JIMMA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

JIMMA INSTITUTE OF TECHNOLOGY

ENVIRONMENTAL ENGINEERING STREAM

PHOSPHATE FIXING CAPACITY OF SOIL BLENDED WITH WASTEWATER

By: FISEHA BEFKADU (Msc)

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Thesis Submitted To the School of Graduate Studies of Jimma University in Partial Fulfillment of the Requirement for the Degree of Master of Science in Environmental Engineering

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I

Declaration

I hereby declare that this thesis:

Phosphate fixing capacity of soil blended with wastewater is my original work and has not been submitted and presented to any other Universities than the University of Jimma for any type of academic degree. `

Name   Signature   Date

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This thesis has been submitted for examination with my approval as university Supervisor

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Acknowledgement

Abstract

The liquid waste discharged from Jimma University Dining Hall contain high amount of phosphate. Based on laboratory experimental result had indicated 10.2 mg/L phosphate concentration. The problem causes a damage aquatic environment, eutrophication and severe disturbance on the downstream community. Phosphorus is an essential plant nutrient and its deficiency limits plant growth. Phosphorus had extracted from wastewater, each treatment combination to determine the amount of Phosphorus fixed. Phosphorus recovered increased with added Phosphorus. The Laterite soil of Serbo area is deficient in available phosphorus, which results in low agricultural productivity. Therefore, it is highly needed to monitor the Phosphorus fixing capacity of these soils. The transformation of applied Phosphorus in soils was examined after treatments with different Phosphorus rates (20, 60 and 180 mg/L) and incubation periods (1, 3, 7, 14 and 28 days) under laboratory conditions. Phosphorus fixing capacity increased with depth throughout the incubation period. The apparatus used to measure phosphorus fixation was Spectrophotometer, and the experimental result showed that Laterite soil was high Fixing capacity. Phosphorus fixed varying between 56-97%. More than 90% of added P had fixed after 28-day incubation. This therefore, reduces the threat of eutrophication. Phosphorus fixed correlated positively with clay and pH, and negatively with organic carbon and available P. Clay had a significant ($p < 0.05$) positive correlation with pH values. Clay and pH could therefore be responsible for phosphorus fixation.

Keywords: *Phosphorus, Laterite soil, wastewater, fixing capacity and depth in Serbo*

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Acronomy

BNR	Biological Nutrient Removal
BOD_5	Biological Oxygen Demand
COD	Chemical Oxygen Demand
CEC	Cation Exchange Capacity
CO_2	Carbon dioxide
H_2S	Hydrogen Sulfide
N_2	Nitrogen
LS	Laterite Soil
MD	Method Detection Limit
NH_3	Ammonia
TOC	Total organic carbon
P	Phosphate
QC	Quality Control
Rec	Recovered
QCS	Quality Control Sample
USEPA	United State Environmental Protection Agency
WW	Wastewater

CHAPTER ONE

Introduction

Wastewater is simply water that has used. It usually contains various pollutants; depending on what it is use for different purposes. It can classify into two major categories by source. The first is domestic or sanitary wastewater. This comes from residential sources including toilets, sinks, bathing, and laundry. The second type of wastewater is industrial wastewater. This is a wastewater discharged during the manufacturing processes of industries and commercial enterprises. Wastewater also includes the discharges from agriculture, storm water and runoffs (Fenta, 2007).

Domestic wastewater together with discharges from industry and agriculture has an impact on environmental conditions in rivers and coastal waters. This is mainly because untreated wastewater usually contains among other contaminants, nutrients mainly nitrogen and phosphorus that can stimulate the growth of aquatic plants, which in turn results in eutrophication problem in rivers and coastal waters (Fenta, 2007).

The impacts of untreated wastewater on the environment (such local rivers and streams) and on human health is clear, then proper wastewater treatment is fundamental for maintaining people's health, protecting the quality of the environment and ultimately promoting economic development (Kaseva 2004; Kyambadde, 2005). For this reason, the treatment of wastewater is not only desirable but also necessary (Fenta, 2007).

Treatment is necessary to correct wastewater characteristics in such a way that the use or final disposal of the treated effluents can take place in accordance with the rules set by the recent legislative bodies without causing adverse impacts on the receiving waster bodies (Njau and Mlay, 2000). To protect human health and water quality, wastewater treatment systems must carefully managed and properly operated. In the last few decades, wastewater engineers have concentrated on conventional wastewater treatment systems (Francis, 2006)).

But most conventional wastewater treatment technologies such as waste stabilization ponds, trickling filter, sequential batch reactors, and activation sludge, which are used in developing countries are not cost effective, need trained manpower for operation and maintenance, and not energy efficient (Fenta, 2007).

Because of this, the research for appropriate technologies in overcoming the wastewater problems which are causing health and environmental risks in developing countries is becoming more and more important (Peter,2005). The best solution for the wastewater problem was the technology that is manageable with the local people, cost effective, low technology and environmentally sound.

 Low technology and low cost wastewater treatment systems are cost effective in developing countries where sufficient land is available for extensive natural or artificial wastewater treatment facilities (Fenta, 2007).

Without phosphorus in the environment, no living organism could exist. Phosphorus is present in all plant and animal tissues. It has now well understood that P-nutrition of crop plants is more of a soil problem and a higher dose of P is necessary for soils having high P fixing capacities. In view of the economic desirability of having single fertilizer applications, the P-fixation capacity of our soils are of considerable importance in determining the requirement for applied P and may be indicative of possible adverse environmental effect (Lalijee, 1997).

The P fixation in soils depends up on many factors, namely the pH of the soil, organic matter content, type of clay and sesquioxides. Owusu Bennoah and Acquaye (1989) studied the phosphate sorption characteristics of some Ghanaian soils and found that the phosphate sorption maxima were highly correlated with the soil properties in the order: Al_2O_3, clay content, free Fe_2O_3 and organic carbon (Morel, 1989).Therefore, the aim of this research was be to determine Phosphate. Fixing Capacity of Soil Blended with Wastewater from Dining Hall of University. Student at different depths under laboratory condition, decrease the phosphorus fixing capacity of the Laterite soil while maximizing its availability (Lalijee, 1997). Study conducted on the investigation of phosphate fixing capacity of soils by the isotopic exchange techniques in north-east France reported that there was a significant correlation between amount of reported the significant correlation between amount of P fixed, pH, exchangeable cations, clay content and soluble phosphate (Soon, 1990). Sample depth also has effect on the P fixing of soils. Sampling depths of 10 and 15 cm frequently resulted in lower P fertilizer recommendation than those of 30-cm depth (Koenig et al., 2000).

1.1 Statement of the Problem

The liquid waste discharged from University Dining Hall contain high amount of phosphate based on laboratory experimental result showed which is 10.2 mg/L in concentration. Therefore, the problem leads to disturbing the ecosystem and eutrophication. Phosphorus is an essential plant nutrient and its deficiency limits plant growth. Phosphorus enhances a good development of the

root system particularly of the fibrous and lateral rootlets, a route through which the other nutrients can made available to plants. Ethiopia is one of the countries, which located in sub Saharan Africa and one of the global hot spots of malnutrition and an area likely to be most sensitive to climate change. Agriculture is the main source of livelihood to over whelming Ethiopia.

However, most Ethiopian soils are low in available phosphorus. However, recommendation of the high rates of mineral N and P fertilizers application is not viable option for farmers because most of them lack financial resources. Studies show that the total P status of some representative major soil types in Ethiopia is low (Picolo and A., 1985). Most of the Vertisols in the Ethiopian highlands, 70% of the cases, are reported low in available P content, below 5 ppm (Dirk van der Eijk et al., 2006).

P fractionation results show low levels of the available forms in the Ethiopian highland is Vertisols. P sorption studies indicated high sorption capacity of Vertisols and other soils in Ethiopia which is mainly controlled by content of Fe and Al oxides (Dirk van der Eijk et al., 2006).

The presence of Al^{+3} and Fe^{+3} is the main factors which affect available phosphorus for plant in Laterite soil. In Laterite, soils availability of phosphorus is reduced which in turn affects crop development and yields. Infertile soils may correct through liming or the use of organic fertilizers (manures). Thus to decrease the amount of mineral fertilizers required there is a need to adopt integrated soil fertility management technologies which combine wastewater with small amounts of mineral fertilizer and build up soil conditions to enhance P fixation. Therefore, the goal of the study was to determine Phosphate Fixing Capacity of Soil Blended with Wastewater from Jimma x Dining Hall of University Student.

CHAPTER TWO

LITRATURE REVIEW

2.1 Wastewater constituents

Wastewater had characterized in terms of its physical, chemical and biological composition. The most important physical characteristics of wastewater is its total solids content, which is composed of floating matter, settle able matter, colloidal matter and matter in solution. Other important physical characteristics include particle size distribution, turbidity, color, temperature and conductivity.

The chemical constituents of wastewater typically classified as inorganic and organic. Inorganic constituents mostly related with pH, nutrients like phosphorus and nitrogen, chloride, sulphur, heavy metals, and gases like methane, carbon dioxide (CO_2), oxygen (O_2), nitrogen (N_2), hydrogen sulphide (H_2S) and ammonia (NH_3).

The organic constituent is the combination of carbon, hydrogen and oxygen together with nitrogen in some cases. The most widely used parameter of organic pollution in wastewater is biochemical oxygen demand (BOD_5), chemical oxygen demand (COD) and total organic carbon (TOC). In addition to the above mentioned chemical constituents, a variety of emerging compounds have been identified (Ganesh and Nabelsi, 2013).

Serious problems due to eutrophication has led to governmental regulatory pressure for lowering phosphorus concentrations from wastewater (Kadlec and Wallace, 2008) in order to reduce the negative effects of overloading the ecosystems with P as well as reducing the high costs that accompany the mining and processing of P (Adam et al., 2007, Vohla et al., 2011). Further research is necessary to investigate various techniques and materials that could contribute to the removal as well as recycling of P (Adam et al., 2007). Constructed wetlands had evolved as one simple ecologically adapted technique for control of water pollution (Ganesh and Nabelsi, 2013).

