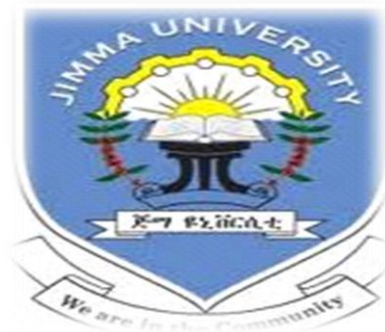


JIMMA UNIVERSITY
JIMMA INSTITUTE OF TECHNOLOGY (JiT)
SCHOOL OF GRADUATE STUDY
DEPARTMENT OF WATER RESOURCE AND HYDRAULIC ENGINEERING



SORPTION OF PHOSPHATE FROM WASTEWATER USING TERMITE SOIL

BY HAILU ASHEBIR

A THESIS SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES OF JIMMA
UNIVERSITY INSTITUTE OF TECHNOLOGY IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF MASTER OF ENVIRONMENTAL
ENGINEERING PROGRAM

NOVEMBER, 2015

JIMMA, ETHIOPIA

SORPTION OF PHOSPHATE FROM WASTEWATER USING TERMITE SOIL

BY: HAILU ASHEBIR

A THESIS SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES OF JIMMA UNIVERSITY INSTITUTE OF TECHNOLOGY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF ENVIRONMENTAL ENGINEERING PROGRAM

ADVISORS: Dr.-Ing. FEKADU FUFA (PhD)

Dr. DEJENE BEYENE (PhD)

JIMMA, ETHIOPIA

NOVEMBER, 2015

Abstract

Wastewater which contains pollutants like phosphate above its permissible level and released into environment without treatment is a headache of our world today. So, the aim of this study was to investigate phosphate (P) removal efficiency of Termite mounds which is locally available, low cost adsorbent under batch experimental study. Various parameters studied including contact time, adsorbent dosage, pH, initial concentration, shaking speed, particle size, temperature and the presence of competing anions were considered. The result of this study showed that the optimum contact time for adsorption of P on termite mounds reached to equilibrium after 60 min with removal efficiency of ~96%, at optimum adsorbent dose of 10 g/l, optimum pH ~7, equilibrium initial concentration of 3 mg/L, equilibrium shaking speed 200 rpm and grain size <0.075 mm. And also, the increases of temperature also increase the removal efficiency of adsorbent.

The sorption kinetics was found to follow pseudo-second-order model $R^2 = 0.997$ rate and the experimental equilibrium sorption data fitted well to Langmuir model with $R^2 = 0.978$ the equilibrium adsorption, giving a sorption capacity of 4.32 mg/g for central part of termite mounds.

The presences of competing anions (carbonate and bicarbonate) significantly influence P adsorption efficiency while sulfate, chloride and nitrate were interfering slightly. The adsorbent was reduced P concentration of real wastewater from 9.03 mg/L to 0.97 mg/L which was below its permissible limits. Regenerablity of adsorbent was tested using NaOH solution and the re-adsorption efficiency after third adsorption/desorption was >73%. From the results of this study it is concluded that the application of TMs for adsorptive removal of P is highly favorable and a spontaneous process. Therefore, it can be likely that termite mound (TM) can be used as a low cost locally available together with highly efficient adsorbent for removal of P from wastewater.

Key words: Phosphate, Termite mound, Sorption and Kinetics

Acknowledgements

First and foremost the Glory goes to the Almighty God; through Him all things are possible. In Him, I put all my trust for protection and guidance!

And then, I am very grateful to express my sincere thanks to my advisors Dr.-Ing. Fekadu Fufa and Dr. Dejene Beyene for their intellectual inspiration, invaluable help, constant suggestions and comments which proved to be helpful in ensuring the successful completion of this paper, may you receive my special gratitude for your academic guidance and endless support.

Furthermore, special thanks go to my friends and fellow classmates for their cooperation during laboratory work, continuous discussion program and material support.

Lastly but no list I would like to thanks all my family for their initiation, support and encouraged me during the study period.

Table of Contents

Abstract.....	III
Acknowledgements.....	IV
List of Table.....	VIII
List of Figures.....	IX
List of Abbreviations, Acronyms and Symbols.....	XI
CHAPTER ONE.....	1
INTRODUCTION.....	1
1.1 Back ground.....	1
1.2 Statement of the problem.....	3
1.3 Significance of study.....	4
CHAPTER TWO.....	5
LITERATURE REVIEW.....	5
2.1 General description.....	5
2.2 Forms of phosphate found in wastewater.....	6
2.3 Basics of phosphate source control.....	7
2.4 General Descriptions of Termites.....	7
2.6 Influence of termite activities on physico-chemical soil properties.....	8
2.6.1 <i>Influence on soil texture</i>	9
2.6.2 <i>Influence on soil acidity</i>	9
2.6.3 <i>Influence on organic carbon</i>	10
2.6.4 <i>Influence on the cation exchange capacity and exchangeable basic cations</i>	10
2.6.5 <i>Influence on phosphorus availability</i>	11
2.8 Variability of termite activities in different zones of the mound.....	12
2.10. Factors affecting phosphorus adsorption by soils.....	12
2.10.1 <i>Soil Mineral Type</i>	13
2.10.2 <i>Amount of clay</i>	13
2.10.3 <i>Adsorption thermodynamics</i>	14
2.10.5 <i>Effect of soil pH</i>	15
2.10.6 <i>Exchangeable Al³⁺</i>	15
2.10.7 <i>Effect of organic matter</i>	16
2.10.8 <i>Effect of Coexisting Ions,</i>	16
2.11 Regeneration.....	17

CHAPTER THREE	19
OBJECTIVE	19
3.1. General Objective	19
3.2 Specific objectives	19
3.3 Research hypotheses	19
CHAPTER FOUR.....	20
MATERIALS AND METHODS.....	20
4.1 General description of the study site and Period	20
4. 2. Study Design.....	20
4. 3. Study variables.....	20
4.3.1. <i>Independent variables</i>	20
4.3.2 Dependent variable	20
4. 5. Real wastewater analysis	21
4. 6.Preparation of P solutions and analytical methods	21
4.7 Batch adsorption experiments.....	22
4.7.1 <i>Effect of contact time</i>	22
4.7.2 <i>Adsorption kinetics</i>	23
4.7.3. <i>Effect of solution pH</i>	24
4.7.4 <i>Effect of adsorbent dose</i>	24
4.7.5 <i>Effect of initial concentration and Adsorption Isotherms</i>	24
4.7.6 <i>Effect of shakin speed</i>	25
4.7.7 <i>Effect of co-existing ions</i>	26
4.7.8 <i>Effect of termite activity</i>	26
4.7.9 <i>Effect of temperature</i>	26
4.8. Regeneration of adsorbent	26
4.9 Data Quality	27
4. 10. Dissemination of plan	27
CHAPTER FIVE	28
RESULT	28
5.1. Adsorbent.....	28
5.1.1. <i>Characterization</i>	28
5.2.4 <i>Effect of TM dosage on adsorption</i>	29
5.2.3 <i>Effect of shaking speed</i>	29
5.2.1. <i>Effect of contact time and Adsorption Kinetics</i>	30

5.2.5 <i>Effect of particle size of the adsorbent</i>	33
5.2.6 <i>Effect of initial concentration</i>	34
5.2.6 <i>Intraparticle diffusion of P</i>	35
5.2.7 <i>Adsorption thermodynamics</i>	35
5.2.8 <i>Effect of termite activity</i>	36
5.2.8 <i>Effect of temperature</i>	36
5.3 <i>Effect of coexisting ions</i>	37
5.4 <i>Regeneration of adsorbent</i>	38
CHAPTER SIX.....	40
Discussion.....	40
CHAPTER SEVEN	47
Conclusion and Recommendation	47
6.1 <i>Conclusions</i>	47
6.2 <i>Recommendations</i>	48
References.....	49
ANNEX I: BATCH EXPERIMENTS PROCEDURE	57
ANNEX II <i>Tables contain more information's</i>	58

List of Table

Table 1 Characterization of chemical properties of TMs.....	28
Table 2 Physical properties of TMs (clay, silt and sandy)	28
Table 3 some important chemical properties of TMs with its depth from external to the center	28
Table 4 some important physicochemical properties of real ww taken from Jimma University waste discharge sewer line Jimma, Ethiopia.....	29
Table 5 Isotherm parameters of the equilibrium adsorption of $[\text{PO}_4^{3-}]$ on TM.....	32

List of Figures

Fig. 1 Effect of adsorbent dose	29
Fig. 2 Effect of shaking speed	30
Fig. 3 Effect of contact time on adsorption: (a) 3 mg/L and (b) 10 mg/L	31
Fig. 4 Pseudo-first-order plots of: (a) 3 mg/L and (b) 10 mg/L and pseudo-second-order (c) 3 mg/L and (d) 10 mg/L.....	32
Fig. 5 Effect of pH on adsorption: (a) q_e (mg/g) and (b) A(%).....	33
Fig. 6 Effect of particle size on adsorption.....	34
Fig. 7 (a) Effect of initial concentration (b) Isotherms of equilibrium adsorption	35
Fig. 8 Intraparticle diffusion plots: (a) 3 mg/L and (b) 10 mg/L.....	35
Fig. 9 Effect of temperature on adsorption	37
Fig. 10 Effect of competing ions on adsorption of phosphate	38
Fig. 11 Regenerability of adsorbent (a) effect of agitation time on desorption; (b) amount desorbed with cycle.....	39

List of Abbreviations, Acronyms and Symbols

CEC	Cation Exchange Capacity
FAO	Food and Agriculture Organization of the United Nations
HWS	Highly Weathered Soils
Ha	Hectare
UV-SSPM	Ultra Violet Spectrophotometer
K	Potassium
M	Meter
MSc	Master of Science
N	Nitrogen
OC	Organic carbon
P	Phosphorus
SOM	Soil Organic Matter
WRB	World Reference Base for soil Resources
Fe-Zr	Iron–Zirconium
GFH	Granular Ferric Hydroxide
ECEC	Effective Cation Exchange Capacity
CEC	Cation Exchange Capacity
EC	Electro Conductivity
ΔG	Gibbs free energy Change
ΔH	Enthalpy Changes
ΔS	Entropy Change
STPP	Sodium Tripolyphosphate
NTA	Nitriloacetic Acid

CHAPTER ONE

INTRODUCTION

1.1 Back ground

Phosphorous (P) is a constituent of many organic and inorganic compounds found widely distributed in the environment. It is a widely distributed naturally occurring element that can be found in the earth's crust, water, and all living organisms. However, it is limiting element in nature, because of its widely use, it is introduced to environment from different sources such as fertilizer, boiler, water conditioners, drinking water treatment aids, detergents and other laundering products (Tomar, 1999, Millus, 2009). Since it is a limiting nutrient it causes many problems after entering into aquatic environment such as eutrophication, Oxygen depletion and overgrowth of algal bloom and then cause's loss of aquatic life's and water bodies. Effluents that contain P beyond its permissible limits and released into aquatic environment can cause this problem.

