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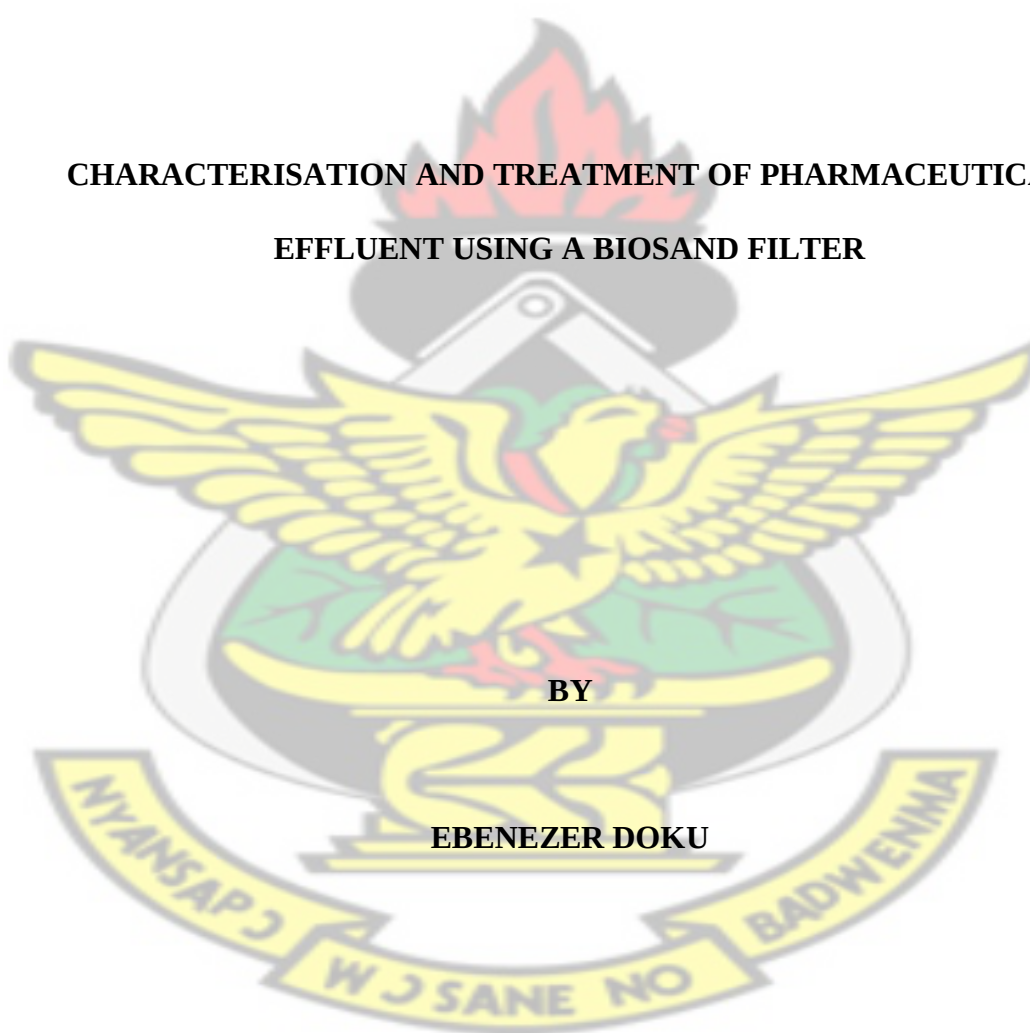
DEPARTMENT OF THEORETICAL AND APPLIED BIOLOGY

KNUST

**CHARACTERISATION AND TREATMENT OF PHARMACEUTICAL
EFFLUENT USING A BIOSAND FILTER**

BY

EBENEZER DOKU



FEBRUARY, 2019

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EFFLUENT USING A BIOSAND FILTER**

**A DISSERTATION SUBMITTED TO THE DEPARTMENT OF
ENVIRONMENTAL SCIENCE IN PARTIAL FULFILMENT OF THE
REQUIREMENT
FOR THE AWARD OF
MASTER OF SCIENCE DEGREE IN ENVIRONMENTAL SCIENCE**

BY

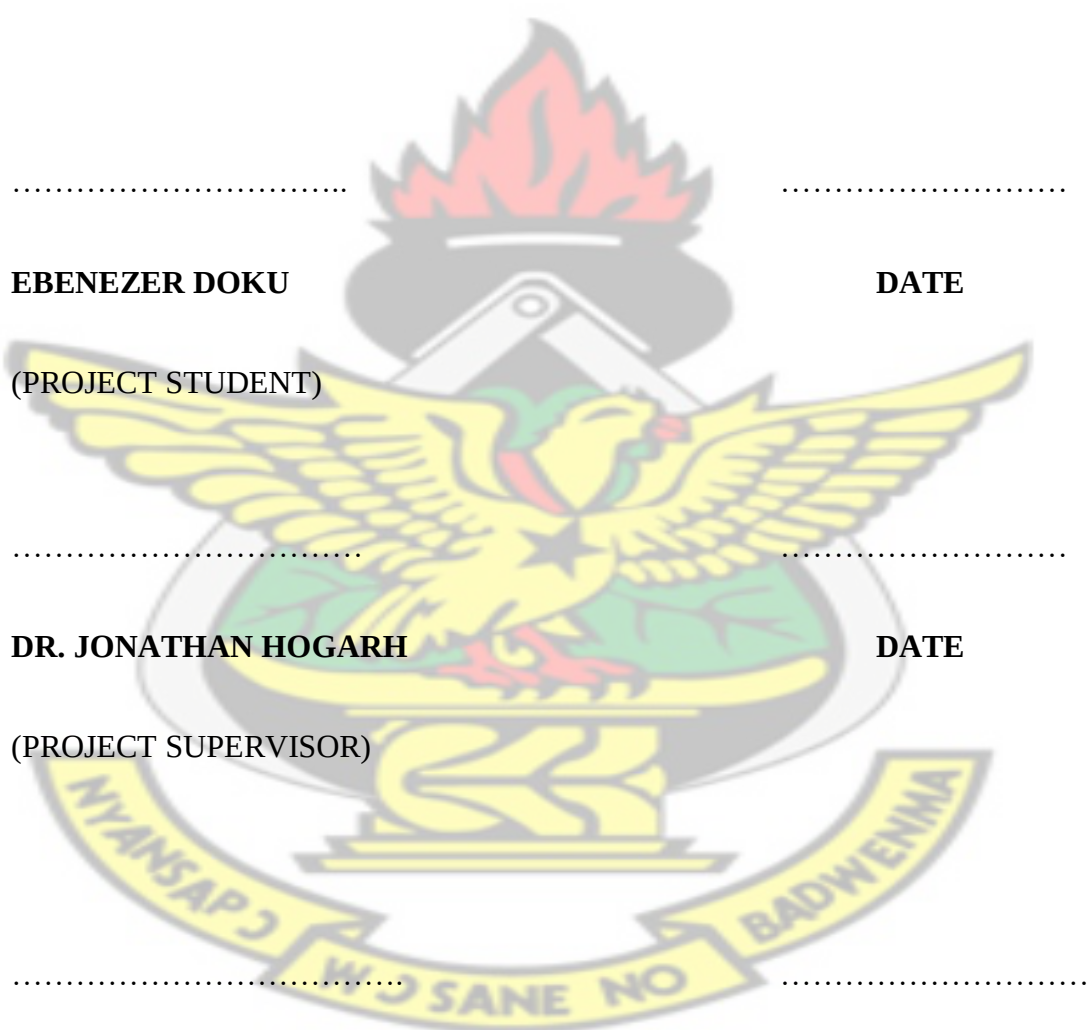
EBENEZER DOKU

FEBRUARY, 2019

DECLARATION

I hereby declare that this report is my own work and to the best of my knowledge does not contain any material previously published by another person nor material which has been accepted for the award of any other degree of the university except where it has been duly acknowledged.

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(HEAD OF DEPARTMENT)

DEDICATION

I dedicate this project to my father, Mr. Henry Tetteh Doku. You were very supportive in the movement of materials to make this work a success.

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ACKNOWLEDGEMENT

I would like to express my sincerest gratitude to Dr. J. N. Hogarh for his guidance and direction during this project and preparation of this thesis.

I am also indebted to the Ghana Atomic Energy Commission for their cooperation during the project.

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ABSTRACT

An emerging group of pollutants known as pharmaceutical and personal care products (PPCPs) are present in effluents from pharmaceutical companies. Most pharmaceutical companies in Ghana release their effluents directly into nearby public drainage systems, without any form of treatment and this has dire public health concerns. However, energy consuming effluent treatments plants are financially unsustainable for small scale pharmaceutical companies so cost effective measures to manage effluents are required. This project investigated the potential of the biosand filter to treat pharmaceutical effluent as a cheaper alternative to conventional methods.

Two filters were built and run according to standard design criteria. Removal of four common active pharmaceutical ingredients (APIs) i.e. ciprofloxacin hydrochloride, cefuroxime axetil, amoxicillin trihydrate and diclofenac sodium were monitored. The filters were fed pharmaceutical effluent dosed with 1g of each API. The results showed that the biosand filter was efficient in removing APIs from the effluent water. The average removal of ciprofloxacin hydrochloride, cefuroxime axetil, amoxicillin trihydrate and diclofenac sodium at the recommended flow rate were 93.32%, 91.05%, 89.33% and 92.42% respectively. The removal of the APIs by the biosand filters may have been achieved through a combination of mechanisms like settlement, sand straining and charcoal adsorption.

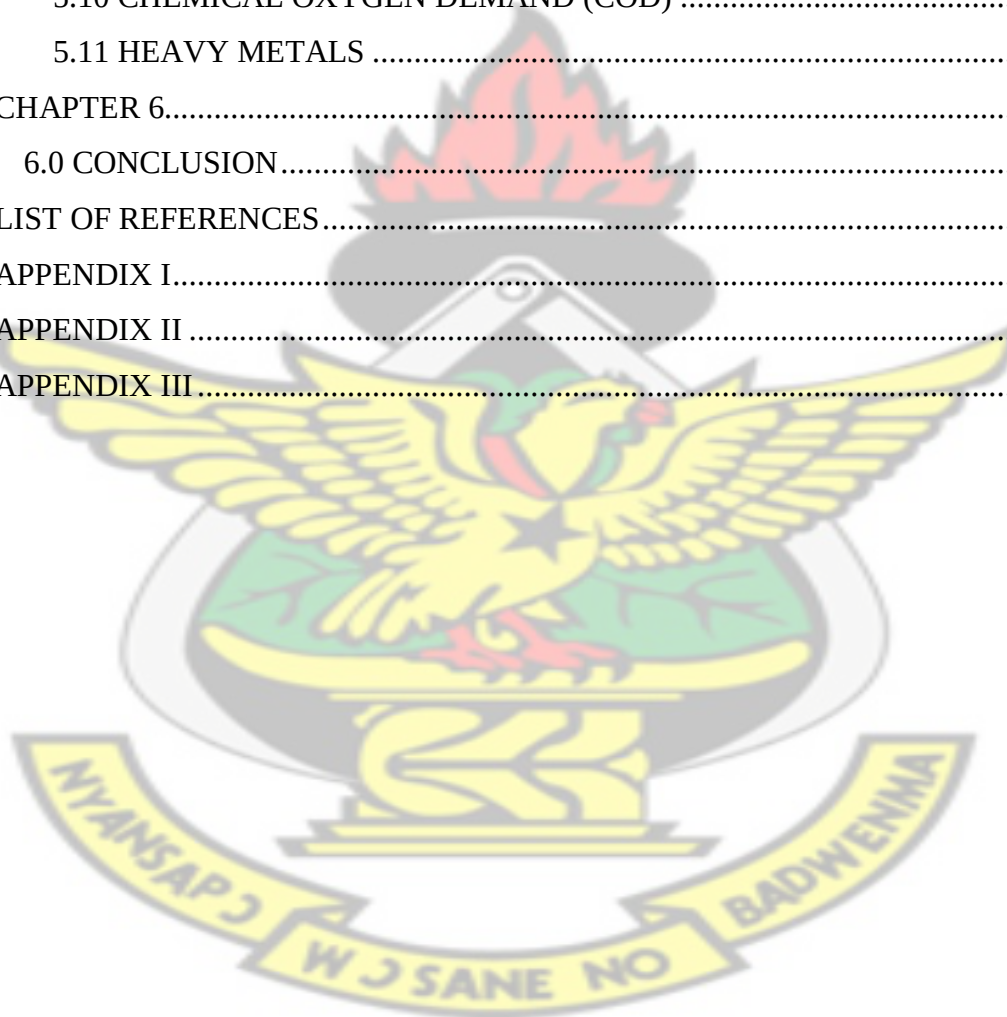
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ACRONYMS

PPCP – Pharmaceutical and personal care product

API – Active pharmaceutical ingredient

EPA – Environmental protection agency

EDC - Endocrine disrupting chemicals

SOP – Standard operating procedure

RMG – Rapid mixer granulator

FBD – Fluid bed dryer

AMA – Accra metropolitan assembly

PVC – Polyvinyl chloride

FDA – Food and drugs authority

NF – Nano filtration

RO – Reverse osmosis

PAC – Powdered activated carbon

GAC – Granular activated carbon

AOP – Advanced oxidation process

BSF – Biosand filter

TDS – Total dissolved solids

TSS – Total suspended solids

BOD – Biochemical oxygen demand

COD – Chemical oxygen demand

CHAPTER 1

1.0 INTRODUCTION

1.1 BACKGROUND

For plants and animals 50-97% of their weight is made of water whereas 70% of the human weight is made of water. This demonstrates that water is an essential part of all life forms (Allan, 1995). Even though water is available in huge quantities on the earth, of the 3% that is fresh water, only 5% is available for human use (Usharani et al., 2010). Water being an essential resource for manufacturing, agriculture and other human needs, it is important that it is protected. However wrongful disposal of industrial wastes have contributed substantially to the loss of water quality in urban areas (Mathuthu et al., 1997).

Pharmaceutical industries pollute the air and water bodies via the emission of unpleasant gases and through the discharge of liquid effluents. Pharmaceutical industry wastes are generally composed of both organic and inorganic matter in various quantities and different levels of concentration. It contains acids, bases, toxic materials, and suspended solids. Generally, the most appropriate way to clean highly contaminated and toxic wastewater from industries is by treating them at the source (Peringer, 1997). Another option is to apply onsite treatment at the production lines and by recycling treated effluent (Hu et al., 1999). For industrial wastes, pre-treatment is required to produce a less polluted effluent that meets regulatory requirements (Lokhande et al., 2011).

In instances where pharmaceutical effluents are contaminated with toxic heavy metals, human health could be affected adversely and this could result in acute or chronic diseases. Many industrial organic substances reach water bodies and this leads to failure

in reproduction among fish, shellfish, and other wildlife or may even cause their death. Heavy metals also accumulate in animal and fish tissue, they are absorbed in sediments or they may contaminate supplies of drinking water and pose health risks to humans in the long term (Alam et al., 2007).

In order for pharmaceuticals to work properly they must retain their potency in the adverse conditions present in the human body. For this reason, the active compounds in many pharmaceutical products do not breakdown after they are excreted or disposed of. Thus even after being passed through some treatment plants it is not uncommon to detect pharmaceutical compounds in wastewater (Keil, 2008). The means by which pharmaceuticals enter water bodies include the following: excretion, disposal down the drain, through hospital wastes disposal and by industrial effluent disposal (Deziel, 2014), spanning the time of their production in factories to their use or disposal. Pharmaceuticals may be classified as antibiotics, antidepressants, and anti-inflammatory.

The health risks emanating from industrial effluents mean that these effluents must be treated to meet standards set by the EPA (Kumar, 1996). Many pharmaceutical companies in Ghana however do not have effluent treatment plants, thereby releasing untreated effluents directly into the public drainage system. The few that have these plants do not use it due to the associated cost of operation. It is therefore imperative to develop cheaper means to fairly reduce the contaminants to comply with national EPA guidelines.

1.2 PROBLEM STATEMENT

Of great concern has been the adverse environmental effects associated with industrial waste disposal activities. Some pharmaceutical industries in Ghana dispose of their wastes directly into municipal waste streams without any prior treatment. These wastes are mostly composed of contaminants including heavy metals, active pharmaceutical ingredients, various acids, alkalis, colours and other chemicals which greatly change the physico-chemical properties of water.

Current effluent treatment systems are financially unsustainable for small scale pharmaceutical companies. There is the need to explore simple and cheap methods to reduce the pollutant load in pharmaceutical effluents in order to protect the environment.

1.3 AIM AND OBJECTIVES

The aim of the study was to determine the effectiveness of treating pharmaceutical effluent using a biosand filter.

The objectives are:

- To determine the physico-chemical properties of pharmaceutical effluent.
- To assess the potential of applying biosand filter to remove active pharmaceutical ingredients (APIs) from wastewater.
- To evaluate the efficiency of the treatment.

CHAPTER 2

2.0 LITERATURE REVIEW

2.1 PHARMACEUTICALS

2.1.1 Introduction

Pharmaceuticals are bioactive chemicals used for the treatment of diseases, reducing symptoms and maintaining a good health. They are found in effluents from sewage treatment plants, surface water, seawater, groundwater, soil, sediment and fish. Their presence in the environment can be linked to an increasing population density and a widespread use of self-administrated medications and drugs. Improper disposal of pharmaceuticals and insufficient or non-treatment of waste water are also some of the causes of pharmaceutical residue proliferation and toxicity (Rivera-Utrilla et al., 2013).

Various pharmaceutical products are prescribed all around the world. Over the past few decades there has been a marked rise in the concern in the existence and fate of these pharmaceuticals in the environment. The major reason for this has been the increasing rate at which medical preparations are being consumed as well as the progressive development of both semi synthetic and synthetic derivatives of these pharmaceuticals (Vaňková, 2010). The chemical derivatives of compounds which are otherwise naturally occurring are specifically designed to be potent and species selective or with a broad range of target organisms. This leads to an increased toxicity and better membrane penetration. Constant exposure affects human, plant, and animal health and cause the development of resistant strains of bacteria.

Pharmaceuticals are categorised as emerging pollutants. Emerging pollutants are those pollutants which are released into the environment and yet remain unregulated. This is due to a lack of information with regards to their toxicity, their occurrence and a lack

of an appropriate analytical procedure for their determination in environmental media. In Ghana, the Environmental Protection Agency does not have specific analytical methods for pharmaceuticals and their guidelines do not isolate pharmaceutical effluents for monitoring activities. However since such emerging pollutants are possibly poisonous even at trace levels, optimization of their analytical methods is critical to regulate and reduce their impacts.

Estimates indicate that almost half of the effluents produced from pharmaceutical industries around the world are not subjected to any form of treatment prior to their disposal into the environment (Enick and Moore, 2007). The removal of many active pharmaceutical ingredients has been ignored even though some attention has been placed on endocrine disrupting chemicals (EDCs). An array of modern and innovative technologies is currently available however beyond being very expensive for small pharmaceutical companies to manage, the right know-how and practical experience are still critical for a successful implementation of these technologies.

Break down of pharmaceuticals can happen via biotic processes i.e. biological degradation as well as abiotic processes such as photochemical reactions and hydrolysis. The biodegradation stage in wastewater treatment plants is integral in the removal of some chemicals and other potential pollutants. Studies have indicated that many pharmaceuticals like caffeine and ibuprofen are eliminated mostly by biodegradation (Ternes, 2007).

2.1.2 Properties of Active Pharmaceutical Ingredients

A typical characteristic of most APIs is their hydrophilic behaviour. This is important to ensure easy absorption by human bodies. Even though a work by Radjenović et al. (2008) indicated that APIs are biologically active chemicals which have high

persistence in order to avoid their degradation before having any effects on the patients taking them, Nikolaou et al. (2007) explained that pharmaceutical residues are still in the environment because high release rates overcome the rates of transformation although they have low volatility and low persistence. A reduced amount of pharmaceuticals in the environment can also be an indication of sorption to soil particles and sorption of antibiotics is dependent on the amount of free and suspended particles, pH, soil organic matter and soil minerals (Thiele-Bruhn, 2003).

These properties have a very important effect on their biodegradability and results in rather high biological degradation rates for example paracetamol or elimination rates tending to zero for example diazepam (Ternes et al., 2004). However in a work by Vaňková, (2010) all tested antiviral drugs, antimalarial drugs, antiparasitics, antifungals, antituberculous, antibacterials, and antiulceratives were determined to be non-degradable and thus likely to be persistent in the environment and may affect the efficiency of effluent treatment plant processes. Only two drugs from among the seventeen drugs under study were readily biodegradable.

Pharmaceuticals are classified in several ways. This classification could be based on either their pharmaceutical purpose or biological activity. They are also classified based on the API and the chemical structure of the small molecules which determine the solubility of the compounds and their effects in the environment. Pharmaceuticals are removed from the body as hydrophilic metabolites in urine and gall but also pass through the body unchanged (Rivera-Utrilla et al., 2013). They are small, complex and polar molecules with different functionalities.

2.1.3 Manufacture of Pharmaceutical Products

The manufacturing process involves: sifting, mucilage preparation, dry mixing, granulation, drying, sifting & milling, lubrication, compression and coating (for coated tablets). These stages change depending on the particular formulation i.e. tablet (coated and uncoated), capsule or dry syrup. The manufacture of pharmaceutical products at COMPANY A involves the following stages for tablets, dry syrups and capsules. This study is therefore restricted to these formulations.

2.1.3.1 Dry Syrups and Capsules

After a line clearance to prevent a mix up with previous batch, all active pharmaceutical ingredients and excipients are weighed. The raw materials are sifted separately and mixed in an SBH blender. For Dry syrups, the mixture is filled in bottles and in the case of capsules, they are filled in empty capsules as indicated in figure 2.1. Spillages which occur are cleaned and the machines are washed for a change over when the batch is completed. All waste water is collected in the effluent reservoir.