2.2 Phosphorus cycle

The cycle of phosphorus in ecosystems varies from that of carbon, hydrogen, oxygen and nitrogen, which have much faster cycles (Holtan et al., 1988).The phosphorus binding process by iron (Fe) and aluminum (Al) oxide and oxyhydroxide phases is of vast importance in

terrestrial ecosystems, and had extensively studied in soil Science. Its importance refers to the fact that phosphorus can be a limiting nutrient for algeal growth in terrestrial ecosystems, and the removal of natural phosphorus or its use as fertilizer can influence the health and production level of crops and forests (K. C. Ruttenberg, 2003).

The phosphorus had found as organic and inorganic phosphate in soil. Inorganic p had connected to phosphorus minerals originated. The organic Phosphate originally originated from plant residues but also might been produced by human excreta and animal manure (Lusk et al., 2011). There is a consideration that plants can uptake their P only from inorganic sources and that organic P compounds mineralized before their uptake by plants. There had been a focus on the inorganic rather than the organic P in soil, and this refers to the limited knowledge of the specific nature of most of the organic bound P in soils (Ganesh and Nabelsi, 2013).

The inorganic phosphate compounds in soil had classified into two groups: (a) calcium compounds and (b) iron and aluminum compounds. The calcium compounds in alkaline soils, while the iron and aluminum compounds mainly exist in acidic soils. As soil pH decreases, the degree of calcium compounds dissolution becomes high such as apatite. Apatite is the less soluble among the calcium phosphate (Ganesh and Nabelsi, 2013).

The inorganic phosphate had also referred as "available or reactive P" (Lusk et al., 2011). However, Phosphorus is unavailable in high and low pH ranges of soil solution (Ahmed, 2007). The dissolved forms of inorganic P included H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} (Lusk et al., 2011). The distribution of these species is pH dependent and can reflect the P availability for plants. The most favorable pH for P availability is near neutral to slightly acid. Phosphorus absorbed by plants largely as $H_2PO_4^-$, HPO_4^{2-} and $PO4^{3-}$. Most of the P absorbed by plants is in the monovalent orthophosphate form; H_2PO^{4-} was predominant at pH values below 7.2 and is typical of most agricultural soils.

At pH above 7.2, the HPO_4^{2-} is more dominant, and might been used by some plants. When the pH is too high, the concentration of the tertiary orthophosphate $PO4^{3-}$ will be high, which makes this form of P a significant source in plant nutrition. Even at a pH of 12 the HPO_4^{2-}, concentration is still greater than that of $PO4^{3-}$. From this relationship, the hydrogen ion activity was to a great extent influence all phosphate reaction systems. Some plants may also absorb certain soluble organic phosphates but these are very minute amounts (Ganesh and Nabelsi, 2013).
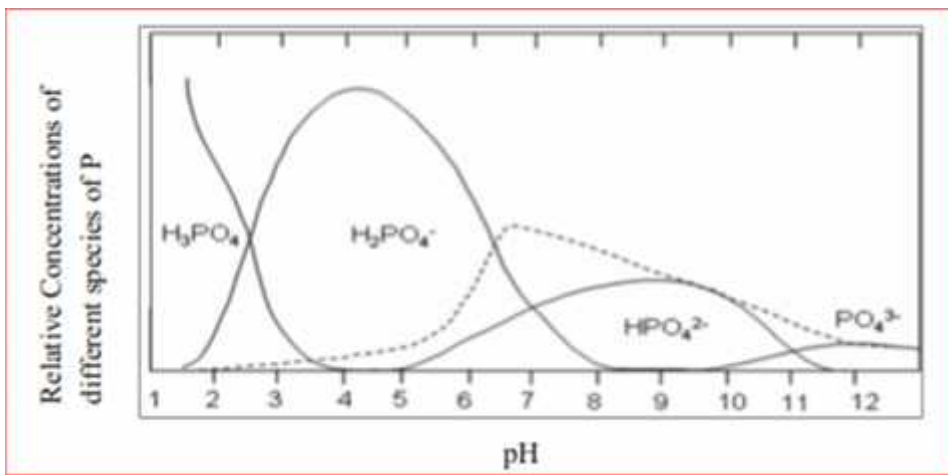
Fig 1.the available forms of P ions and their relative concentrations at different pH values.

2.1.3 Forms of phosphorus in soil and in the soil solution

Phosphorus occurs in nature almost exclusively as phosphate, in all known minerals more specifically as orthophosphate with an ionic form of PO_4^{3-}. The distribution of the different species of orthophosphate is pH-dependent and the dissociation of the ortho-phosphoric acid in aqueous systems as a function of pH.
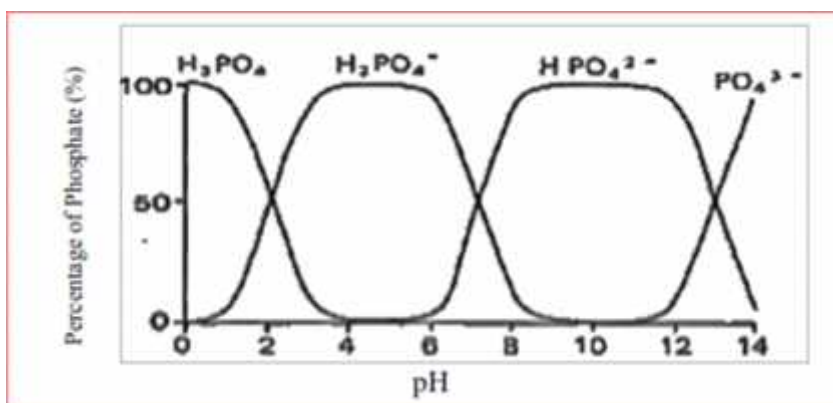
Fig 2. Distribution of phosphate species with pH (Holtan et al., 1988)

2.1.4 Soil characteristics and constraints

For any crop, soil characteristics are very important as environment provided by soil and climate governs the growth of the crop. Cotton being a commercial crop, its soil site suitability characteristics had worked out (Sehegal et al., 1989) and soils are grade from most suitable to unsuitable based on the characteristics.

Black soil

These soils have pH values ranging from 7.8 to 8.7, which may reach up to 9.4 in sodic soils. These soils have cation exchange capacity (35-55 cmol (p/kg) and rich in base status. Although the black soils have relatively high moisture holding capacity (150-250 mm/m), yet water is not available to plants because the water held tenaciously by the smectitic clay. These

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soils have low permeability and the bulk density of these soils is generally high (1.5 to 1.8 mg/m^3) because of shrinkage on drying. The main constraints in this soil to cotton production are due to their narrow range of workable moisture, low infiltration and poor drainage when wet leading to water logging and high runoff and soil loss during heavy down pour. Otherwise, these soils suffer from moisture stress during drought. These soils are poor inorganic carbon, nitrogen, sulfur and phosphorus. Water holding capacity is a major problem in shallow soils. Whereas deep soils when irrigated are very much prone to salinity and sodicity particularly in the subsoil. The calcareous nature of these soils affects the availability of many micronutrients.

Red soil:

These soils were mostly deriving from crystalline granite and metamorphic rocks, such as gneisses, schists, mainly of Achaean period. Occasionally, the red soils developed on micaceous schiests, sand stone, limestone and shales. Morphologically the red soil classified as in to two broad sub groups i.e. (a) Red loam and (b) Red earth. The main constraints in these soils include surface crusting and low soil depth under up land conditions. These soils are low in water holding capacity and have high soil-erosion potential and surface runoff. They have compacted subsurface layer due to eluviation's, which may lead to restricted root development. The soils have low CEC and high P fixing capacity. These soils are low in N, P, Ca, Z and S.

Alluvial soil

These soils mainly developed from coastal alluvium or deltaic alluvium. These soils are generally variable in color depending on the source of parent material and are calcareous. The depth of this soil depends on the geomorphic position of landscapes. Their texture varies from very coarse to fine. These soils are rich in P and K but low in N and organic carbon. These soils are generally alkaline in reaction but may be acidic when rainfall exceeds potential evapo-transpiration. These soils are best agricultural soils. The main constraints in these soils include low content of N, P, S, Zn and organic matter and development of salinity and or sodicity under injudicious use of irrigation water.

Laterite soil

These soils are deeply weathered soils and the depth of weathering may extend up to several meters. They have high clay content (especially in the B-horizon) which is not due to migration of clay but due to in situ alteration of weather able minerals. With depth and

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between pH ranges of 6.0 to 6.8, there is a decreasing intensity of red color and clay content. With pronounced leaching, they lose bases (Ca, Mg, Na, and K) and silica with relative accumulation of sesquioxides and the soils develop acidic reaction. Kaolinite is the dominant clay of these soils. In laterite soil, the base saturation is less than 40% whereas in lateritic soils it is more than 40% with CEC. The major constraints of these soils are deficiency of P accentuated by high P fixing capacity of Fe and Al phosphates, high acidity, toxicity of Al and Mn and deficiency of K, Ca, Mg, Zn and B (Bandyopadhyay et al., 2007). Fixation is a generic word used to designate the transformation of soluble soil phosphate forms into in soluble ones.

Phosphorus (P) is the eleventh in order of abundance element on Earth; under most conditions, it can exclusively combine with four oxygen molecules, forming the phosphate oxyanion. Phosphorus is essential for all living organisms, as it represents the energy currency for organisms at cell level, and its availability often controls biological productivity; for that reason, in excess quantities it is the cause of eutrophication *(corre et al., 2009).*

Eutrophication can be described as nutrient enrichment of surfaces waters, leading to an excessive production of toxic algae, and is responsible for turning water green in lakes, reservoirs, rivers, coastal waters and the marine environment in general (Burke et al., 2004).