However, there are different methods of P removal methods from wastewater and aquatic environments including chemical precipitation, crystallization such as magnesium ammonium phosphate and hydroxyl apatite processes and biological methods which are widely studied for a long period of times by different researchers. Even though chemical treatment is more effective for P removal than other methods but still it is subjected to high costs, complex technology, problems of sludge handling, its disposal and neutralization of effluent (Biswas, 2008a, Dursun et al., 2006a). This and other problems initiate researchers of developing countries to focus on low cost locally available materials to remove this pollutant from wastewater focus on a removal technology called as adsorption. Adsorption is one of newly developed technology investigated effective pollutant removal using locally available low cost materials. In this study locally available material called termite mound was used.

Termite mounds are types of soil constructed by insects called termite. Termites are social insects that exert significant influence on the physical, chemical and biological properties of tropical and sub-tropical soils (Semhi et al., 2008). Their feeding habit, food processing and mound construction operations introduce significant modifications to the soils organic and mineralogical content on which the mound is built (Konate et al., 1999). Because of its chemical composition,

high clay contain and modified physical properties of their mounds, it is looked as good adsorbent materials. Studies have shown that termite mounds in tropical and sub tropical have higher values for exchangeable some minerals like Al^{3+} , Ca^{2+} , Mg^{2+} and K^{+} , effective cation exchange capacity (ECEC), water holding capacity and water infiltration rates (Rupela et al., 2006). In another related research, termite-mound soil was reported to contain as much as 20% of the total nitrogen as inorganic nitrogen, an average organic carbon content of 9.30% and 2.25 times more total P than the adjacent soils (Abdus and Itiola, 2012, Lamoureux and O'Kane, 2012). This is why termites have been categorized as one of the main soil engineers (Bignell and Eggleton, 2000a). Since they modify soil physico-chemical properties, the promotion of microbial metabolism in nest materials and increased mobilization of nutrients in the neighborhood of the nest (Abbadie et al., 2009; Jouquet et al., 2004).

1.2 Statement of the problem

The pollution of surface waters by phosphate is the main cause for eutrophication and was recognized as a problem in the middle of the twentieth century. This was identified through survey on the extent of the problem on a global level has found that in Europe, 53% of lakes and reservoirs are eutrophied. The proportions for Africa, South East Asia, North and South America are 28%, 54%, 48%, and 41%, respectively (ILEC, 2009). Eutrophication is a natural process and took centuries to transform water body into a dry land. Nowadays, this process is greatly accelerated by human activities causes eutrophication within a decade's (Panasiuk, 2010). This short term consequences of eutrophication are promoting growth of excess toxic algal blooms which can kills fish , harm wildlife and livestock by reducing the oxygen content of water (anoxia) or through the production of toxins and leading to a destabilized aquatic ecosystem (Singh et al., 2012; Dursun et al., 2006b). Recent reports indicated that more than 80% of wastewater containing P generated is directly discharged into surface and ground water bodies without any treatment (Liu et al., 2014).

While sewage discharges are gradually tackled, the relative importance of diffused phosphorus sources such as agriculture and soil erosion will increase. Even though, improvements in discharge and surface water quality in recent years, phosphorus pollution remains a significant issue in developed countries. Developing countries have also severe eutrophication problems driven by increased use of fertilizer, as well as very poor treatment of urban wastewater from increasing populations (WHO, 1997)

However, our country Ethiopia is under rapid growth of industries and towns, all liquid wastes containing high concentration of P from old as well as new factories, commercial, public and domestic utilities release untreated into any receiving water body (Aschale et al., 2015; MoWIE, 2015). These habits are one of the main causes of soil and water contamination and consequently cause of public health problem (MoWIE, 2015; WHO, 1997).

In general, removal of phosphorous from wastewater is very difficult to remove by biological method in which removal efficiency is not greater than 20%; in the other way, chemical treatment is effective for P removal even though construction and sludge treatment are too expensive. So, the aim of this research is to apply recently developed technology known as adsorption using TM which is locally available adsorbent.

1.3 Significance of study

This study gives a great advantage for developing countries those have low income and can't access high technology for their liquid waste treatment. It alarms them to use locally available material (TMs) with low cost but high efficiency of pollutant (P) removal to meet internationally permissible guide linesfor wastewater to release into environment.

Specially, for tropical and sub tropical countries where TMare abundantly found it gives good information to use as one of P removal technology.

Since our country Ethiopia is one of low income sub-Saharan country with accelerated economic growth and industrial establishments but difficulty of waste treatment, this research gives a key to use locally available material for waste treatment.

CHAPTER TWO

LITERATURE REVIEW

2.1 General description

Wastewater which contains pollutants beyond its permissible limit generated from both point and non point sources released into environment without treatment is a fret of our world today. Wastewater containing high concentration of P discharge from sewage and industries are major component of water pollution, contributing to oxygen demand and nutrient loading of the water bodies, promoting toxic algal blooms and leading to a destabilized aquatic ecosystem (Singh et al., 2012; Dursun et al., 2006b). Recent reports indicate that worldwide more than half of the population of less developed countries does not have access to sanitation and more than 80% of the waste water generated is directly discharged into surface and ground water bodies (Harris, 2002). Different national and international institutions try to develop permissible limit for all hazardous chemical and elements released in waste water and inter into river, stream and stagnant water bodies (Maduakor et al., 1995; Tekalign and Haque, 2007; WHO, 1997). P is one of those elements which limit the growth and if in excess cause the loss of aquatic life and death of water bodies.

The general purpose of P removal is to eliminate the excess P content from wastewater discharged to receiving waters and then to utilize this excluded P load in the way which is the most proper for the natural phosphorus cycle in nature. This method should prevent surface waters against Eutrophication-related problems (Rybicki, 1997b).

P is a naturally occurring element that can be found in different parts of earth's crust, water bodies, and in all living organisms (Millus, 2009). P is one of 16 elements that are essential for plant growth and it is found in natural environment in the form of condensed phosphate (polyphosphates), organic phosphates and orthophosphates (Guan, 2005). The excess content of P in receiving waters leads to extensive algal growth which is called Eutrophication. The phenomenon of Eutrophication usually decreases the water quality and as a result it may increase significantly the cost of water treatment at treatment plants for surface water. The load of phosphorus discharged to receiving waters comes from various groups of sources of point source and non point sources of which the main sources are agricultural use of fertilizers, domestic and industrial wastewater, and atmospheric deposition (Rybicki, 1997a).

A lot of researchers were reported on the sources of P and the ways used to reduce this pollutant from wastewater using different technologies. According to the findings >80% P was from domestic wastewater which is the dominating source of P in municipal discharges in densely populated regions (Spellman, 2003). As presented by van Starckenburg and Rijs (1988) in the Netherlands 18 million tons per year of P comes from domestic wastewater while only 4.2 million tons per year comes from industrial discharges as reviewed by (Rybicki, 1997b). Similar report for Poland showed that as much as 85% of the total P load comes from domestic sources (Rybicki, 1996). The finding also reports amount of P released per capita per person for different countries with the average of 1.4 g P/cap*day (Boller, 1993). Even though the amount and type of waste produced in households is influenced by culture, lifestyle and standard of living of the inhabitants as well as the technical and juridical framework by which people are surrounded (Henze, 2008). These sources mainly come from house hold because of excess uses of detergents containing high concentration of P.

Another important source which takes the second priority of P concentration was industrial and commercial wastewater with >17.1% P content (Wentzel, 1995). The effects of mining P and manufacturing fertilizer have been controversial for decades, but until relatively recently no one was willing to take on the industry. Even though developed countries used high technology to treat their waste still it is difficult to remove such like of P and nitrate from wastewater through biological treatment methods.

2.2 Forms of phosphate found in wastewater

Phosphate is found in water environment in different forms; below it was discussed in short as great importance in wastewater:

- Organic P (with -P-O-C- bonds), usually constituents of dissolved and suspended compounds of wastewater. Their input to total phosphorus is estimated as approx. 4%, mostly from plastifiers for plastics or pesticides. In a water environment these compounds are degraded chemically and/or biologically to orthophosphates. Forms of compounds: parts of cell walls (Phospholipids), phosphoramides, toxic phosphate esters, phosphororganic insecticides

- Condensed inorganic Phosphate (with -P-O-P- bonds), including both chain-bonded polyphosphates and cyclic bonded metaphosphates. Polyphosphates being basic constituents of detergents and water softeners are the most common inorganic condensed polyphosphates in municipal wastewater
- Inorganic orthophosphates PO_4^{3-} ions.

2.3 Basics of phosphate source control

As discussed above the main sources of P was from reducing domestic, industries and commercial area which mainly come from detergent used for cleaning and small was for another purpose. According to Wentzel, (1996) recommendation of P concentration from wastewater was possible to eliminate or significantly reduce this source of contamination several sodium tripolyphosphate (STPP) substitutes have been proposed e.g. nitriloacetic acid (NTA), zeolites, unsaturated sulphonated organic acids etc(Wentzel, 1991).

Even though it is possible to reduce P concentration in wastewater by replacing with another alternatives of detergents, these methods of P elimination occurred to be not as simple as it had been recognized previously because of:

- The impact of STPP on environmental was not studied and well known yet;
- There were no clear agreements on the ecological safety of NTA is still being under question as this compound cannot be fully removed in biological treatment plants;
- Substitutes of newly developed detergents decreasing washing performance and may reduce life times machine and clothing (Wentzel, 1991)
- To conclude even though some amounts of pollutant decreased by using alternative detergents (30-40%) for those left in wastewater another technology will be required such as chemical precipitations, biological methods and adsorption which are focus of this study and will be discussed in detail

2.4 General Descriptions of Termites

Termite mounds are built by different types of mound-building termite species that significantly modify the physicochemical properties of soil (Fufa et al., 2013; Semhi et al., 2008). It is widely distributed throughout the world including our country Ethiopia (Abbadie et al., 2009; Getahun and Degaga, 2014; Bignell and Eggleton, 2000b). In Ethiopia, TMs are found widely distributed

almost in all regions. In the northern part of Amhara region (Tekalign and Haque, 2007), Southern Tigray (Hadgu et al., 2014), SNNP (Getahun and Degaga, 2014) and Oromia (Wellega, Borana, Jimma, great rift valley area of Ethiopia, Northern shewa (Sellale) is where it is found widely distributed (Itanna et al., 2011; Abdus and Itiola, 2012; Fufa et al., 2013; Debelo and Degaga, 2014). Average mound soil weight per a single mound is estimated ~ 5 tons per hectare (Getahun and Degaga, 2014) and ~12 mounds per hectare are found according to (Fufa et al., 2013, Tilahun et al., 2012). In Ethiopia, it's also reported as termites are the main causes for deterioration of crop products in the farming lands are estimated in millions (Hadgu, 2014).

Termites are social insects that exert significant influence on the physical, chemical and biological properties of tropical and sub-tropical soils (Semhi et al., 2008). The feeding habit, the food processing and mound construction operations introduce significant modifications to the soils organic and mineralogical content on which the mound is built (Konate et al., 1999). Termites perform several activities that qualify them as soil engineers. They collect organic material as food source and for nest construction, transport it to their nest, and alter it during digestion. For the transportation, they build galleries into the soil and also on the soils surface. The physico-chemical characteristics of soils largely influence the parameters of adsorption process and this eventually governs the availability of nutrient ions to the growing plants. Among the soil properties affecting the P adsorption capacity are soil texture, organic matter content, soil pH and sesquioxides of the soil. The surface charge of clay minerals and oxides is partly pH.