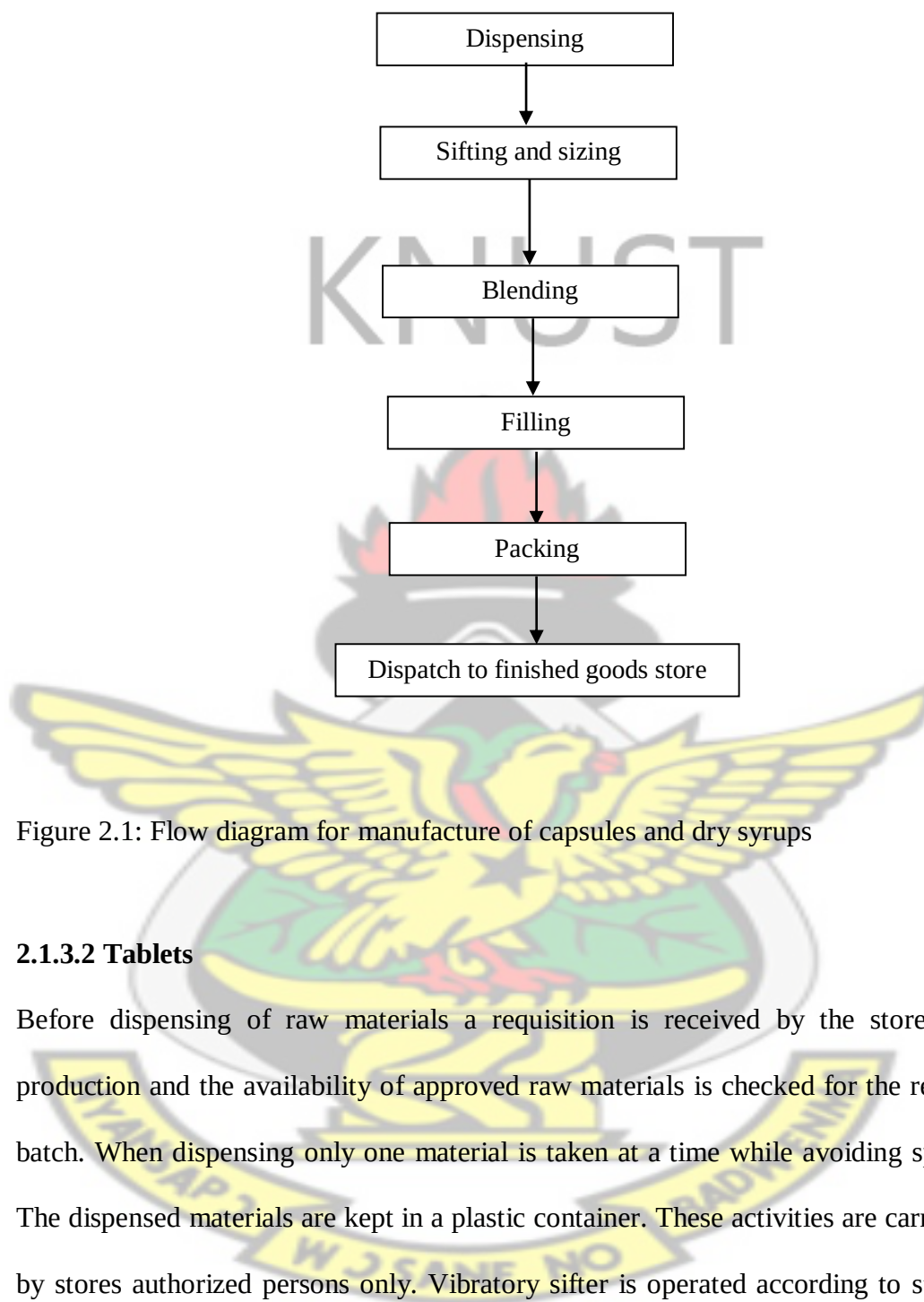


Figure 2.1: Flow diagram for manufacture of capsules and dry syrups

2.1.3.2 Tablets

Before dispensing of raw materials a requisition is received by the stores from production and the availability of approved raw materials is checked for the requisite batch. When dispensing only one material is taken at a time while avoiding spillage. The dispensed materials are kept in a plastic container. These activities are carried out by stores authorized persons only. Vibratory sifter is operated according to standard operating procedure (SOP), putting appropriate sieve and checking its integrity before and after sifting operation. The residues are checked for appearance and quality and sifted materials are collected in polythene bags.

Sub-lot quantities of APIs and excipient are transferred in a rapid mixer granulator (RMG) and mixed. A starch mucilage is prepared and added in the RMG and mixed. Contents are then discharged into Fluid Bed Dryer (FBD) bowls which are transferred for drying. The dried mixture with huge grains are milled and sifted directly into polythene lined drums and added to lubricants in an SBH blender where it is mixed evenly for 20 minutes. Blended granules are discharged into stainless steel containers and transferred to a compression and coating area. The granules are compressed and these compressed tablets may be coated before being blistered onto PVC and aluminium foil for packing. Spillages which occur are cleaned and the machines are washed for a change over when the batch is completed. The manufacturing flow diagram for the whole process is shown in figure 2.2 below. All waste water is then collected in the effluent reservoir.

Pharmaceutical industry wastewaters are composed of APIs, organic solvents, catalysts, additives, reactants, intermediates and other raw materials. When pharmaceuticals, in the manufacturing process are incorrectly disposed to a sewage system or a dumpsite or when they appear in wastewater they exist in active forms either as suspended solids or in the dissolved state. Monitoring is however ineffective in developing countries due to the usage of centralized sewage systems, insufficient sanitation and unavailability of reliable data or inaccurate data on concentrations of pharmaceuticals consumed unknown or inaccurate quantities of pharmaceuticals consumed.

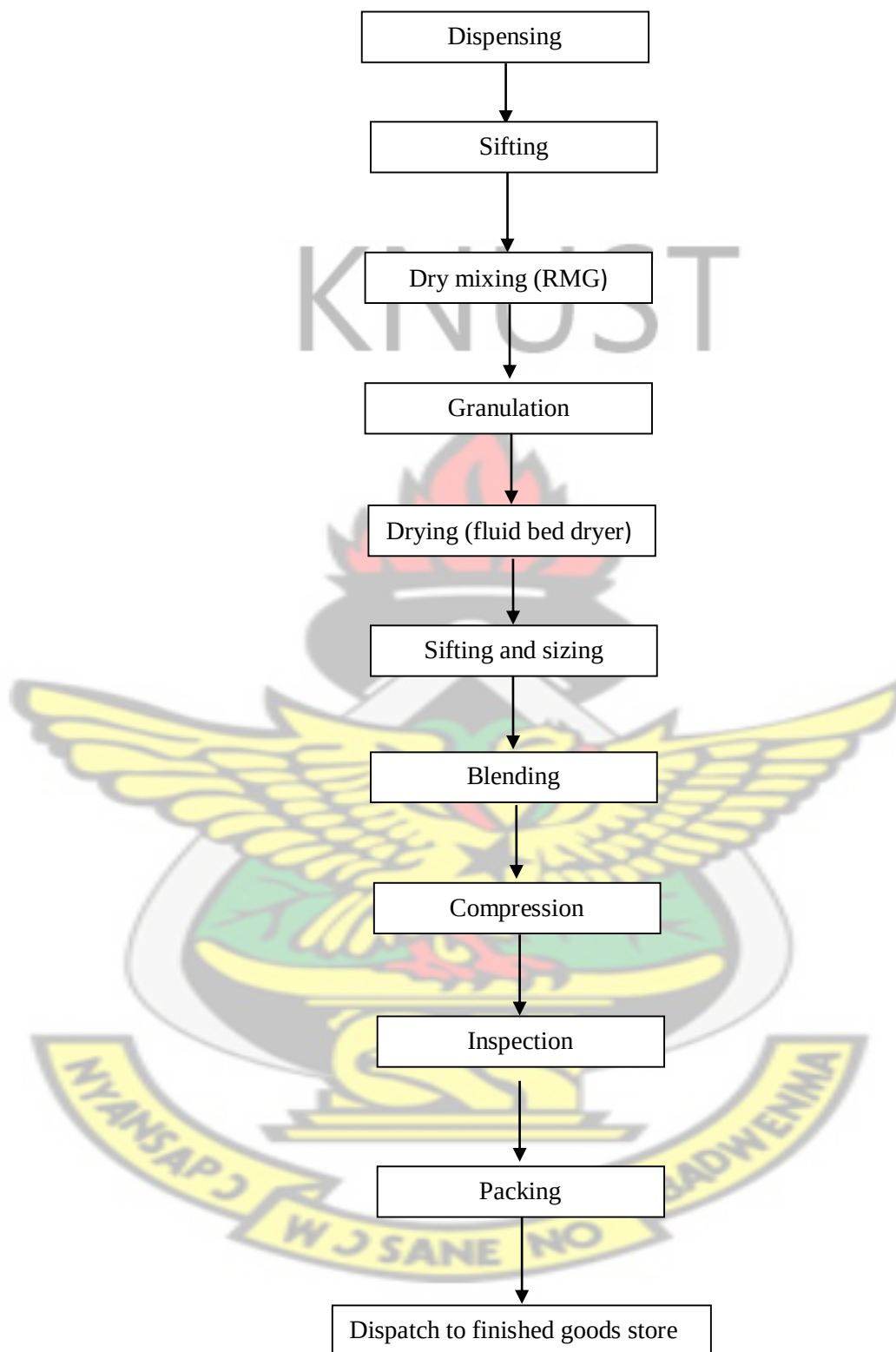


Figure 2.2: The manufacturing flow diagram for tablets

2.1.4 Targeted Active Pharmaceutical Ingredients

Of all the 20 pharmaceutical products manufactured in COMPANY A, four active pharmaceutical ingredients were chosen based on their therapeutic use, ease of chemical analysis and the number of batches produced annually. They are; amoxicillin trihydrate, cefuroxime axetil, ciprofloxacin hydrochloride and diclofenac sodium.

2.1.4.1 Amoxicillin Trihydrate

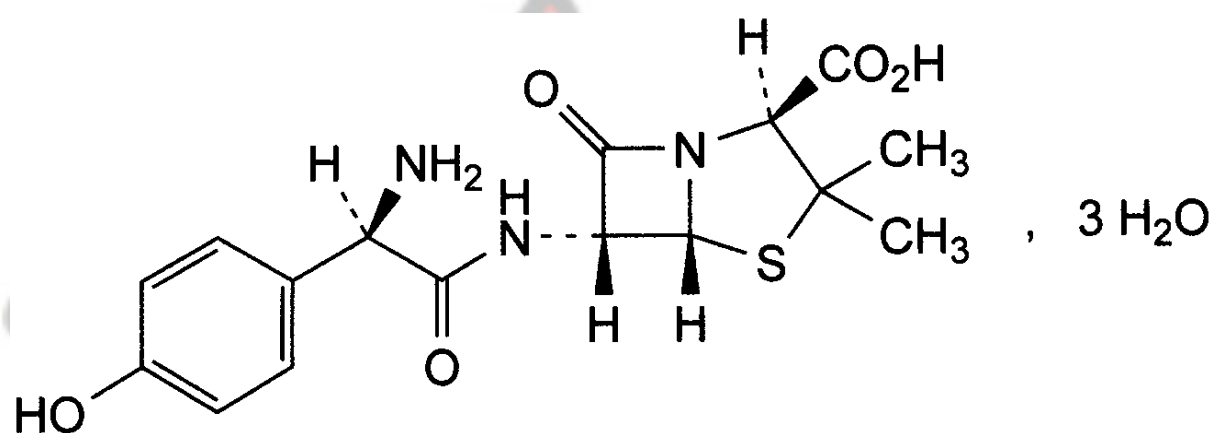


Figure 2.3: Chemical structure of amoxicillin trihydrate (British Pharmacopoeia, 2013).

Amoxicillin trihydrate (Figure 2.3) is a semi synthetic penicillin antibacterial product which is derived from a fermentation product. It is a white crystalline powder which is partially soluble in water, very slightly soluble in ethanol and practically insoluble in fatty oils. It is however soluble in dilute acids and dilute solutions of alkali hydroxides. It is stored in an airtight container and it is used for the manufacture of amoxicillin oral suspension at COMPANY A. The suspension is a wide spectrum antibiotic that is used for the treatment of common infections caused by bacteria, including upper respiratory tract infections, acute bronchitis, chronic bronchitis and skin and soft tissue infections.

2.1.4.2 Cefuroxime Axetil

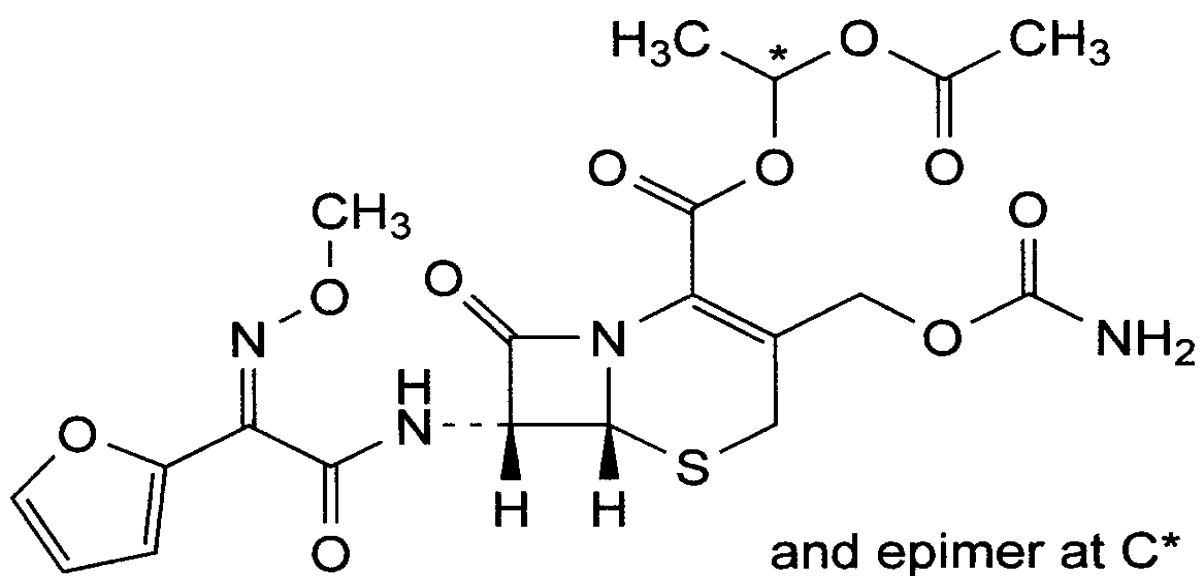


Figure 2.4: Chemical structure of cefuroxime axetil (British Pharmacopoeia, 2013).

Cefuroxime axetil is a semi synthetic cephalosporin antibacterial product derived from another fermentation product. It is a white powder which is partially soluble in water, soluble in acetone, soluble in ethyl acetate and also soluble in methanol. It is also partially soluble in ethanol. It is stored in a container which is airtight and protected from light. It is used for the manufacture of cefuroxime axetil oral suspension. It is classified as a cephalosporin and is used for the treatment of infections of the ear, chest, nose and throat.

2.1.4.3 Ciprofloxacin Hydrochloride

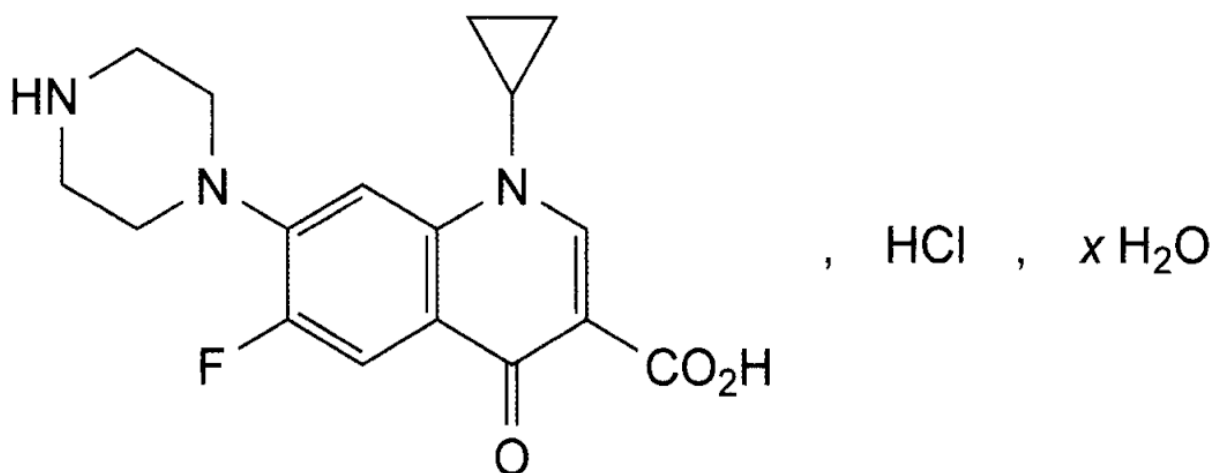


Figure 2.5: Chemical structure of ciprofloxacin hydrochloride (British Pharmacopoeia, 2013).

Ciprofloxacin hydrochloride is a crystalline, pale yellowish, antibacterial which is slightly hygroscopic powder. It readily dissolves in water, it is slightly soluble in methanol, very slightly soluble in anhydrous ethanol and insoluble in acetone, in ethyl acetate and methylene chloride. Figure 2.5 shows the structure of ciprofloxacin hydrochloride. It is stored in a container which is airtight and protected from light. Ciprofloxacin hydrochloride is used for the manufacture of Ciprofloxacin tablets. It is a very potent, wide spectrum, synthetic antibacterial compound belonging to a class of drugs referred to as fluoroquinolone. It acts against bacterial by inhibiting the A subunit of DNA gyrase, a critical enzyme involved in the DNA. It is used for the treatment of urinary tract infections, surgical infections as well as sexual transmitted diseases.

2.1.4.4 Diclofenac Sodium

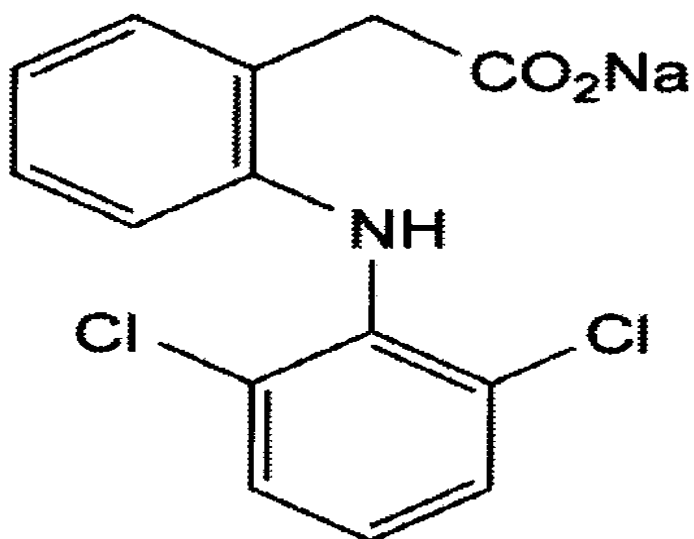


Figure 2.6: Chemical structure of diclofenac sodium (British Pharmacopoeia, 2013).

Diclofenac sodium is an inhibitor of cyclo-oxygenase, an analgesic and a chemical with inflammatory properties. It is a yellowish, slightly hygroscopic, crystalline powder. Diclofenac sodium is sparingly soluble in water, it readily dissolves in methanol and it is soluble in ethanol. It is also partially soluble in acetone. It has a melting point of 280 °C with decomposition and stored in a container which is airtight and is protected from light. It is used to manufacture gastro-resistant diclofenac tablets and its structure is shown in figure 2.6 above. It is indicated for the treatment of mild to moderate pain including period pains, back ache and symptomatic relief of sprains.

2.1.5 Exposure to Pharmaceuticals

The existence of pharmaceuticals in the environment can be attributed to the release of both active and partially active metabolites of pharmaceuticals through faeces and urine into the influent of wastewater treatment plants. For water bodies, the major routes of entry include human wastes, pharmaceuticals from industry as well as pharmaceuticals

used for agricultural purposes (Klavarioti et al., 2009). Soil is also contaminated by medication used for treating farm animals as a result of run off from fields and groundwater (Khetan and Collins, 2007). According to Kessler (2010), the single biggest source of very high concentrations of pharmaceuticals to the environment is the pharmaceutical manufacturing industry. The contribution from drugs usage while significant, is dwarfed by those from the pharmaceutical industries.

Pharmaceuticals manufacturing factories discharge large quantities of wastewater to effluent treatment plants which are subsequently released into the environment. This is the main route by which pharmaceuticals enter the environment. Conventional treatment procedures for which involve stage-wise primary, secondary and tertiary processes have been demonstrated to be inefficient in removing many pharmaceuticals from wastewater. Some pharmaceuticals are non-biodegradable and thus tend to build up in the environment even after using conventional effluent treatment methods (Vieno et al., 2007). In the pharmaceutical industry the manufacturing process is a batch-wise and multistage process and therefore lead to the generation of large quantities of effluent wastewater. The production and administration of pharmaceuticals is also expected to increase as a consequence of development, improvement of life expectancy and the advancement of lifestyle across the globe (Goossens et al., 2007).

