

	Variation of COD with coagulant dosage for PAC				Variation of COD with coagulant dosage for $Fe_2(SO_4)_3$			
Coagulant dose mg l^{-1}	(Trial 1) Vol FAS	(Trial 2) Vol FAS	Ave Vol FAS	**COD (mg/l)**	(Trial 1) Vol FAS	(Trial 2) Vol FAS	Ave Vol FAS	**COD (mg/l)**
Blank	23.0	21.7	22.35		23.0	21.7	22.35	
Raw effluent	17.6	17.2	17.40	396.0	17.6	17.2	17.40	396.0
5	17.9	18.0	17.95	352.0	17.8	17.7	17.75	368.0
10	18.1	17.6	17.85	360.0	1.8.0	18.1	18.05	344.0
15	18.6	18.4	18.50	308.0	18.3	18.5	18.40	316.0
20	18.5	18.1	18.30	324.0	18.2	18.3	18.25	328.0
25	18.2	18.0	18.10	340.0	18.0	18.4	18.20	332.0
30	17.8	18.1	17.95	352.0	18.1	18.2	18.15	336.0

	Variation of COD with pH for PAC (15 mg/l)				Variation of COD with pH for $Fe_2(SO_4)_3$ (15 mg/l)			
pH	(Trial 1) Vol FAS	(Trial 2) Vol FAS	Ave Vol $Na_2S_2O_3$	**COD (mg/l)**	(Trial 1) Vol FAS	(Trial 2) Vol FAS	Ave Vol FAS	**COD (mg/l)**
2	NA	NA	0.00	0.0	18.3	18.1	18.20	332.0
3	17.5	17.7	17.60	380.0	18.3	18.3	18.30	324.0
4	18.1	17.9	18.00	348.0	18.5	18.3	18.40	316.0
5	18.4	18.5	18.45	312.0	18.3	18.4	18.35	320.0
6	18.6	18.6	18.60	300.0	18.2	18.2	18.20	332.0
7	18.6	18.7	18.65	296.0	18.0	18.1	18.05	344.0
8	18.8	18.8	18.80	284.0	NA	NA	0.00	0.0
9	18.9	18.7	18.80	284.0	NA	NA	0.00	0.0

Effect of pH on TSS for PAC (15 mg/l)				Effect of pH on TSS for Fe2(SO4)3 (15 mg/l)			
	Weight before filtration (g)	Weight after filtration (g)	TSS (mg/l)		Weight before filtration (g)	Weight after filtration (g)	TSS (mg/l)
pH				**pH**			
3	3.5150	4.2060	34.55	**3**	3.8263	4.3133	24.35
4	3.4375	4.0265	29.45	**4**	3.6483	3.9981	17.49
5	3.7753	4.1587	19.17	**5**	3.9464	4.3033	17.85
6	3.7843	4.0939	15.48	**6**	3.8263	4.4015	28.76
7	3.8264	4.2153	19.45	**7**	3.8364	4.4136	28.86
8	3.7526	4.1973	22.24	**8**	3.5838	4.2236	31.99

Effect of pH on Turbidity (NTU)

	15 mg/l PAC only Turbidity (NTU)			15 mg/l $Fe_2(SO_4)_3$ only Turbidity (NTU)		
pH	Trial 1	Trial 2	Turbidity(NTU)	Trial 1	Trial 2	Turbidity (NTU)
3	9	10	9.5	9	10	9.5
4	9	10	9.5	7	7	7.0
5	7	8	7.5	8	7	7.5
6	7	7	7.0	9	9	9.0
7	9	9	9.0	9	11	10.0
8	8	9	8.5	9	8	8.5

Effect of pH on TOC (mg/l)

pH	**PAC TOC (mg/l)**	**$Fe_2(SO_4)_3$ TOC (mg/l)**
2	NA	107.5
3	118.10	92.00
4	107.30	80.00
5	90.30	85.00
6	75.80	95.70
7	70.10	99.80
8	85.20	NA
9	89.00	NA