2.6 Influence of termite activities on physico-chemical soil properties

In their life, mound-building termites implement different forms and grades of activity that can influence soil nutrient cycles or soil physico-chemical properties. The significance of termite activities to the modification of soil properties is said to be dependent on temporal and spatial dynamics of their activities in the soil (Lisa et al., 1995). Their building and feeding activities influence soil properties by modification and redistribution of the soil materials (Lavelle et al., 1992), due to selection of fine particles for construction (Jouquet et al., 2002b; 2007). As a result of ensuring the stability of their mounds, termites modify the soil by increasing the clay and SOM content (Holt and Lepage, 2000; Mora et al., 2003) hence, modifying other chemical properties of the soil. Other studies have reported accumulation of nutrients such as C, N, P and

exchangeable basic cations in termite mounds compared to unaffected soils (Abbadie and Lepage, 1989; Black and Okwakol, 1997; Lopez-Hernandez, 2001).

2.6.1 Influence on soil texture

Soil texture refers to the particle size distribution in a soil. The particle sizes are in three groups according to the USDA systems of textural classification; sand (2-0.05 mm), silt (0.05-0.002 mm) and clay (< 0.002 mm) but many researchers use ASTM particle size classifications of (> 4.75, 2 to 4.75, 0.425 to 2 and 0.075 to 0.425) (ASTM, 1986). The soil texture affects water percolation and retention in the soil, nutrient retention and leaching, aeration, erosion behavior and organic matter dynamics of the soil. It is so important to analyze the soil texture for assessing the quality of the soil and its sustainability for agricultural management activities (Kettler et al., 2001). Termite distribution and activity can be both affected by and affect soil texture. Termites affect surface processes by transporting soil from various depths in the profile to the surface, where they build epigeal mounds and other structures (Ross et al., 1992). It has been argued that termites select small particle materials from the soil profile and bring them to the target area of construction; hence the mounds are commonly of fine texture (Boyer, 1982).

2.6.2 Influence on soil acidity

An acidic pH ≤ 5.0 is a characteristic feature of Ferralsols. Due to this reason, problems such as aluminum toxicity, weak cation exchange capacity, and retention of phosphorus are commonly reported for these soils (WRB, 2006). Elevating the pH of the soil towards neutrality combats the Al toxicity problem, lowers anion exchange capacity and raises the cation exchange capacity (McBride, 1994 many studies have observed changes in pH of the termite mounds compared to the control soil. The increased pH that is commonly found in termite mound samples compared to the control soil may be due to translocation of less weathered soil from subsoil during the mound building (Lepage and Darlington, 2000). Due to being less weathered, this soil can be expected to have higher levels of basic cations as compared to the control soil which is deeply leached out and dominated by acidic cations e.g. Al^{3+} . These basic cations partly neutralize the soil acidity and thus elevate the pH. A more recent study by Mujinya et al., (2011) research work, confirmed the higher pH levels in the mound are due to the accumulation of pedogenic carbonates in the mounds.

2.6.3 Influence on organic carbon

Termites are among the factors that affect the dynamics of soil organic matter (SOM) in tropical ecosystem. Although their function is of great importance, it is still not well documented. A few studies show that there is a variation of SOM content between the mound soil and the control soil. In some cases, organic carbon levels in the epigeal termite structures are reported to be higher than those of the soil from which they were formed (Abbadie and Lepage, 1989; Jouquet et al., 2003; Ruckamp, et al., 2011). The high levels of SOM in the termite structures are thought to depend on inclusion of feces during building (Lavelle et al., 1992) and due to feeding on plants (Lee and Wood, 1971). On the other hand, lower SOM content in the termite mound compared to the control soil is reported by other studies (Fall et al., 2001; Jouquet et al., 2004). However, Jouquet et al., (2007) suggested that termites are able to change the level of SOM depending on the part or zone of the mound constructed (fungus comb chamber walls, inner section and the rest of the mound parts) and the species of termites. This was confirmed by Mujinya et al., (2013), who found the OC was higher in the mound foot, followed by the outer crust, and the remaining parts which had low levels, though still higher than the control soil.

2.6.4 Influence on the cation exchange capacity

The cation exchange capacity (CEC) is a measure of the ability of a soil to attract, retain and exchange cations, among which nutrients for plant growth or adsorbed on colloidal soils around. For this reason, the CEC is a good indicator of soil quality and productivity. It is the expression for the negative charge per unit mass of soil that arises at surfaces of colloidal particles, mainly clay and organic matter of the soil which can be occupied by cations. This expresses the potential capacity of soil to retain nutrients on the soil colloids. As a result CEC can be used to assess the potential fertility of a soil and its possible response to fertilizer (Landon, 1984). According to Troeh, (1995), states that the strength of CEC and types of soil found around as following:

Colloid CEC, cmol/kg

- Kaolinite 3 – 15
- Illite 20 – 40
- Montmorillonite 60 – 100
- soil organic matter, humus 100 – 300

Soil clay minerals and organic matter tend to be negatively charged, thus attracting positively charged ions (cat-ions) on their surfaces by electrostatic forces. As a result, the cations remain

within the soil root zone and are not easily lost through leaching. The adsorbed cations may easily exchange with other cations in the soil solution, hence the term “cation exchange.” The adsorbed cations replenish the ions in the soil solution when concentrations decrease due to the occurrence of high adsorption capacity around (Troeh et al., 1993)

When soil is highly weathered its pH becomes acidic. Then exchangeable aluminum dominates the soil and occupies the exchange complex of the soil instead of the exchangeable basic cations which are leached out. The CEC clay indicates the stage of soil weathering and is related to the clay mineralogy of the soil. If the CEC clay is low, the clay fraction could be dominated by low-activity clays (e.g. kaolinite). Where the CEC clay is high, high activity 2:1 clay minerals, e.g. smectites or vermiculite, are expected to dominate the soil. For humid tropical soils, the soil CEC is generally low due to being highly weathered and as a result the soil is dominated by Al and Fe oxy-hydroxides and 1:1 minerals which have variable surface charges depending on the pH. It has been argued that due to the higher clay and SOM contents in the mound soil than in the control soil, there is a higher CEC and an enrichment of basic cations (Ca^{2+} , Mg^{2+} , K^+ and Na^+) and mineral nutrients such as NH_4^+ and NO_3^- in the mound (Summer and Miller, 1996). Other studies observed mineralogical alteration of the clay by termites that lead to the formation of unstable illite which is finally transformed into vermiculite (Koch et al., 1992). On the other hand, Jouquet et al., (2007) suggested the formation of smectite layers from illite due to termite activities. The formation of smectites and vermiculites due to alteration of illite would also cause an increase in CEC in the mound soil compared to the control soil.

2.6.5 Influence on phosphorus availability

Effective management of P in soils requires an understanding of the factors affecting availability of soil native P and applied fertilizer P. Among the factors that affect soil P availability, pH is a major factor that determines the availability of soil P. The forms of available P for plant uptake are primary H_2PO_4^- and secondary HPO_4^{2-} orthophosphates. Primary orthophosphate which dominates in slightly acidic soil is reported to be more readily taken up by plants than the secondary form which dominates in slightly alkaline conditions. When the pH exceeds 7.5, P is increasingly fixed with Ca while at a pH below 5.5 it binds with soluble Al and Fe, and adsorbs to positively charged sesquioxides. Soil P sorption and adsorption dynamics are important for P

availability (Mamo and Wortmann, 2009). Ferralsols, being HWS with many sesquioxides and a low pH, are characterized by a strong retention or sorption of phosphorus.

Few studies have looked at the dynamics of biogenic elements P, C, and N in termite mounds compared to associated soils, and some studies suggest that mounds act as sinks for some elements (Wood and Sands, 1978). Though, findings on P content of termite mounds in relation to associated soils are contradictory (Lopez-Hernandez, 1989). A study on mound structures of termites in Australia found that there were only small differences in P concentration between termite mound and the soil from which it was built (Lee and Wood, 1971). Another study encountered a significantly greater amount of extractable P in the in the same Australian termite mounds compared to associated soils (Okello-Oloya et al., 1985). However, for the effects of termite activities on soil P status, it is suggested to be related to the materials use for construction and the feeding habits. In regard to the feeding habits, it was found that there is a high level of both total and available P in termite mounds of the plant-feeding termites compared to surrounding soil (Lopez-Hernandez, 1989).

2.8 Variability of termite activities in different zones of the mound

Comparatively a few authors have wrote the different activities of termite activities in different parts of mounds that influence variability in soil properties among the different parts of mounds compared with non termite soils. Ruckamp et al., (2012) suggested the termite effects are higher below the mounds due to long time period the soil was exposed to the termite activities. They also suggested that the variation was due to redistribution of soil particles in the mound during different termite activities. Jouquet et al., (2002) found that there was more carbon and nitrogen in the fungus-comb chamber walls than in the galleries. Mujinya et al., (2010) also reported a higher CEC and pH in the chamber wall, followed by the central hive and mound foot. Contrasting to the previous findings, a few studies have reported no differences in C content among different zones of the mounds, despite the fact that all contained higher amounts than the control soil (Mora et al., 2003; Jouquet et al., 2003; Ndiaye et al., 2004).

2.10. Factors affecting phosphorus adsorption by soils

Depending on its characteristics soil can influence P adsorption depending on the amount and type of clay content, soil pH, soil OM content, reaction time, exchangeable Al^{3+} , soil redox

condition (Sanchez and Uehara, 1980), and root exudates. These and other factors play a great role on P adsorption/desorption process. Same factors are review in detail under the following sub titles.

2.10.1 Soil Mineral Type

Numerous studies show that clay minerals play an important role in P sorption by soils. In summary, those clay minerals that possess greater anion exchange capacity due to a positive surface charge have a greater affinity for P ions (Harrell and Wang, 2006). The surface charge of clay minerals and oxides are partly pH dependent so there is an inverse relationship between pH and anion exchange capacity. Soils with significant contents of iron and aluminum oxides have large P fixation/adsorption capacities because of their high surface areas. Tisdale *et al.*, (1985) supported that crystalline hydrous metal oxides are usually capable of retaining more phosphorus than layer silicates.

The higher Al and Fe oxide contents of soil clay and less crystalline more amorphous the soil minerals, the greater an acid soil's P fixation capacity. This is largely attributed to the greater surface area which these conditions represent (Gilkes and Hughes, 1994; Quintero *et al.*, 1999). Among the layer silicate clays, 1:1 type clays have a greater phosphate retention capacity than 2:1 type clays. Soils containing large amounts of kaolinite group clay minerals will retain larger quantities of added P than those containing the 2:1 type clay minerals.

2.10.2 Amount of clay

In recent reports clays are not the only indicators of CEC but also play a great role for P availability in soil through its high adsorptions capacity (Hardy, 1995). The clay content of a soil has impact on P adsorption. When it is compared to the control soil, Soils containing higher percentage of clay adsorbs more P than those with less clay content. In other words, since clay soils are very silty in size it has more surface area that exposed with a given adsorbent, so, it has the greater tendency to retain P. Many studies have shown that there are close relationships between clay content and P sorption (Soils and Torrent, 1989; Pena and Torrent, 1990) Pena and Torrent, 1990). In short, the soil components affecting P adsorption include iron and aluminum oxides, clay and clay sized amorphous materials. The specific surface

area of the calcium carbonate is also responsible for P adsorption in calcareous soils. Higher clay contents also result in greater P fixation (Harris, 2002; Voundi et al., 1997; Grassi et al., 2012).