2.1.6 Fate of Pharmaceuticals

When a pharmaceutical molecule enters the environment it goes through certain structural changes by biotic and non-biotic processes, such as biotransformation, biodegradation, photo transformation and hydrolysis, transforming the parent compound into new molecules with less toxicity. (Nikolaou et al., 2007). Different pharmaceuticals in the environment have different fates, with the main removal process in the environment being sorption and biodegradation even though photo-degradation

and hydrolysis are significant (Kummerer, 2009). APIs can persist for years in our surroundings. This is dependent on the toxicity of such compounds as well as their stability in the presence of light and air. Eckel (1993) detected pentobarbital in an anaerobic ground water plume which was 21 years old. Sarafloxacin has also been detected in fish farm sediments several months after they had been applied to the water. Pharmaceuticals have also been detected in groundwater which had been contaminated by manufacturing residues and landfill leachates (Halling-Sørensen, 1998).

Due to their inherent biological activity, active pharmaceutical ingredients within the environment can have fatal consequences and thus are of emerging concern (Huerta, 2012). Since the amount of pharmaceutical residues in an effluent is not part of EPA's requirement most of the effluents released from pharmaceutical companies in Ghana are discarded without any treatment.

2.1.7 Effects of Pharmaceuticals

In a study to determine the potential effect of pharmaceutical levels on humans, human embryos were exposed to a mix of 13 different pharmaceuticals in a manner that mimics the levels that are likely found in treated effluent wastewater (Potami et al., 2006). The work sought to account for the effect on people when these various pharmaceuticals are consumed in such an instance as wastewater reuse. Physical changes to the shapes and appearances of the cells were observed, an indication that even such low levels of pharmaceuticals have a potential effect on humans (Potami et al., 2006). The results of the study are however difficult to compare to the interaction that would be recorded when fully developed humans are involved.

When persistent pharmaceutical residues which are biologically active are present in irrigation water and organic fertilizers they are accumulated and stored in soils. These could be taken up by plants and lead to a re-exposure to animals and humans. The presence of these xenobiotics in plants could disrupt growth and development. For example Boxall et al. (2006) found a decline in plant growth when lettuce and carrots were exposed to phenylbutazone, oxytetracycline and enrofloxacin. A study by Kumar et al, 2005 found that cabbage, green onion and maize fertilized using affected manure, contained some amount of chlortetracycline.

At concentrations as low as 150 µg/ml ibuprofen, an anti-inflammatory drug has a potential antimicrobial activity against *Staphylococcus aureus*. It inhibits its growth. (Halling-Sørensen et al, 1998)

Endocrine disrupting chemicals are chemicals that can interfere with endocrine (or hormone) systems at certain doses and the presence in aquatic systems is of considerable concern due to their potency in disrupting the endocrine system (Anderson, 2005). When pharmaceuticals are released into the aquatic environment, they persist and result in microorganisms developing antibiotic resistant strains. Once in the environment they inhibit the oxidation of nitrites and methanogenesis. Some pharmaceuticals increase the toxicity of metabolites and other chemical combinations (Dalrymple et al, 2007).

Feminization in some species of fish due to exposure to pharmaceuticals in the aquatic environment has been reported (Orlando et al., 2004) and the near extinction of the vulture population in India has been attributed to the presence of the pharmaceutical diclofenac (Oaks et al., 2004).

2.2 WASTE MANAGEMENT AT COMPANY A

COMPANY A is a pharmaceutical manufacturing company which has been in operation for the past 10 years. The plant is located at Bubiashie, near Kaneshie, a suburb of Accra which lies 10 km away from the capital, Accra. Formulations manufactured include tablets, dry syrups and capsules. It is a relatively small company with a production batch size of 5000 x 70ml bottles for dry syrups and 300,000 for tablets and capsules. COMPANY A however does not have a wastewater treatment plant and thus releases its effluent wastewater without prior treatment into the public drainage system, thereby posing potential health risk to residents.

Waste management at the facility is carried out by the Accra Metropolitan Assembly (AMA.), the Food and Drugs Authority (FDA) and the Environmental Protection Agency (E.P.A.). Each institution performs a separate function. The AMA is responsible for public health and environmental sanitation on the outer surroundings of the plant and it conducts regular inspections to enforce by-laws. Removing PVC wastes, aluminium foils, corrugated boxes and other 'non-chemical' wastes are within its mandate.

The FDA regulates the pharmaceutical industry and pharmaceutical wastes like expired raw materials and products and other ingredients that do not meet specification. They have particular interest in how such wastes are disposed of. The FDA continues to landfill pharmaceutical wastes even though a literature review by Kümmerer (2009) indicated that burning of pharmaceuticals is better for the environment compared to landfilling. The effluent from landfills, if not treated, can pollute surface and groundwater. The EPA supervises the treatment and disposal of industrial effluent to ensure that they meet the agency's specifications stipulated in its guidelines.

2.3 MECHANISMS FOR PHARMACEUTICALS REMOVAL

A number of advanced techniques have been available for the removal of pharmaceuticals and their derivatives from effluent wastewater. Majority of these processes have however not been implemented on a large scale successfully. They include the following: Membrane separation, activated carbon, chlorination and oxidation.

2.3.1 Membrane Separation

Microfiltration, ultra-filtration, nano-filtration (NF) reverse osmosis (RO), electro dialysis reversal and membrane bioreactors are some of the membrane processes which have been applied both at pilot level and full scale basis for the removal of APIs. Even though pressure driven, nano-filtration and reverse osmosis studies for the removal of pharmaceuticals is limited since most of the studies rather employed NF and RO membranes for tertiary treatment in wastewater recycling plant or for the treatment of saline groundwater (Snyder et al., 2007).

Snyder et al, 2007 indicated that different configurations of RO have demonstrated efficient removal of pharmaceuticals to levels below detection limits. Since the pore sizes involved in microfiltration and ultra-filtration are far larger than the micro pollutants, they easily slip out and therefore they are not as effective in the removal of organic contaminants.

2.3.2 Activated Carbon

Activated carbon is recognized as a technology applied for the removal of synthetic and natural organic materials. It is usually applied in its granular form in packed bed filters or as a powdered feed making it very useful in adsorption and filtration. Carbon regeneration and disposal are however of environmental concern. Snyder et al. (2007)

discovered that both the granular activated carbon (GAC) and powdered activated carbon (PAC) (5 mg/L) removed more than 90% of oestrogens (100-200 ng/L initial concentrations). PAC removed greater than 90% of 19 of some 26 APIs tested and these included trimethoprim, carbamezapine and acetaminophen.

Before the treatment of micro pollutants using PAC, it is important to filter (Hartig et al., 2001). This filtration stage is required because it reduces the carbon demand of wastewater due to a reduced blockage by high molecular weight compounds of the micro pores present on charcoal. PAC is therefore only suitable for the treatment of wastewater which had been pre-treated and or those wastewaters with very low organic loads. To improve the performance of PAC the contention time must be increased (Westerhoff et al., 2005).

2.3.3 Chlorination

Chlorine dioxide has been shown to be effective for removing sulfamethoxazole, ethinylestradiol, roxithromycin and diclofenac (Khetan and Collins, 2007). According to a work by Lee and Von Gunten (2009) 90% conversion of oestrogen and ethinylestradiol was achieved with chlorine. Diclofenac, acetaminophen, sulfamethoxazole and fluoroquinolone are oxidized when subjected to chlorination.

When acetaminophen is oxidized during chlorination the by-products include the toxic N-acetyl-p-benzoquinine imine and 1, 4-benzoquinone. Both Metoprolol and sulfamethoxazole form carcinogens such as chloramines as one of their oxidation products because ammonia chlorination is about a thousand time faster than phenol chlorination (Pinkston and Sedlak, 2004)

2.3.4 Oxidation

Higher removal rates have been shown as a result of the development of oxidation processes and are used to augment conventional wastewater treated systems to improve the removal of organic pollutants like pharmaceuticals (Khetan and Collins, 2007). Oxidation processes require chemicals like transition metals, ozone, hydrogen peroxide, and metal oxides as well as energy sources like ultraviolet visible radiation or electric current. This mechanism involves the free radical production, specifically the hydroxyl radical which facilitates the conversion of pollutants to less toxic and more biodegradable product compounds (Ikehata et al., 2006).

Ultimately the objective of the oxidation process is to mineralize pollutants by converting them to carbon dioxide, water and other minerals. Several studies have demonstrated the potential of advanced oxidation processes (AOPs) in the removal of pharmaceuticals (Ternes et al., 2002). Oxidation processes affect a compound's polarity and the number of functional groups and thus change the functional potency of the pharmaceutical compound in the body of a human. The original modes via which pharmaceuticals effect their action then disappear, for example hydroxylated antibiotics do not promote the formation of resistant strains (Ternes et al., 2003). Since some degradation products may be more toxic than the parent compounds, degradation products must be identified and monitored throughout the treatment process.

2.3.5 Biosand Filtration

The biosand filter is mostly used for treating water for domestic consumption. Research on its ability to remove active pharmaceutical ingredients from effluent wastewater is limited.

2.4 BIOSAND FILTER

2.4.1 Introduction

The Biosand Filter was invented by Dr. David Manz at the Calgary University and has since been introduced in a number of countries (Earwaker, 2006) like Canada, the USA and Mexico. It is also used in El Salvador, China, the Philippines and Brazil (University Technologies International, 1998). It is a household water filter that makes dirty water safe to drink. The biosand filter is an adapted version of slow sand filters which have been used for community water treatment for several years in many parts of the world. The container of the filter may either be made of plastic or concrete, before being filled with carefully prepared layers of sand and gravel or charcoal in some augmented versions.

The BSF is designed to support a biofilm during intermittent flow, unlike a slow sand filter. In the design of the biosand filter, there are two elements that are responsible for the preservation of the biofilm. While at rest, the BSF holds about 5 cm of water above the top surface of the sand column. This 5 cm resting water level is the head height at which the bio-layer receives maximum oxygen while ensuring that there is adequate protection from incoming water. It is necessary that a constant aquatic environment is provided to ensure the survival of the microorganisms present in the layer. It is important that the water layer is not too deep since it might prevent oxygen from diffusing and this may lead to the suffocation and death of the microorganisms. The other element of the design that protects the biofilm is the presence of a diffuser plate or basin which prevents input water from disturbing the top layer of the sand (Ritenour, 1998).

The BSF has been reported to have removed 15-20 % of dissolved carbon dioxide and 90-95 % iron (Ngai and Welewijk, 2003), up to 1 NTU turbidity (Buzunis, 1995), 50-

90 % of organic and inorganic contaminants (Palmateer et al., 1999) and less than 47 % arsenic (Collins, 1998) the BSF has thus been shown to be effective in the reduction of turbidity and pathogens from drinking water but its performance in terms of chemical pollutants from industrial effluents have not been reported.

2.4.2 How Biosand Filter Works

Various filtration processes occur within the biosand filter and these include straining, settlement, filtration, the removal of organics, the inactivation of microorganisms and chemical change (Huisman and Wood, 1974). The biosand filter works based on gravity and does not require any prior treatment. Two features that control the flow rate of water from a biosand filter is the height of the water column above the sand bed as well as the porosity of the sand bed (Barnes et al., 2009).

When particles are too large to pass through the interstices between the grains that form the biosand filter media, they are trapped and this process is referred to as surface straining. This is the major mechanism by which turbidity is reduced in the BSF (Harhoff and Cleasby, 1991). In order to trap particles of 15 % the grain size, it is proposed to use spherically shaped grains (Huisman and Wood, 1974). With a hypothesis based on a research on slow sand filters, Mohammed et al. (1996) and Collins (1998) found that BSFs may remove some heavy metals.

According to Huisman and Wood (1974), Effective purification is provided by a complex biological layer called the schmutzdecke whereas the underlying sand provides a support medium. They explain that food is provided in the form of deposited organic matter. To provide the energy that they require for metabolism, the bacteria oxidize part of the food through dissimilation and convert a fraction into cell material for growth through assimilation. The products of the dissimilation process are

transported by water for reuse at greater depth by some other organisms. An equivalent dying off also accompanies the assimilation process. These processes contribute to the freeing up of organic matter which, at lower depths become available to other bacteria. Through these mechanisms, there is a gradual breakdown and conversion of the entire degradable organic matter present in the raw water into water, carbon dioxide and inorganic salts like sulfates, nitrates and phosphates to be discharged and collected in the biosand filter effluent.

Studies by Weber-Shirk and Dick (1997) also attribute the removal of pathogenic microorganisms to a phenomenon referred to as bacterivory. This phenomenon is the consumption of bacteria by predators such as protozoa and rotifers. Sites for the attachment of future bacteria are potentially freed up when predators graze on attached bacteria whereas those predators that feed on suspending bacteria directly remove particles from the mobile phase.

2.4.3 Maturation of the Biological Layer

Maturation of the bio-layer is a process which involves both physical and biological mechanisms. According to Bellamy et al. (1985). While filtration is taking place several microbial growth made up of bacteria, algae, and zooplankton occurs within the gravel layer and within the sand. During this maturation period, the efficiency of bacteria removal is low within the filter. The sand bed of a freshly prepared removes 85 % the coliform bacteria present in an influent. The percentage removal however increases to 99 % for coliform bacteria as the sand bed matures (Bellamy et al., 1985). The BSF is usually considered to have ripened after a period of one or two weeks (Jellison et al., 2000).

2.5 CHARCOAL FILTER

The charcoal filter involves the use of local charcoal or industrial grade activated charcoal. Charcoal is made elemental carbon in its graphite modification and it is used for the purification of water. During the treatment of water, contaminants diffuse into the charcoal pores and are attached to the surface of the charcoal. Several reactive sites for the attachment of various dissolved compounds are provided by the porosity and large surface area charcoal provide. Due to Van der Waals forces, both targeted and non-targeted organic compounds dissolved in water are attracted to these reactive sites.

Non-problematic dissolved organic matter which happen to be present in every water from natural sources occupy sites on the charcoal surface and block the attachment of those contaminants of concern. The binding of non-target contaminants in the charcoal filters is mitigated by earlier processes like the sand and gravel filtration which remove a huge fraction of such background dissolved organic matter from the influent before any interaction with the charcoal. To achieve a high level of treatment prior to reaching the charcoal filter, it is critical to secure the carbon for the removal of targeted dissolved organic compounds. Some of these compounds must have made it through the previous treatment stages.

In the charcoal filter a biofilm readily establishes on the surface of the filter media. Even though the biofilm contributes to the percolation of natural organic matter in the column and therefore contributes to non-target binding to reactive sites of charcoal, the development of pathogenic colonies in the media is inhibited by environmental microorganisms which constitute the biological layer through predation and competition.

Dissolved contaminants are attenuated by carbon, allowing time for the biological layer to break them down. Additional adsorption takes place due to the availability of free sites on carbon as a consequence of the breakdown. The duration of the filter media is thus extended. In some long running carbon bio-filters certain compounds which are generally classified as non-biodegradable are degraded. Some environmentally unfriendly compounds are broken down as a result of the constant exposure of microorganisms to contaminants retained by carbon. Over long periods the microorganisms tend to acclimatize and develop those enzymatic pathways required to breakdown these recalcitrant contaminants. Thus there is a net removal of certain hazardous chemical contaminants from the effluent due to a synergy between biodegradation processes and adsorption.

According to the USA EPA national drinking water standards, the following water contaminants can be reduced to acceptable standards by activated carbon filtration; chromium and mercury complexes, inorganic mercury, benzene, endrin, lindane, methoxychlor and organic arsenic (Water quality association, 1989).

CHAPTER 3

3.0 MATERIALS AND METHODS

3.1 DESIGN OF THE BIOSAND AND CHARCOAL FILTERS

The biosand and charcoal filters were both fabricated at COMPANY A based on guidelines given in literature (CAWST, 2009). Both filters were constructed with 100 L drums and orderly arranged to allow filtrate from the biosand filter to pass through the charcoal filter before collection, as indicated in figure 3.1. In both filters, drainage gravel has a depth of 5 cm from the base of drum and separating gravel occupies the next 5 cm from surface of drainage gravel. Filtration sand and standing water occupy 40 cm and 5 cm respectively in the biosand filter whereas filtration sand and charcoal occupy 15 cm and 30 cm respectively in the charcoal filter. In both filters, the size of filtration sand was less than 0.7 mm, separating gravel was between 0.7 mm and 6 mm and drainage gravel was between 6 mm and 12 mm.

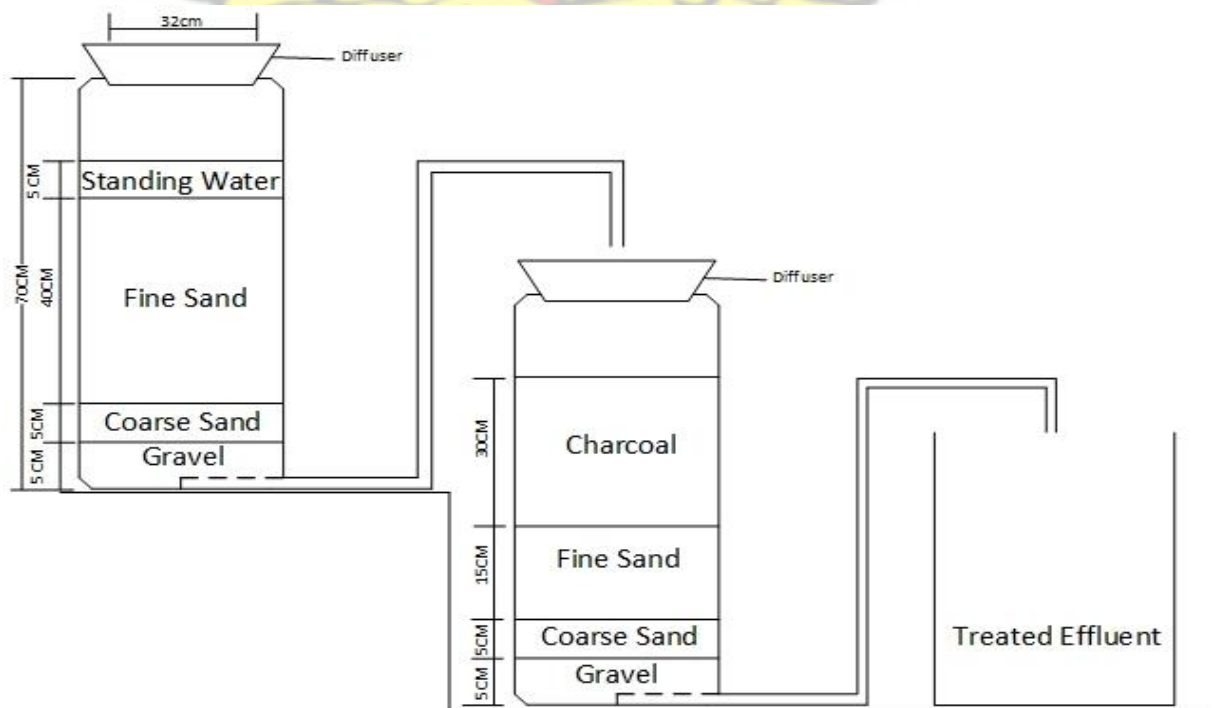


Figure 3.1: A schematic representation of the setup of biosand filter and charcoal filter.

3.2 SAND AND GRAVEL LOCATION

Crushed granite was obtained from Eastern Quarries Limited in the Shai Hills area of the Greater Accra Region. The selection of quarry dust and chippings was to improve treatment efficiency of the filters since they potentially contain lower levels of contaminants compared to other readily available sources. They are considered to be less contaminated because they are least exposed.

3.3 CONSTRUCTING THE FILTER CONTAINER

The filter containers for both the biosand filter and the charcoal filter were made of 100 L plastic drums with height of 70 cm and opening 32 cm wide. A 2.5 cm diameter incision was made on the lower part of each drum, 1 cm from base for setting the standpipe. PVC pipes with 2.5 cm diameters were cut to differing lengths and joined with elbows. The portion of the PVC fitted to the base of the interior of the bucket was drilled with 1 mm holes using an electrical drill. One end was fixed onto the interior section of the bulkhead fitting and the other open end was capped to avoid clogging during the filtration process. The standpipe portion of the PVC was tightly fixed to the exterior section of the bulkhead fitting to prevent leakages. After all glues had dried and fasteners were fixed the filter container was filled with water to locate possible leakages and ensure the flow rate is 1 L/min.

3.4 BUILDING THE DIFFUSER

In order to prevent water poured into the filter from disturbing the biological layer, a diffuser was built using a plastic basin. The diffuser basin was drilled to perforate it with 2 mm sized circular holes 2 cm apart, with the help of an electrical drill. Gridlines intersecting at 2 cm intervals were drawn underneath the basin to ensure evenly distributed holes. A rule and a knife were used to draw the lines. The diffuser basin at

a steady rate, distributes and maintains the flow rate of the biosand filter. It also traps large particles like grass and leaves (Barnes et al., 2009).

3.5 SIEVING THE SAND AND GRAVEL

The quarry dust was dried and cleaned to allow easy flow through the sieves and to ensure the removal of leaves, grass or other material from it. It was put through the 12 mm sieve and any rocks that stayed on top of the 12 mm sieve was thrown away as they were too big to use in the filters. All the material that went through the 12 mm sieve was picked up and put through the 6 mm sieve. The gravel that stayed on top of the 6 mm sieve was stored and used as drainage gravel that went inside the filter. The material that went through the 6 mm sieve was put through the 0.7 mm sieve. The gravel that stayed on top of the 0.7 mm sieve was stored and used as a separating gravel inside the filter. All the sand that fell through the 0.7 mm sieve was used as a filtration sand.

3.6 WASHING THE FILTRATION SAND

Some sieved filtration sand was placed in a bucket and filled half full with clear water. The sand was swirled around in the water with the hand and the water decanted into a drain. The sand was held back with the hand to prevent it from falling out of the bucket. The washing procedure was repeated and a jar test was used to determine if the sand had been washed clean. During the jar test a little sand was placed in a clean, transparent glass beaker, filled with water and covered with a lid. The filtration sand was stirred for 1 min in the water and observed after allowing it to rest for 4 secs. The top of the sand could be seen but not clearly, an indication that the washing was good.