Appendix IV: Optimization of bentonite

Coagulant dosage of 15 mg/l								
	Variation of COD with bentonite dosage for PAC				**Variation of COD with bentonite dosage for $Fe_2(SO_4)_3$**			
Bentonite g/l	(Trial 1) FAS	(Trial 2) Vol FAS	Ave Vol FAS	**COD (mg/l)**	(Trial 1) Vol FAS	(Trial 2) Vol FAS	Ave Vol FAS	**COD (mg/l)**
Blank	23.00	21.70	22.35		23.00	21.70	22.35	
Raw effluent	17.60	17.20	17.40	396.00	17.60	17.20	17.40	396.00
2.50	19.50	19.30	19.40	236.00	19.00	19.00	19.00	268.00
5.00	19.90	19.70	19.80	204.00	19.40	19.50	19.45	232.00
7.50	20.50	20.50	20.50	148.00	20.20	20.20	20.20	172.00
10.00	21.00	21.00	21.00	108.00	20.70	20.60	20.65	136.00
12.50	19.50	19.50	19.50	228.00	19.20	19.20	19.20	252.00
15.00	19.30	19.20	19.25	248.00	19.00	18.90	18.95	272.00
17.50	19.00	19.00	19.00	268.00	18.80	18.70	18.75	288.00
20.00	18.90	18.70	18.80	284.00	18.50	18.50	18.50	308.00
22.50	NA	NA	0.00	0.00	NA	NA	0.00	0.00
25.00	NA	NA	0.00	0.00	NA	NA	0.00	0.00

Variation of TSS with bentonite dosage for PAC				Variation of TSS with bentonite dosage for $Fe_2(SO_4)_3$			
Bentonite g/l	**Weight before filtration (g)**	**Weight after filtration (g)**	**TSS (mg/l)**	**Bentonite g/l**	**Weight before filtration (g)**	**Weight after filtration (g)**	**TSS (mg/l)**
0.00	4.2123	6.1323	96.00	**0.00**	4.2123	6.1323	96.00
2.50	3.9765	4.3783	20.09	**2.50**	3.9846	4.6876	35.15
5.00	3.6825	3.9792	14.84	**5.00**	3.6864	4.1386	22.61
7.50	4.0063	4.2451	11.94	**7.50**	3.8745	4.2868	20.62
10.00	3.8865	4.1192	11.64	**10.00**	3.9004	4.2302	16.49
12.50	3.9542	4.2289	13.74	**12.50**	3.4746	3.8849	20.52
15.00	3.6387	3.9849	17.31	**15.00**	4.0921	4.5994	25.37
17.50	3.6912	4.0932	20.10	**17.50**	3.8835	4.4793	29.79
20.00	4.0027	4.4618	22.96	**20.00**	3.9643	4.5787	30.72

Variation of Turbidity with bentonite dosage

Bentonite g/l	Turbidity (NTU) PAC	Turbidity (NTU) Ferric sulfate
0 (blank)	84.00	84.00
2.50	16.00	19.00
5.00	12.00	15.00
7.50	9.00	13.00
10.00	9.00	12.00
12.50	10.00	12.00
15.00	12.00	14.00
17.50	12.00	14.00
20.00	12.00	14.00

Variation of TOC with bentonite dosage

Bentonite g/l	TOC (mg/l) PAC	TOC (mg/l) $Fe_2(SO_4)_3$
Raw effluent	120.10	120.10
2.50	68.80	70.50
5.00	58.20	59.70
7.50	49.40	51.20
10.00	45.10	55.00
12.50	49.00	55.80
15.00	52.60	62.20
17.50	57.40	66.70
20.00	69.50	69.80

Appendix V: Results for chemical coagulation and bentonite pre-treatment

This section contains data that was obtained for TSS, Turbidity, COD, TOC, BOD and HPLC analysis for chemical coagulation and bentonite clay pre-treatment.

Effect of coagulant dosage on TSS without bentonite pre-treatment

Coagulant (mg/l)	PAC ONLY			Fe2(SO4)3 only		
	Wt before filtration (g)	Wt after filtration (g)	TSS (mg/l)	Wt before filtration (g)	Wt after filtration (g)	TSS (mg/l)
0	4.2123	6.1323	96.00	4.2123	6.1323	96.00
5	3.5590	4.2294	33.52	4.4027	5.2434	42.04
10	3.9482	4.3766	21.42	3.7483	4.3527	30.22
15	3.8503	4.1966	17.32	3.6138	4.0504	21.83
20	3.7595	4.0951	16.78	3.9883	4.3328	17.23
25	4.6931	5.0297	16.83	4.0552	4.3933	16.91
30	3.8443	4.1785	16.71	4.2613	4.6015	17.01
35	4.2847	4.6252	17.03	3.9068	4.2515	17.24
40	4.0738	4.4204	17.33	3.8744	4.2150	17.03