2.10.3 Adsorption thermodynamics

Thermodynamic parameters such as Gibbs free energy change (ΔG), enthalpy changes (ΔH) and entropy change (ΔS) are among the most important features involved in an adsorption system.

The positive values of ΔS (J/mol K) revealed the affinity of adsorbent for the adsorbate being tested and increased randomness at the solid–solution interface during adsorption of adsorbate onto the active sites of adsorbent. If the negative ΔG obtained for the adsorption of adsorbate onto adsorbent indicates spontaneous nature and feasibility of the adsorption process with high preference of adsorbate onto adsorbent (Bello and Ahmad 2011).

The entropy term is therefore subtracted from the enthalpy term when calculating ΔG° for a reaction. Because of the way the free energy of the system is defined, ΔG° is negative for any reaction for which ΔH° is negative and ΔS° is positive. ΔG° is therefore negative for any reaction that is favored by both the enthalpy and entropy terms. We can therefore conclude that any reaction for which ΔG° is negative should be favorable, or spontaneous. Favorable or spontaneous reactions $\Delta G^\circ < 0$ and Unfavorable or non-spontaneous reactions $\Delta G^\circ > 0$

2.10.4 Adsorption mechanisms

Adsorption rate is known to be controlled by several factors including

1. Diffusion of the solute from the solution to the film surrounding the particle,
2. Diffusion from the film to the particle surface (external diffusion)
3. Diffusion from the surface to the internal sites (surface diffusion or pore diffusion) and
4. Uptake which can involve several mechanisms such as physicochemical adsorption, ion exchange, precipitation or complexation (Gercel et al. 2007; Wu et al. 2001). Adsorption kinetics are usually controlled by different mechanisms, of which the most limiting ones are the diffusion mechanisms, including the initial curved portion, which is attributed to rapid external diffusion or boundary layer diffusion and surface adsorption, and the linear portion, i.e., a gradual adsorption stage due to intra-particle diffusion, followed by a plateau to equilibrium where the intra-particle diffusion starts to decrease due to the low concentration in solution as well as fewer available adsorption sites (Venkata et al. 2002). In the present study, non-linear plots were obtained, the first one is bulk diffusion, the second is external mass transfer resistance and the

third is intra-particle mass transfer resistance. Mass transfer is governed by several relationships, taking into account the diffusion mechanisms and their related equations, the coupling between liquid and solid phases and the initial and boundary conditions. Therefore, it means that the rate of attainment to equilibrium may be particle-diffusion controlled (Yang and Al-Duri 2005). And also Weber and Morris, (1963), discuss that if intraparticle diffusion is a rate controlling step, then the plots should be linear and pass through the origin then the intraparticle diffusion is not complex and it is a rate controlling step.

2.10.5 Effect of soil pH

Soils pH has profound effect on the amount and manner in which soluble phosphate become adsorbed. Soil P sorption capacity is correlated with metal oxides, carbonates, soil solution pH, and ionic strength and composition (Tsadilas et al., 1996; Harrell and Wang, 2006). Adsorption of P by iron and aluminium oxides declines with increasing pH (White, 1980). Gibbsite [t-Al(OH)_3] adsorbs greatest amount of P between pH 4 and 5. P adsorption by goethite ($\alpha\text{-FeOOH}$) decreases steadily between pH 3 and 12 (Huang, 1975; Bowden et al., 2009). Phosphate availability in most of the soils is at a maximum in the pH range of 6.0 to 6.5 (Tisdale et al., 1985). At lower pH values the retention results from the reaction with iron and aluminum and their hydrous oxides. Above pH 7.0 the ions of calcium, and magnesium and their carbonates cause precipitation of added phosphorus, which decreases its availability. The presence of calcium and magnesium ions must accompany high pH values. If the increase of these soils ion continued, there will be a decrease in solubility of soil phosphorus. However, liming acid soils increases the solubility of phosphorus.

2.10.6 Exchangeable Al^{3+}

In highly weathered and acid soils, exchangeable Al^{3+} is the main factor determining the pattern of P sorption with changing pH (Chen and Barber, 1990). Haynes, (1984) said that one should expect liming to increase P sorption in soils that are initially high in exchangeable Al^{3+} but to decrease P sorption in soils with low exchangeable Al^{3+} content. When soils with low exchangeable Al^{3+} are limed, the neutralization and precipitation of Al^{3+} ion and of hydroxy-Al species to form Aluminum hydroxide reduces the number of P-sorption sites. Where exchangeable Al^{3+} is initially high, the formation of amorphous hydroxyl Al with highly active

sorbing surfaces may exceed any decrease in the sorption capacity of the original sorbing surfaces, resulting in increasing P sorption as pH increases.

2.10.7 Effect of organic matter

In highly weathered soils, the phyto-availability of P can be greatly reduced through sorption to sesquioxides (Pushparajah, 1998). Organic matter (OM) interacts with P in soils in a variety of ways that potentially influence these P sorption reactions (Saunders, 1965). A lot of researchers noted correlation between OC and the amount of P adsorbed by soils (Woodruff and Kamprath, 1965). According to Tisdale et al, (1985) the availability of phosphorus increased from decomposition of organic residues has been due to:

1. The formation of phosphohumic complexes which are more easily assimilated by plants
2. Anion replacement of the phosphate by the humate ions and
3. The coating of sesquioxide particles by humus to form a protective cover and thus reduce the P retention capacity of the soil. It was suggested that certain organic anions form stable complexes with iron and aluminium, thus preventing their reaction with phosphorus by blocking the adsorption sites (Guppy et al., 2005; Leaver and Russell, 1957). It was further stated that these complex ions release P previously retained by the same mechanism. Haller, (1969) suggested that it is OH groups in OM which affects P adsorption through anion exchange, while the results of Appelt et al, (1975) showed that it is the Al and to lesser extent the adsorbed by the organic colloids which are active in P adsorption. OM does lower the adsorption of P. it also provides a method of increasing the P availability without the use of fertilizers. The evolution of carbon dioxide after the decomposition of organic residues has a favorable effect on P availability. The gas is dissolved in water to form carbonic acid which is capable of decomposing certain primary soil minerals. On the basis of available evidence, it is clear that the addition of organic materials to mineral soils may increase the availability of soil P. Soils with a high content of OM (colloidal) had very low capacities to adsorb P (Fox and Kamprath, 1971).

2.10.8 Effect of Coexisting Ions,

Both organic and inorganic anions compete with phosphate for adsorption to varying extent. In some cases it may result in a decrease in the adsorption of added phosphate or desorption of retained phosphate (Grassi et al., 2012). Researchers have proposed an ion-exchange reaction as

a possible mechanism for phosphate adsorption on different types of soils and treated wastes as effective adsorbent (Zhang et al., 1987). But P adsorption efficiency was significantly affected by co-existing ions like Fluoride, carbonate, sulfate, nitrate and bicarbonate which is found in waste water within different concentration range. According to, Chubar et al., (2009) study of phosphate uptake by HUD and Al-HUD as a function of the initial concentrations of the coexisting ions the uptake of phosphate increased slightly, without any trend, in the presence of chloride, nitrate, or sulfate ions but significantly affected in the presence of carbonate and bicarbonate. Another study state that selectivity of the fluoride adsorption onto three samples was reported as 25–50 times greater than phosphate adsorption (Hamdi and Srasra, 2008). Also Panasiuk, (2010) in his study divided co-existing ions into two: those that form outer-sphere complexes (chloride, nitrate, and sulfate) and those that form inner-sphere complexes with binding surfaces, e.g., fluoride. According to the result of this study the quantities of phosphate adsorbed on HUD and Al-HUD decreased from 48.85 and 56.6 mg/g to 35.9 and 29.1 mg/g in the presence of co-existing ions, respectively. The decrease of P sorption in the presence of co-existing ion show that both ions (P and co-existing ions) compete for the same active site of adsorbent.

2.11 Regeneration

Adsorption is recently developed technology for water and waste water treatments to remove pollutants still the regeneration (desorption) of adsorbent needs further study. The word desorption is mainly used to explain the regenerability of adsorbent to use more than once by treating with strong base and acid like NaOH, NaCl and H_2NO_4 (Koutarou et al., 2015; Kose and Kivanc, 2011). And also, Onyango et al., (2007) state desorption as a valuable resource recovery and desorption of P ions from HUD and Al-HUD adsorbents was carried out at various pH values. According to his report the pH of the solution was adjusted using either nitric acid or sodium hydroxide which is similar with (Onyango et al., 2007). Even though desorption depends on the pH of solution; Solution with strong pH acid/base desorbs effectively while close to neutral negligible in their desorption capacity. Consequently, a pH increase due to the use of caustic agents such as NaOH shifts the adsorption equilibrium and can result in desorption of the adsorbed solute. If the adsorption capacity can be regained in this process, the adsorbent can be regenerated. In several studies, sodium NaOH solution has been shown as suitable regenerant for

metal oxide adsorbents as well as hybrid anion exchange resins. Donnert and Salecker, (2005) reported regeneration of activated alumina for phosphate adsorption by 0.5 M NaOH. Zhu and Jyo, (2012) used a zirconium loaded phosphoric acid chelating resin for phosphate removal. According to this study more than 90 % of the removed phosphate could be eluted within 20 bed volumes using 0.5 M NaOH. Phosphate adsorption behavior was not adversely affected by repeated adsorption/desorption cycles. Mohammed and Rashid, (2012). Chitrakar et al., (2015) used synthetic akaganeite for selective phosphate adsorption from seawater and regenerated with 0.1 M NaOH. Almost no loss in capacity after up to 12 adsorption/desorption cycles was reported. Also, Genz et al., (2011) studied phosphate adsorption from MBR effluents onto GFH and activated alumina followed by regeneration with 0.6 M NaOH and reported as no decrease in adsorption efficiency after third adsorption/desorption cycles.

CHAPTER THREE

OBJECTIVE

3.1. General Objective

The main objective of this study is to investigate the adsorption capacity and mechanisms that promote removal of phosphate by using TMs from wastewater under batch experimental setup

3.2 Specific objectives

- ✓ To characterizes physicochemical properties of TM by part from outside to the center
- ✓ To determine factors affecting sorption(time, pH, shaking speed, dose, initial concentration particle size coexisting ions and temperature)
- ✓ To check the reusability of adsorbent and physicochemical properties of wastewater
- ✓ To assess the adsorption equations that best fit to describe the relationship between solution phosphate and adsorbed phosphate

3.3 Research hypotheses

- i. Mound-building termites influence the adjustment on mineralogical and physico-chemical properties of the soil.
- ii. Termite activity affects the availability and content of phosphorus in mound soil.
- iii. Termite mound can remove phosphate
- iv. The impact of the termites on the soil properties differs among different parts of the mound (mound foot, outer mantle and the inner section).

CHAPTER FOUR

MATERIALS AND METHODS

4.1 General description of the study site and Period

The data analysis was conducted in Jimma zone, Oromia regional state, South West Ethiopia which is located 356 km from Addis Ababa with an estimated area of 19,506.24 km^2 and the elevation ranges between 1000-3500 m. The zone constitutes three major climates belonging to subtropical, temperate and tropical zones, respectively (Haddis et al., 2014; Tilahun et al., 2012). The study was conducted at environmental health science main campus and soil laboratory of Agricultural College of Jimma University from April 2014 to November 2015.