Phosphates represent the main source of P and commonly used in fertilizers, detergents or insecticides. (Morse et al. 1993) reported that the overdose of P in European Union (E.U) countries water essentially comes from human sources in sewage and from livestock. Since 1991, European legislation has approached this pollution problem by establishing a new directive (EC Urban Wastewater Treatment Directive (Dirk van der Eijk et al., 2006).

The fixation of P in wastewater discharged to sensitive areas now regulated and minimum P concentrations in effluents had imposed, depending on the size of discharge. The legislative pressure has led to more discussions on how to integrate P fixation processes in wastewater treatment plants. Traditional P removal processes are based on phosphorus fixation in activated sludge either by a biological (biological nutrient removal, BNR) or chemical (precipitation by metal salts) method (Lalijee, 1997).

According to (Booker et al., 1999), this process was efficient in the sense that they can reduce the P concentration in wastewater effluents to less than 1 mg/L. but they lead to the accumulation of phosphorus in sludge, an increase in sludge volumes, and contribute by reaction with magnesium and ammonium ions to the precipitation of magnesium ammonium phosphate hex hydrate most commonly known as struvite *($_{CORRE}$ et al., 2009).*

Any phenomenon that causes a decrease in the orthophosphate ion concentration in a solution in contact with the soil is responsible for the fixation (Catani and Gloria, 1964). Many authors (Dean, 1949; Kurtz, 1953; Olsen, 1953; Hemwall, 1952; Catani & Pellegrino, 1957; Catani & Gallo, 1957; Hsu & Jackson, 1960; Wright & Peech, 1960) agree that in soils having much iron and aluminum, phosphorus shows a tendency to bind to those elements. In other words, both iron and aluminum compounds (hydrated oxides) present in the soil are the main responsible for the phosphorus "fixation. All the methods of evaluation of phosphorus fixation capacity by the soil are conventional and furnish variable results, according to the work conditions. (Jackson, 1958), describes several methods for determining the phosphate exchange capacity of soils (Catani and Gloria, 1964).

The amount of phosphorus fixed by a soil depends on a series of factors, as phosphate concentration in the solution, solution pH, reacting time, temperature, relation between the weight of the soil sample and the volume of the solution, and physico-chemical characteristics of the soil itself (Catani and Gloria, 1964).In many areas of the tropics, population and demand for food are rapidly growing.

Therefore, production of subsistence crops could augment. Unfortunately, most tropical soils have low levels of chemical soil fertility, often caused by low levels of available phosphorus. Furthermore, many tropical soils are able to fix large quantities of fertilizer P, which is consider a main factor lowering the recovery of fertilizer P by plants. The low P status of many tropical soils is in sharp contrast to the situation in some areas of the western world where because of repeated application of animal manure and P fertilizers, soils have become P saturated. Despite often large P retention capacity of soils, excessive applications of P may lead to P leaching to ground and surface waters and may contribute to eutrophication of surface waters (Ghosal et al., 2011).

2.1.5 Phosphorus in the aquatic environment

Once phosphorus in dissolved or particulate form has entered, the aquatic environment complex reactions between the water columns occur. Particulate P can accumulate on bottom sediments through sedimentation if water flow is slow the suspended particle can settle or trapped in vegetation buffers. Suspension of particulate dispersed by wind induced water turbulence sand high stream flow conditions (Clayson, 2007). In a similar way benthic invertebrates living in the fresh water can disturb these suspend particles (Simsetal., 2004).Sediment P is not readily available, but it can be a long-term source of P for aquatic biota. The exchange of phosphorus across the sediment water interface is regulated by

fixation, adsorption-desorption, precipitation, dissolution, microbial mineralization, immobilization and plant uptake processes (Clayson, 2007). Phosphorus from the wastewater could incorporate in to these dement by biotic and a biotic pathways. Abiotic pathways include adsorption and desorption reactions. The adsorption reaction had defined as the removal of P from a solution by concentrating it in, or on, a solid phase.

2.1.6 Phosphorus fixation by clay minerals

The availability of P in alkaline soils was determine principally by the solubility of the various Ca- phosphate compounds present and the reactions of P with clay minerals causing p fixation in soil had studied. Al is one of the elements, which associated with clay, and it is responsible for this fixation (Hemwall, 1957). It was deduced that P fixation by clay minerals was clearly related with the sesquioxides Al content of the clays not the intact aluminium silicate clay minerals (Coleman, 1944). The amount of P fixed in clay mineral was indicated to be proportional to the amount of free Al oxide on the clays; and that fixation occurs as long as due to Al availability in clay substance. Additional support for the hypothesis is that free aluminium oxides are necessary for clay minerals to fix P was provided by demonstration that montmorillonite will not fix P once all Fe and Al oxides are removed from the clay (Ellis and Troung, 1955).

It was shown that the presence of fluoride or aluminium tricarboxlic acid, both strong complexing agents for aluminium, inhibits the fixation of P by montmorillonite (Hemwall, 1957). Moreover, the X- ray diffraction evidence showed that fixed P is not sorbed between the lamellae of the clay minerals and does not interfere with the swelling properties of the clay. An experimental procedure for developing a P retention characteristic of soil layers has been developed (Pant et al., 2002).

The P adsorption maxima were positively correlated with oxalate aluminium and citrate dithionite bi carbonate extractable aluminium under conditions, but there was no significant correlation with either oxalate extractable iron or citrate dithionite bi carbonate extractable iron. The X- ray diffraction patterns indicated that smectite was the dominant mineral in the clay size fraction. It is likely that the permanent negative charge of smectite limits its concentration to P adsorption.

2.1.6 Wastewater treatment in soils

The purpose of wastewater treatment is to reduce the pollutants in wastewater that can contaminate ground and surface waters. Without proper treatment, wastewater can cause public health problems and environmental contamination from potential spread of bacteria, viruses and pathogens. Wastewater may contain bacteria, viruses, protozoa, nitrogen compounds, and toxic organic compounds, which can cause disease in humans. Chemical constituents in wastewater: oxygen-demanding substances nitrogen, phosphorus, chloride, sulfate, sodium, heavy metals, toxic organic compounds, detergent surfactants, and suspended solids can adversely affect the environment.

Most on-site systems treat and dispose of wastewater. Depending on a number of factors, the soil can reduce or remove these pollutants. This section describes the process of wastewater treatment in soils. Most of the organic solids in domestic sewage were remove by sludge settling in the septic tank. Some of these solids were partially biodegrade in the tank. Wastewater effluent that exits the septic tank and enters the soil receives most of its treatment in the unsaturated aerobic regions under the treatment and disposal field (Jagessar and Alleyne, 2012).

2.1.7 Tertiary or Advanced wastewater treatment and wastewater reclamation:

To remove the specific wastewater constitutes which could not remove by secondary treatment including toxic substances, elements and solid particles. Nutrient control or removal is a treatment, which removes nitrogen and phosphorus by chemical, biological, or a combination of both. Also some physic- chemical treatment like sedimentation, chemical coagulation, filtration and flocculation decreases the water quality (Kordrostami, 2015).

All of these processes may occur independently or together for any given wastewater constituent. Wastewater from various facilities can contain a wide variety of contaminants. Common domestic sewage has at least minor levels of the pollutants as discussed below. Contaminants present in wastewater from other facilities, such as commercial and industrial establishments, vary widely and depend on the type of activities taking place in the facility generating the wastewater. Sodium may be a problem if high levels found in the wastewater. Sodium cations had adsorbed to the soil aggregates, which had held together by organic matter and clay. When sodium levels in wastewater are too high, the sodium may disperse the organic matter and clay in the soil. Such soil dispersion changes the soil structure and reduces

the rate of water movement through the soil, which can cause failure of an on-site system (Bomans E. et al., 2005*)*.

Detergent surfactant as we currently do not use many "soaps are removed from wastewater effluent by adsorption into soil particles and by biodegradation. Aerated soil conditions enhance biodegradation and increase the treatment of surfactants. Fixation of surfactants not only removes them from the wastewater, but also increases the time for additional biodegradation to occur.

2.1.8 Phosphorous retention by laterites

Laterite contain high proportions of iron- and aluminum- oxides (Wood & Mc Atamney 1996; Gerritse 2000) and it is these compounds that allow phosphorous to readily fix (Peters & Donohue 2001), and be removed from the water column. The mechanism for this Phosphorous fixation done through a process called ligand exchange (Wood & Mc Atamney 1996). A ligand is a molecule, which is bound to a metal ion to form a complex ion (Silberberg 2000). Ligand exchange occurs when the ligand bound to the metal ion could replace by another ligand (Cotton et al. 1999). In this case, the orthophosphate molecule acts as a ligand, binding at the hydrous oxides of iron and aluminum (Wood & Mc Atamney 1996), replacing the current ligands, (the hydroxides) (Clayson, 2007).

2.1.9 Characterization of soils phosphorous uptake

Generally, phosphorous uptake for soils had investigated in India. Kothandaraman and Hrishnamoorthy (1978) investigated phosphorous fixation for three local soils, including laterite, to determine phosphorous availability and phosphorous fertilizing requirements for the area. They determined that laterite material had the highest uptake of the three and that all soils had initial fast reactions followed by slow reactions (Clayson, 2007).

2.2 Phosphorous in on-site Systems

Phosphorus can enter a wastewater system in a variety of forms. Organic and synthetic phosphorus had transformed by bacteria to the simple orthophosphate form. Because excess phosphorus can stimulate eutrophication, the excessive growth of algae and aquatic plants in streams, rivers, and lakes it is important that phosphorus not enter water bodies in high concentrations. Fortunately, orthophosphate could usually immobilized by a number of processes in the soil. Phosphate immobilization processes in the soil include adsorption to the soil particles or biomat, precipitation in the soil or biological uptake. Most soils in North Carolina have high phosphorus fixing capacity.