Effect of coagulant dosage on TSS with bentonite pre-treatment

Coagulant (mg/l)	PAC with bentonite			Fe2(SO4)3 with bentonite		
	Wt before filtration (g)	Wt after filtration (g)	TSS (mg/l)	Wt before filtration (g)	Wt after filtration (g)	TSS (mg/l)
0	4.2123	6.1323	96.00	4.2123	6.1323	96.00
5	3.7639	3.8273	3.17	3.9258	3.9898	3.20
10	3.9027	3.9611	2.92	3.8777	3.9387	3.05
15	4.3996	4.4521	2.62	3.8816	3.9386	2.85
20	3.8489	3.8737	1.24	3.9294	3.9880	2.93
25	4.2501	4.2989	2.44	4.2088	4.2681	2.96
30	3.9006	3.9514	2.54	4.3256	4.3879	3.12
35	4.0639	4.0932	1.47	3.9735	4.0132	1.99
40	4.7263	4.7510	1.24	3.7349	3.7875	2.63

Turbidity results from coagulation treatment

Coagulant (mg/l)	PAC only			$Fe_2(SO_4)_3$ only		
	Trial 1	Trial 2	Turbidity (NTU)	Trial 1	Trial 2	Turbidity (NTU)
0 (Raw effluent)	82.0	86.0	84.0	82.0	86.0	84.0
5	15.0	14.0	14.5	20.0	19.0	19.5
10	12.0	12.0	12.0	15.0	14.0	14.5
15	6.0	8.0	7.0	12.0	9.0	10.5
20	6.0	9.0	7.5	8.0	11.0	9.5
25	7.0	6.0	6.5	7.0	8.0	7.5
30	8.0	7.0	7.5	8.0	8.0	8.0
35	6.0	8.0	7.0	9.0	8.0	8.5
40	8.0	6.0	7.0	7.0	8.0	7.5

Turbidity results from bentonite pre-treatment and coagulation tests

Coagulant (mg/l)	PAC with bentonite			$Fe_2(SO_4)_3$ with bentonite		
	Trial 1	Trial 2	Turbidity (NTU)	Trial 1	Trial 2	Turbidity (NTU)
0 (Raw effluent)	82.0	86.0	84.0	82.0	86.0	84.0
5	1.0	2.0	1.5	2.0	2.0	2.0
10	2.0	1.0	1.5	1.0	1.0	1.0
15	1.0	1.0	1.0	1.0	2.0	1.5
20	1.0	1.0	1.0	1.0	1.0	1.0
25	1.0	1.0	1.0	1.0	1.0	1.0
30	1.0	1.0	1.0	2.0	1.0	1.5
35	1.0	1.0	1.0	1.0	1.0	1.0
40	1.0	1.0	1.0	1.0	1.0	1.0

TOC results from treatment with coagulants and bentonite pre-treatment

Coagulant dose mg l^{-1}	PAC Only TOC (mg/l)	$Fe_2(SO_4)_3$ only TOC (mg/l)	PAC with bentonite TOC (mg/l)	$Fe_2(SO_4)_3$ with bentonite TOC (mg/l)
0.0	120.1	120.1	120.10	120.10
5.0	90.4	95.8	52.10	62.10
10.0	80.6	82.9	44.40	55.00
15.0	72.4	84.7	45.50	55.30
20.0	78.8	86.4	44.20	52.10
25.0	81.7	95.9	45.80	52.30
30.0	82.5	99.9	47.10	55.30
35.0	85.3	99.8	46.50	55.80
40.0	86.1	102	45.80	55.50

COD results from treatment with coagulants only FAS - 0.1 mole/l

	PAC only					$Fe_2(SO_4)_3$ only				
Coagulant (ml)	(Trial 1) Vol FAS	COD (1) mg/l	(Trial 2) Vol FAS	COD (2) mg/l	**COD (mg/l)**	(Trial 1) Vol FAS	COD (1) mg/l	(Trial 2) Vol FAS	COD (2) mg/l	**COD (mg/l)**
0 (Raw effluent)	17.6	380.0	17.2	412.0	396.0	17.6	380.0	17.20	412.0	396.0
5	17.9	356.0	17.7	372.0	364.0	17.8	364.0	17.40	396.0	380.0
10	18.0	348.0	18.1	340.0	344.0	17.9	356.0	18.00	348.0	352.0
15	18.2	332.0	18.2	332.0	332.0	18.2	332.0	18.10	340.0	336.0
20	18.3	324.0	18.2	332.0	328.0	18.3	324.0	18.30	324.0	324.0
25	18.7	292.0	18.4	316.0	304.0	18.4	316.0	18.40	316.0	316.0
30	18.7	292.0	18.7	292.0	292.0	18.6	300.0	18.40	316.0	308.0
35	18.7	292.0	18.8	284.0	288.0	18.7	292.0	18.50	308.0	300.0
40	18.9	276.0	18.8	284.0	280.0	18.8	284.0	18.50	308.0	296.0