4.2. Study Design

Laboratory based experimental study design was used. Soil sample constructed by TM species was taken to laboratory and air dried at room temperature. Then all important preparation and physico-chemical analyses for soil sample was made and the powder of soil was ready for synthetic laboratory test. The next step was conducting synthetic experiment for all parameters. Finally real waste water was taken and the removal efficiency of adsorbent was checked.

4.3. Study variables

4.3.1. Independent variables

- pH
- Contact time
- Initial phosphate concentration
- Co-existing ions
- Adsorbent dose
- Temperature

4.3.2 Dependent variable

- Adsorption capacity

4.4 Adsorbent preparation

Samples of mound soil were collected from two TMs surrounding of Agaro town, Jimma Zone, Oromia Regional and National State, South West Ethiopia. The sampling area is covered with big trees and surrounded by farming land with 7 km radius. A sample was taken by dividing a single mound into three equal parts with difference of 92 cm and control soil (non termite) was taken within 50 m away from TMs. The first outer part was used for all synthetic laboratory tests and then for middle, center and control soil was conducted with initial P concentration to compare its P removal efficiency from outside to center with each other and termite soil with non termite. Particle size analysis of the soil sample was performed according to (ASTM D 422) and soil textural classification system used was (ASTM, 1996). Then soil sample was air dried for five days at room temperature and crushed by hand in a mortar, and sieved to different particle size > 4.75, 1-0.425, 0.425 – 0.075 and <0.075 mm particle size. Then the sieved sample was packed in an air-tight plastic bag for later investigation. The moisture content was determined by heating in an oven at 105 °C for 24 h. The pH of the adsorbent was measured using a Microprocessor pH meter (pH 196, WTW, Germany) at a 1:2.5 TM/water ratio according to the standard method (Appel and Ma 2002).

4.5. Real wastewater analysis

A wastewater sample with P concentration of 9.03 mg/L was collected from Jimma University waste discharge sewer line Jimma town which is located in the Oromia regional state, south west Ethiopian. Using the wastewater sample without adjusting its pH and keeping another all parameters at optimum and equilibrium, adsorption experiments were carried out with particle size of <0.075 mm. In addition to this all important physicochemical parameters were measured both at the field and in laboratory using standard water and wastewater sampling and analyses methods (Stephenson et al., 1985).

4.6. Preparation of P solutions and analytical methods

The salt used is: Anhydrous Potassium dihydrogen phosphate KH_2PO_4 (0.2195 g) was prepared in 1000 ml and this stock solutions further diluted with distilled water to desired working solution with concentrations of (0.5, 1, 3, 5, 10, 15 and 20 mg/L) were prepared. Phosphate was determined by using the ascorbic acid method according to standard methods for the examination

of water and wastewater analyses methods (Stephenson et al., 1985). Ammonium molybdate and antimony potassium tartrate reacts in acidic medium with Orthophosphate to form a heteropoly acid (phosphomolibdic acid) that is reduced to intensely colored molybdenum blue by ascorbic acid and measured by using double bin spectrophotometer (V-630, Japan) at $\lambda = 880$ nm.

All the chemicals and reagents used in this study were of analytical grade. All glassware and sample bottles were soaked in diluted 0.01 M H₂SO₄ solution for 24 hrs, washed and then rinsed three times with distilled water and dried in an oven at 105 °C for 2 hrs and after conducting one parameter the bottles were washed well and filled with distilled water over night for next parameter to minimize contamination according to (Maduakor et al., 1995). All experiments were conducted in duplicate and the average values were used for data analysis. Also blank and controls were used for correction of color developed and interference leached from instrument and adsorbent (Stephenson et al., 1985). The pH of solution was adjusted using 0.1 M NaOH and/or 0.1 M HCl. In order to widen the applicability of proposed method, it was tested for the removal of P from wastewater.

4.7 Batch adsorption experiments

Series of batch adsorption experiments were carried out using 1000 ml solution of PO₄²⁻ with initial concentration of 3 mg/L. The adsorbent with a concentration of 10 g/L TM was added in the bottle and agitated on an orbital shaker (Type SM 30 C, Germany) agitated at a rate of 200 rpm and the supernatant solution samples were waiting for ten minutes to allow sedimentation of adsorbent in solution followed with centrifugation at speed of 5000 rpm by using (Eppendorf AG 22331 Hamburg, Germany) for fifteen minutes. After that it is filtered by using Whatman filter paper (0.45µm) and then all important reagents prepared was added. Then it is read by using double bin spectrophotometer (V-630, Japan) with in thirty minutes after adding reagents.

4.7.1 Effect of contact time

Equilibrium agitation times were optioned by adjusting with different contact time of (5, 10, 15, 30, 45, 60, 75, 90 and 120 min) until equilibrium was achieved. A known concentration of the adsorbate, 3 mg/L in synthetic aqueous solutions at desired pH ~7 was shaken with a desired amount of the adsorbent, 10 g/L and shaking speed of, 200 rpm. Then supernatant solution was

taken to determine equilibrium time. The percentage of P adsorbed and the P adsorption capacity of TMs were calculated using (Eqs. 1 and 2), respectively (Sun et al. 2011).

$$q_t = \frac{(C_0 - C_t) * V}{M} \quad (1)$$

Where q_t is the P adsorption capacity TMs (mg/g), C_0 is initial P concentration (mg/L), C_t is P concentration at time t (mg/L), V is volume of the solution (L) and M is mass of the TMs used (g).

$$A(\%) = \frac{(C_0 - C_t) * 100}{C_0} \quad (2)$$

Where A (%) is the percentage of P adsorbed, C_0 is initial P concentration (mg/L), and C_t is P concentration at time t (mg/L).

4.7.2 Adsorption kinetics

The adsorption kinetics of the system was explained by pseudo-first-order and pseudo-second-order equation (Eqs. 3 and 4) when the removal of an adsorbate from aqueous solution increases during the initial agitation time, and followed by a slow increase until the equilibrium time was reached (Lagergren, 1898).

$$q_t = q_e [1 - \exp(-k_f t)] \quad (3)$$

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (4)$$

Where q_t (mg/g) is the amount of P adsorbed per unit mass of the adsorbent at any time t (minutes), q_e (mg/g) is the calculated equilibrium capacity, and k_2 (g/mg/min) is the equilibrium rate constant based on the pseudo-second-order equation. Integrating (Eq. 4) for the boundary conditions $q_t = 0$ to $q_t = q_t$ at $t = 0$ to $t = t$ is simplified and linearized to obtain (Eq. 5).

$$\frac{t}{q_e} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} (t) \quad (5)$$

The values of k_2 and q_e were calculated from the intercept and the slope of the plot of t/q_t versus t , respectively.

4.7.3. Effect of solution pH

Solution pH was investigated to determine the optimum pH for maximum adsorptive removal of P over the pH range of (3, 4, 5, 6, 7, 8, 9, 10 and 11) by allowing a known adsorbent of dose, 10 g/L, shaking speed of, 200 rpm, agitation time, 60 min, initial P concentration, 3 mg/L, particle size <0.075 mm and clear supernatant was taken to determine effective optimum pH.

4.7.4 Effect of adsorbent dose

To determine the optimum dose required for reduction of average P concentration released from different sources of pollution in wastewater to its acceptable level, different adsorbent doses were tested ranging (2, 5, 10, 15, 20, 30, and 50 g/L) was separately added into solution at pH ~7, containing a desired adsorbate concentration of 3 mg/L, shaking speed at 200 rpm, agitation time of 60 min and particle size <0.075 mm. at the end clear supernatant solution was taken to determine effective dose.

4.7.5 Effect of initial concentration and Adsorption Isotherms

The effect of initial concentration was tested varying initial concentration of P ions ranging at (0.5, 1, 3, 5, 10, 15 and 20 mg/L) while maintaining the solution pH ~7, adsorbent dose, 10 g/L, shaking speed, 200 rpm, equilibrium contact time, 60 min and particle size <0.075 mm then the effect of initial concentration was analyzed by well known isotherm parameters.

Adsorption Isotherms was used to evaluate the P sorption capacity of TM, the relationship between the amount of P adsorbed at equilibrium per unit mass of the adsorbent and the concentration of P in the aqueous phase at equilibrium was analyzed by applying adsorption isotherm models. The nonlinear forms of the two widely used isotherms namely, the Langmuir (Eq. 6) and the Freundlich (Eq. 8) were used to estimate the P adsorption capacity of the adsorbent.

$$q_e = \frac{Q_{\max} bC_e}{1 + bC_e} \quad (6)$$

C_e is the equilibrium concentration (mg/L) and q_e the amount adsorbed at equilibrium (mg/g). The Langmuir constants q_e (mg/g) represent the monolayer adsorption capacity and b (L/mg) relates the heat of adsorption (Chen et al., 2013; Gandhi et al., 2014). In order to evaluate the feasibility

of the process, the Langmuir isotherm can be described in terms of the dimensionless constant; separation factor or equilibrium parameter;

$$R_L = \frac{1}{1 + bC_0} \quad (7)$$

b (L/mg) is the Langmuir isotherm constant and C_0 (mg /L) is the initial concentration of P. There are four probabilities for the R_L value:

For favorable adsorption $0 < R_L < 1$, unfavorable adsorption $R_L > 1$, linear adsorption $R_L = 1$ and irreversible adsorption for $R_L = 0$ (Foo & Hameed, 2010).

$$q_e = K_F C_e^{1/n} \quad (8)$$

K_f indicates adsorption capacity (mg/g) and $1/n$ an empirical parameter related to the intensity of adsorption, which varies with the heterogeneity of the adsorbent. For values in the range $0.1 < 1/n < 1$, adsorption is favorable. The greater the values of K_f better is the favorability of adsorption (Attar, 2010).

Thermodynamic parameters such as Gibbs free energy change (ΔG), enthalpy changes (ΔH) and entropy change (ΔS) are among the most important features involved in an adsorption system.

The positive values of ΔS (J/mol K) revealed the affinity of adsorbent for the adsorbate being tested and increased randomness at the solid–solution interface during adsorption of adsorbate onto the active sites of adsorbent. If the negative ΔG obtained for the adsorption of adsorbate onto adsorbent indicates spontaneous nature and feasibility of the adsorption process with high preference of adsorbate onto adsorbent (Eq. 9) below used to calculate Gibbs free energy (Bello and Ahmad 2011).

$$\Delta G_o = -RT \ln K_d \quad (9)$$

Where K_d is the equilibrium partition constant calculated as the ratio between sorption capacity (q_e) and equilibrium concentration (C_e), R is the gas constant (8.314 J/mol/K) and T is the temperature in Kelvin (K).

4.7.6 Effect of shaking speed

Effect of agitation speed on P adsorption was analyzed at different shaking speed (100, 150, 200 and 250 rpm) while another parameters kept to their optimum and equilibrium agitation time, 60

min, solution pH ~7, Initial P concentration, 3 mg/L, adsorbent dose, 10 g/L and particle size <0.075 mm then optimum agitation speed were determined.

4.7.7 Effect of co-existing ions

In addition to all described parameters above also effect of co-existing ions of Potassium salts of bicarbonate, carbonate, chloride, nitrate, and sulfate anions were used in the investigation of the effects of competing ions by varying their concentrations in to (10, 100 and 300 mg/L) at constant initial P concentration of 3 mg/L, dose of 10 g/L, pH ~7, shaking speed, 200 rpm and agitation time, 60 min and particle size <0.075 mm. Then supernatant was taken to determine the effect of interference.