Research by Uebler (1984) has shown that phosphorus was reduce to undetectable levels 12 inches below the nitrification trench in a Cecil clay soil. Detergent surfactants as we currently do not use many "soaps" are removing from wastewater effluent by adsorption in to soil particle sand by biodegradation. Aerated soil conditions enhance biodegradation and increase the treatment of surfactants. Adsorption of surfactants not only removes them from the wastewater, butal so creases the time for additional biodegradation to occur.

Toxic carcinogenic compounds, such as pesticide sand non-biodegradable organic compounds degrade slowly. Since these compounds usually are not adsorbing by the soil, they may leak into and contaminate the groundwater. The best way to minimize the impact of these chemicals is to keep them out of the on-site system.

Heavy metals in high concentrations are usually toxic. Such metals can slow or stop the bacterial action in these the treatment and disposal trench. These metals could not put in the on-site system. In addition, these tend to be more common treated in the sludge layer or removed when the sludge is pump out.

Viruses

Viruses can remove by adsorption, filtration, precipitation, biological enzyme attack, and natural die-off in soils. Because of their smaller size, viruses may move much further in soils than other pathogens in some instances, from meters to miles. Greater clay content, low pH, low soil moisture content, and low effluent loading rates are important factors that decrease the possibility of viral contamination of ground water from on-site systems.

Bacteria

Reside and often re-grow in the septic tank. Fortunately, bacteria had effectively removed in the soil, primarily through filtration, adsorption, and natural die-off. If the soil is unsaturated, bacteria are not usually transported more than3feet if the soil is aerobic. Aerobic soil does not favor the survival of anaerobic bacteria that may cause disease. If however saturated flow occurs, bacteria can move farther. Saturated flow, high wastewater effluent rates, shallow depth to soil wetness conditions or fractured bedrock may contribute to bacterial contamination from on-site systems.

Protozoa

Cyst sand worm eggs are largely removing by settling in septic tank sludge. Few disease out breaks by microbes have been reported other than bacteria and viruses from subsurface wastewater disposal systems. It appears that these biological agents had removed in the tank or treated in the soils.

2.2.1 Role and behavior of P in soil, plant, animals

In the natural environment, phosphorus was supplies through the weathering and dissolution of rock sand minerals with very slow solubility. Therefore, P is usually the critical limiting element for plant and animal production, and throughout the history of natural production and human agriculture, P has been largely in short supply.

Many natural ecosystems and low-input farming systems have adapted to low P supply by recycling from litter and soil organic materials. Increases in productivity require external nutrient inputs if they are not to cause a decline in fertility. External P-inputs have become available on large scale with the mining of phosphate deposits. This has decoupled patterns of supply, consumption and waste products from natural nutrient cycles, and has made them dependent one economics (Tiessen, 1995).

Phosphorus plays a series of functions in the plant metabolism and is one of the essential nutrients required for plant growth and development. It has functions of a structural nature in macromolecules such as nucleic acid sand of energy transfer in metabolic pathways of biosynthesis and degradation. Unlike nitrate and sulphate, phosphate was not reduce in plants but remains in its highest oxidized form (Marchner, 1993).

Phosphorus deficiency often appears early in plant growth as stunting, with purple or reddish leaf and vegetative tissues of corn, barley, and some mustard crops. Within the plant, phosphorus compounds from older leaves can be relocating to younger leaves and developing buds. However, as the deficiency becomes more severe, the symptoms first seen in the older leaves can progress to the youngest leaves. Deficiency in wheat was generally show by a thinner than normal wheat leaf and stunting. Deficiency in potatoes often resembles late blight symptoms.

Phosphorus deficiency can sometimes be induced through situations that inhibit root growth, such as soil compaction or cold soil temperatures. A deficiency of phosphorus affects not only plant growth and development and crop yield, brutal so the quality of the fruit and the formation of seeds. Deficiency canal so delay the ripening of crops, which can set back the harvest, risking the quality of the production. However successfully produce the next generation of plants, seeds and grains must store phosphorus. Then, as the root system develops, the growing plant was able to take up the phosphorus it requires from the soil, providing there are adequate reserves.

In common with other major elements, the concentration of total P in soils is high relative to both crop requirements and to the available P fraction. The typical range for total P content of agricultural oils had estimated as 0.20to2.0g/kg (McGrath, 1994).Phosphorus exists in soils either in the dissolved (i.e. solution) or solid form (particulate P), with the solid form being dominant.

Dissolved P is typically less than 0.1 percent of the total soil P and usually exists as ortho-phosphate ions, inorganic polyphosphates and organic P (Magette and Carton,1996). Phosphorus are absorbed by plants from the soil solution as monovalent (HPO_4) and divalent (H_2PO_4) Organic P compounds undergo mineralization (into inorganic forms) and immobilization with the aid of soil bacteria and growing plants.

In the soil, two sources of inorganic phosphorus exist: inorganic phosphorus is set free form organic matter by microorganism sand mineral fertilizers bring in inorganic phosphate. Microbial organisms immobilize part of the phosphate by using it for their own growth. Different forms of P had also partitioned as between soluble P, labile soil P and non-labile soil P. Soluble P represents P in the soil solution that was readily extract with either water or weak salt and measures the concentration of ortho-phosphates ions in solution.

Labile P describes forms of P had chemically mobile, exchangeable and reactive in soil and water Labile P can replenish the soil solution P concentrations for uptake of P by the crop. Non-labile P had thought to represent a fraction of P, which had physically encapsulated within a mineral compound (e.g. apatite) in complexes of metal oxides and hydroxide. These latter forms of P are protected from chemical reactions and can only be released by very strong chemical treatments (Clayson, 2007).

2.2.2 Phosphorus in the Environment

Although phosphorus is a nutrient essential to the growth of plants, too much of a good thing can be harmful to the environment (Mueller and Helsel, 1996). Enriched phosphorus levels can accelerate the growth of algae and other plants that impair the suit ability of the water for municipal, recreational, and fishery use.

To control eutrophication, the USEPA has established a recommended limit of 0.05 mg/L for total phosphates in streams that enter lakes and 0.1 mg/L for total phosphorus in flowing waters (Clayson, 2007). A USEPA study (Omernik, 1977) of 928 basins around the Nation found that basins that were more than 90 percent forested had stream water with a median

total phosphorus concentration of 0.018 mg/L. This same study identified no relation between rock type and phosphorus concentration.

Dissolved phosphate occurs in small concentrations in water because it has low solubility, is readily taken up by biota, and adsorbs to metal oxides in soils (Litke, 1999). Large total phosphorus concentrations generally are associated with runoff events, which carry a substantial proportion of suspended sediment to which phosphorus could attach. Yields of phosphorus therefore can, vary considerably from year to year in both natural (Lewis and others, 1984) and developed environments (Svendsen and others, 1995), depending on water yield.

2.2.3 P-losses to the environment

Some 25 years ago, reports of undesirable changes in the freshwater environment in several countries led to a growing concern for the aquatic environment in general. These changes could consider related to the increasing concentration of nutrients in the water. Nitrogen, phosphorus, carbon and in some cases silicon are the nutrients of concern in relation to eutrophication. However, because phosphorus is the limiting nutrient in freshwater environment, it attracts the most attention when the problem of eutrophication is considered in relation to fresh water (Clayson, 2007).

2.2.4 Phosphorous control strategies

It is a common management action to reduce nutrient (including phosphorous) loads entering the system (Ryding & Rast 1989; Hart et al. 2003; Thompson & Hosja 1996). If elimination or sufficient reduction at the source is not possible, the control of nutrients entering the water body may be accomplished by reducing or preventing effluent discharges or runoff from agricultural land (Clayson, 2007).

2.2,5 Phosphorus transport

Phosphorus can enter the surface water from point and non-point sources. Point source inputs of P have been greatly reduced over the past decades with detergent reformation and improved Wastewater treatment therefore non-point source pollutions from urban and agriculture land have been identified as the major source of P in many eutrophic waters.

Non-point sources include both natural and human sources. Natural sources for P inputs can be the weathering of Phosphate rich rocks, which contribute through erosion and leaching to higher P concentrations and sediments in lakes and reservoirs, which release P during seasonal overturn. The loss of P in agricultural runoff increases the risk of surface water

eutrophication and are affecting by a number of factors including hydrology, soil type, soil P content and amount and placement of P added as fertilizer or manure (Carpenter et al., 1998). Phosphorus in livestock manures is more slowly available in comparison to the inorganic P in fertilizers, but is generally consider becoming very available in the long term (von and Prein, 2005).

2.26 Organic compound in Wastewater

Organic matter in terms of COD or BOD is one concern in the treatment of any types of wastewater. Its disposal to water bodies might cause oxygen depletion that will have harmful effects to living resources like fishes, or eventually make the environment anaerobic(Fanta Hun, 2005; Hoshino et al., 2005). Typical organic composition of domestic wastewater is 40-60% proteins, 25-50% carbohydrates and 10% lipids (Lacina and Spiros, 2003).

Biological degradation of organic compounds during solid waste or wastewater treatment proceeds in the presence of molecular oxygen by respiration, under anoxic conditions by denitrification, or under anaerobic conditions by either methanogens or sulfidogenesis (Claudia and Josef, 2005). Aerobic degradation of organic compounds such as carbohydrates, proteins, fats, or lipids in activated sludge systems leads to the formation of carbon dioxide, water, and a significant amount of surplus sludge. Some ammonia and may be H_2S formed during degradation of sulfur-containing amino acids or heterocyclic compounds (Mamo, 2008).

Conductivity

Defined as the ability or power to conduct or transmit heat, electricity or sound. The conductivity of wastewater had directly linked to the conductivity of the ions & their mobility. The ion in wastewater acts as electrolytes & conducts the electricity. Conductivity depends on the value of the PH; on the amount of $co_2$was dissolve in the wastewater to form ions.

CHAPTER THREE

OBJECTIVES

3.1 General objectives

The general objective of this study was to evaluate the effect of blending wastewater in to laterite soil on P fixing trend.