3.7 WASHING THE GRAVEL

The sieved separation gravel and drainage gravel was put in a bucket and the bucket was filled half full with clear water. The gravel was swirled around in the water with

the hand and the water is poured out of the bucket into a drain while holding back the gravel to prevent it from falling out of the bucket. This washing procedure was repeated until the gravel is completely clean and the water dumped out is clear. The cleaned gravel was stored in a dry, clean place.

3.8 PREPARATION AND WASHING OF THE CHARCOAL

The charcoal was obtained from the market and broken down into smaller pieces in order to increase the surface area. The charcoal chips were sifted through a 6 mm sieve to get rid of dust particles. The chips retained on the sieve were stored and used in the charcoal filter. The charcoal chips were put in a bucket and the bucket was filled half full with clear water. The charcoal was swirled around in the water with the hand and the water poured out of the bucket into a drain while holding back the charcoal to prevent them from falling out of the bucket. This washing procedure was repeated until the charcoal was completely clean and the water dumped out is clear. The cleaned charcoal was stored in a dry and clean place.

3.9 FILTER INSTALLATION

Each filter was placed on a flat, level platform in an area away from sunlight where there was enough room to manoeuvre. 10 litres of water was put in the filter before addition of other components to prevent air pockets and dry spots in the sand. As shown in figure 3.2, the charcoal filter was positioned in front of the biosand filter to allow filtrate from the biosand filter to pass through the charcoal filter.

3.9.1 Biosand Filter

The drainage gravel was placed in the plastic filter container to the 5 cm mark and topped with the separation gravel to the 10 cm mark. The clean filtration sand was quickly added until it reached the 50 cm mark on the drum. The diffuser was fixed and

some more water was added to allow the filter to run until the water stopped flowing from the outlet. A standing water of 5 cm is allowed in the biosand filter to support a biolayer.

3.9.2 Charcoal Filter

The drainage gravel was placed in the plastic filter container to the 5 cm mark and topped with the separation gravel to the 10 cm mark. The clean filtration sand was quickly added until it reached the 25 cm mark on the drum before topping up with charcoal chippings to the 55 cm mark. The diffuser was fixed and some more water was added to allow the filter to run until the water stopped flowing from the outlet.

3.10 BULK SAMPLING AND SPIKING OF EFFLUENT

Samples of effluent were collected weekly for four weeks at regular intervals. 50 L of effluent samples were collected each week in a sampling bucket over the period from COMPANY A. For collection, bucket was cleaned with tap water, uncovered and effluent was collected at the valve of an effluent reservoir. The bucket was tightly covered immediately after sampling. One gram each of diclofenac sodium, ciprofloxacin hydrochloride, cefuroxime axetil, and amoxicillin trihydrate was added and samples were taken in bottles.

3.11 SAMPLING SPIKED EFFLUENT

Spiked effluent was stirred and samples were collected in appropriately labelled 500 ml bottles for the study. The samples were refrigerated at 4 °C to preserve them, ensuring that no other chemicals are added. The samples were warmed to room temperature (25 °C) prior to analyses. Parameters such as API concentration, temperature, and pH were determined soon after sampling.

3.12 FILTRATION AND SAMPLING TREATED EFFLUENT

During this study, a total of 200 L of spiked pharmaceutical effluent was filtered. The spiked effluent was passed through the filters, filling the biosand filter slowly and at intervals to avoid an overflow. Filtrate from the biosand filter was allowed to pass through the charcoal filter and treated effluent samples were collected in bottles only after more than half of the volume of untreated effluent had passed through both filters. Collection was at the outlet of charcoal filter. Each sample bottle was labelled with the appropriate information and the effluent was characterized by determining the physico-chemical characteristics. Samples were refrigerated at 4 °C to preserve them, while ensuring that no other chemicals are added. The samples were warmed to room temperature (25 °C) prior to analyses. Parameters such as API concentration, temperature and pH were determined soon after sampling.



Figure 3.2: The experimental set up during the filtration process

3.13 DETERMINATION OF CONCENTRATIONS OF APIs

To determine the concentration of each API in the effluent, known concentrations of standard APIs were prepared. A blank and the results of 1 to 10 mg/L API reference standards prepared by dissolving in respective solvents were used to generate calibration curves. Cefuroxime axetil and diclofenac sodium standards were dissolved in methanol whereas ciprofloxacin hydrochloride and amoxicillin hydrochloride were dissolved in R.O. water and 0.1 M sodium hydroxide solution respectively. The absorbance of standard cefuroxime axetil, diclofenac sodium, ciprofloxacin hydrochloride and amoxicillin hydrochloride was determined at 247 nm, 285 nm, 276 nm, and 247 nm respectively with the UV-visible (SHIMAZO 1700 PharmaSpec) spectrophotometer. Effluent samples were centrifuged at 2,000 rpm for 3 minutes and filtered through 0.7 μ m filter paper to remove suspended solids before the concentration of APIs were determined.

3.13.1 Amoxicillin Trihydrate

To 5.0 ml of effluent sample 5.0 ml of 0.1 M sodium hydroxide was added and the mixture was shaken for 10 mins. The absorbance at 247 nm was read and the concentration was determined. Triplicate readings were taken for the sample.

3.13.2 Cefuroxime Axetil

To 5.0 ml of effluent sample 5 ml of methanol was added and the mixture was shaken for 10 mins. The absorbance at 247 nm was determined and the concentration calculated. Triplicate readings were taken for the sample.

3.13.3 Ciprofloxacin Hydrochloride

To 5 ml of effluent sample 5 ml of R.O. water was added, the mixture was shaken for 10 mins and the absorbance at 276 nm was read. The concentration of the API was calculated. Triplicate readings were taken for the sample.

3.13.4 Diclofenac Sodium

To 5 ml of effluent sample 5 ml of methanol was added, the mixture was shaken for 10 mins and the absorbance at 285 nm was read. The concentration was determined for the API and three readings were taken.

3.14 PHYSICO-CHEMICAL ANALYSES

3.14.1 Determination of pH

pH was electrometrically measured using an MFRS digital pH meter; model number, CAT no: CL-54. Three different buffer solutions of pH 4, 7 and 10 were used to calibrate the pH meter before it was used for the analyses. To use the pH meter, the protective cap was removed from the tip of the probe and the probe was washed with deionized water. The probe was then stirred into a beaker containing 100 ml of the effluent sample until a stable reading was displayed. The reading was recorded as pH.

3.14.2 Determination of Temperature

A calibrated 30 cm long mercury-in-glass thermometer was used to measure the temperature of the four effluent samples both before and after treatment. The measurement was done immediately after sampling by inserting the thermometer into the sample and leaving it for 2 mins. The reading on the thermometer was noted and recorded.

3.14.3 Determination of Electrical Conductivity

The electrical conductivity was determined by using a calibrated WTW Cond 3210 conductivity meter. The meter was calibrated by immersing the probe in a potassium chloride solution with known electrical conductivity of 1413 $\mu\text{S}/\text{cm}$. The electrical conductivity of the effluent was then determined by inserting the probe of the meter in 100 ml of the effluent sample until it was fully covered. The reading was noted and recorded.

3.14.4 Determination of Turbidity

To determine the turbidity of the samples, a Hach DR/890 Portable Colorimeter. Distilled water was placed in the cuvette to zero the instrument, ensuring that the clear face of the cuvette is in the path length. 10 ml of the sample was placed in the colorimeter and the reading was recorded.

3.14.5 Determination of Total Dissolved Solids (TDS)

To determine the TDS, an H2550 pH / ORP α EC / TDS / NaCl Meter was used. The probe of the meter was immersed in 100 ml of the sample, ensuring that the sensor was fully submerged until the reading was stabilized. The reading was recorded.

3.14.6 Determination of Total Suspended Solids (TSS)

TSS was measured by using a Hach DR/890 Portable Colorimeter. Distilled water was placed in the cuvette to zero the instrument, ensuring that the clear face of the cuvette is in the path length. 25 ml of the sample was placed in the colorimeter and the reading was recorded.

3.14.7 Determination of Biochemical Oxygen Demand (BOD)

The Winkler method was used to determine the BOD. A 500 ml sample of spiked effluent was kept in a BOD incubator at 20 °C for five days and another 500 ml sample was immediately analysed for its biochemical oxygen demand. The bottles were filled carefully to avoid formation of air bubbles and stoppered carefully. Effluent sample was fixed by adding 1ml each of Winkler I and Winkler II solutions. Winkler I is composed of manganous sulphate and water, whereas Winkler II is an alkaline-iodide-azide reagent. To 50 ml portion of the fixed sample in a conical flask, 5 ml of concentrated sulphuric acid was added, followed by three drops of starch indicator. The contents of the conical flask was titrated against sodium thiosulphate until a colour change from blue to colourless was observed at the endpoint. Titre value was noted and recorded. The procedure was repeated for the sample kept for 5 days and the titre value recorded.

$$\text{BOD} = \frac{(D1 - D5)}{P}$$

Where D1 is the dissolved oxygen of sample on day 1, mg/l

D5 is the dissolved oxygen of sample after 5 days of incubation at 20 °C, mg/l

P is the decimal volumetric fraction of sample used

3.14.8 Determination of Chemical Oxygen Demand (COD)

To 10 ml of spiked effluent sample in a clean conical flask, 3 ml of potassium dichromate was added and the mixture was acidified with 3 ml of concentrated sulphuric acid. The content was covered with a lid and heated for five minutes. While ensuring that drops of the content underneath the lid and the walls of the conical flask were washed back into the flask, 20 millilitres of distilled water was added. The mixture

cooled to room temperature and three drops of ferroin (1, 10 phenanthroline ferrous sulfate) indicator was added. In a direct titration using 0.025 M ferrous ammonium sulfate (FAS) as the titrant until a colour change is observed at the endpoint, the amount of dichromate was determined. The titre value was noted and recorded. A blank was prepared in the same manner as the sample solution using distilled water instead of the sample.

The COD was determined as shown below:

$$\text{COD (mg/L)} = \frac{(A - B) \times N \times 8000}{V}$$

V

A is the volume of FAS required for the titration of the blank

B is the volume of FAS required for the titration of the sample

N is the normality of the FAS

V is volume of effluent used

3.15 HEAVY METAL ANALYSES

To analyse the heavy metals cadmium, copper, chromium, zinc and lead, a VARIAN AA240FS Fast Sequential Atomic Absorption Spectrophotometer (AAS) was used. Pure metal standards of the ions (1000 mg/L) were acquired from the Ghana Atomic Energy Commission and used to prepare working standards at the Ghana Atomic Energy Commission Chemistry Laboratory. Effluent samples were taken in 500 ml propylene bottles. To 50 ml of the effluent sample 15 ml of 15.44 mol/L HNO_3 was added and slowly heated to a volume of about 20 ml. 5 ml of the concentrated HNO_3 was again added and the mixture was diluted with distilled water to 50 ml. The mixture was gently heated until complete digestion was obtained, indicated by a lighter coloured

solution. After being allowed to cool, it was transferred into a 50 ml volumetric flask and diluted to the mark. Samples were then analysed three times each for chromium, Cadmium, Copper, Lead, and Zinc using the Atomic Absorption Spectrophotometer. The absorption wavelengths were 228.802 nm for Cadmium, 324.753 nm for Copper, 538.304 nm for Chromium, 196.026 nm for Lead, and 213.856 nm for Zinc.

3.16 DETERMINATION OF TOTAL REMOVAL

The percentage removal of each pollutant was determined using the formula below

$$\text{Removal (\%)} = \frac{(I - F)}{I} \times 100$$

I

Where I is the value of pollutant before treatment

F is the value of pollutant after treatment

3.17 ANALYSES OF DATA

All metal and API concentrations were determined as milligrams per litre. Raw data collected for physico-chemical, APIs and heavy metals were analysed using Microsoft spreadsheet version 2013. Paired t-test was used to test for any significant difference between contaminant levels in untreated and treated effluents with p-values less than 0.05 considered to be statistically significant. The results were presented in the form of graphs.

CHAPTER 4

4.0 RESULTS

The results were analysed with Microsoft excel, using the paired t-test to determine if there are significant differences in the results for each parameter. The flow rate for the filter was 425 ml/minute for week one, 416 ml/minute for week two, 402 ml/minute for week three and 397 ml/minute for week four. The UV spectra for the effluents showed high absorbance between 260 nm and 320 nm and the maximum wavelength of absorbance was recorded at 280 nm. There was a high reduction in absorbance along the entire wavelength after treatment. The treatment efficiencies have been determined and presented.

4.2 PHARMACEUTICAL ANALYSES

4.2.3 Amoxicillin Trihydrate

The amoxicillin trihydrate concentrations in the effluent before treatment, for the four weeks were as follows: 138.44 mg/L, 123.43 mg/L, 182.48 mg/L and 100.73 mg/L for weeks 1, 2, 3 and 4 respectively. Post treatment, the concentrations reduced to 13.74 mg/L, 15.85 mg/L, 12.92 mg/L and 12.92 mg/L for week 1, week 2, week 3, and week 4 respectively as shown in Figure 4.1. The percentage reductions recorded for week 1, week 2, week 3 and week 4 were 90.08%, 87.16%, 92.92% and 87.17%, translating into a 89.33% average treatment efficiency over the treatment period. The variations in concentration before and after the filtration were determined to be statistically significant ($P < 0.05$) over the four week period.

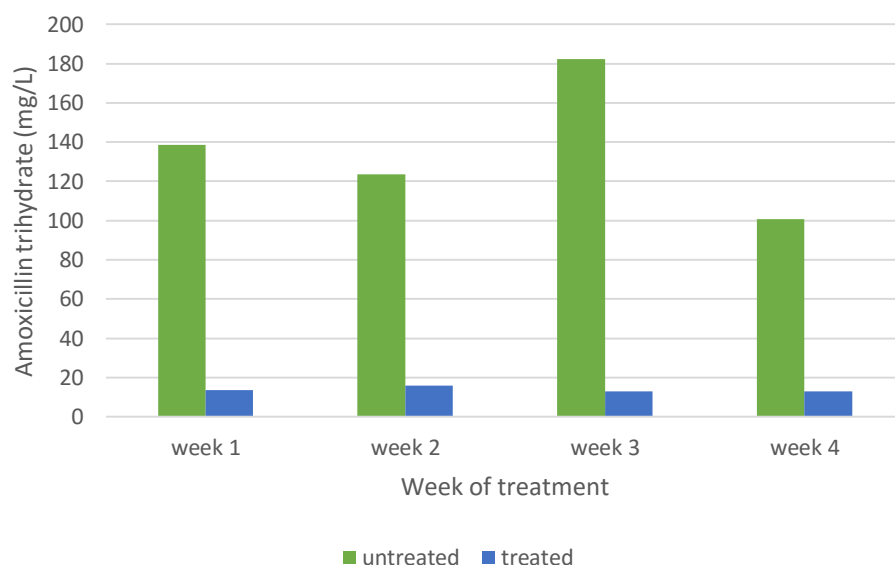


Figure 4.1: Weekly levels of amoxicillin trihydrate in pharmaceutical effluent before and after passing through biosand filter.

4.2.2 Cefuroxime Axetil

Cefuroxime axetil concentration in the untreated effluent recorded were 159.28 mg/L, 121.38 mg/L, 227.81 mg/L and 110 mg/L for week 1, week 2, week 3, and week 4 respectively. After treatments the following concentrations were recorded for week 1, week 2, week 3, and week 4 respectively; 13.21 mg/L, 15.54 mg/L, 11.62 mg/L and 10.57 mg/L. This translates into a cefuroxime axetil removal of 91.71 %, 87.20 %, 94.90 % and 90.39% for week 1, week 2, week 3 and week 4 respectively. The differences in concentration before and after passing through the biosand filter were determined to be statistically significant ($P < 0.05$).

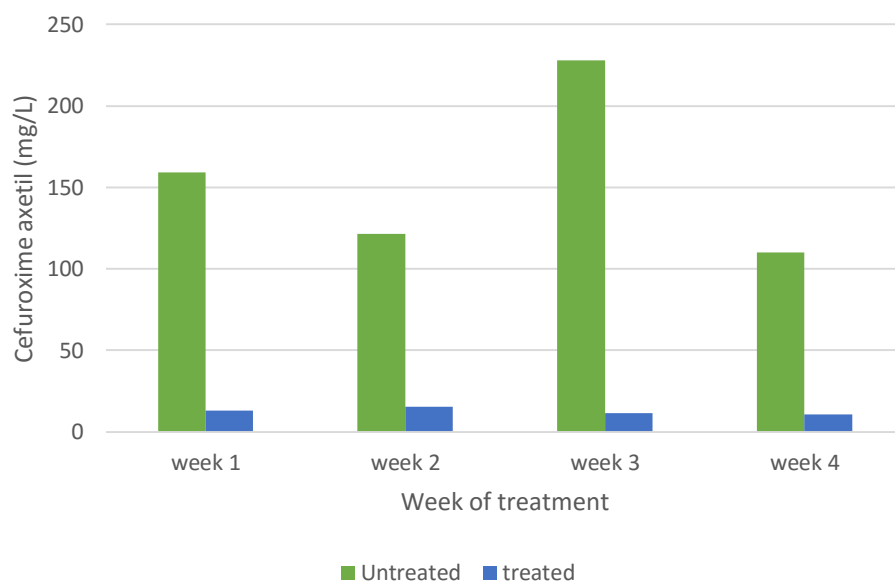


Figure 4.2: Weekly levels of cefuroxime axetil in pharmaceutical effluent before and after passing through biosand filter.

4.2.3 Ciprofloxacin Hydrochloride

The concentration for ciprofloxacin hydrochloride in the untreated pharmaceutical effluent ranged between 38.73 mg/L and 61.25 mg/L. Week 1, week 2, week 3 and week 4 concentrations were 51.01 mg/L, 38.73 mg/L, 61.25 mg/L, and 42.24 mg/L respectively. The concentrations however reduced to 2.59 mg/L, 4.09 mg/L, 4.13 mg/L and 2.05 mg/L from weeks 1 to 4 respectively. The percentage of ciprofloxacin hydrochloride removed over the four week period was 95.46%, 89.44%, 93.24% and 95.15% for week 1, week 2, week 3 and week 4 respectively. The differences in concentrations before and after treatment were determined to be statistically significant ($P < 0.05$).

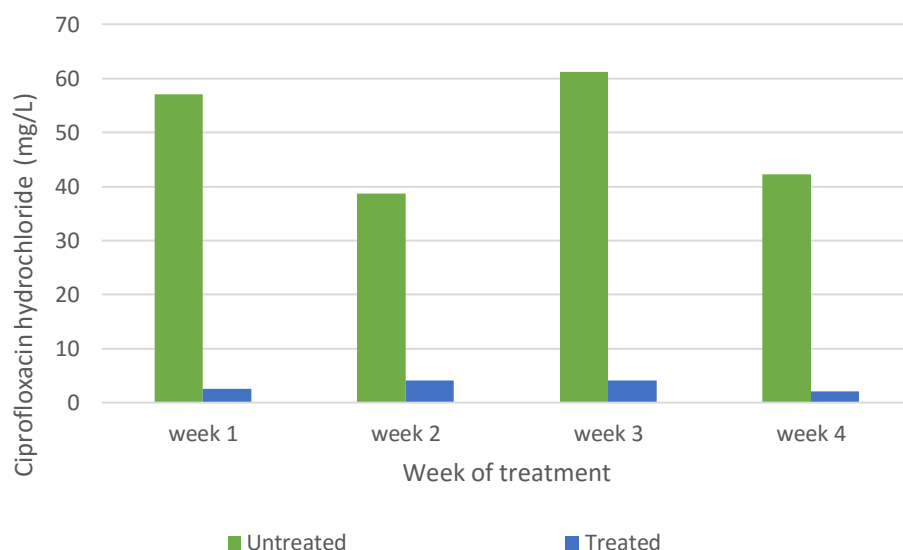


Figure 4.3: Weekly levels of ciprofloxacin hydrochloride in pharmaceutical effluent before after passing through biosand filter.

4.2.4 Diclofenac Sodium

The concentration for diclofenac sodium in the untreated pharmaceutical effluent ranged between 111.71 mg/L and 177.77 mg/L. Week 1, week 2, week 3 and week 4 concentrations were 171.70 mg/L, 111.71 mg/L, 177.77 mg/L and 116.46 mg/L respectively. The concentrations however reduced to 9.96 mg/L, 12.76 mg/L, 14.19 mg/L and 5.94 mg/L from weeks 1 to 4 respectively. The percentage of diclofenac sodium removed during the treatment period was 94.20%, 88.58%, 92.02% and 94.90% for week 1, week 2, week 3 and week 4 respectively. The variations in concentrations before and after treatment were determined to be statistically significant ($P < 0.05$).

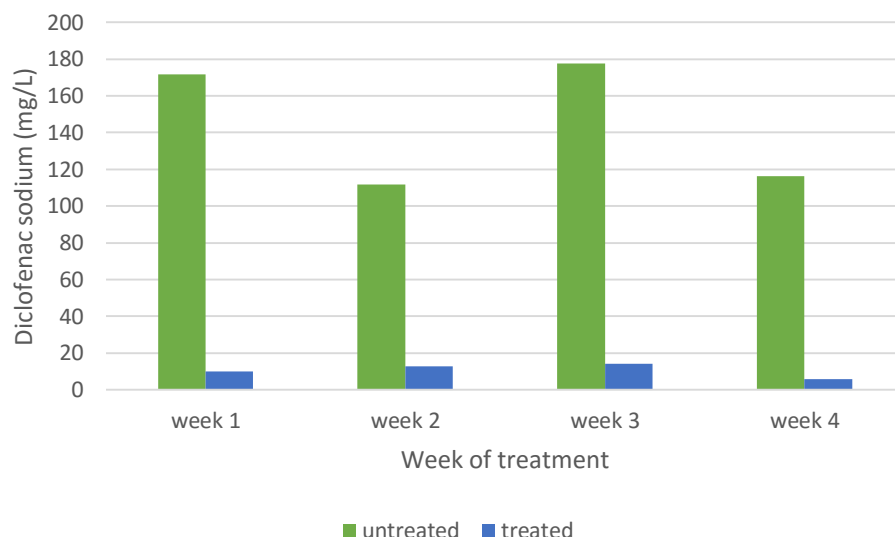


Figure 4.4: Weekly levels of diclofenac sodium in pharmaceutical effluent before and after passing through biosand filter.