4.7.8 Effect of termite activity

Effect of Termite activity on phosphate removal was analyzed by dividing a single TM into three equal parts. The outer part was taken within the depth of 0 – 10 cm; the middle part was taken from middle by measuring 92 cm from outside to the center and the center/hill was taken from the center of the mound with similar variation. Finally the control soil was taken with the distance of 50 m away from TM and sorption capacity of each part was compared with each another and with control soil.

4.7.9 Effect of temperature

Effect of temperature on phosphate sorption was analyzed by varying its temperature to (25, 35 and 45 °C) at constant initial P concentration of 3 mg/L, dose of 10 g/L, pH ~7, shaking speed, 200 rpm and agitation time, 60 min and particle size <0.075 mm. Then supernatant was taken to determine the effect of interference (Wuber, 2009).

4.8. Regeneration of adsorbent

To investigate the reusability of adsorbent, desorption was investigated using 10 g/L TMs of particle size <0.075 mm used for the adsorption of 3 mg/L P solution. The adsorbent was separated from the solution by filtration using Whatman (0.45 µm) filter paper and washed gently with distilled water to remove unadsorbed P on adsorbent surface. The P loaded TMs was dried in an oven at 105 °C for 24 hrs and then soaked and shaken in 0.1 and 0.2 M

NaOH solution. Then, the amount of desorbed P was measured and desorption ratio of P was calculated using (Eq. 9).

$$\text{Desorption ratio(\%)} = \frac{\text{Amount desorbed}}{\text{Amount adsorbed}} \times (100) \quad (10)$$

4.9 Data Quality

Duplicate experiments were carried out during each set of experiments and average of the duplicate measurements was reported. At every set of experiments calibration was conducted for analysis.

4. 10. Dissemination of plan

The final result of this study will be submitted to Jimma University institute of technology, department of hydraulics and Environmental Engineering and result will be disseminated to all concerning bodies and will be published in national and international peer reviewed journal.

CHAPTER FIVE RESULT

5.1. Adsorbent

5.1.1. Characterization

Chemical and physical properties of the adsorbent was analyzed and presented in (Tables 2and3). Other important physicochemical contents of TMs with its depth and width those important for discussion of this result presented in (Table 1).

Physical properties of TM were conducted. According to the result the outer part contain high clay contents while the middle part contains lower clay present compared with other.

Table 1: Physical properties of TMs (clay, silt and sandy)

Fractions	Control soil	Outer of TM	Middle of TM	Center of TM
Clay %	32	58	48.5	54.5
Silt %	22	29.5	32	24
Sandy %	48	16	19.5	18
Texture	Silt loam	Silty clay	Silty clay	Silty clay

Chemical properties of TM were analyzed in the laboratory and according to the finding the outer part has higher pH while control soil has lower than others; the center part contains higher OC than other parts. Similarly have higher EC, Available P, OM, and CEC than others.

Table 2: Chemical properties of TMs with its depth from external to the center

Fractions	pH	EC (dS/m)	Available P (%)	Organic Carbon (%)	Organic Matter (%)	CEC (cmol(+)/kg)
Control soil	6.71	0.02	0.16	0.92	1.59	17.8
Outer of TM	7.40	0.65	0.27	1.10	1.90	29.45
Middle of TM	7.20	0.64	0.24	2.25	3.88	31.56
Center of TM	7.53	0.96	0.33	3.16	5.45	35.32
Mean	7.23	0.57	0.25	1.86	3.21	28.53

A physicochemical property of real WW was analyzed and according to the laboratory result contains high phosphate concentration, low pH, higher TDS and moderate temperature.

Table 3: Physicochemical properties of WW sample

Parameter	Value	Parameter	Value (mg/l)
T° (°C)	24.6	PO ₄ ³⁻ _P	9.02
EC (μS/m)	11.9	PO ₄ ³⁻	27.06
pH	4.34	NO ₃ ²⁻	1.51
DO	2.43	NO ₃ ²⁻ _N	0.34
BOD	1254.4	HCO ₃ ³⁻	91.5
COD	1568	CO ₃ ²⁻	Nil
Cl ⁻	54.95	SO ₄ ²⁻	Nil
TDS	1148.4	F ⁻	Nil

Note: DO, BOD, COD, CL and TBS are in mg/L

5.2.4 Effect of TM dosage on adsorption

Effect of adsorbent dose on P ions adsorption was investigated under different adsorbent dose and the result is presented graphically on Fig. 1. The result shows that increases of adsorbent dose also increase adsorption removal efficiency. Minimum and maximum removal efficiency obtained was 73.36 and 94.74% for 2 and 50 g/L respectively. It is obvious that as dose increase the active site also increase which are ready to adsorb P ions in the solutions

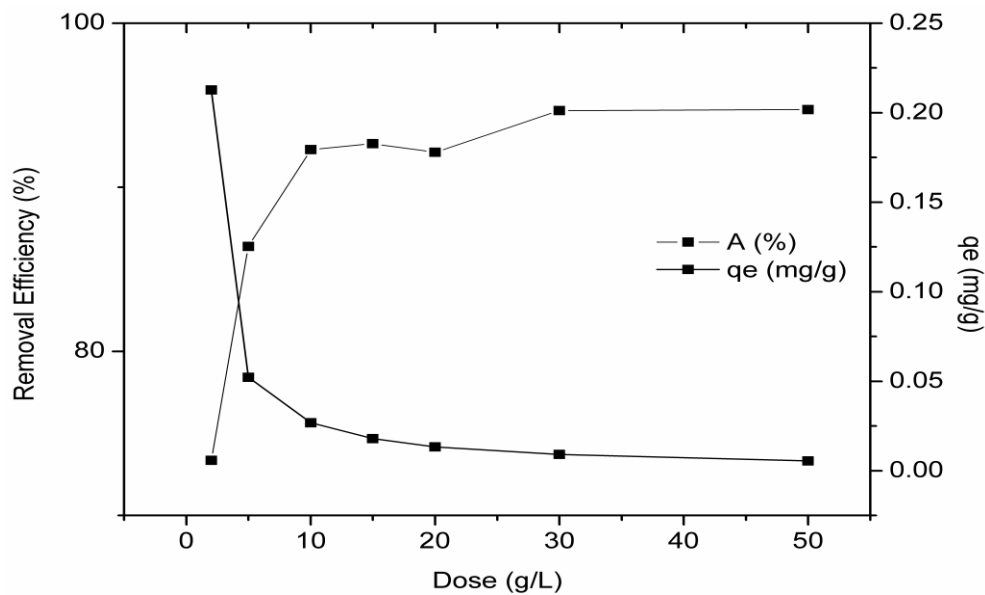


Figure 1: Effect of adsorbent dose

5.2.3 Effect of shaking speed

Effect of shaking speed was tested using an orbital shaker and result is presented graphically on Fig. 2. Result indicates removal efficiency increases with increase of shaking speed. The value obtained was 73.36 and 94.42% for 100 and 200 rpm respectively. But further increases of shaking speed were result in the fall of removal efficiency; for example at 250 rpm it was 91.39% which decreases ~3% compared to 200 rpm and this indicates that over shaking will cause desorption.

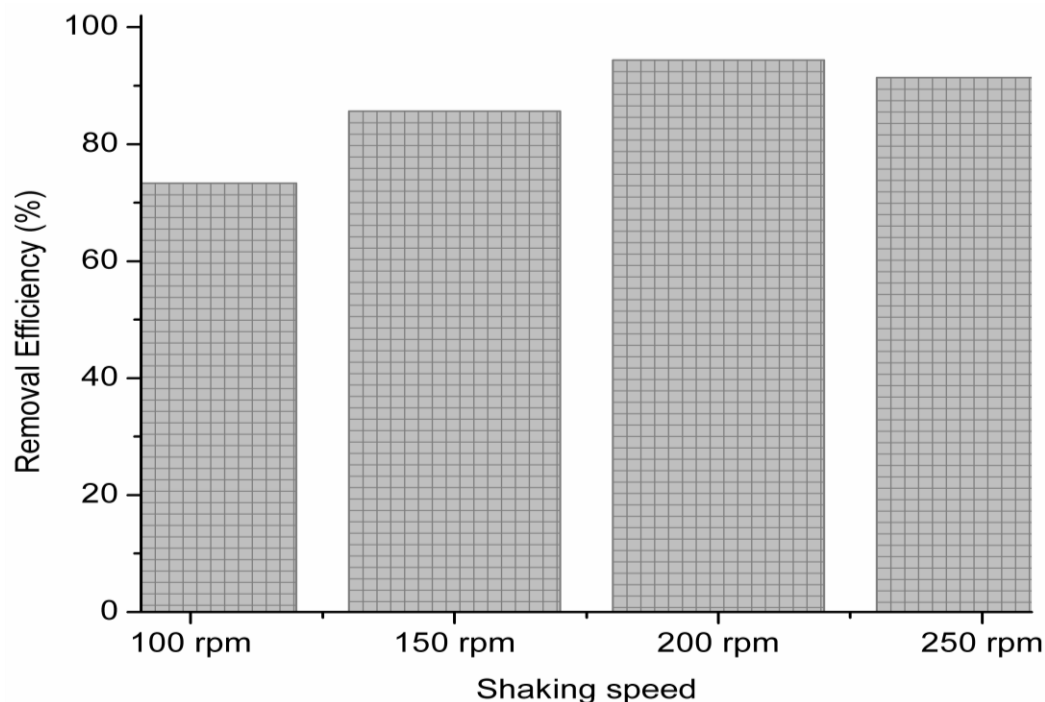


Figure 2: Effect of shaking speed

5.2.1. Effect of contact time and Adsorption Kinetics

The effect of agitation time on the adsorption of P ions by TMs was studied and the result is graphically presented on fig. 1. From the graph initially adsorption was increased sharply up to 30 min and get almost constant after 60 min. The result obtained was 72.25 and 95.76% for 5 and 60 min respectively.

Information on the kinetics of solute uptake is required to select optimal operating conditions for full-scale batch processing. The graph plotted on Fig. 3 shows agitation time of 60 min was sufficient to achieve equilibrium and adsorption did not change significantly with further increases in the contact time. Therefore, the uptake and un-adsorbed P concentrations at the end of 60 min are given as the equilibrium values.