3.2 Specific Objective

- ✓ To study the effect of depth
- ✓ To study the effect of pH
- ✓ To determine the effect of different blending ratios of WW and LS,
- ✓ To examine the effect of incubation period,
- ✓ To analyze the phosphorus fixing capacity of LS

Research Question

1. How the wastewater discharged from Dining Hall affect the ecosystem?
2. What is the effect depth on phosphate fixing soil blended with wastewater?
3. Does the capacity of laterite soil can affect by the presence of maximum amount of phosphate?
4. What is the level effect of phosphate in the environment?

CHAPTER FOUR

Material and Method

4.1 Study Area

The study was conducted at Jimma zone, South Western Ethiopia that is located between 7° 13'- 8° 56 N latitude and 35°49'-38°38'E longitude with an estimated area of 19,506.24 km^2 and the elevation ranges between 1000-3500m. The zone constitute three major climates 78%, 12% and 10% belongs to subtropical, temperate and tropical or thermal zones, respectively.

4.2 Available phosphorus

The Bray number 1 method (IITA, 1985) had used to determine the concentration of available phosphorus. 1:1 ratio of soil sample and wastewater sample One gram (g/g) was weighed into 15 mL centrifuge tube and 7 ml of Bray No. 1 (0.03 M NH$_4$F + 0.025 M HCl) extracting solution will be added and shaken for one minute on a mechanical shaker. The suspension was centrifuge at 200 rpm for 50 minutes. Two milliliters of the clear supernatant were pipette into 25 ml volumetric flask to which 10 ml of distilled water and 4 ml of ascorbic acid added to make up for the volume required. The colour had allowed developing for 15 min and the concentration of phosphorus in solution determined with a Spectrophotometer at 690nm.

$$mgP/kg = mgP/\text{L insolution} \times \frac{\text{Vol.of extrctant}}{\text{Wt.of Soil}} \times \frac{\text{Final vol.of aliquot}}{\text{initial aliquot pipetted}} \qquad (1)$$

4.3 Stannous Chloride Method

Principle: Molybdophosphoric acid had formed and reduced by stannous chloride to intensely colored molybdenum blue. This method is more sensitive than Method C and makes feasible measurements down to seven µg P/L by use of increased light path length. Below 100 µg P/L an extraction step may increase reliability and lessen interference.

Apparatus

Set spectrophotometer at 625 nm in the measurement of benzene- isobutanol extracts and at 690 nm for aqueous solutions. If the instrument is not equipped to read at 690 nm, use a wavelength of 650 nm for aqueous solutions, with somewhat reduced sensitivity and precision.

Reagents

Phenolphthalein indicator aqueous solution

Strong-acid solution: Prepare as directed in Section 4500-P.B.2b2). Ammonium molybdate reagent I: Dissolve 25 g $(NH_4)_6 Mo_7 O_{24}$. $4H_2O$ in 175 mL distilled water. Cautiously add 280 mL conc H_2SO_4 to 400 mL distilled water. Cool, add molybdate solution, and dilute to 1L.

Stannous chloride reagent I:

Dissolve 2.5 g fresh $SnCl_2 2H_2O$ in 100 mL glycerol. Heat in a water bath and stir with glass rod to hasten dissolution this reagent is stable and requires neither preservatives nor special storage. Standard phosphate solution:

Ammonium molybdate reagent II: Dissolve 40.1 g $(NH_4)_6 Mo_7 O_{24} 4HO$ in approximately 500 mL distilled water. Slowly add 396 mL ammonium molybdate reagent I. Cool and dilute to 1L.

Alcoholic sulfuric acid solution: Cautiously add 20 mL conc H_2SO_4 to 980 mL methyl alcohol with continuous mixing.

Dilute stannous chloride reagent II: Mix 8 mL stannous chloride reagent I with 50 mL glycerol. This reagent is stable for at least 6 months (Source Standardard Water and Wastewater).

4.4 Sampling methods

4.4.1 Laterite soil

Three samples of laterite soil & wastewater was be collected from different sites at Jimma locality, Kersa district, Jimma Zone, Oromia Regional State, and South West Ethiopia according to standard soil sampling procedures. Composite sample had used. Laterite soil was prepared by thoroughly mixing the samples in a 1:1 ratio. The composite sample were analysed for the grain size distribution using sieve analysis (ASTM).

4.4.2 Wastewater

Composite samples had collected over time, either by continuous sampling or by mixing discrete samples. A composite sample represents the average wastewater characteristics during the compositing period. A time composite sample consists of equal volume discrete sample aliquots

collected at constant time intervals into one container. A time composite sample could collect either manually or with an automatic sampler (USEPA, 2013).

4.1.3 Sample collection and preservation

Samples should be collected in glass bottles and using Agar. All bottles had thoroughly cleaned and rinsed with reagent water. Volume collected should be sufficient to insure a representative sample, allow for duplicate analysis (if required), and minimize waste disposal.

Preservation techniques

To minimize the potential for volatilization or biodegradation between sampling and analysis, keep sample as cool as possible without freezing. Pack samples in crushed or cubed ice before shipmen or use refrigeration system set at $4°_C$. Use chemical preservatives only when they are shown not to interfere with the analysis being made. Analyze samples as quickly as possible at the laboratory.

Quality control

Each laboratory using this method was required to operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, and the periodic analysis of laboratory reagent blanks, fortified blanks and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that had generated.

Initial demonstration of performance

Quality Control Sample (QCS): when beginning the use of this method, on a quarterly basis or as required meeting data-quality needs, verify the calibration standards and acceptable instrument performance with the preparation and analyses of a QCS. If the determined concentrations are not within ±10 percentage of the stated values, performance of the determinative step of the method is unacceptable. The source of the problem could identify and corrected before either proceeding with the initial determination of MDLs or continuing with on-going analyses.

Method Detection Limit (MDL)

MDLs had established for all analytes, using reagent water (blank) fortified at a concentration of two to three times the estimated instrument detection limit. To determine MDL values, take 20 duplicate aliquots of the fortified reagent water and process through analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units.

Calibration

Prepare standard curve by plotting instrument response against concentration values. A calibration curve fitted to the calibration solutions concentration/response data-using computer or calculator based regression curve fitting techniques. Acceptance or control limits should established using the difference between the measured value of the calibration solution and the "true value" concentration.

After the calibration was established, it could verified by the analysis of a suitable quality control sample (QCS). If measurements exceed ±10 percentage of the established QCS value, the analysis terminated and the instrument recalibrated. The new calibration had verified before continuing analysis.

Data quality

The quality of the data was assuring through duplicate the samples by using standard operating procedures. To check the accuracy and validity of data instrument calibration and verification as checked, and the duplicate data averaged and mean ± SD/SE reported.

Data Analysis

Experimental data analysis had utilized to this end; Microsoft **Excel 2010** employed. Therefore based on that, the finding reported as using table**.**

CHAPTER FIVE

Results and Discussions

The common effluent quality parameters were orthophosphate, total phosphorus, wastewater pH, conductivity and the soil texture had measured. Orthophosphate, total phosphorus were measured calorimetrically by spectrophotometer (DR/ 2010, USA) according to HACH instructions. In addition, pH was measure off-site after sampling time and using pH meter.

To evaluate the treatment performance of phosphorus fixation from wastewater, selected parameters from the effluent had measured. These were $PO4^{3-}$, TP, and pH, from wastewater. During the entire period of the study, 20 samples for both wastewater and soil were analyze by using Spectrophotometer and duplicate the samples were used as average value.

The biological processes are typically solar-driven as light and carbon sources (from the substrate) are using to derive the microbial and plant processes. Nevertheless, fixation can seems to be appropriate in Ethiopia, which influences the treatment process in wastewater. The result showed that total phosphorus, orthophosphate effluent concentration values were not within the standard discharge limit values set by the National Environmental Quality Standard for domestic wastewater effluent (EEPA, 2003). Therefore, this showed that the effectiveness of fixation in fulfilling the regulatory limit values to discharge the effluent in to surface at downstream and inland water bodies.

Laterite soil had the potential to detain contaminants due to less void space usually characterized by low flow rates. The key to govern reduction is the retention time of the contaminants in the soil. Since the soil textural result indicated that 70% clay, therefore the soil have high water holding capacity. Fixation system operates using experimental processes and usually do not require substantial energy inputs.

5.1 Wastewater Characterization

The results of the experiment of P fixing the capacity WW were present in the results show that 6.43% PH, which is slightly acidic to the soil that we used. WW contain 5.43 $_pH$, 8.56 OC, 12.73 OM, 5.79 EC and 74.35 available P therefore, the WW have high amount of organic matter and available p, which described below.

Table 1.Wastewater Characterization

Parameter	Unit		Value	Remarks
pH (H_2O)			6.43	Slightly acidic
OC	%		8.56	High
OM	%		12.73	High
EC	ds/m		5.79	Non saline
Available P	mg/L		74.35	High

5.2 Mineralogical Characterization of LS

From the result of the investigation using silicate complete analysis, LS characterization for different parameters carried out among them SiO_2, AlO_3, and FeO_3 has high content chemical. This chemical leads to lack of fertility of the soil and but the rest is low content in this soil described below.

Table 2. Mineralogical Characterization of LS

Parameter	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	MnO	P_2O_3	TiO_2	H_2O	LoI
Percentage	63.52	13	9.78	0.78	< 0.01	0.82	< 0.01	0.38	0.18	1.79	1.25	8.25

5.3 Soil texture Characterizations

The result soil textural class indicates that 70% Clay, 6% Sand and 24% Silt. Therefore, the high content of this soil is responsible for holding the water without passing through due to low pore space. The results of the experiment of P fixing the capacity of LS were present in the results shown that 5.43% PH, which is slightly acidic to the soil that we used. WW contain 5.43 $_P$H, 2.35 OC, 3.98 OM, 0.32 EC, CEC 38.56 and 46.57 available P therefore, the LS have high amount of clay, which is describe in the below.