4.3 pH

Before treating the pharmaceutical effluent the following pH values were recorded for each successive week; 8.38 for week 1, 7.36 for week 2, 7.45 for week 3 and 7.36 for week 4. After passing through the filter the pH values changed to 8.03 on the first week, 7.80 on the second week, 7.81 on the third week and 8.10 for the final week. The highest pH value was recorded on week 1 from the untreated effluent whereas the lowest pH value was from untreated samples from weeks 2 and 4.

4.4 ELECTRICAL CONDUCTIVITY

The values for electrical conductivity of the pharmaceutical effluent prior to treatment were 589 $\mu\text{S}/\text{cm}$, 656 $\mu\text{S}/\text{cm}$, 634 $\mu\text{S}/\text{cm}$ and 711 $\mu\text{S}/\text{cm}$ for week 1, week 2, week 3 and week 4 respectively. After treating the effluent samples the electrical conductivity readings reduced to the following; 504 $\mu\text{S}/\text{cm}$ for week 1, 510 $\mu\text{S}/\text{cm}$ for week 2, 574 $\mu\text{S}/\text{cm}$ for week 3 and 536 $\mu\text{S}/\text{cm}$ for week 4. This resulted in a removal efficiency of

14.43% for week 1, 22.26% for week 2, 9.46% for week 3 and 24.61% for week 4. The average treatment efficiency was 17.69% over the four week period. The variations in values of electrical conductivity before and after treatment were determined to be statistically significant ($P < 0.05$).

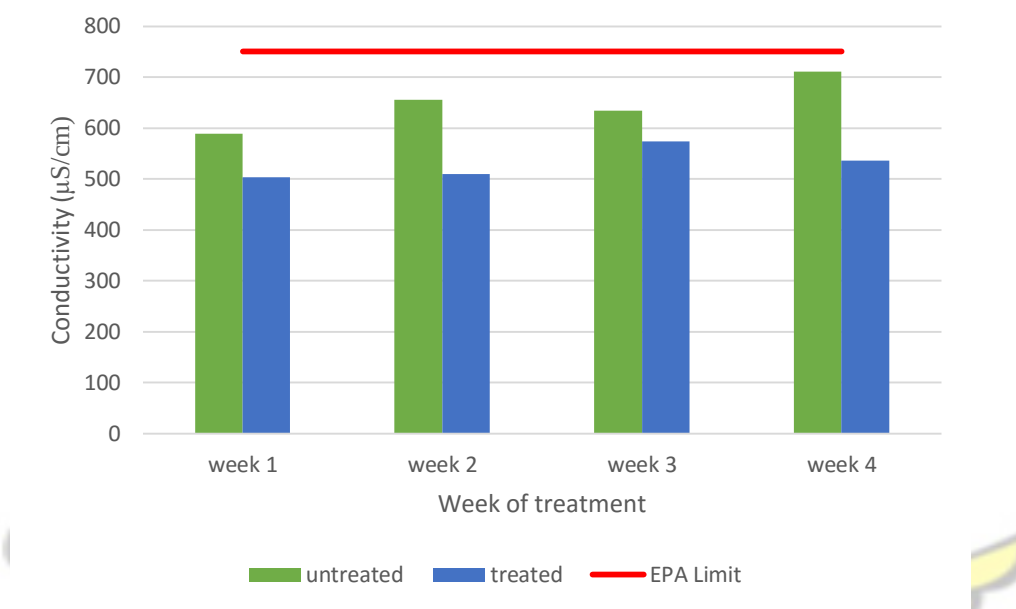


Figure 4.5: Weekly variations in electrical conductivity of pharmaceutical effluent before and after passing through biosand filter.

4.5 TOTAL DISSOLVED SOLIDS (TDS)

Prior to passing the spiked effluent through the filter, total dissolved solids from week 1 to week 4 were as follows; 336 mg/L, 368 mg/L, 363 mg/L and 398 mg/L respectively (Figure 4.6). Total dissolved solids reduced to 289 mg/L, 292 mg/L, 327 mg/L and 312 mg/L at a removal efficiency of 13.99%, 20.65%, 9.92% and 21.61% respectively for weeks 1, 2, 3, and 4. The variations recorded before and after each treatment over the four week period was determined as statistically significant ($P < 0.05$).

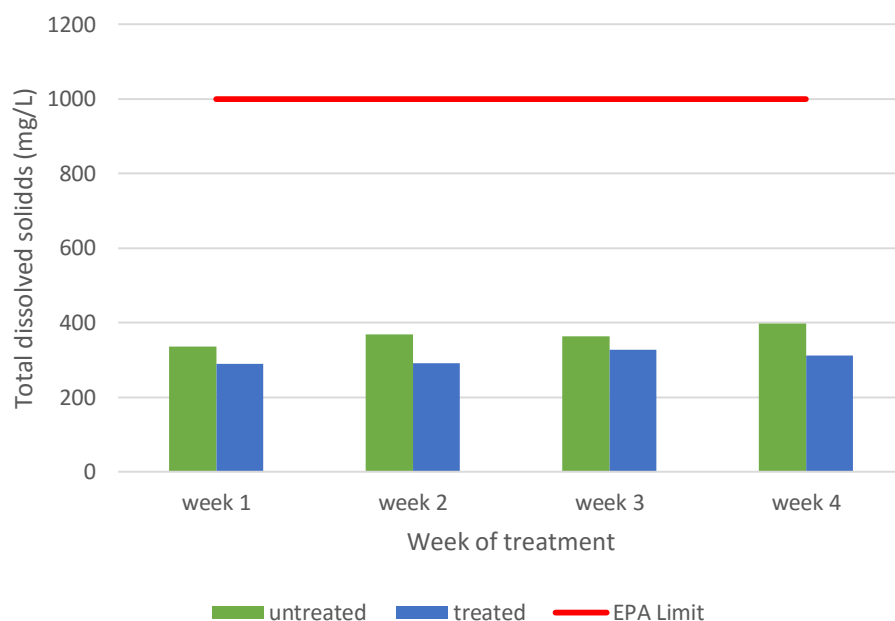


Figure 4.6: Weekly variations in total dissolved solids of pharmaceutical effluent before and after passing through biosand filter.

4.6 TOTAL SUSPENDED SOLIDS (TSS)

The following values were recorded as total suspended solids for the effluent samples before treatment; 227 mg/L, 121 mg/L, 287 mg/L and 38 mg/L for week 1, week 2, week, 3 and week 4 respectively. After treatment the TSS values reduced to 11 mg/L, 8 mg/L, 1 mg/L and 7 mg/L for each week. The treatment efficiencies were as follows for each week; 95.15% for week 1, 93.39% for week 2, 99.65% for week 3, and 81.57% for week 4. The average treatment efficiency was 95.08% over the four week period. The differences between the values for untreated and treated effluents were determined to be statistically significant ($P < 0.05$).

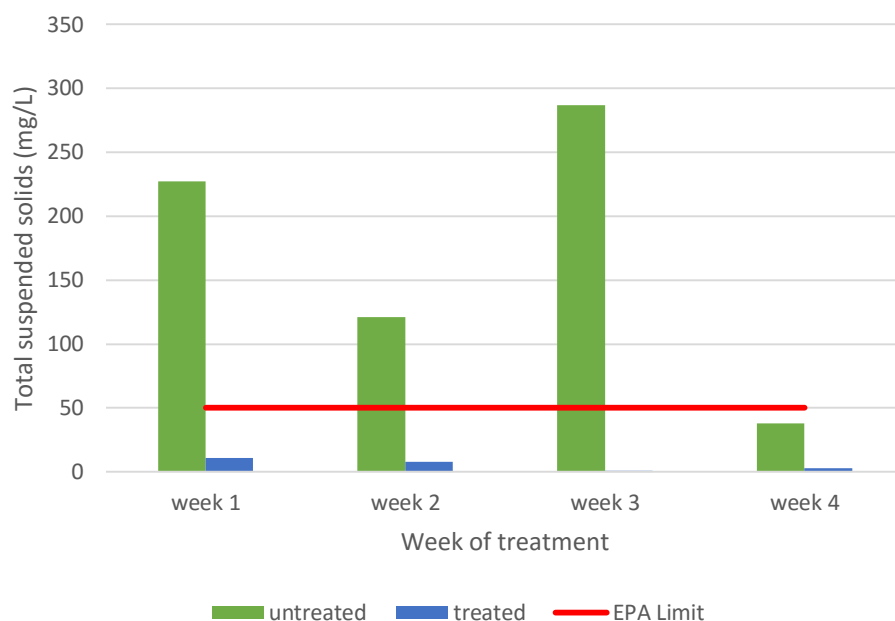


Figure 4.7: Weekly variations in total suspended solids of pharmaceutical effluent before and after passing through biosand filter.

4.7 TEMPERATURE

The temperature of the effluent for each week immediately after sampling was 30.3 °C, 30.2 °C, 30.9 °C and 29.7 °C from week 1 to week 4 and 30.1 °C, 30 °C, 30.8 °C and 29.5 °C respectively after passing through the filter. There was no significant change in the temperature between untreated and untreated effluent samples.

4.8 TURBIDITY

The turbidity for both treated and untreated effluent ranged from 1 NTU to 615 NTU over the four week period. For untreated effluent the turbidity values were as follows from week 1, week 2, week 3 to week 4 respectively; 264 NTU, 247 NTU, 615 NTU and 42 NTU. Upon passing through the biosand filter the turbidity changed to the following over the same period; 17 NTU, 13 NTU, 1 NTU and 3 NTU (Figure 4.8). These resulted in treatment efficiencies of 93.56% for week 1, 94.74% for week 2,

99.84% for week 3 and 92.86% for week 4. The differences between turbidity values before and after passing through the filter were determined to be statistically significant over the four week period ($P < 0.05$).

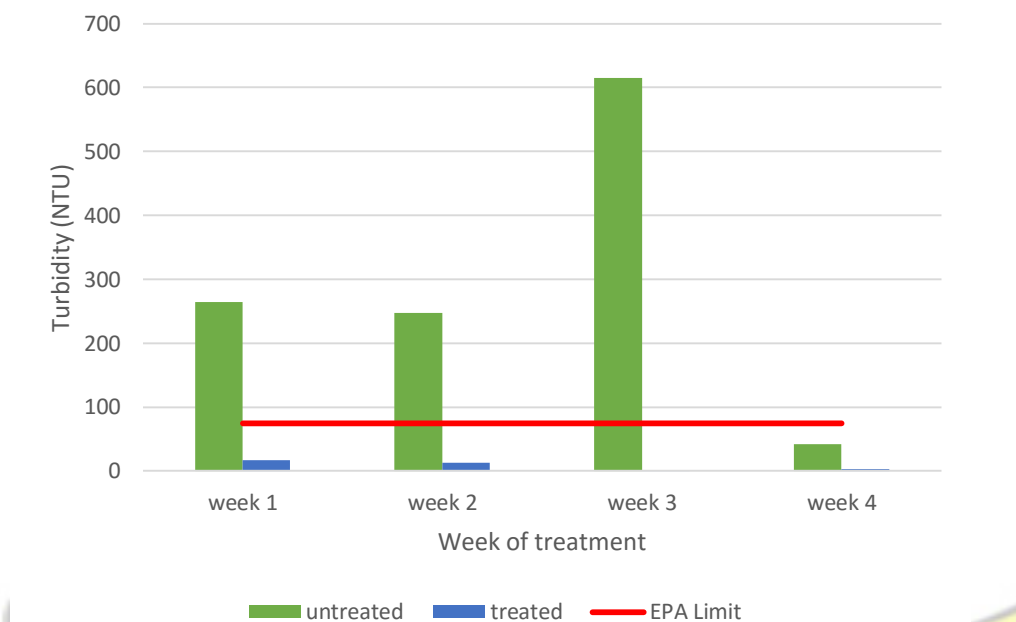


Figure 4.8: Weekly variations in turbidity of pharmaceutical effluent before and after passing through biosand filter.

4.9 BIOCHEMICAL OXYGEN DEMAND (BOD)

The BOD values recorded before the treatment were as follows 24.38 mg/L for week 1, 16.23 mg/L for week 2, 10.16 mg/L for week 3 and 4.06 mg/L for week 4. After the treatment the same BOD value of 2.032 mg/L for each week. This translates into a percentage reduction of 91.67%, 87.5%, 80% and 50% for each week. Even though all BOD values recorded before and after passing through the filters were below the EPA specification of 50 mg/L as shown in figure 4.9, the average treatment efficiency over the four week period was recorded as 77.29%. The difference between BOD values for

untreated and treated effluent samples were determined to be statistically significant ($P < 0.05$).

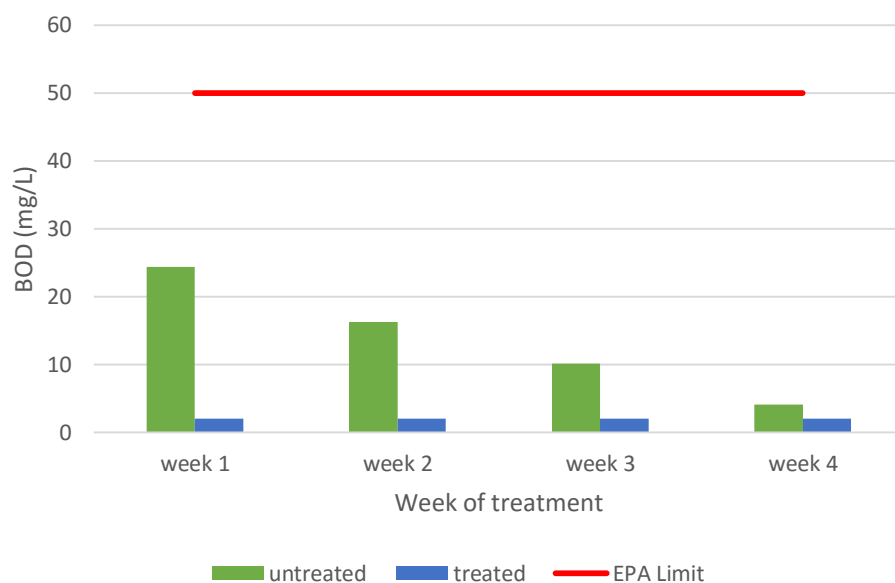


Figure 4.9: Weekly variations in biochemical oxygen demand of pharmaceutical effluent before and after passing through biosand filter.

4.10 CHEMICAL OXYGEN DEMAND (COD)

The recorded values for COD over before treatment are; 104.28 mg/L, 113.76 mg/L, 110.6 mg/L and 94.8 mg/L for week 1, week 2, week 3 and week 4. These values reduced to the following 79 mg/L, 90.5 mg/L, 91.64 mg/L and 66.36 mg/L for week 1, week 2, week 3 and week 4 as shown in figure 4.10. The percentage reduction after the treatment for week 1, week 2, week 3 and week 4 are as follows; 24.24%, 20.45%, 17.14% and 30%. There was a treatment efficiency of 22.96% over the four week period and the variations between COD values for untreated and treated effluent samples were determined to be statistically significant ($P < 0.05$). All COD values recorded were however below the EPA limit of 250 mg/L.

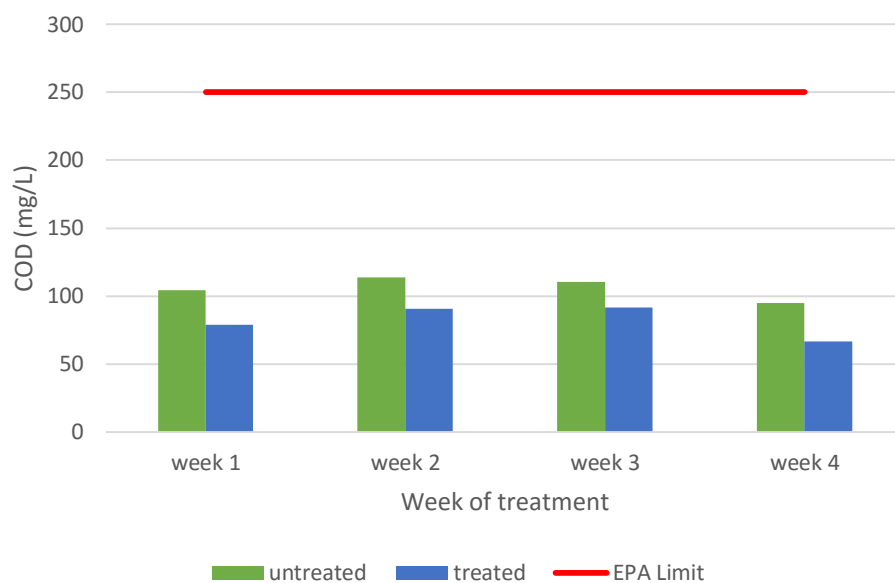


Figure 4.10: Weekly variations in chemical oxygen demand of pharmaceutical effluent before and after passing through biosand filter.

4.11 HEAVY METALS

4.11.1 Chromium

The concentration for chromium in the untreated pharmaceutical effluent was between 0.021 mg/L and 0.056 mg/L. Week 1, week 2, week 3 and week 4 concentrations were 0.045 mg/L, 0.056 mg/L, 0.044 mg/L and 0.021 mg/L respectively. After passing through the filter, the concentrations reduced to 0.021 mg/L, 0.023 mg/L, 0.029 mg/L and 0.018 mg/L from weeks 1 to 4 respectively. The percentage of chromium removed over the four week period was 53.33%, 58.93%, 34.09% and 14.29% for week 1, week 2, week 3 and week 4 respectively. The average treatment efficiency during the treatment period was 40.16%. The variations in concentrations before and after treatment were determined to be statistically significant ($P < 0.05$).

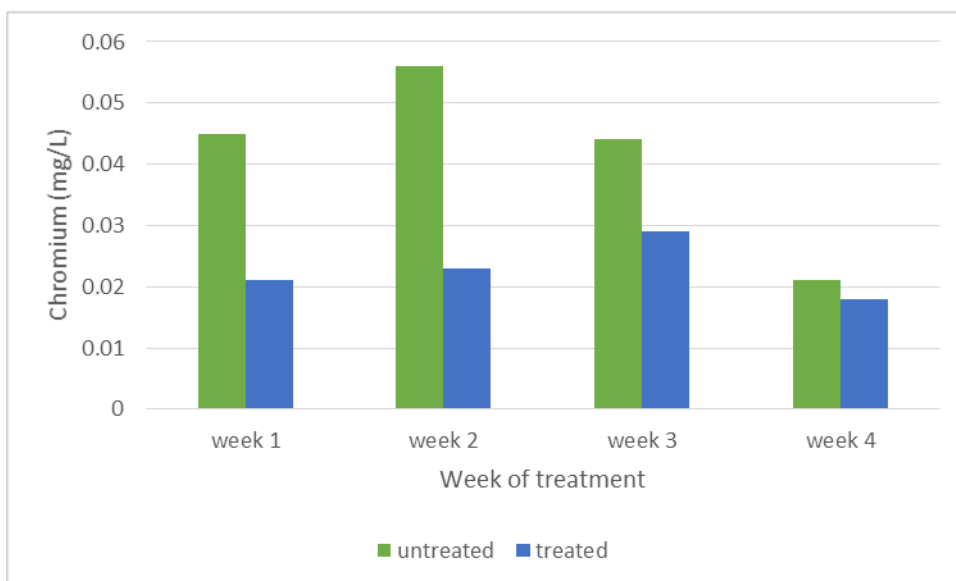


Figure 4.11: Weekly levels of chromium in pharmaceutical effluent before and after passing through biosand filter.

4.11.2 Cadmium

The concentrations for cadmium in the untreated pharmaceutical effluent for week 1, week 2, week 3 and week 4 were 0.002 mg/L, 0.008 mg/L, 0.003 mg/L and 0.002 mg/L respectively. The concentration recorded after passing through the filter was 0.002 mg/L for each week. The average treatment efficiency of cadmium over the four week period was 27.08%. The differences in concentration of cadmium in effluent samples before and after treatment were determined to be statistically insignificant ($P > 0.05$).

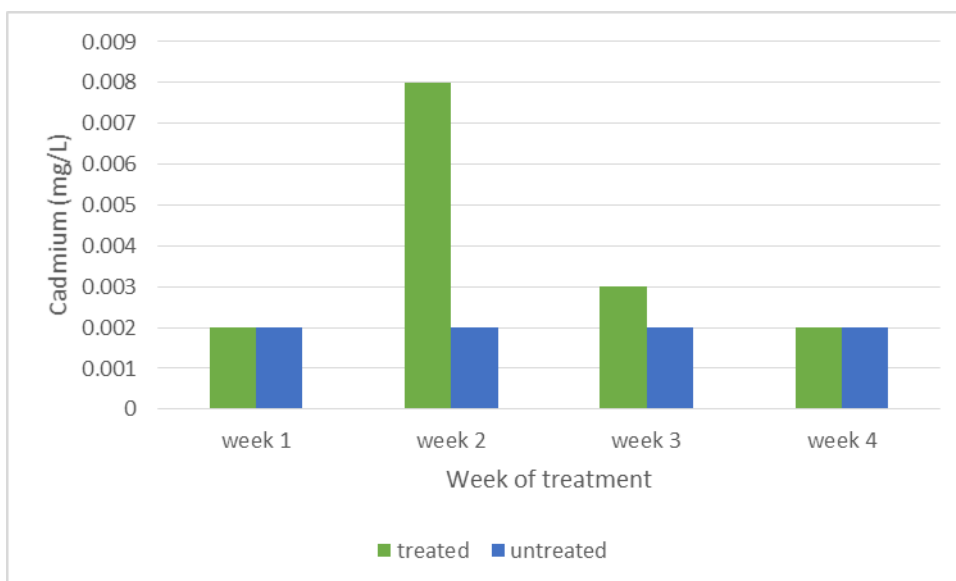


Figure 4.12: Weekly levels of cadmium in pharmaceutical effluent before and after passing through biosand filter.