COD results from coagulation with bentonite clay pre-treatment FAS - 0.1 mole/l

	PAC with bentonite					**$Fe_2(SO_4)_3$ with bentonite**				
Coagulant (ml)	(Trial 1) Vol FAS	COD (1) mg/l	(Trial 2) Vol FAS	COD (2) mg/l	**COD (mg/l)**	(Trial 1) Vol FAS	COD (1)	(Trial 2) Vol FAS	COD (2)	**COD (mg/l)**
0	17.6	380.0	17.2	412.0	396.0	17.6	380.0	17.2	412.0	396.0
5	18.9	276.0	19.0	268.0	272.0	18.4	316.0	18.2	332.0	324.0
10	19.9	196.0	19.7	212.0	204.0	18.9	276.0	18.9	276.0	276.0
15	20.3	164.0	20.2	172.0	168.0	19.4	236.0	19.7	212.0	224.0
20	20.8	124.0	20.5	148.0	136.0	19.9	196.0	19.7	212.0	204.0
25	21.3	84.0	20.8	124.0	104.0	20.3	164.0	20.4	156.0	160.0
30	21.2	92.0	20.8	124.0	108.0	20.5	148.0	20.5	148.0	148.0
35	21.0	108.0	21.2	92.0	100.0	20.7	132.0	20.5	148.0	140.0
40	21.3	84.0	21.0	108.0	96.0	20.6	140.0	20.7	132.0	136.0

BOD RESULTS FROM COAGULATION TESTS (mg/l)

	Sample (ml)	Initial DO	Final DO	Depletion	Seeding factor	Dilution factor	BOD $_5$ (mg/l)	Ave BOD_5
Coagulant (mg/l)								
0 (Raw effluent)	25	82.00	51.00	31	6.8250	12.0	290.100	273.225
	50	85.00	34.00	51	6.8250	6.0	265.050	
	100	119.00	24.00	95	6.8250	3.0	264.525	
20 (PAC)	25	80.50	50.50	30.0	6.8250	12.0	278.100	261.225
	50	97.00	45.00	52	6.8250	6.0	271.050	
	100	123.00	38.00	85	6.8250	3.0	234.525	
40 (PAC)	25	79.00	52.00	27	6.8250	12.0	242.100	243.225
	50	87.50	40.50	47	6.8250	6.0	241.050	
	100	118.00	29.00	89	6.8250	3.0	246.525	
20 (Fe)	25	82.50	53.50	29	6.8250	12.0	266.100	262.575
	50	89.00	39.00	50	6.8250	6.0	259.050	
	100	102.00	8.00	94	6.8250	3.0	261.525	
40 (Fe)	25	77.00	49.00	28	6.8250	12.0	254.100	253.725
	50	98.50	47.00	51.5	6.8250	6.0	268.050	
	100	124.00	37.50	86.5	6.8250	3.0	239.025	
20 (PAC + Bentonite)	25	79.00	46.00	33	6.8250	12.0	314.100	247.5375

BOD RESULTS FROM COAGULATION TESTS (mg/l)

	Sample (ml)	Initial DO	Final DO	Depletion	Seeding factor	Dilution factor	BOD $_5$ (mg/l)	Ave BOD_5
	50	85.50	36.00	49.5	6.8250	6.0	256.050	
	100	108.00	21.50	86.5	6.8250	3.0	239.025	
40 (PAC + Bentonite)	25	79.00	52.00	27	6.8250	12.0	242.100	242.225
	50	89.50	42.00	47.5	6.8250	6.0	244.050	
	100	113.00	26.00	87	6.8250	3.0	240.525	
20 (Fe + Bentonite)	25	80.00	52.50	27.5	6.8250	12.0	248.100	246.225
	50	93.50	44.00	49.5	6.8250	6.0	256.050	
	100	114.00	29.00	85	6.8250	3.0	234.525	
40 (Fe+ Bentonite)	25	78.00	50.00	28	6.8250	12.0	254.100	249.225
	50	92.00	46.00	46	6.8250	6.0	235.050	
	100	115.00	22.00	93	6.8250	3.0	258.525	