Table 3. Soil texture Characterizations

Parameter	Unit	Soil class	Value	Remarks
Texture	%	Sand	6	
		Silt	24	Clayey
		Clay	70	
pH (H_2O)			5.61	Slightly acidic
OC	%		2.106	Medium
OM	%		3.631	Medium
EC	ds/m		0.104	Non saline
CEC	cmol/kg		38.43	High
Available P	mg/kg		46.56	Low

5.4 Effect of incubation Time

In order to determine the incubation time at which the fixation completed, the time dependent fixation of p on Laterite soil was be carried out with 1g of the adsorbent and 10.2 mg/ L p solution. The mixtures was be stirred at speed of 200 rpm for different time intervals (10-100 min), centrifuged at pH 4-11 and the amount of p fixed per unit mass of laterite soil, and the percentage of p fixed was be computed respectively using equation given below:-

The P fixed (Pf) and percent P fixed (%Pf) were calculated using the following formula

$$Pf = P_i - P_x \tag{2}$$

$$\%\ Pf = \frac{P_i - P_x}{P_i} \times 100 \tag{3}$$

Where: Pf- phosphorus fixed

Pi- Applied phosphorus (20, 60, and 180 mg/L)

Px- Phosphorus treatment in x^{th} fraction at (20, 60 and 180 mg/L)

Native adsorbed P was be not determined or included in the fixation measurement (Tening et al., 2013).The results from laboratory experiment for samples for 28 days incubation of operation had shown 98.86 % P fixed, for Laterite soil and 88.55 % for both laterite soil and wastewater total phosphorus and orthophosphate fixation. Soils of Serbo region have the ability to fix P with the amount fixed increasing with increasing supply of P. More than 90% of added P fixed after 28 day of incubation below.

Table 4. Effect of incubation Time

Depth (cm)	Time (days)	P concentration (mg/L)					
		20		**60**		**180**	
		Rec (mg/L)	% Fixed	Rec (mg/L)	% Fixed	Rec (mg/L)	% Fixed
0-15	1	8.25	57.55	60.70	61.95	22.63	66.25
	3	6.89	64.54	53.40	65.70	20.40	70.30
	7	6.06	68.81	43.42	72.47	16.37	75.85
	14	5.45	71.95	31.08	74.47	15.27	82.71
	28	2.52	87.02	4.41	91.92	4.81	90.55
15-46	1	7.25	58.62	52.14	78.08	15.65	75.68
	3	4.85	68.12	47.23	84.50	12.65	82.42
	7	4.10	73.41	32.12	88.48	9.45	88.64
	14	3.14	83.24	22.42	95.82	6.75	93.82
	28	2.45	93.74	1.89	96.94	1.46	92.14
46-92	1	5.45	64.78	40.32	81.68	9.84	87.64
	3	2.45	76.06	32.14	91.86	6.28	92.91
	7	2.10	85.69	21.03	94.36	3.24	96.58
	14	0.95	94.85	14.25	97.01	2.14	98.47
	28	0.24	96.34	0.02	98.78	0.01	98.86

5.6 Effect of dose:

The result of this study increasing of LS dose was result with high fixation efficiency. it was observed that the fixation percentage of P ions onto the LS increased rapidly with the increasing of concentration. This result had expected because the increase of dose leads to greater surface area. When the fixation concentration was increasing from 0.5 to 50 g/L, the percentage of P fixation increased from 88.55% to 98.86%.

From the table it had observed that, as the dose of WW increases, amount of P fixed decreases sharply and attains the minimum. The point where maximum P fixed attained had taken as optimum dosage at 2 g. In this experiment, available P was increase with increasing WW dose .This increase might be due to high OM content of WW. Hue (1992) and Abreha (2013) reported that adsorption of organic anions on hydrous Fe and Al surfaces, and release of hydroxyl ions from OM increase pH and reduce P fixation.

Table 5. Effect of dose on p fixation

Dose (g)	Co (mg/L)	C_f (mg/L)	(%) fixed
2	10.2	0.773	66.25
5	10.2	0.293	70.30
10	10.2	0.223	75.85
15	10.2	0.213	82.71
20	10.2	0.228	90.55
30	10.2	0.154	92.21
50	10.2	0.153	96.7

5.7 PH Adjustment for phosphorus fixation

The results of the investigation of P fixing capacity pH had presented as 88.58% P fixed in the first day of incubation from 20 mg/L P added into the solution. The percent P fixed of LS and LS + WW in 20, 60, and 180 mg/L after the incubation of 1, 3, 7, 14 and 28 days is presented below**.**

Table 6. PH Adjustment for phosphorus fixation

P in solution (mg/L) pH Solution P fixed LS (mg/L)								
.	4	5	6	7	8	9	10	11
P rec	rec	rec	rec	rec	rec	rec	rec	rec
20	4.67	11.46	18.35	7.32	7.8	8.59	9.88	10.88
60	6.32	24.45	23.56	7.25	8.2	9.22	10.19	10.915
180	4.78	51.41	17.94	7.13	8.3	9.03	10.3	10.18
P fixed LS blended with Wastewater at various pH values (mg/L)								
	4	5	6	7	8	9	10	11
P rec	rec	rec	rec	rec	rec	Rec	rec	rec
20	2.34	9.23	6.56	6.81	6.79	6.88	8.12	9.79
60	5.23	18.34	17.39	5.93	6.93	8.71	9.37	8.38
180	3.12	43.22	12.31	5.285	6.195	8.43	8.89	8.17

Table 7. Capacity of Laterite soil for Phosphorus fixation with d/t incubation

Time	P Concentration (mg/L)					
	20		**60**		**180**	
	Recovered mg/L	% Fixed	Recovered mg/L	% Fixed	Recovered mg/L	% Fixed
1	12.85	33.84	34.13	42.61	77.52	56.89
3	11.31	41.75	23.16	61.06	42.47	76.38
7	8.89	54.23	20.75	65.11	34.35	80.90
14	8.16	58.01	19.13	67.82	28.37	84.22
28	6.96	64.17	17.69	70.26	20.54	88.58

Table 8. Capacity of laterite soil with wastewater for Phosphorus fixation with d/t incubation

Time (days)	P concentration (mg/L)					
	20		60		180	
	Rec (mg/L)	Fixed (%)	Rec (mg/l)	Fixed (%)	Rec (m /L)	Fixed (%)
1	8.25	23.34	22.63	31.23	56.45	44.43
3	6.89	18.45	20.40	43.56	34.23	57.12
7	6.06	32.45	16.37	47.67	26.45	72.45
14	5.45	43.23	15.27	54.21	14.34	76.12
28	2.52	48.54	4.81	63.45	4.41	78.32

This finding is in agreement with the report of Erich et al. (2002) that deprotonation of carboxylate group (COOH), phenolic and alcoholic hydroxyls (OH) reduce soil acidity. The lowest fixation was obtained when 20 mg/L of P was added for LS and LS + WW. The low P-fixing capacity of the LS + WW as compared to the LS may be due to the presence of more organic matter in the WW. Organic molecules released on decomposition of organic matter form complexes with Fe and Al in the soil thereby blocking the sites which are mainly responsible for fixation of P in the soil (Juo and Fox, 1977; Ghosal et al., 2011;

Brouwere, 2003).

Banik et al. (2006) also report that addition of organic manure markedly increased the availability of P in the soil. In addition, the decrease P fixation in LS +WW could be associated to the fact that WW has a large quantity of organic matter to the soil. This finding was similar with the study of (Kasongo et al., 2011) P fixation had reduced due to the increasing soil water holding capacity, alkalinity of soil humus with increasing WW. The percent P fixed in LS and LS +WW we also correlated with LS properties at various incubation periods and concentrations of applied.

CHAPTER SIX

CONCLUSION AND RECCOMENDATION

The finding from lab experiment thus it would not to use directly apply soil having p fixation.

Detail characterization of LS experimental investigation to know the techniques of wastewater application to the soil.

Soils of the Serbo have the ability to fix P with the amount fixed increasing with increasing supply of P and depth.

More than 90% of added P had fixed after 28 day of incubation. Phosphorus is therefore a hazard to contaminate groundwater supplies in this sub-region if not properly managed.
To reduce the impact of phosphorus in the wastewater, one must identify and recognize the influence of the primary factors affecting the environment.

The result of the "the experiment and factor agrees with the fact the management system suffers from the lack of trained and skilled workers.

Training of workers is very valuable, especially in a country like Ethiopia with waste handling system before discharging the downstream.

The availability of the liquid waste and their ease of handling" is highly increase productivity if properly allocate to required irrigable land.

Low quality of soil with nutrient availability will cause malnutrition; this affects the production rate and decreases the output.

Necessary and Sufficient supervision will increase the static value; result in safe in the environment, and increase productivity.

Field investigation will require for practical application.

Recommendations

Based on the results of this experiment, study and other research outputs done in other countries (with similar conditions) and in order to use this Fixation in our country as alternative wastewater treatment technology, the following points must recommend-

For effective wastewater treatment performance, Fixation should critical.

To make safe the environment we need to use low cost technology overcoming the problem.

Very significant decision-making factors must need to discharge the clarified wastewater in to use surface water and ground water.

Laterite soil were deficient phosphorus they do not used as agriculture but due to proper fixation of phosphorus from wastewater it is possible to use for agriculture and maximize production.

For the safe wastewater treatment, the University properly manages and applies the waste to soil, which is deficient in phosphate.

In addition, an advocacy and awareness creation works done by concerned institutions in the country on the methods of wastewater treatment that are cheap and highly effective like fixation.

Based on the substances of the wastewater, it is advised to consider which kind of treatment (Preliminary, Primary, secondary or Tertiary) should be used before the ultimate disposal.