4.11.3 Copper

The concentrations for copper in the untreated pharmaceutical effluent were 0.04 mg/L, 0.06 mg/L, 0.055 mg/L and 0.03 mg/L respectively. The concentrations however reduced to 0.016 mg/L, 0.007 mg/L, 0.01 mg/L and 0.005 mg/L from weeks 1 to 4 respectively after passing through the biosand filter. The treatment efficiencies of copper were 60%, 88.33%, 81.81% and 83.33% for week 1, week 2, week 3 and week 4 respectively. The average treatment efficiency was 78.37%. The variations in concentrations of copper in effluent samples before and after treatment were determined to be statistically significant ($P < 0.05$).

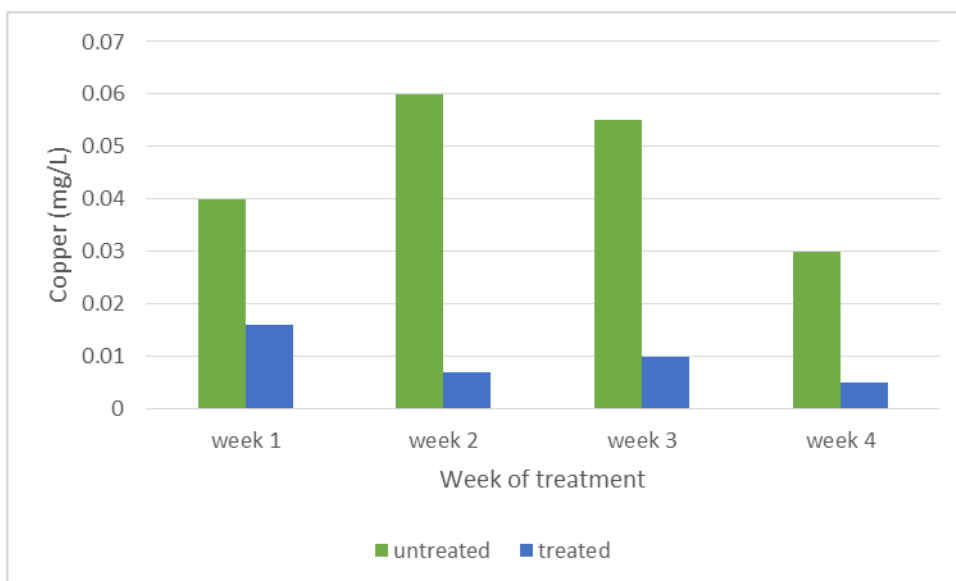


Figure 4.13: Weekly levels of copper in pharmaceutical effluent before and after passing through biosand filter.

4.11.4 Lead

The concentration of lead in the untreated pharmaceutical effluent ranged between 0.001 mg/L and 0.03 mg/L. Week 1, week 2, week 3 and week 4 concentrations were 0.001 mg/L, 0.03 mg/L, 0.001 mg/L and 0.001 mg/L respectively. After treatment, the concentration remained 0.001 for those samples which recorded 0.001 mg/L prior to treatment however the concentration reduced to 0.01 mg/L week 2. The treatment efficiency of lead in week 2 was 66.67%. With an average percentage reduction of 16.67%, the differences in concentrations of lead in effluent samples before and after treatment were determined to be statistically insignificant ($P > 0.05$).

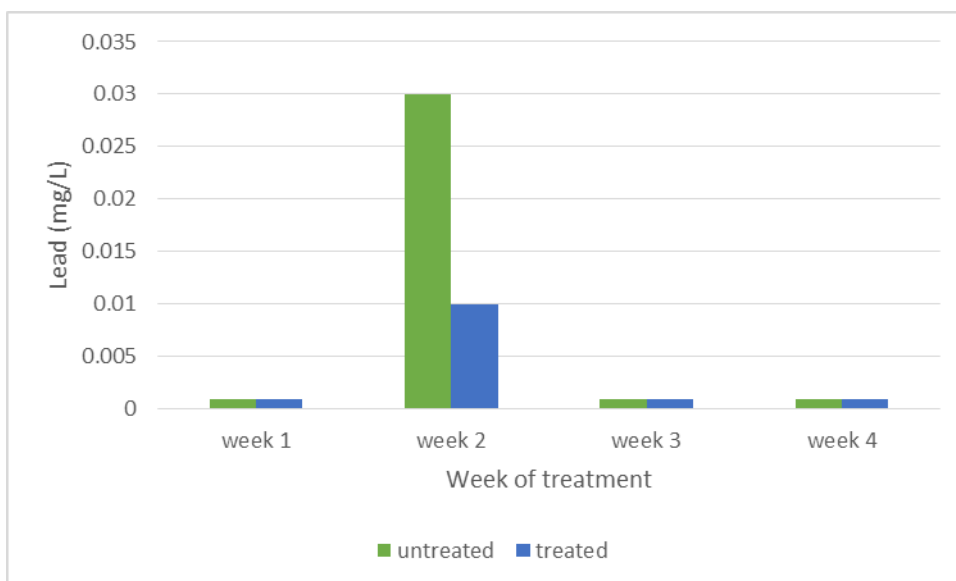


Figure 4.14: Weekly levels of lead in pharmaceutical effluent before and after passing through biosand filter.

4.11.5 Zinc

The concentration for zinc in the untreated pharmaceutical effluent for week 1, week 2, week 3 and week 4 were 0.04 mg/L, 0.013mg/L, 0.066 mg/L and 0.062 mg/L respectively. The concentrations however reduced to 0.018 mg/L, 0.0081 mg/L, 0.062 mg/L and 0.025 mg/L from weeks 1 to 4 respectively after passing through the biosand filter. The treatment efficiencies were 55%, 38.64%, 6.06% and 59.68% for week 1, week 2, week 3 and week 4 respectively. The average treatment efficiency over the four week period was 39.84%. The variations in concentrations of zinc in effluent samples before and after treatment were determined to be statistically insignificant ($P>0.05$).

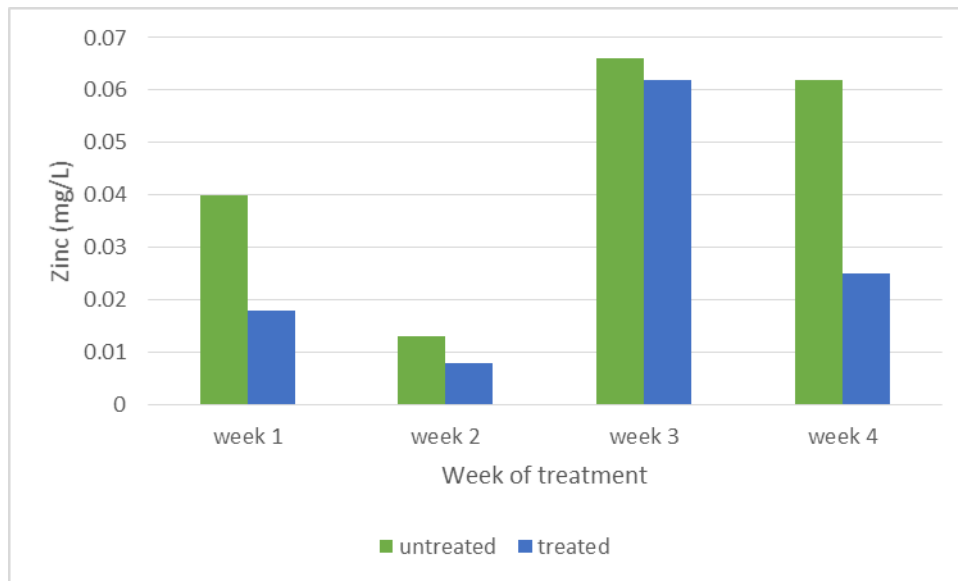
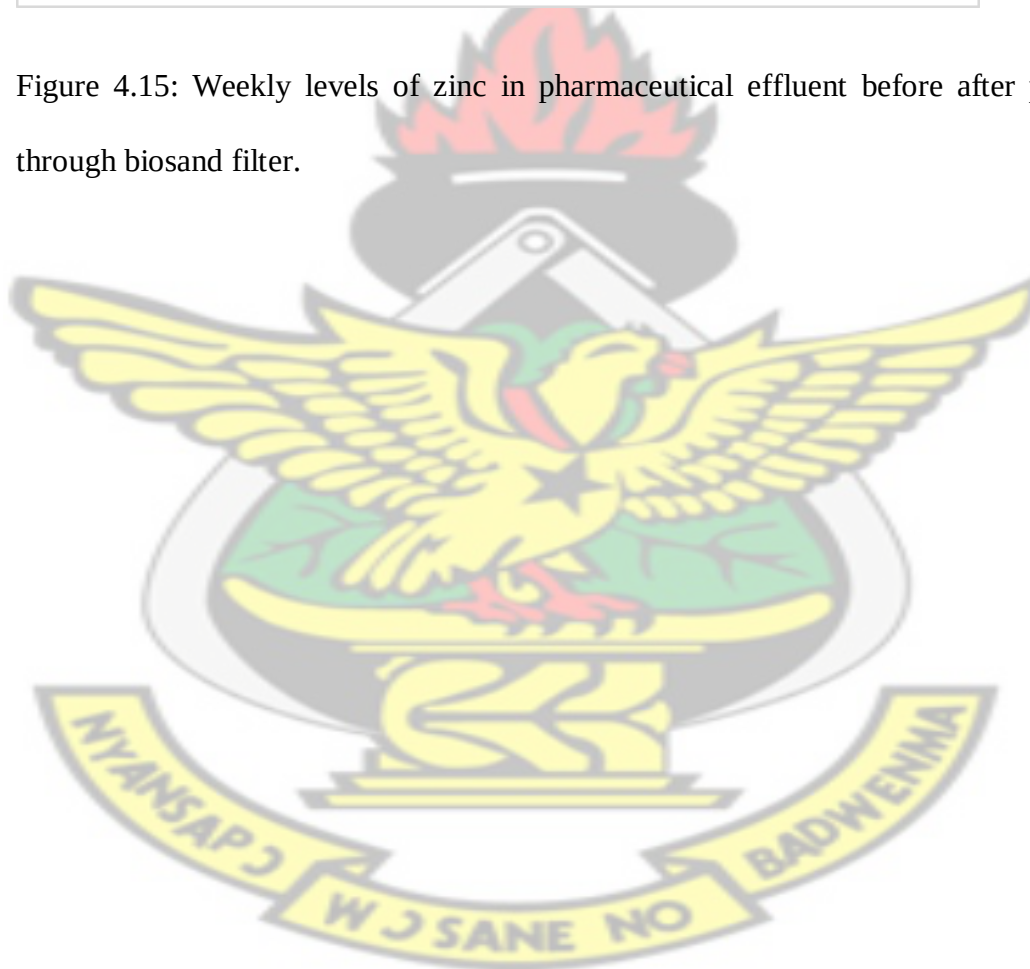


Figure 4.15: Weekly levels of zinc in pharmaceutical effluent before after passing through biosand filter.



CHAPTER 5

5.0 DISCUSSION

As the volume of effluent passed through the filter increased, the flow rate decreased but remained within an acceptable range. The reduction in flow rate may be attributable to clogging caused by the turbidity of effluent as it passed through the filter over the four week period. A possible breakup of the charcoal into smaller particles may also have contributed to the reduced flow rate.

5.1 UV-VISIBLE SPECTRA OF EFFLUENT

The presence of aliphatic compounds with different chromophores as well as aromatic constituents was demonstrated by absorbance at 280 nm. The most likely compounds present may be APIs and other organic excipients used in the manufacture of the products. The particularly high absorbance in the region between 260 nm and 320 nm suggests that the effluent is not fit to be disposed in the public drainage system as these effluents may result in increase of organic load. After treatment however the absorbance reduced at all regions of the spectrum, indicating that significant amount of contaminants had been removed during the treatment.

5.2 PHARMACEUTICAL ANALYSES

5.2.1 Amoxicillin Trihydrate

Compared to the four other APIs, amoxicillin trihydrate recorded the lowest average removal of 89.33% over the treatment period. Being an antibiotic, having recorded this reduction in concentration upon passing through the filter (Figure 4.1) also demonstrates that the sand straining process and charcoal surface pore adsorption phenomena were the two most likely mechanisms by which amoxicillin trihydrate was

removed because even though a reduction due to biodegradation was found for penicillin G, only 27% was removed after 28 days according to a study by Ahmad et al. (1999). Amoxicillin trihydrate has a comparatively high molecular weight of 419.449 g/mol so even though the API was extracted with 0.1 M sodium hydroxide, it is slightly soluble in water and therefore has a moderate affinity to water molecules. This means that it passed through the filtration sand with the strain barely removing the particles. The largest proportion of removal may have taken place in the second filter due to the presence of charcoal, where the amoxicillin trihydrate molecules must have been made accessible to the charcoal surfaces for adsorption to take place.

5.2.2 Cefuroxime Axetil

The average removal of cefuroxime axetil of 91.04% was significantly higher than what was observed for penicillin G in studies by Ahmad et al which showed that a reduction due to biodegradation was found for penicillin G, with 27% removed after 28 days. This is evidence that a higher proportion of the antibiotic was removed by the straining process of the filter than biodegradation in the biolayer. The filtration process may also have been influenced by molecular size of the API because cefuroxime axetil has a molecular weight of 510.475 g/mol and this could have resulted in the high average removal observed. In some other biodegradation study by Vankova (2010) it was recorded from a list of pharmaceutical therapeutic groups including antifungals, antiretrovirals, antibacterials, antimalarials, anthelmintics, antituberculosics, antiulceratives and glucocorticoids only the anti-inflammatory drug aspirin and glucocorticoid hydrocortisone acetate were determined to be readily biodegradable.

Cefuroxime axetil was most likely also removed by the detoxifying properties of charcoal via adsorption onto surface pores of charcoal. The removal rate of 90.39% at the end of the treatment in week four was lower than the 91.70% removed in the first

week of treatment and this may have been due to a blockage of some charcoal pores week after week of treatment. Cefuroxime axetil has low solubility in water and was extracted with methanol. Its average percentage removal of 91.04% is consistent with the 92.42% treatment efficiency of methanol soluble diclofenac sodium. The removal of cefuroxime axetil may have been comparatively lower because it is an antibiotic whereas diclofenac sodium is an analgesic and thus was taken up more by the biolayer. Even though an average treatment efficiency of 91.04% is significant, it is difficult to determine whether it is satisfactory because the EPA does not have guidelines on pharmaceuticals in industrial effluents.

5.2.3 Ciprofloxacin Hydrochloride

The average removal of ciprofloxacin hydrochloride of 93.32% shows that the biosand filter was efficient in removing the API. Ciprofloxacin hydrochloride is soluble in water and its significant removal rate may be because of the detoxifying properties of charcoal because a study by Vankova (2010) recorded a 0.5% biodegradation for ofloxacin. Ofloxacin is a fluoroquinolone like ciprofloxacin. They have similar characteristics but minor differences are observed in their antimicrobial activity pharmacokinetic and interaction profiles and their clinical utilities. The pores of charcoal must have adsorbed ciprofloxacin hydrochloride on their surfaces as the effluent passed through the filter because charcoal has been demonstrated to be efficient at removing some other organic contaminants like phenols.

In a study which explored the application of activated carbon and wood charcoal in the removal of phenols from water environment, 98% and 90% percentage removal efficiencies were obtained at specified adsorption conditions using activated carbon and wood charcoal respectively (Mukherjee et al., 2007). Here, the breakdown was

attributed to adsorption or aerobic and anaerobic degradation. Even though studies performed by Al-Ahmad et al. (1999) indicated that the antibiotic ciprofloxacin hydrochloride had no biodegradation even after 28 days, the current study recorded very high removal rates as indicated in figure 4.3. This could be due to the fact that as an antibiotic, removal of this API was largely due to adsorption to sand in the first filter and charcoal in the second filter. Adsorption to the charcoal will not lead to the formation of by-products but would require a longer treatment time, especially for the most soluble pharmaceutical compounds like ciprofloxacin hydrochloride. The required treatment time would however depend on the properties of the pharmaceutical compound and its affinity with the charcoal surfaces. The bio-layer therefore played an insignificant role during the treatment period as indicated by the weekly levels of this API before and after treatment as shown in figure 4.3.

It was expected that ciprofloxacin hydrochloride would record the lowest average removal due to its solubility in water, however it recorded the highest removal rate. This may be because its molecular weight of 367.805 g/mol and other chemical properties could have affected its uptake from the effluent. The high percentage removal may also have been because of the high affinity of the API to water and its ready accessibility to the active surfaces of the charcoal. Even though the average removal was determined to be significant there are no EPA guidelines for regulating pharmaceuticals in industrial effluent.

5.2.4 Diclofenac Sodium

Analgesic diclofenac sodium has comparatively lower solubility in water and may remain dispersed but insoluble as a solid material in the effluent. An average removal of 92.42% was recorded for diclofenac sodium after passing the effluent through the

biosand filter. This is higher compared with a 58% biodegradability recorded by Vankova (2010) for anti-inflammatory aspirin. Being a pain killer without any anti-microbial properties, some proportion of diclofenac sodium was most likely biodegraded during the treatment. Some of the particles may also have been filtered out by surface straining through the filtration sand in the biosand filter and another portion may have been removed by adsorption to the charcoal surface as it passed through the second filter in the setup.

In some studies, reported removal rates for pharmaceuticals including diclofenac ranged between 43% - 92% (Zhou et al., 2009) and 6% and 98% (Santos et al., 2007) which are consistent with the results of the current study. The highest removal of 94.90% recorded in week four differs from the records of the three antibiotics. The average removal of the antibiotics appeared to depend mostly on the physico-chemical characteristics of pharmaceutical compounds i.e. their high solubility and their acidity in water with very low solid liquid partition. This factor cause a poor sorption of these contaminants onto carbon and thus leaves them soluble in the aqueous phase (Gracia-Lor et al., 2012).

Since diclofenac sodium has the smallest molecular weight of 318.129 g/mol among the APIs under study it was expected that its removal would be lower, however the API also has a very low affinity for water and this may have contributed significantly to the average removal of 92.42%. A large proportion of the molecules were likely strained out during the filtration process and some were adsorbed onto the charcoal pores.

5.3 pH

pH is defined as the negative logarithm of the molar concentration of hydrogen ions. It measures the amount of hydrogen ions present in water. Both treated and untreated effluent samples tested were alkaline and are consistent with EPA range of 6 to 9. The mean pH of untreated effluent of 7.64 was increased to a pH of 7.94 after treatment and this could be attributed to the presence of charcoal in the second filter as the effluent passed through.

5.4 ELECTRICAL CONDUCTIVITY

Electrical conductivity is a measure of the ability of water to conduct electricity. The mean value of electrical conductivity for untreated effluent of 647.5 $\mu\text{S}/\text{cm}$ was reduced by 17.99% to 531 $\mu\text{S}/\text{cm}$ after treatment. This was consistent with percentage reduction for total dissolved solids and demonstrates the relationship between both parameters. The reduction may be due to microbial decomposition of organic and inorganic components of the effluent during the filtration process. Charcoal, as an effective adsorbent also removes some materials. The electrical conductivity of water is a more-or-less linear function of the concentration of dissolved ions. The highest conductivities recorded for untreated and treated effluents of 711 $\mu\text{S}/\text{cm}$ and 504 $\mu\text{S}/\text{cm}$ respectively were satisfactory compared to EPA limit of 750 $\mu\text{S}/\text{cm}$ and this is most likely due to the fact that much of the water used in the manufacturing facility is deionized water.

5.5 TOTAL DISSOLVED SOLIDS (TDS)

Total dissolved solids is a measure of the amount of salts, metals, minerals, cations or anions dissolved in the wastewater. It comprise inorganic salts like magnesium, calcium, sodium, potassium, chlorides, sulphates, chlorides, and bicarbonates as well as small quantities of organic matter present in wastewater. The highest value recorded

for the total dissolved solids in untreated effluent of 398 mg/L was below the EPA limit of 1000 mg/L. This could be because much of the water used for manufacturing the medicines is already deionized through reverse osmosis. However, the mean value of 366.55 mg/L was reduced by 16.72% to 305 mg/L possibly due to the ability of charcoal to adsorb such ions and other dissolved materials in the pores on their surfaces. This may also be due to a limited oxidation of dissolved substances by microorganisms in the filter.

5.6 TOTAL SUSPENDED SOLIDS (TSS)

Total suspended solids is an estimation of the amount of particles suspended in a wastewater column and it indicates the clarity of wastewater. The mean effluent over the four week period recorded was 168.25 mg/L and this was higher than the 50 mg/L recommended guideline of the EPA. However after treatment there was a 96.58% mean reduction in total suspended solids, reducing it to 5.75 mg/L, a figure below the EPA limit. This could be attributed to surface straining as indicated by Harhoff and Cleasby (1991). A mechanical filtration process occurs at the surface when particles larger than the pore sizes within each component of the filter are physically blocked from flowing further as the biosand filter is filled with effluent. The TSS values thus indicate likely transportation of pharmaceutical compounds and other pollutants with the effluent since organic matter and harmful substances adsorb to sediments. The 96.58% reduction is consistent with a 96% reduction reported when a modified biosand filter augmented with zeolite was applied to remove chemical contaminants from water by Mahlangu et al. (2011).