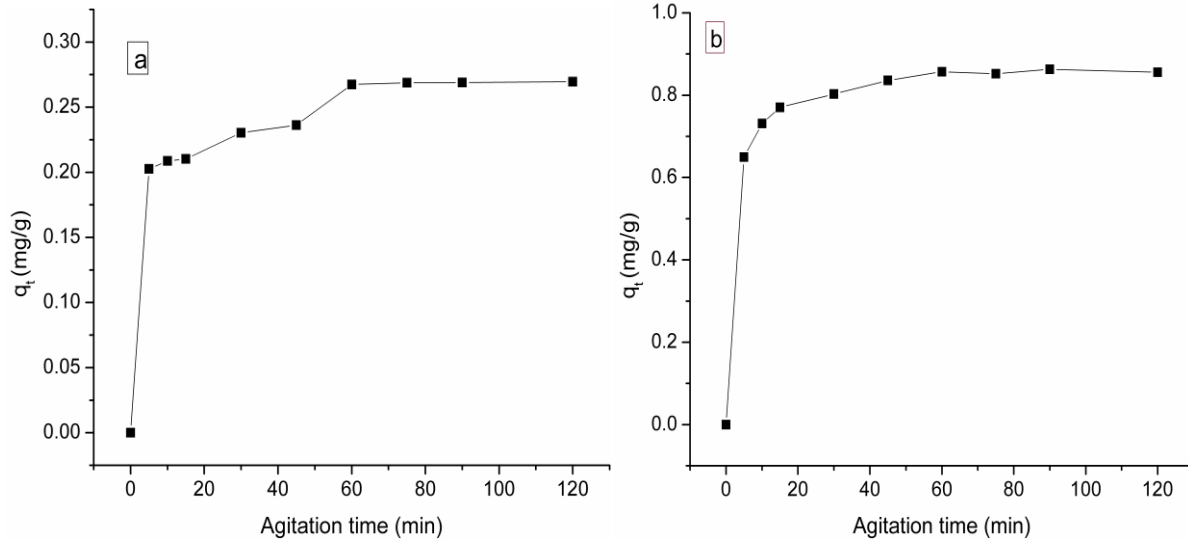


Figure3: Effect of contact time on adsorption: (a) 3 mg/L and (b) 10 mg/L

The kinetic values of adsorption were analyzed using pseudo-first-order and pseudo-second-order models. These models correlate solute uptake to predict the required reactor volume. The pseudo-first-order rate constant, k_1 can be obtained from the slope of the graph of $\log(q_e - q_t)$ versus time on fig. 4a. The calculated k_1 values and corresponding linear regression correlation coefficient values are shown in table 5. The linear regression correlation coefficient value $R_1^2 = 0.961$, which indicates that this model cannot be applied to predict the adsorption kinetics.

Fig. 4b shows the linear relationship of the graph plot of t/q_t versus time, from which q_e and k can be determined from the slope and intercept, respectively. The linear regression correlation coefficient $R_2^2 = 0.997$ was higher than R_1^2 in table 5. These results confirm that the adsorption data were well represented by the pseudo-second-order kinetic model, this means that the adsorption rate is proportional to the concentration of P. As shown in fig.3, in the beginning, there is high concentration of P ions so the adsorption rate is fast until reach 45 min then the rate become slowly until it reach 120 min. Adsorption did not change significantly with further increase in the contact time after 60 min which is considered as equilibrium time.

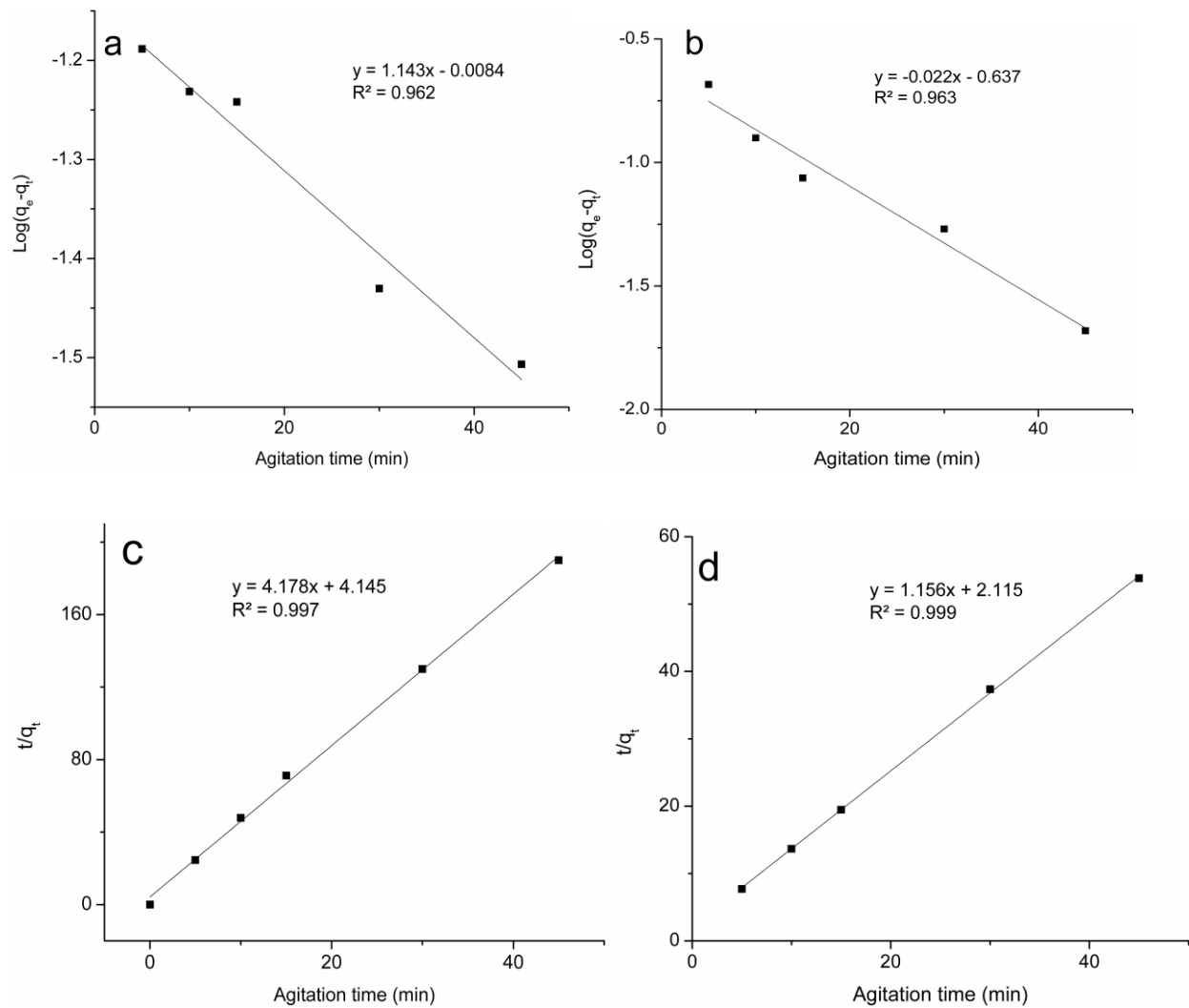


Figure 4: Pseudo-first-order plots of: (a) 3 mg/L and (b) 10 mg/L and pseudo-second-order (c) 3 mg/L and (d) 10 mg/L

Table 4: Isotherm parameters of the equilibrium adsorption

Model Parameter	PO ₄ ³⁻ concentration			
	3 (mg/L)	Value	10 (mg/L)	Value
Pseudo- first Order	q _{e,exp} (mg/g)	0.279	0.857	
	q _{e,cal} (mg/g)	0.072	0.231	
	k ₂ [g/(mg.min)]	0.019		0.051
	R ²	0.963		0.962
Pseudo-second Order	q _{e,exp} (mg/g)	0.268		0.857
	q _{e,cal} (mg/g)	0.280		0.881
	k ₂ [g/(mg.min)]	0.827		0.319
Intraparticle	R ²	0.998		0.999

diffusion	k_p [mg/(g.min ^{0.5})]	0.009	0.092
	C (mg/g)	0.181	0.276
	R ²	0.921	0.684

5.2.2 Effect of pH

The effect of pH on P ions removal from wastewater solution analyzed with synthetic solution was investigated and presented on Fig. 5 and the lowest adsorption was observed at pH ~ 11 and the highest is at pH ~ 7. Also the pH observed was low at lower pH value. The minimum and maximum adsorption efficiency was ~ 43 and 96% respectively. From the result it is observed that adsorbent can effectively remove >80% of P ions within the range of wide pH 3 to 9. This shows that pH is important parameters which can influence the adsorption process.

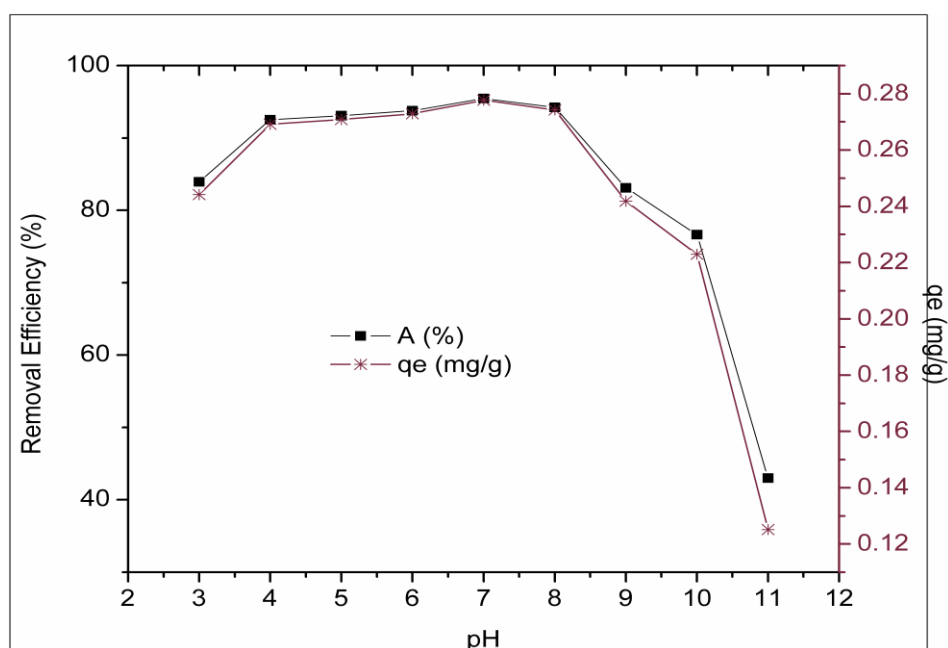


Figure5: Effect of pH on adsorption

5.2.5 Effect of particle size of the adsorbent

Effect of particle size of the adsorbent on P adsorption was investigated under different particle size and result is presented graphically on Fig. 6. From the result adsorption capacity increases as particle size get smaller and smaller. For comparison at particle size >4.75 mm removal

efficiency is 84.81% but when particle size is < 0.075 mm removal efficiency was increases to 96.68%. Generally, it is obvious that as particle size decrease surface area of adsorbent increases.

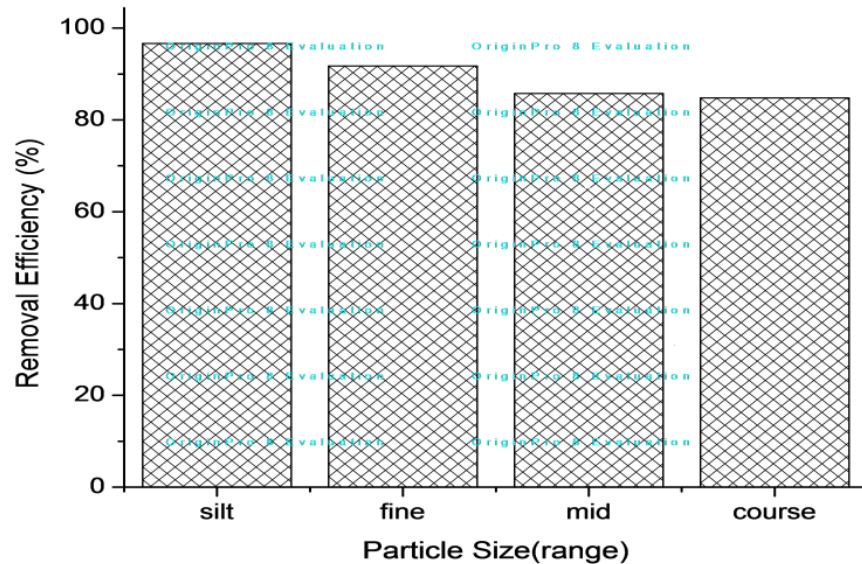


Figure 6: Effect of particle size on adsorption

5.2.6 Effect of initial concentration

Effect of initial P concentration and adsorption isotherm to assess adsorption capacity of the TMs and adsorption isotherm, the experiments were conducted by varying initial P concentration from 0.5 to 20 mg/L while maintaining all the other optimized parameters constant. As a result was presented graphically on Fig.7a P removal was high at lower initial concentration and starts to decrease as initial concentrations start to increase. Result of removal efficiency for 0.5 mg/L was 98.56% but it was decrease to the contrast when P concentration increase and result was 62.12% for 20 mg/L. This can be concluded that the active site of adsorbent was limited with constant adsorbent dose but continues increases of P ions remain excess in solution.