The need for improvement and conservation of the environment in Ethiopia is necessitating the provision of energy and cost effective secondary wastewater treatment facilities for small communities such as schools, hospitals, military camps, colleges, farms, industries, and universities where on-site wastewater disposal technology is predominant.

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ANNEX

Procedure

For testing the given wastewater sample first the reagents are to be prepared.

Then the conductivity meters required calibration.

Preparation of Reagents

Potassium chloride solution (0.1N)

Switch on the electronic balance; keep the weighing pan set the reading to zero.

Measure 50mL of distilled water & transfer it to the beaker.

Weigh 0.7456g of potassium chloride

Transfer the 0.7456g of potassium chloride to the beaker contains distilled water &mix it by the glass rod until it dissolves thoroughly.

Transfer the contents to 100mL standard flask

Make up the volume tp 100mL, by adding distilled water & shake the contents well. This solution used to calibrate the conductivity meter.

Testing of wastewater sample

Rinse the electrode thoroughly with deionized water & carefully wipe with a tissue paper.

Measure 200mL of wastewater sample & transfer it to a beaker & place it on the magnetic stirrer.

Dip the electrode in to the sample solution taken in a beaker & wait for a steady reading.

Note down the reading in the display directly, which was expressed in millisiemens. The reading was 5.97 millisiemens.

Procedure

Preliminary sample treatment: To 100 mL sample containing not more than 200 µg P and free from color and turbidity, add 0.05 mL (1 drop) phenolphthalein indicator. If sample turns pink, add strong acid solution drop wise to discharge the color. If more than 0.25 mL (5 drops) is required, take a smaller sample and dilute to 100 mL with distilled water after first discharging the pink color with acid.

Color development:

Add, with thorough mixing after each addition, 4.0 mL molybdate reagent I and 0.5 mL (10 drops) stannous chloride reagent I. Rate of color development and intensity of color depend on temperature of the final solution, each 1°C increase producing about 1% increase in color. Hence, hold samples, standards, and reagents within 2°C of one another and in the temperature range between 20 and 30°C.

Color measurement: After 10 min, but before 12 min, using the same specific interval for all determinations, measure color photo metrically at 690 nm and compare with a calibration curve, using a distilled water blank. Light path lengths suitable for various concentration ranges are as follows:

Approximate P Range (mg/L)	Light Path
0.3–2	0.5
0.1–1	2
0.007–0.2	10

Always run a blank on reagents and distilled water. Because the color at first develops progressively and later fades, maintain equal timing conditions for samples and standards. Prepare at least one standard with each set of samples or once each day that tests are made. The calibration curve may deviate from a straight line at the upper concentrations of the 0.3 to 2.0 mg/L range.

Table 9 Standard Solution

Concentration	Absorbance
0	0.085
0.5	0.369
1	0.592
1.5	0.899
2	1.12
2.5	1.53

$$y = 0.5591x + 0.0669$$
$$R^2 = 0.9924$$
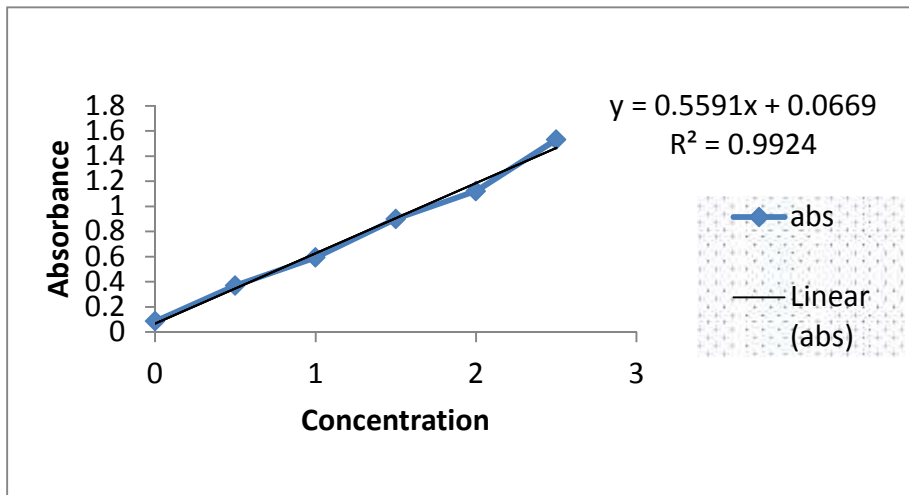
Fig 3 Calibration

Procedure for mechanical analysis of soil

The following summarizes the procedure for the mechanical analysis of a soil.

Step 1: Weigh a 50 g sample of the soil.

Step 2: Disperse the soil in 1 L of water.

Step 3: After suspending the soil, take the hydrometer reading at 40 sec and at 2 h.

Step 4: Apply the correction factor if the room temperature is above or below 20°C.

Step 5: Using the hydrometer readings, calculate the sand, silt, and clay percentages.

Step 6**:** Using the textural triangle find the texture of the soil.

Now we use and identify the texture of a laterite soil sample.

Soil Texture

Determination of soil texture by hydrometer method was calculated the percentage of sand, silt, and clay in a soil sample. Based on these percentages, were determining the texture of the soil by using a textural triangle. Hence, the hydrometer reading (g/L) represents silt and clay. The silt size particles had settled in about 2 h. Now only clay particles remain in suspension. The hydrometer reading represents (g/L) after 2 h of suspension was represent clay. One should note that the room temperature was having an effect on the settling rate of the particles in a liquid.

I was assuming the room temperature to be 25°c.

The mass of the soil sample to be 50 g

Time: 40 sec

Hydrometer reading: 7 g per L

Time: 2 h

Hydrometer reading: 7 g per L

What is the percentage of sand?

The hydrometer reading at 40 sec represents silt and clay in the suspension. Hence, to determine the amount of Clay, subtract this reading from the sample mass. Use the following equation to calculate the percentage of sand in the soil sample.

$$Sand \% = \frac{Sample\ mass - 40\ \sec hydrometer\ rereading}{Sample\ mass} \times 100\ \%$$

$$Silt \% = \frac{40\ \sec hydrometer\ reading}{Sample\ mass} \times 100$$

From the triangle Sand (%) = 6% and Silt (%) = 24%

$$Clay \% = 100 - Sand \% - Silt \% \hspace{3cm} (6)$$

Clay (%) =   100 - Sand % - Silt %

100 – 6% -24%

$Clay \% = 70\%$

Standard Operating Procedure

Procedure for Determining Soil Particle Size Using the Hydrometer Method

MATERIALS

Standard hydrometer, ASTM no. 152 H, with Bouyoucos scale in g/L

Electric stirrer (malted-milk-type)

Plunger or rubber stoppers for 1000 mL sedimentation cylinders

Sedimentation cylinders with 1000 mL mark

600 mL beakers or quart mason jars

Pentanol

Sodium-hexametaphosphate (HMP) solution (50 g/L)

Sieve 2 mm screen

Electric oven and weighing jars or. 5-pint mason jars

Balance

Stopwatch/ timer

100 mL and 2 L volumetric flasks

Mortar and pestle

Safety goggles

Latex gloves

Dust mask

Distilled water

Submersible Thermometer

Conductivity

Experimental Significance of conductivity

Electrical conductivity measurements often employed to monitor desalination plant.

To assess the source of pollution

To assess the suitability of wastewater for disposal on land based on the experimental result the conductivity of the wastewater was 5.97millisiemens.

Conductivity value was gives us a rapid & in expensive way of determining the ionic strength of a solution.

Material Method

Conductivity meter with electrode (ACT probe)

Magnetic stir with stirring bead

Standard flask

Measuring jar

Beaker 250mL

Funnel

Tissue paper

Chemical required

Potassium chloride

Distilled water

Determination of Organic Carbon

Apparatus

Conical flask 500 ml

Pipettes 2 ml, 10 ml, & 20 ml capacity

Burette 50 ml capacity

Volumetric measuring flask (1 Lit. capacity)

Reagent bottles

Asbestos sheet

 Reagents:

1 N potassium dichromate: Dissolve 49.04 AR grade $K_2Cr_2O_7$ (dry) in distilled water and make up the volume to one litre.

Concentrated sulphuric acid (Sp. Gravity 1.84, 96%): If the soil contains chloride, then 1.25% silver sulphate had added in H_2SO_4.

Orthophosphoric acid

Sodium Fluoride (chemically pure)

0.5 N Ferrous ammonium sulphate Dissolve 196.0 gm of AR grade ferrous ammonium sulphate in distilled water, add 20 ml of concentrated $H_2SO_4$and make volume to one litre. The ferrous ammonium sulphate should be from a fresh lot and light green in colour. (**Source Standardard Water and Wastewater).**

Determination of Organic Carbon in Soil

The determination of organic carbon in soil serves indirectly as measure of available nitrogen. The organic matter content of a typically well-drained mineral soil is low varying from one to 6% by weight in the top soil and even less in the subsoil. The influence of organic matter (OM) on soil properties and consequently on plant growth is far greater even though the percentage of organic matter (OM) is higher in the soil.

Walkley and Black Method:

Organic carbon oxidized with potassium dichromate in the presence of concentrated sulphuric acid. Potassium dichromate produces nascent oxygen, which combines with the carbon of organic matter to produce CO_2. The excess volume of $K_2Cr_2O_7$ is titrated against the standard solution of ferrous ammonium sulphate in presence of H_3PO_4, using ferroin to detect the first appearance of unoxidized ferrous iron and thus volume of $K_2Cr_2O_7$ had found out, which is actually required to oxidize organic carbon.

$$\% \text{ Organic carbon} = \frac{(B - S) \times N \times 0.003 \times 100}{\text{Wt. of soil (oven dry)}} \qquad (8)$$

Where, B = ml of std. 0.5 N ferrous ammonium sulphate required for blank.

S = ml of std. 0.5 N ferrous ammonium sulphate required for soil sample.

N = Normality of std. ferrous ammonium sulphate (0.5N).