5.7 TEMPERATURE

Temperature controls metabolic rate and reproductive activities of microorganisms which may be present in the effluent. Mean effluent temperature for both treated and untreated effluent of 30.28 °C and 30.10 °C respectively were compliant with the EPA limit of 30 °C. This could be because the manufacturing activities associated with producing the medicines in the facility are carried out in fully air-conditioned production areas.

5.8 TURBIDITY

Turbidity is an indicator of the amount of colloidal and residual suspended matter present in wastewater and it measures its light transmitting properties. Its removal is dependent on the suspended particles entrapped in the biosand filter. A 96% reduction in turbidity recorded by Mahlangu et al. (2011) was consistent with values obtained during this current work. The mean percentage efficiency after four weeks was 95.25%. The highest value of 99.84% was recorded in the third week and this may be due to the cleaning of the filter after the second week. Both turbidity and total suspended solids recording similar values of 95.25% and 95.08% respectively is an indication of the dependence of turbidity on the TSS. Haarhoff and Cleasby (1991) attributed the mechanism of these reductions to surface straining. Here, the schmutzdecke improved filtration by reducing the filtration rate, it enhanced particle straining and removed major suspended impurities from the effluent. The removal rate may also be due to an adsorption phenomenon which is a critical feature in the attachment of suspended particles in the biosand filter.

The values as shown in figure 4.8 indicated that the efficiency of the biosand filter with charcoal as an additional adsorbent during the four week treatment period reduced the

turbidity to a level far below the EPA permissible limit of 75 NTU. The adsorption process was very important in the removal of turbidity because it occurs under molecular and physicochemical forces which cause bridging between particles. This bridging influences the particle charge on electro kinetic forces and are responsible for the attachment between sand grains and contaminants (Zhang B., et al.). It would be important to pre-treat the effluent in a settlement chamber before pouring into a biosand filter otherwise if the level of source water turbidity is high it would lead to more clogging.

5.9 BIOCHEMICAL OXYGEN DEMAND (BOD)

Biochemical oxygen demand is a measure of the amount of oxygen required by bacteria to decompose organic material under aerobic conditions. The highest of 24.38 mg/L was recorded in week one before treatment and this was consistent with EPA guidelines. After treatment each week the BOD values were reduced significantly with a mean treatment efficiency of 85.19%. The 85.19% efficiency is consistent with an 83% to 97% efficiency recorded by Dalahmeh (2013) where greywater treatment by charcoal filters reduced their organics content to acceptable irrigation levels. She attributed this reduction in BOD to the large specific surface area of the charcoal, which provided capacity for an intermediate-high removal of organic matter. This signifies that a lot of organic matter had undergone biodegradation or adsorbed in the filter. Some of the material may also have been trapped by the charcoal in the second filter as it passed through the column.

Charcoal has been shown to have a large capacity for adsorption of organic compounds (Mukherjee et al., 2007). The removal efficiency of the filter of 85.19% also compares with a 93% removal efficiency recorded by Agyemang et al (2013) where the treatment

efficiency of a conventional wastewater treatment plant was studied. Both treated and untreated effluent samples may have been within EPA limits due to spiking with antibiotics. Antibiotics is one of the medicines produced in this production facility and it may have inhibited biological activity thus affecting results of BOD. The BOD value reducing from week one to week four could be attributed to the presence of varying types of organic compounds in the effluent, each with a different rate and ease of biodegradability over the treatment period.

5.10 CHEMICAL OXYGEN DEMAND (COD)

Chemical oxygen demand measures the amount of oxygen required to completely breakdown organic material into carbon dioxide and water. In the determination of COD there is no distinction between biologically available and inert organic matter. An average COD of 105.86 mg/L for untreated effluent was reduced to 81.88 mg/L, both values lower than the recommended EPA limit of 250 mg/L. The reduction however corresponds to a treatment efficiency of 22.66 %, an indication that there are some particles within the effluent that remained unremoved even after the treatment. The disparity with BOD values indicates that there is a significant portion of the effluent consisting of inert organic material which may not be biologically available for decomposition. The pores in the charcoal may also have contributed to the reduction. The factory produces antibiotics effective against a broad range of bacteria and the low COD values may also be a result of spiking the effluent with antibiotics. The effluent contained a large proportion of non-biodegradable organic matter as shown by the ratio of BOD: COD which ranged from 0.02 to 0.23. A BOD: COD ratio less than 0.5 indicates the presence of a large percentage of non-biodegradable matter in the effluent.

5.11 HEAVY METALS

Even though the concentrations of the heavy metals under study complied with EPA limits, the average removal of Cu, Cr, Pb, Cd and Zn after passing effluent through the biosand filter were 78.37%, 40.16%, 16.67%, 27.08% and 39.84% respectively. Compared with a work by Muhammad (1998), percentage removal of 99.6%, 97.2%, 100% and 96.6% for Cu, Cr, Pb and Cd respectively were obtained in a slow sand filter. These high removal percentages when slow sand filters were applied suggest that majority of metal removal does not occur in the schmutzdecke but through the whole depth of a biosand filter. The results also demonstrate that accumulation of metal is not uniform for all metals. It may relate to the degree of toxicity of the metal to microorganisms. For instance Pb and Cd are known to be more toxic than Cu. Consequently the trapping of Cu in the biosand filter is higher than Pb and Cd which recorded the lowest removal percentages. The accumulation of metals in the schmutzdecke therefore depends on the effect of metal toxicity on microbial activity and confirms the importance of microorganisms on the accumulation of metals in the schmutzdecke. The high removal percentages may also be as a result of the presence of strong covalent coordination bonds between the metal ions and the surface functional groups of charcoal, such as carboxylic and hydroxyl because a research work by Babel et al. (2004) also found that there was a significant Cr adsorption by nitric-treated charcoal from 85% at equilibrium pH of 6.5.

The main mechanism of removal appeared to be their adsorption and electrostatic attachment to the sand and charcoal. Removal percentages of 16.67%, 27.08% and 39.84% for Pb, Cd and Zn respectively suggests that the biosand filter was relatively ineffective at adsorbing Pb, Cd and Zn from the effluent. These low removal rates were below expectation but could be due to the very low initial concentrations of the metals

in the effluent samples passed through the filter. A possible reason for the higher removal rates recorded for Cu and Cr may also be due to the availability of Cu and Cr ions in the effluent. Active sites of the charcoal were more likely to attach the Cu and Cr ions as compared to the Pb, Cd and Zn ions.

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CHAPTER 6

6.0 CONCLUSION

Aside from the heavy metal, COD and BOD levels, effluent from the pharmaceutical company did not meet the generally accepted standards of discharge into public drainage systems without pre-treatment. Allowing this pharmaceutical wastewater to be released untreated into public drainage systems would result in a continuous exposure to these contaminants which could lead to the development of resistant strains of bacteria. Consequently, these resistant strains would increase the need for more potent therapeutics thereby increasing the negative effect on the environment.

From the observations, the biosand filter was efficient in the removal of APIs from pharmaceutical effluents. Ciprofloxacin hydrochloride recorded the highest average removal of 93.32%, while the lowest average removal of 89.33% was recorded for amoxicillin trihydrate. The average removal of cefuroxime axetil and diclofenac sodium at the recommended flow rate were 91.05% and 92.42% respectively. The removal of the APIs by the biosand filters may have been achieved through a combination of mechanisms like settlement, sand straining and charcoal adsorption. One drawback of biosand filtration however is the limitation placed on the efficiency of the filter by the turbidity of the source effluent. It is recommended that pre-treatment steps be included in the biosand filter set-up to help remove sludge which could clog the filter and reduce the flow rate.

LIST OF REFERENCES

Ademoroti, C. M. A. (1979). Studies on physico-chemical methods of wastewater treatment. Ph.D Thesis. University of London.

Agyemang, E. O., Awuah, E., Darkwah, L., Arthur, R, and Osei G. (2013). Water quality assessment of a wastewater treatment plant in a Ghanaian Beverage Industry. *International Journal of Water Resources and Environmental Engineering*, Vol. 5 (5), pp. 272-279.

Alagarsamy, S. R., Navaneetha Gopalakrishnan, A. and Gandhirajan, M. (1983). Treatment of wastes from pharmaceutical industry – a case study. *Journal of the IPHE, India*. (4): 81-87.

Al-Ahmad, A., Daschner, F. D. & Kümmerer, K. (1999). Biodegradability of Cefotiam, Ciprofloxacin, Meropenem, Penicillin G and Sulfamethoxazole and Inhibition of WasteWater Bacteria. *Archives of Environmental Contamination and Toxicology*, vol. 37, pp. 158-163.

Alam, A. S. M. M., Hossain, K. M., Hossain, B., Ahmed, A. and Hoque, M. J. (2007). A Study on Industrial Waste Effluents and Their Management at Selected Food and Beverage Industries of Bangladesh. *J. Appl. Sci. Environ. Manage.* Vol. 11(4) 5 – 9

Allan, J. D. (1995). *Stream ecology of running waters*. Kluwer; Academic publishers, London, UK.

Anderson, P. D. (2005). Technical Brief: Endocrine Disrupting Compounds and Implications for Wastewater Treatment, WERF Report: Surface water quality, 04-WEM-6; IWA: London.

Babel, S., Agustiono, K. T. (2004). Cr (VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan. *Chemosphere* 54, 951-967.

Barnes, D., Collin, C., Ziff, S. (2009). *The Biosand Filter, Siphon Filter and Rainwater Harvesting: Strategic recommendations for new water treatment technologies and safe water storage to pure home water*. MSc Thesis, Massachusetts Institute of Technology.

Bellamy, W. D., Silverman, G. P., Hendricks, D. W., & Logsdon, G. S. (1985), 'Removing Giardia cysts with slow sand filtration, *Journal of American Water Works Association*, vol. 77, no. 2, pp. 52-60

Boxall, A. B. A., Johnson, P., Smith, E. J., Sinclair, C. J., Stutt, E., Levy, L. (2006). Uptake of Veterinary Medicines from Soils into Plants. York, UK: American Chemical Society - *Journal of Agriculture and Food Chemistry* 54, pp.2288-2297

British Pharmacopoeia, 2013

Buzunis, B. (1995). Intermittently Operated Slow Sand Filtration: A New Water Treatment Process. Department of Civil Engineering, University of Calgary, Canada.

Centre for Affordable Water and Sanitation Technology (2009). Biosand filter manual - Design, construction, installation, operation and maintenance. 12, 2916 – 5th Avenue, Calgary, Alberta, T2A 6K4, Canada

Collins R. M. (1998). Assessing slow sand filtration and proven modifications. In: Small Systems Water Treatment Technologies: State of the Art Workshop. NEWWA Joint Regional Operations Conference and Exhibition. Marlborough, Massachusetts.

Dalahmeh, S. (2013). Bark and Charcoal Filters for Greywater Treatment: Pollutant Removal and Recycling Opportunities. Doctoral Thesis, Swedish University of Agricultural Sciences, Uppsala.

Dalrymple, O. K., Yeh, D. H., Trotz, M. A. (2007). Removing pharmaceuticals and endocrine-disrupting compounds from wastewater by photocatalysis. J. Chem. Technol. Biotechnol. 82, 121– 134.

Deshmukh S. B., Gadgil, J. S. and Subrahmanyam, P. V. R. (1984). Treatment and disposal of wastewaters from synthetic drugs plant (I.D.P.L.), Hyderabad part – II biological treatability. Indian J. Environ. Hlth. 26 (1): 20-28.

Deziel, N. (2014). Pharmaceuticals in Wastewater Treatment Plant Effluent Waters. Scholarly Horizons: University of Minnesota, Morris Undergraduate Journal. Vol I, Issue 2. Article 12

Earwaker, P. (2006). Evaluation of Household BioSand Filters in Ethiopia. Master of Science thesis in Water Management (Community Water Supply). Institute of Water and Environment, Cranfield University, Silsoe, United Kingdom.

Eckel, W. P., Ross, B., Isensee, R. (1993). Pentobarbital Found in Ground Water. s.l.: Ground Water Vol.31, No.5, pp. 801-804

Enick, O. V., Moore, M. M. (2007). Assessing the assessments: Pharmaceuticals in the environment. Environ. Impact Assess. Rev. 27, 707–729.

Gilbert, T. W., Behymer, T. D., Castaneda, H. B. (1982). Determination of dissolved oxygen in natural and wastewater, American Laboratory, pp. 119-134.

Goossens, H., Ferech, M., Coenen, S., Stephens, P. (2007). Comparison of outpatient systemic antibacterial use in 2004 in the United States and 27 European countries. Clin. Infect. Dis. 44, 1091–1095.

Gracia-Lor, E., Sancho, J. V., Serrano, R., Hernandez, F. (2012). Occurrence and removal of pharmaceuticals in wastewater treatment plants at the Spanish Mediterranean area of Valencia. Chemosphere 87 (5), 453–462.

Haarhoff, J., Cleasby, J. L. (1991). Biological and physical mechanisms in slow sand filtration. In: *Slow Sand Filtration*. Gary Logsdon (ed.). American Society of Civil Engineers, New York, pp. 19-98.

Halling-Sørensen, B., Nielsen, S. N., Lanzky, P. F., Ingerslev, F., Lützhøft, H. C. H, Jørgensen, S. E. (1998). Occurrence, Fate and Effects of Pharmaceutical Substances in the Environment-A Review. Copenhagen, Denmark: Elsevier - *Chemosphere* 36, pp. 357-393.

Hartig, C.; Ernst, M.; Jekel, M., (2001). Membrane filtration of two sulphonamides in tertiary effluents and subsequent adsorption on activated carbon. *Water Res.*, 35 (16), 3998-4003.

Hu, H.-Y., Goto, N. and Fujie, K. (1999). Concepts and methodologies to minimize pollutant discharge for zero-emission production. *Wat. Sci.Tech.* Vol. 10-11, Pp. 9-16.

Huerta, B., Barceló, D. (2012). Pharmaceuticals in biota in the aquatic environment: Analytical methods and environmental implications. *Anal. Bioanal. Chem.* 404, 2611–2624.

Huisman, L., Wood, W. (1974). *Slow Sand Filtration*. WHO, Geneva.

Ikehata, K., Naghashkar, N., El-Din, M., (2006). Degradation of Aqueous Pharmaceuticals by Ozonation and Advanced Oxidation Processes: A Review. *Ozone-Sci. Eng.*, 28 (6), 353-414.

Jellison, K. L., Dick, R. I., Weber-Shirk, M. L. (2000). Enhanced ripening of slow sand filters. *J. Env. Engineering* 126 (12) 1153-1157.

Keil, F. (2008). *Pharmaceuticals for Human Use: Options of action for reducing the contamination of water bodies*. Frankfurt/Main, Germany: Institute for Social-Ecological Research (ISOE) GmbH. 51 p.

Kessler, R. (2010). Pharmaceutical factories as a source of drugs in water. *Environ. Health Perspect.* 118, No. 383.

Khetan, S., Collins, T. (2007). Human Pharmaceuticals in the Aquatic Environment: A Challenge to Green Chemistry. *Chem. Rev.*, 107 (6), 2319-2364.

Klavarioti, M., Mantzavinos, D., Kassinos, D. (2009). Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes. *Environ. Int.* 35, 402–417.

Kumar, A. (1996). Impact of industrial pollution on the population status of endangered Gangetic dolphin (*Platanista gangetica*) in the River Ganga in Bihar, India. *Pol. Arch. Hydrobiol.*, 18(4), 469-476.

Kumar, K., Gupta, S.C., Baidoo, S.K., Chander, Y., Rosen, C.J. (2005). Antibiotic Uptake by Plants from soil Fertilized with Animal Manure. Madison, USA: ASA, CSSA, SSSA - reproduced from *Journal of Environmental Quality* 34, pp. 2082-2085.

Kümmerer, K. (2009). Antibiotics in the aquatic environment: A Review part I. *Chemosphere* 75, 417–434.

Lee, Y., Von-Gunten, U., (2009). Kinetics of the oxidation of phenols and phenolic of 17 α -estradiol and their estrogenic activities, *Environ. Sci. Tech.*, 43 (22), 480–487.

Lokhande, S. R., Singare U. P., Pimple, D. S. (2011). Study on Physico-Chemical Parameters of Waste Water Effluents from Taloja Industrial Area of Mumbai, India. *International Journal of Ecosystem*; 1(1): 1-9

Mahlangu, T. O., Mpenyana-Monyatsi, L., Momba, M. N. B., and Mamba, B. B., (2011). A simplified cost-effective biosand filter (BSFZ) for removal of chemical contaminants from water. *Journal of Chemical Engineering and Materials Science* Vol. 2(10), pp. 156-167

Mathuthu, A.S., Mwanga, K. and Simoro A. (1997): Impact Assessment of Industrial and Sewage Effluents on Water Quality of receiving Marimba River in Harare.

Mohammed, N., (1998). Removal of heavy metals by slow sand filtration, PhD Thesis, Loughborough University, U. K.

Muhammad, N., Ellis, K., Parr, J., Smith M. D. (1996). Optimization of slow sand filtration. Reaching the unreachable: challenges for the 21st century. 22nd WEDC Conference New Delhi, India, pp. 283-285.

Mukherjee, S., Kumar, S., Misra, A. K. & Fan, M. (2007). Removal of phenols from water environment by activated carbon, bagasse ash and wood charcoal. *Chemical Engineering Journal* 129(1-3), 133-142.

Ngai, T., Welewijk, S. (2003). The Arsenic Biosand Filter (ABF) Project: Design of an Appropriate Household Drinking Water Filter for Rural Nepal. Report prepared by RWSSSP and ENPHO.

Nikolaou, A., Meric, S., Fatta, D. (2007). Occurrence patterns of pharmaceuticals in water and wastewater environments, *Analytical and bioanalytical chemistry*, 387(4), 1225-34.

Oaks, J. L., Gilbert, M., Virani, M. Z., Watson, R. T.; Meteyer, C. U., Rideout, B. A., Shivaprasad, H. L., Ahmed, S.; Jamshed, M., Chaudhry, I. (2004). Diclofenac residues as the cause of vulture population decline in Pakistan. *Nature*. 427.

Orlando, E. F., Kolok, A. S., Binzcik, G. A., Gates, J. L., Horton, M. K., Lambrigh, C. S., Gray, L. E., Soto, A. M., Guillette, L. J. (2004). Endocrine-disrupting effects of cattle feedlot effluent on an aquatic sentinel species, the fathead minnow. *Environ. Health Perspect.* 112, 353–358.

Palmateer, G., Manz, D., Jurkovic, A., McInnis, R., Unger, S., Kwan, K. K., Dudka, B., (1999). Toxicant and parasite challenge of Manz intermittent slow sand filter. *Environ. Toxicol*, 14: 217–225.

Peringer, P. (1997). Biologischer Abbau von Xenobiotica. *BioWorld* (1), pp. 4-7.

Pinkston, K.; Sedlak, D. (2004). Transformation of Aromatic Ether and Amine Containing Pharmaceuticals during Chlorine Disinfection. *Environ. Sci. Tech.*, 38 (14), 4019-4025.

Pomati, F., Castiglioni, S., Zuccato, E., Fanelli, R., Vigetti, D., Rossetti, C., and Calamari, D. (2006). Effects of a Complex Mixture of Therapeutic Drugs at Environmental Levels on Human Embryonic Cells. *Environmental Science and Technology*. 40: 2442-2447.

Radjenovi, J., Mato, M., Mijatovi, I., Petrovi, M., Barceló, D. (2008). Membrane Bioreactor (MBR) as an Advanced Wastewater Treatment Technology. *Handbook Env. Chem.* Vol. 5 Part S/2: 37-101

Ritenour, R. (1998), BioSand household water filter: A transfer of slow sand filtration technology to developing countries. 3rd ed. Samaritan's Purse, Canada.

Rivera-Utrilla, J., Sánchez-Polo, M., Ángeles Ferro-García, M., Prados- Joya, G., & Ocampo-Pérez, R. (2013). Pharmaceuticals as emerging contaminants and their removal from water, *Chemosphere*, vol. 93, no. 7, pp. 1268–1287.

Royal Commission Reports. (1974). Effect of industrial effluents in urban areas. Europe. No 23, 1529.

Santos, J. L., Aparicio, I., Alonso, E. (2007). Occurrence and risk assessment of pharmaceutically active compounds in wastewater treatment plants. A case study: Seville city (Spain). *Environ. Int.* 33 (4), 596–601.

Sateesh Babu, N., Dr. Jain, R. K., and Tripathi, R. K. (1994). Environmental management in a basic drug industry. *Journal of the IPHE, India.* (4): 33-42.

Snyder, S.; Adham, S.; Redding, A.; Cannon, F.; DeCarolis, J.; Oppenheimer, J.; Wert, E.; Yoon, Y. (2007). Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals. *Desalination*, 202 (1-3), 156-181.

Ternes, T. A., Janex-Habibi, M., Knacker, T., Kreuzinger, N., Siegrist, H. (2004). POSEIDON Project: Assessment of Technologies for the Removal of Pharmaceuticals and Personal Care Products in Sewage and Drinking Water Facilities to Improve the Indirect Potable Water Reuse. Final Detailed Report Related to the Overall Project Duration: January 1st, 2001 – June 30th, 2004.

Ternes, T. A., Meisenheimer, M., McDowell, D., Sacher, F., Brauch, H., Haist-Gulde, B., Preuss, G., Wilme, U., Zulei-Seibert, N. (2002). Removal of pharmaceuticals during drinking water treatment. *Environ. Sci. Tech.*, 36 (17), 3855- 3863.

Ternes, T.; Stüber, J.; Herrmann, N.; McDowell, D.; Ried, A.; Kampmann, M.; Teiser, B. (2003). Ozonation: a tool for removal of pharmaceuticals, contrast media and musk fragrances from wastewater. *Water Res.*, 37(8), 1976-1982.