	Data from HPLC analysis											
Retention time	**0.417**	**1.363**	**4.429**	**4.438**	**4.801**	**5.079**	**5.395**	**5.604**	**7.021**	**7.338**	**7.519**	**8.579**
Ciprofloxacin					14.983							
Clotrimazole												
Diclofenac												
Sulfamethoxazole							62.831					
Paracetamol												
Ibuprofen												26.543
Trimethoprim			208.302									
Metronidazole									29.922			
5 mg/l $Fe_2(SO_4)_3$ only			208.018		14.978		62.831		29.719			26.135
10 mg/l $Fe_2(SO_4)_3$ only			207.236		14.853		62.763		27.267			24.826
15 mg/l $Fe_2(SO_4)_3$ only			204.743		13.864		61.923		26.827			18.261
20 mg/l $Fe_2(SO_4)_3$ only			201.501		12.954		61.722		26.824			15.022
25 mg/l $Fe_2(SO_4)_3$ only			201.826		12.998		61.992		26.854			15.017
30 mg/l $Fe_2(SO_4)_3$ only			201.984		13.678		62.021		26.801			15.725
5 mg/l $Fe_2(SO_4)_3$ + bentonite			118.298		0		53.053		22.362			0
10 mg/l $Fe_2(SO_4)_3$ + bentonite			117.726		0		52.031		21.150			0
15 mg/l $Fe_2(SO_4)_3$ + bentonite			117.827		0		52.311		21.172			0
20 mg/l $Fe_2(SO_4)_3$ + bentonite			117.992		0		52.342		21.227			0

	Data from HPLC analysis											
Retention time	**0.417**	**1.363**	**4.429**	**4.438**	**4.801**	**5.079**	**5.395**	**5.604**	**7.021**	**7.338**	**7.519**	**8.579**
Ciprofloxacin					14.983							
Clotrimazole												
Diclofenac												
Sulfamethoxazole							62.831					
Paracetamol												
Ibuprofen												26.543
Trimethoprim			208.302									
Metronidazole									29.922			
25 mg/l $Fe_2(SO_4)_3$ + bentonite			116.287		0		53.842		20.832			0
30 mg/l $Fe_2(SO_4)_3$ + bentonite			116.975		0		52.014		20.932			
5 mg/l PAC only			207.928		14.528		62.102		21.862			26.542
10 mg/l PAC only			198.263		4.127		59.384		21.001			18.732
15 mg/l PAC only			196.821		0.000		57.792		20.033			16.434
20 mg/l PAC only			196.002		0.000		57.182		19.929			16.472
25 mg/l PAC only			196.726		1.827		57.928		19.517			16.321
30 mg/l PAC only			196.276		1.119		58.922		19.186			16.925
5 mg/l PAC + bentonite			101.726		0.000		48.286		18.791			0.618
10 mg/l PAC + bentonite			99.102		0.000		45.332		18.764			0.000

	Data from HPLC analysis											
Retention time	**0.417**	**1.363**	**4.429**	**4.438**	**4.801**	**5.079**	**5.395**	**5.604**	**7.021**	**7.338**	**7.519**	**8.579**
Ciprofloxacin					14.983							
Clotrimazole												
Diclofenac												
Sulfamethoxazole							62.831					
Paracetamol												
Ibuprofen												26.543
Trimethoprim			208.302									
Metronidazole									29.922			
15 mg/l PAC + bentonite			98.992		0.000		45.028		18.852			0.000
20 mg/l PAC + bentonite			99.293		0.000		46.183		19.023			0.000
25 mg/l PAC + bentonite			99.273		0.000		46.072		18.817			0.000
30 mg/l PAC + bentonite			99.398		0.000		46.726		18.992			0.000

Appendix VI: Prediction of bentonite dosage

The statistical method of multiple regression was used to predict bentonite dosage for a particular effluent using its characteristics. Optimum bentonite dosages required for treatment of the wastewater samples collected were used as the dependent variables while the parameters TSS, COD, turbidity and TOC were the independent variables.

Optimum bentonite dosages for sample wastewater

Bentonite dosage (g/l)	TSS	COD	Turbidity	TOC
10.00	96.00	396.00	84.00	120.10
4.00	61.50	423.00	72.00	133.70
12.00	230.00	191.00	129.00	98.60
6.00	87.50	388.60	97.00	96.70
10.00	97.50	406.40	75.00	133.40
8.00	84.00	423.20	69.00	116.00
6.00	77.50	430.50	63.00	102.80
8.00	174.60	211.70	118.00	109.00
12.00	226.50	184.20	134.00	90.80