The correction factor 1.3 had multiplied as according to Walkley and Black method only estimated 77% carbon (av. Value). Soil organic matter contains (59%) of organic carbon. The correlation coefficient between organic matter and P fixation was also quite high. This may be due to the formation of phosphohumic compounds (Dolui and Gangopadhyay 1984).

However other workers (Awad and Al-Obaidy 1989) had found that addition of organic matter to soils increases the availability of the element (Dhargawe et al. 1991). The results showed that P-fixation is quite a complex phenomenon depending upon many interacting factors. The relationship between P-fixation and clay content is shown in our soils are mostly old soils. (Oxisols and Ultisols).

Most of them are rich in iron oxides and Aluminium oxide, P-fixation increases with increase in clay content. There was a significant correlation between amorphous Al and P-fixation, and between amorphous Fe and P-fixation.

It seen that the levels of these two elements are quite high in our soils. Thus the high correlation between them is due to the formation of insoluble Al and Fe phosphates, especially in acidic soils. According to Thomazi et al. (1990) describes that iron oxides and clay were the main factors contributing to P-fixation in some Brazilian soils.

Procedure:

Weigh 1 gm. of 0.5 mm sieved soil into dry 500 ml conical flask. Add 10 ml of $K_2Cr_2O_7$into the flask with pipette and swirl.

Add rapidly with a burette 20 ml conc. $H_2SO_4$and swirl gently until soil and reagents are mixing then more vigorously for one minute.

Allow the reaction to proceed for 30 min on asbestos sheet to avoid burning of table due to release of intense heat due to reaction of sulphuric acid.

Add slowly 200 ml of distilled water, 10 ml of concentrated orthophosphoric acid and add about 0.2 `gm NaF (one small teaspoon) and allow the sample to stand for 1.5 hrs. The titration end is clear in a cooled solution.

Just before titration add 1 ml ferroin indicator into the conical flask, the excess $K_2Cr_2O_7$0.5 N ferrous ammonium sulphates until the colour flashes from yellowish green to greenish and finally brownish red at the end.

Simultaneously blank test had run without soil.

UV Spectrophotometer Method:
Apparatus:
UV Spectrophotometer.
Volumetric flask
Reagents:
N potassium dichromate: Dissolve 49.04 AR grade $K_2Cr_2O_7$dry) in distilled water and make up the volume to one litre.
97 % concentrated Sulphuric acid

PH 7-11 Adjustment For LS And WW

	P_H Adjestment =7			P_H Adjestment =8			P_H Adjestment =9			P_H Adjestment =10	
	T_1	T_2		T_1	T_2		T_1	T_2		T_1	T_2
20	6.84	6.78	20	6.84	6.74	20	8.89	8.88	20	9.84	9.78
60	5.98	5.88	60	6.97	6.89	60	8.74	8.68	60	9.42	9.32
180	5.23	5.34	180	6.21	6.18	180	8.38	8.48	180	8.94	8.84

	P_H Adjestment =11	
	T_1	T_2
20	10.84	10.74
60	10.45	10.31
180	10.21	10.13

PH 7-11 Adjustment For LS

	P_H Adjestment =7				P_H Adjestment =8				P_H Adjestment =9		
	T_1	T_2	AVERAGE		T_1	T_2	Average		T_1	T_2	Average
20	7.26	7.38	7.32	20	7.87	7.78	7.825	20	8.76	8.42	8.59
60	7.21	7.29	7.25	60	8.28	8.08	8.18	60	9.32	9.12	9.22
180	7.08	7.18	7.13	180	8.31	8.21	8.26	180	8.94	9.12	9.03

	P_H Adjestment =10				P_H Adjestment =11		
	T_1	T_2	Average		T_1	T_2	Average
20	9.89	9.88	9.885	20	10.94	10.82	10.88
60	10.1	10.24	10.19	60	10.89	10.94	10.915
180	10.4	10.2	10.3	180	10.12	10.24	10.18

Fiseha	DF	Spectro	R^2	m	b
20	10	19.43	0.9924	0.5591	0.0669
60	30	59.47			
180	60	179.83			

Fixation with Different Incubation time only Laterite Soil

			vs	1.6666667		LS 1 day		C_o(mg/l)		100				
0.5591			DF	50	100						R^2	m	b	
0.0669			10					SV (ml)		50 TV(ml)	0.9924	0.5591		0.066
			30										
			60	ABS	Conce	Conce				Dilution			
Co (mg/L)	Abs	DF	Co (mg/L)	T1	T2	T1	T2	STD	Avg.Conc	DF	Cf	%Fixed trial 1	
				0.09	0.155	0.041	0.158	0.046	0.099				
20	1.153	10	19.43	0.767	0.804	1.252	1.318	0.026	1.285	10	12.853	33.84	
60	1.1752	30	59.47	0.822	0.584	1.351	0.925	0.168	1.138	30	34.132	42.61	
180	1.7426	60	179.83	1.094	1.207	1.837	2.039	0.080	1.938	40	77.525	56.89	

For lateite soil only

	20	60	180
Time (days)	%	%	%
1	33.84	42.61	56.89
3	41.75	61.06	76.38
7	54.23	65.11	80.90
14	58.01	67.82	84.22
28	64.17	70.26	88.58

Time (days)	P fixed at					
	20 mg/L		60 mg/L		180 mg/L	
	Value	%	Value	%	Value	%
1	12.85	33.84	34.13	42.61	77.52	56.89
3	11.31	41.75	23.16	61.06	42.47	76.38
7	8.89	54.23	20.75	65.11	34.35	80.90
14	8.16	58.01	19.13	67.82	28.37	84.22
28	6.96	64.17	17.69	70.26	20.54	88.58

Fixation with Different Incubation time containing Laterite Soil and Wastewater

DF	Co (mg/L)		T1 (Abs)	T2 (Abs)	T1 (Conce)	T2 (Conce)	STD	Avg. Conc	Dilution DF	Cf	%Fixed trial 1	
						R² = 0.9924	m = 0.5591	b = 0.0669	DF		100	
			1 day LS +WW	SV (ml)			50	TV(ml)	2.5			
		1.67							C₀ =			
		50										
			0.11	0.12	0.07	0.09	0.01	0.08				1
10	19.43		0.51	0.54	0.80	0.85	0.02	0.82	10	8.25	57.55	3
30	59.47		0.44	0.50	0.73	0.78	0.04	0.75	30	22.63	61.95	7
60	179.83		0.54	0.72	0.85	1.17	0.13	1.01	60	60.70	66.25	14
												28

	LS + WW		
	20	60	180
Time (days)	%	%	%
1	57.55	61.95	66.25
3	64.54	65.70	70.30
7	68.81	72.47	75.85
14	71.95	74.32	82.71
28	87.02	91.92	97.55

Time (days)	P fixed at					
	20 mg/L		60 mg/L		180 mg/L	
	Value	%	Value	%	Value	%
1	8.25	57.55	22.63	61.95	60.70	66.25
3	6.89	64.54	20.40	65.70	53.40	70.30
7	6.06	68.81	16.37	72.47	43.42	75.85
14	5.45	71.95	15.27	74.32	31.08	82.71
28	2.52	87.02	4.81	91.92	4.41	97.55

ANOVA result two factor with replication

SUMMARY	12.85	33.84	34.13	42.61	77.52	56.89	Total
3							
Count	2.00	2.00	2.00	2.00	2.00	2.00	12
Sum	20.21	95.99	43.91	126.17	76.82	157.28	520.367
Average	10.10	47.99	21.95	63.09	38.41	78.64	43.3639
Variance	2.94	77.82	2.91	8.22	32.97	10.19	602.13
14							
Count	2.00	2.00	2.00	2.00	2.00	2.00	12
Sum	15.12	122.18	36.82	138.09	48.91	172.80	533.916
Average	7.56	61.09	18.41	69.04	24.46	86.40	44.493
Variance	0.72	19.03	1.05	2.97	30.69	9.49	929.492
Total							
Count	4.00	4.00	4.00	4.00	4.00	4.00	
Sum	35.32	218.17	80.73	264.26	125.73	330.08	
Average	8.83	54.54	20.18	66.06	31.43	82.52	
Variance	3.38	89.46	5.50	15.56	86.09	26.62	

ANOVA

Source of Variation	SS	df	MS	F	P-value	F critical
Sample	7.65	1.00	7.65	0.46	0.04	4.75
Columns	16175.63	5.00	3235.13	195.09	0.00	3.11
Interaction	473.22	5.00	94.64	5.71	0.01	3.11
Within	198.99	12.00	16.58			
Total	16855.49	23.00				

ANOVA: Two-Factor With Replication

SUMMARY 3	8.25	57.55	22.63	61.95	60.70	66.25	Total
Count	2	2	2	2	2	2	12
Sum	12.94	133.36	36.77	138.17	96.82	146.16	564.22
Average	6.47	66.68	18.38	69.09	48.41	73.08	47.02
Variance	0.35	9.12	8.10	22.87	49.80	15.39	740.26

14

Count	2	2	2	2	2	2	12
Sum	7.97	158.97	20.08	166.24	35.49	180.26	569.01
Average	3.99	79.49	10.04	83.12	17.74	90.13	47.42
Variance	4.28	113.42	54.74	154.78	355.87	110.05	1579.63

Total

Count	4	4	4	4	4	4
Sum	20.92	292.33	56.84	304.41	132.31	326.42
Average	5.23	73.08	14.21	76.10	33.08	81.61
Variance	3.60	95.52	44.15	124.85	448.68	138.75

ANOVA

Source of Variation	SS	df	MS	F	P-value	F critica
Sample	0.96	1.00	0.96	0.01	0.06	4.75
Columns	22953.0	5.00	4590.60	61.29	0.00	3.11
Interaction	1666.93	5.00	333.39	4.45	0.02	3.11

Within	898.77	12.00	74.90
Total	25519.7	23.00	