University Technologies International. (1998). Clean Drinking Water to the World

Usharani K, Umarani K, Ayyasamy P. M, Shanthi K, Lakshmanaperumalsamy P. (2010) Physico-chemical and bacteriological characteristics of Noyyal River and ground water quality of Perur, India. J Appl Sci Environ Manag 14 (2):29–35

Vaňková, M., (2010). Biodegradability analysis of pharmaceuticals used in developing countries; screening with OxiTop® - C 110. Final thesis, Department of Chemistry and Environmental Engineering, Tampere University of Technology.

Vieno, N.; Tuhkanen, T.; Kronberg, L. (2007). Elimination of pharmaceuticals in sewage treatment plants in Finland. Water Res. 14, 1001–1012.

Water Quality Association, (1989). Recognized treatment techniques for meeting the National Primary Drinking Water Regulations with the application of point-of-use systems; and, Water Quality Association, 1989. Recognized treatment techniques for meeting the National Secondary Drinking Water Regulations with the application of point-of-use systems.

Weber-Shirk, M. L., and Dick, R. I. (1997), 'Biological Mechanisms in Slow Sand Filters' Journal American Water Works Association, vol. 89, no.2, pp. 72-83.

Westerhoff, P., Yoon, Y., Snyder, S., Wert, E. (2005). Endocrine disruptor, pharmaceutical, and personal care product fate during simulated drinking water treatment processes. Environ. Sci. Tech., 39 (17), 6649–6663.

Zhang, B., Gao L., Fazal, S., Mahmood, Q., Laghari, M., & Sayal, A. (2015). Biosand Filter Containing Melia Biomass Treating Heavy Metals and Pathogens. Pol. J. Environ. Stud. Vol. 25, No. 2, 859-864.

Zhou, J.L., Zhang, Z.L., Banks, E., Grover, D., Jiang, J.Q. (2009). Pharmaceutical residues in wastewater treatment works effluents and their impact on receiving river water. J. Hazard. Mater. 166 (2–3), 655–661.

APPENDIX I

Absorbance of ciprofloxacin hydrochloride in water at 276 nm

Concentration (mg/L)	Absorbance			
	1st	2nd	3rd	average
0	0	0	0	0
1	0.0941	0.0946	0.0947	0.094467
2	0.1993	0.1954	0.1934	0.196033
3	0.2992	0.2993	0.2993	0.299267
4	0.4146	0.4144	0.4146	0.414533
5	0.4965	0.4966	0.4965	0.496533
6	0.6145	0.6149	0.6155	0.614967
7	0.7134	0.7131	0.7134	0.7133
8	0.7654	0.7654	0.7661	0.765633
9	0.8593	0.8664	0.8593	0.861667
10	0.9564	0.9564	0.9583	0.957033

Absorbance of cefuroxime axetil in methanol at 247 nm

Concentration (mg/L)	Absorbance			
	1st	2nd	3rd	average
0	0	0	0	0
1	0.0309	0.0313	0.0311	0.0311
2	0.0502	0.0502	0.0501	0.050167
3	0.0636	0.0634	0.0636	0.063533
4	0.0841	0.0852	0.0859	0.085067
5	0.1047	0.1053	0.1051	0.105033
6	0.1272	0.1271	0.127	0.1271
7	0.1473	0.1472	0.1472	0.147233
8	0.1661	0.1661	0.1663	0.166167
9	0.1948	0.1947	0.1949	0.1948
10	0.2201	0.2203	0.2203	0.220233

Absorbance of amoxycillin trihydrate in 0.1M NaOH at 247 nm

Concentration (mg/L)	Absorbance			
	1st	2nd	3rd	average
0	0	0	0	0
1	0.0474	0.0475	0.0466	0.047167
2	0.078	0.0776	0.0773	0.077633
3	0.0968	0.0972	0.0975	0.097167
4	0.1312	0.1316	0.1323	0.1317
5	0.1658	0.166	0.165	0.1656
6	0.1949	0.1951	0.1956	0.1952
7	0.2196	0.22	0.2202	0.219933
8	0.2495	0.2498	0.249	0.249433
9	0.2988	0.299	0.2988	0.298867
10	0.3247	0.3257	0.3251	0.325167

Absorbance of diclofenac sodium in methanol at 285 nm

Concentration (mg/L)	Absorbance			
	1st	2nd	3rd	average
0	0	0	0	0
1	0.0309	0.0309	0.0311	0.030967
2	0.0623	0.0629	0.063	0.062733
3	0.0933	0.0934	0.093	0.093233
4	0.1251	0.1257	0.126	0.1256
5	0.1561	0.1565	0.1565	0.156367
6	0.187	0.1879	0.1874	0.187433
7	0.2239	0.2242	0.2242	0.2241
8	0.2544	0.2548	0.2544	0.254533
9	0.2842	0.2832	0.2839	0.283767
10	0.3192	0.3193	0.3195	0.319333

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APPENDIX II

Ciprofloxacin hydrochloride

	Untreated		Treated		Difference	
Week of treatment	Absorbance	Concentration (mg/L)	Absorbance	Concentration (mg/L)	Concentration (mg/L)	Percentage
week 1	2.7558	57.01142	0.1353	2.587747	54.42368	95.461
week 2	1.8755	38.72897	0.2076	4.089304	34.63967	89.44123
week 3	2.9597	61.24611	0.21	4.139148	57.10696	93.24178
week 4	2.0447	42.24299	0.1094	2.049844	40.19315	95.14749

Cefuroxime axetil

	Untreated		Treated		Difference	
Week of treatment	Absorbance	Concentration (mg/L)	Absorbance	Concentration (mg/L)	Concentration (mg/L)	Percentage
week 1	1.6755	159.2762	0.1418	13.20952	146.0667	91.70653
week 2	1.2776	121.381	0.1663	15.54286	105.8381	87.19498
week 3	2.3951	227.8095	0.1251	11.61905	216.1905	94.89967
week 4	1.1581	110	0.1141	10.57143	99.42857	90.38961

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Amoxicillin trihydrate

Week of treatment	Untreated		Treated		Difference	
	Absorbance	Concentration (mg/L)	Absorbance	Concentration (mg/L)	Concentration (mg/L)	Percentage
week 1	2.1807	138.4395	0.2229	13.73885	124.7006	90.07591
week 2	1.9451	123.4331	0.256	15.84713	107.586	87.16136
week 3	2.8721	182.4777	0.2101	12.92357	169.5541	92.91773
week 4	1.5887	100.7325	0.2101	12.92357	87.80892	87.17041

Diclofenac sodium

Week of treatment	Untreated		Treated		Difference	
	Absorbance	Concentration (mg/L)	Absorbance	Concentration (mg/L)	Concentration (mg/L)	Percentage
week 1	2.7372	171.6991	0.1575	9.962382	161.7367	94.19777
week 2	1.7803	111.7053	0.2021	12.75862	98.94671	88.57832
week 3	2.8341	177.7743	0.225	14.19436	163.5799	92.01552
week 4	1.8561	116.4577	0.0934	5.943574	110.5141	94.89637

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APPENDIX III

Ciprofloxacin hydrochloride (mg/L)	week 1	week 2	week 3	week 4
Untreated (mg/L)	57.01142	38.72897	61.24611	42.24299
Treated (mg/L)	2.587747	4.089304	4.139148	2.049844
Difference (mg/L)	54.42368	34.63967	57.10696	40.19315
Treatment efficiency %	95.461	89.44123	93.24178	95.14749
Average %	93.32288			
Mean (mg/L)	46.59086			
API SD	10.88888			
n	4			
df	3			
t	8.557513			
p-value	0.001677			
Mw	367.805 g/mol			

Cefuroxime axetil (mg/L)	week 1	week 2	week 3	week 4
Untreated (mg/L)	159.2762	121.381	227.8095	110
Treated (mg/L)	13.20952	15.54286	11.61905	10.57143
Difference (mg/L)	146.0667	105.8381	216.1905	99.42857
Treatment efficiency %	91.70653	87.19498	94.89967	90.38961
Average %	91.0477			
Mean (mg/L)	141.881			
API SD	53.66784			
n	4			
df	3			
t	5.287374			
p-value	0.006598			
Mw	510.475 g/mol			

Amoxicillin Trihydrate (mg/L)	week 1	week 2	week 3	week 4
Untreated (mg/L)	138.4395	123.4331	182.4777	100.7325
Treated (mg/L)	13.73885	15.84713	12.92357	12.92357

Difference (mg/L)	124.7007	107.586	169.5541	87.80893
Treatment efficiency %	90.07591	87.16136	92.91773	87.17041
Average %	89.33135			
Mean (mg/L)	122.4124			
API SD	34.8559			
n	4			
df	3			
t	7.023913			
p-value	0.002964			
Mw	419.449 g/mol			

Diclofenac sodium (mg/L)	week 1	week 2	week 3	week 4
Untreated (mg/L)	171.6991	111.7053	177.7743	116.4577
Treated (mg/L)	9.962382	12.75862	14.19436	5.943574
Difference (mg/L)	161.7367	98.94668	163.5799	110.5141
Treatment efficiency %	94.19777	88.57832	92.01552	94.89637

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Average %	92.422
Mean (mg/L)	133.6944
API SD	33.78484
n	4
df	3
t	7.914459
p-value	0.002103
Mw	318.129 g/mol

CONDUCTIVITY ($\mu\text{S}/\text{cm}$)		week 1	week 2	week 3	week 4
Untreated ($\mu\text{S}/\text{cm}$)	589		656	634	711
Treated ($\mu\text{S}/\text{cm}$)	504		510	574	536
Difference ($\mu\text{S}/\text{cm}$)	85		146	60	175
Limit ($\mu\text{S}/\text{cm}$)	750		750	750	750
Treatment efficiency %	14.43124		22.2561	9.463722	24.61322
Average %	17.69107				
Mean ($\mu\text{S}/\text{cm}$)	116.5				

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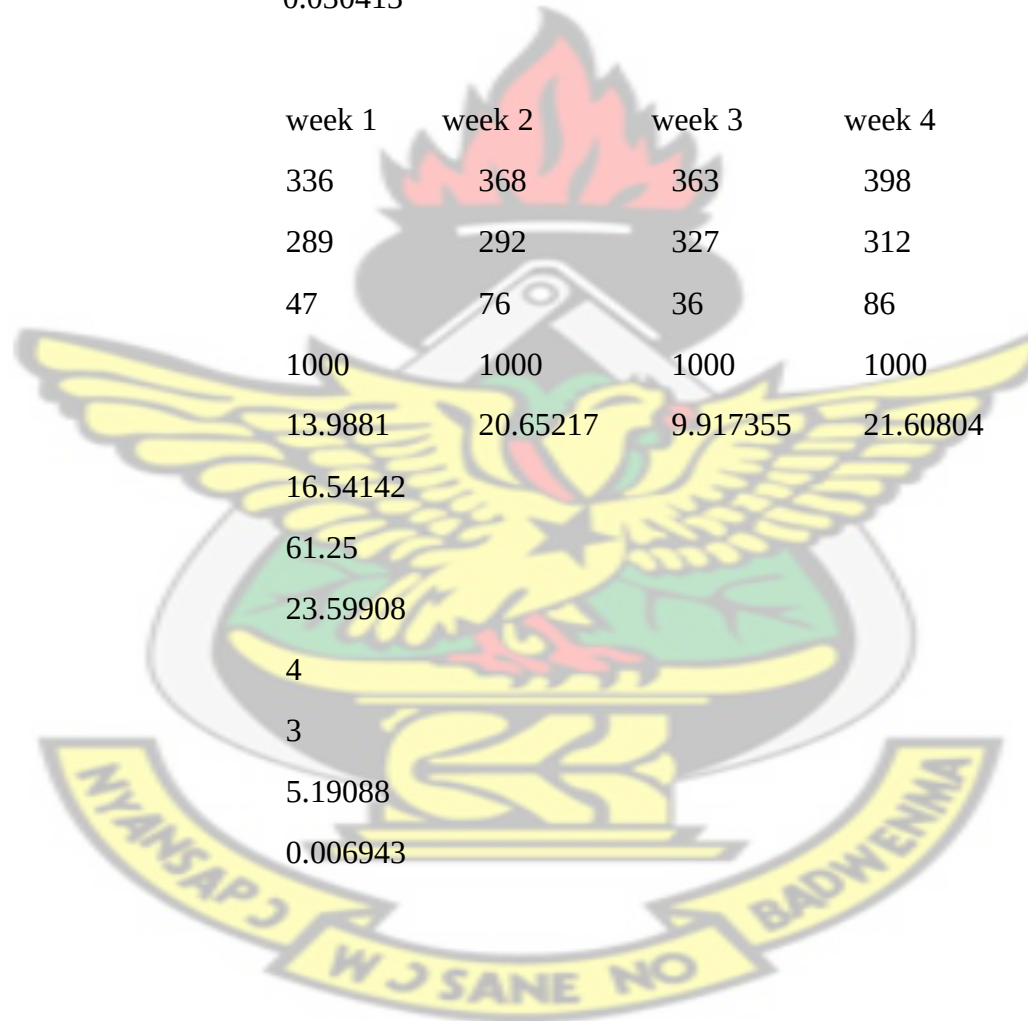
API SD	53.157
n	4
df	3
t	4.383242
p-value	0.010993

	week 1	week 2	week 3	week 4
TSS (mg/L)				
Untreated (mg/L)	227	121	287	38
Treated (mg/L)	11	8	1	3
Difference (mg/L)	216	113	286	35
EPA limit (mg/L)	50	50	50	50
Treatment efficiency %	95.15419	93.38843	99.65157	92.10526
Average %	95.07486			
Mean (mg/L)	162.5			
API SD	110.7866			
n	4			
df	3			

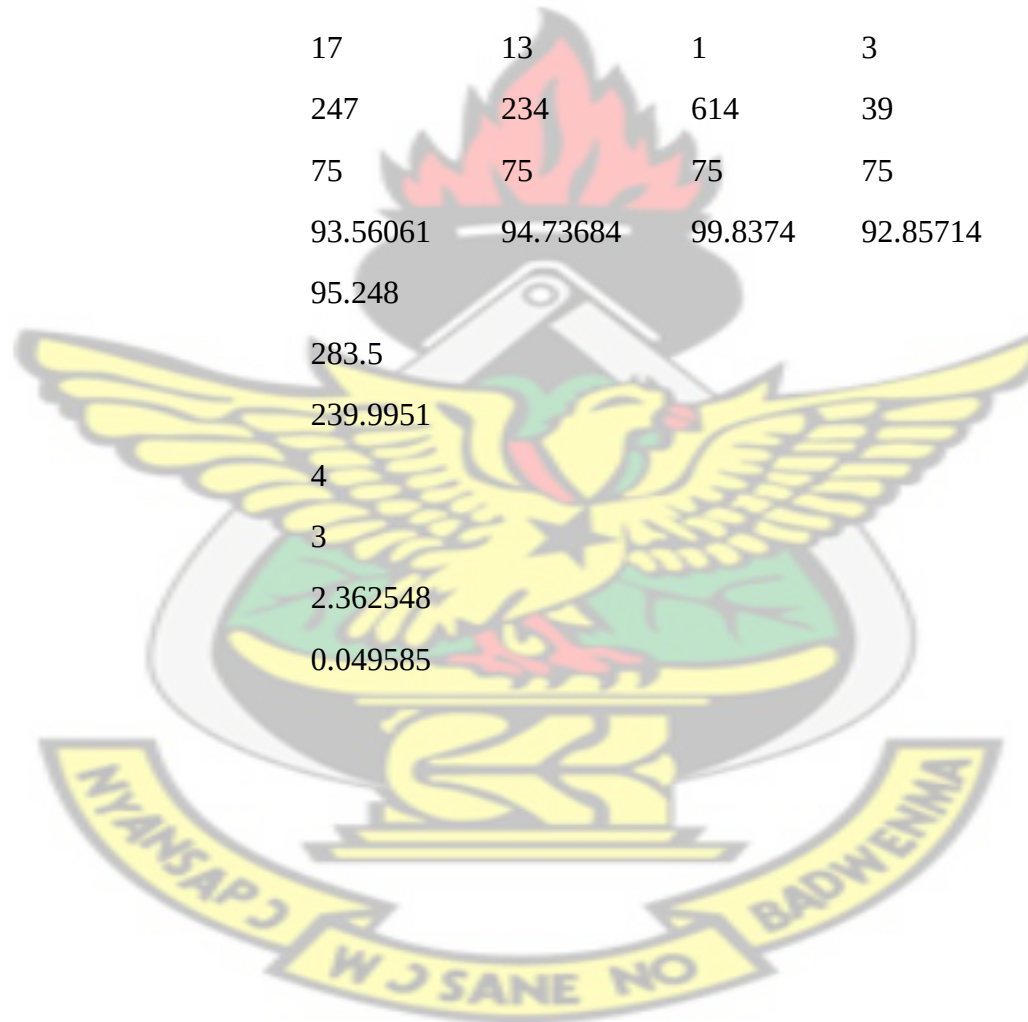
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t 2.933568
p-value 0.030413

	week 1	week 2	week 3	week 4
TDS (mg/L)				
Untreated (mg/L)	336	368	363	398
Treated (mg/L)	289	292	327	312
Difference (mg/L)	47	76	36	86
EPA Limit (mg/L)	1000	1000	1000	1000
Treatment efficiency (%)	13.9881	20.65217	9.917355	21.60804
Average (%)	16.54142			
Mean (mg/L)	61.25			
API SD	23.59908			
n	4			
df	3			
t	5.19088			
p-value	0.006943			



	week 1	week 2	week 3	week 4
Turbidity (mg/L)				
Untreated (mg/L)	264	247	615	42
Treated (mg/L)	17	13	1	3
Difference (mg/L)	247	234	614	39
EPA Limit (mg/L)	75	75	75	75
Treatment efficiency (%)	93.56061	94.73684	99.8374	92.85714
Average %	95.248			
Mean (mg/L)	283.5			
API SD	239.9951			
n	4			
df	3			
t	2.362548			
p-value	0.049585			



BOD (mg/L)	week 1	week 2	week 3	week 4
Untreated (mg/L)	24.384	16.256	10.16	4.064
Treated (mg/L)	2.032	2.032	2.032	2.032
Difference (mg/L)	22.352	14.224	8.128	2.032
EPA Limit (mg/L)	50	50	50	50
Treatment efficiency	91.66667	87.5	80	50
Average %	77.29167			
Mean (mg/L)	11.684			
API SD	8.680708			
n	4			
df	3			
t	2.691946			
p-value	0.037146			

Chromium (mg/L)	week 1	week 2	week 3	week 4
Untreated (mg/L)	0.045	0.056	0.044	0.021
Treated (mg/L)	0.021	0.023	0.029	0.018

Difference (mg/L)	0.024	0.033	0.015	0.003
EPA Limit (mg/L)	1.001	1.001	1.001	1.001
Treatment efficiency (%)	53.33333	58.92857	34.09091	14.28571
Average (%)	40.15963			
Mean (mg/L)	0.01875			
API SD	0.012816			
n	4			
df	3			
t	2.926029			
p-value	0.030598			

Cadmium (mg/L)	week 1	week 2	week 3	week 4
Untreated (mg/L)	0.002	0.008	0.003	0.002
Treated (mg/L)	0.002	0.002	0.002	0.002
Difference (mg/L)	0	0.006	0.001	0
EPA Limit (mg/L)	0.5	0.5	0.5	0.5
Treatment efficiency	0	75	33.33333	0

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Average %	27.08333
Mean (mg/L)	0.00175
API SD	0.002872
n	4
df	3
t	1.218544
p-value	0.15505

	week 1	week 2	week 3	week 4
Copper (mg/L)				
Untreated (mg/L)	0.04	0.06	0.055	0.03
Treated (mg/L)	0.016	0.007	0.01	0.005
Difference (mg/L)	0.024	0.053	0.045	0.025
EPA Limit (mg/L)	2	2	2	2
Treatment efficiency (%)	60	88.33333	81.81818	83.33333
Average %	78.37121			
Mean (mg/L)	0.03675			

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API SD	0.014523
n	4
df	3
t	5.060948
p-value	0.007445

Lead (mg/L)	week 1	week 2	week 3	week 4
Untreated (mg/L)	0.001	0.03	0.001	0.001
Treated (mg/L)	0.001	0.01	0.001	0.001
Difference (mg/L)	0	0.02	0	0
EPA Limit (mg/L)	250	250	250	250
Treatment efficiency	0	66.66667	0	0
Average %	16.66667			
Mean (mg/L)	0.005			
API SD	0.01			
n	4			

KNUST

df 3
t 1
p-value 0.195501

Zinc (mg/L)	week 1	week 2	week 3	week 4
Untreated (mg/L)	0.04	0.0132	0.066	0.062
Treated (mg/L)	0.018	0.0081	0.062	0.025
Difference (mg/L)	0.022	0.0051	0.004	0.037
EPA Limit (mg/L)	0.252	0.252	0.252	0.252
Treatment efficiency (%)	55	38.63636	6.060606	59.67742
Average %	39.8436			
Mean (mg/L)	0.017025			
API SD	0.015659			
n	4			
df	3			
t	2.174476			

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p-value

0.05898

COD (mg/L)

week 1

week 2

week 3

week 4

Untreated (mg/L)

104.28

113.76

110.6

94.8

Treated (mg/L)

79

90.5

91.64

66.36

Difference (mg/L)

25.28

23.26

18.96

28.44

EPA Limit (mg/L)

250

250

250

250

Treatment efficiency (%)

24.24242

20.44655

17.14286

30

Average %

22.95796

Mean (mg/L)

23.985

API SD

3.970739

n

4

df

3

t

12.08088

p-value

0.00061