Adsorption isotherms state about the equilibrium relationship between amounts of adsorbate adsorbed q_e (mg/g), and the amount of adsorbate in solution C_e (mg/L) at room temperature. Both models Freundlich and Langmuir were fitted to the experimental values. Table 4 shows the values of Langmuir and Freundlich models fitted to the homogenous and heterogeneous surface respectively fig.7b. And table6 shows Freundlich and Langmuir isotherm parameters correlation results. The maximum removal capacity (1.486 mg/L) with $R^2 > 998$ was occurred on the result of outer parts of TMs, while the smallest 1.28 mg/L with $R^2 = 0.732$ obtained for control soil taken 50 m away from TMs.

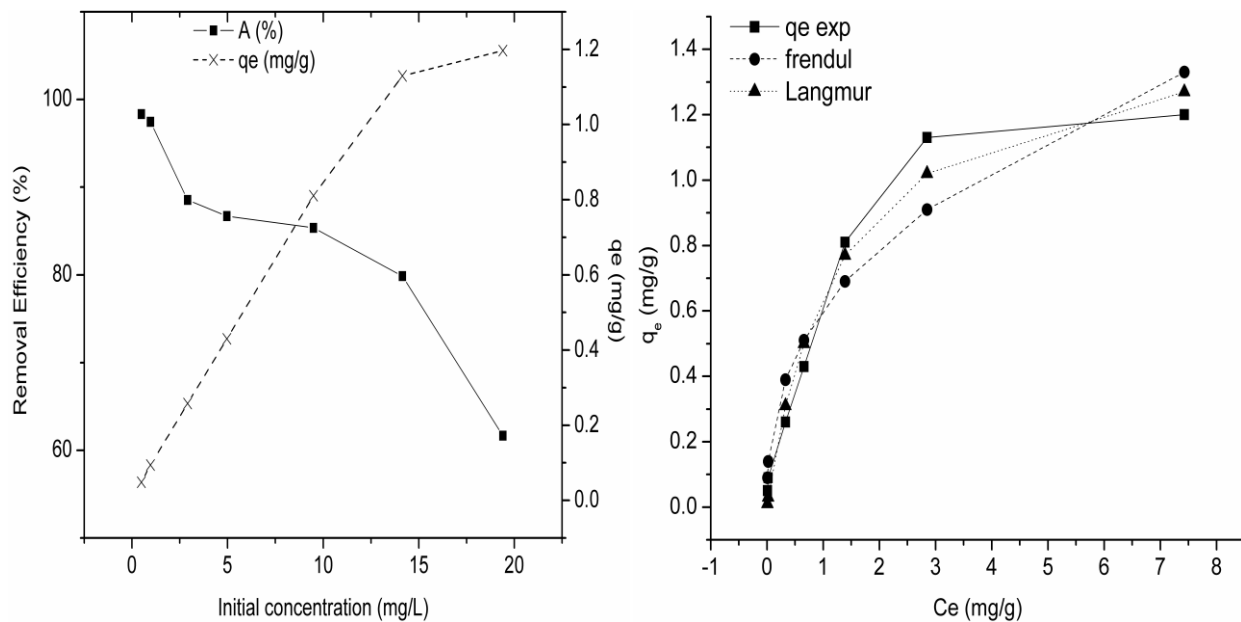


Figure 7: (a) Effect of initial concentration (b) Isotherms of equilibrium adsorption

5.2.6 Intraparticle diffusion of P

Effects of intraparticle diffusion were calculated from result of agitation time and result is presented in table 4 and fig. 8. The intraparticle diffusion rate constant (k_p) value estimated from the slope of plot of q_t versus square root of time was found to be $0.009 \text{ min}^{1/2}$ for the initial P concentration of 3 mg/L with $R^2 = 0.912$. From the results plot it is linear and pass through the origin and this indicate that reaction is not complex but it is a rate controlling step.

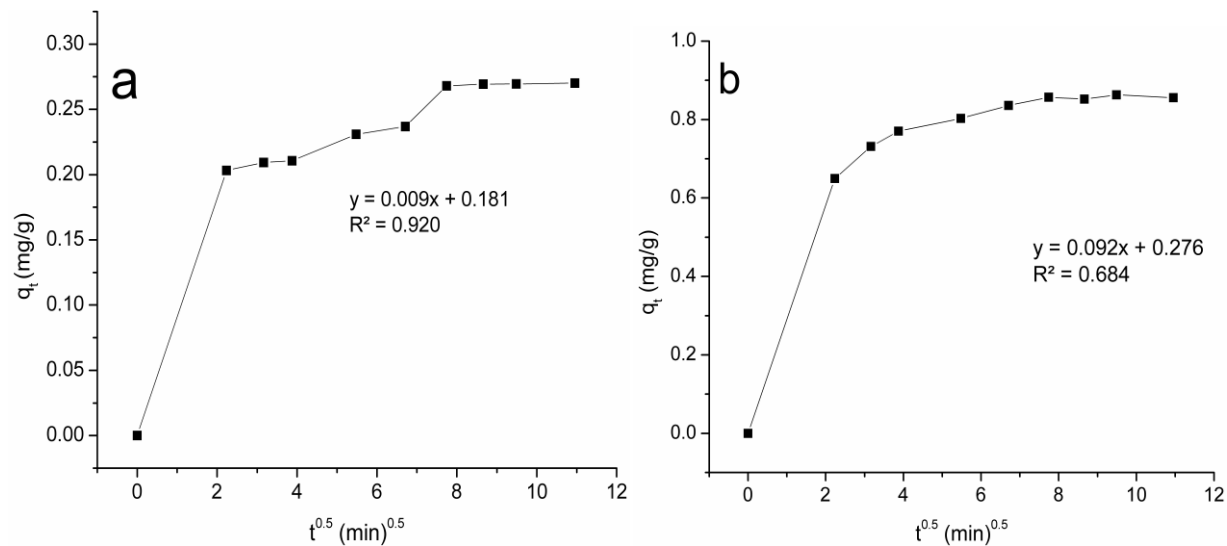


Figure8:Intraparticle diffusion plots: (a) 3 mg/L and (b) 10 mg/L

5.2.7 Adsorption thermodynamics

Thermodynamic parameters of Gibbs free energy change (ΔG), was tested to know the value and condition of adsorptions using eq. 8. The result obtained was negative ($\Delta G = -1.23$ kJ/mol) and it shows as adsorption of P ions onto TM indicates spontaneous nature and feasibility of the adsorption process with high preference onto TM.

5.2.8 Effect of termite activity

Effect of termite activities on sorption of phosphate was investigated for each partition of mounds. According to the laboratory result the outer parts of the mound has higher removal capacity than middle and center of mounds.

Table 6: Langmuir and Freundlich isotherm parameters

Soil by part	Freundlich			Langmuir		
	1/n	K_F [(mg ^{1-1/n} L ^{1/n})/g]	R ²	Q _{max} (mg/g)	R ²	b (L/mg)
Control	0.765	0.155	0.981	1.277	0.732	0.552
External	0.393	0.604	0.924	1.486	0.978	0.784
Middle	0.422	0.465	0.989	1.299	0.996	0.589
Central	0.825	0.465	0.757	1.354	0.998	0.033

5.2.8 Effect of temperature

The effect of temperature on P adsorption was investigated under different temperature range and result is graphically presented on fig. 9. From the result increase of temperature also result in increase of adsorption capacity of adsorbent with removal capacity of 1.2, 1.34 and 1.5 mg/g for 25, 35, and 45°C respectively.

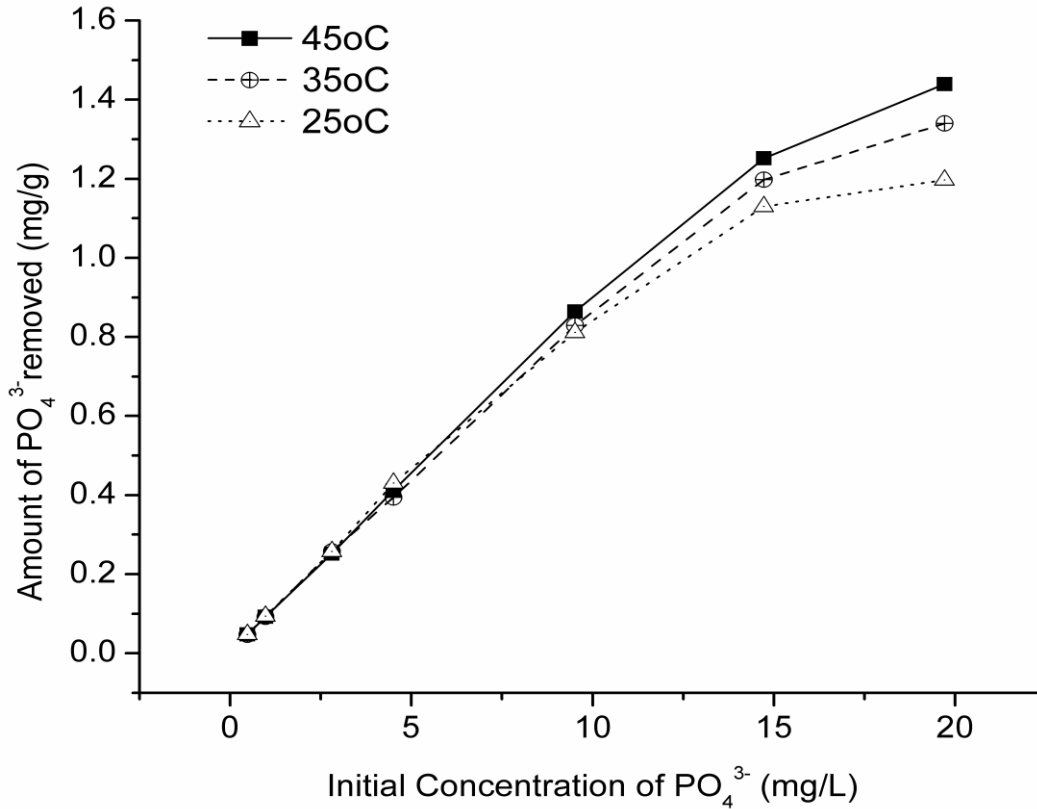


Fig. 9 Effect of temperature on adsorption

5.3 Effect of coexisting ions

The interference of competing anions was investigated by varying the concentration of anions at 10, 100 and 300 mg/L under 3 mg/L P concentration at pH ~ 7. The results of the effects of coexisting anions on the adsorption of P on TM are graphically presented in fig. 10. It was observed that from the graph the presence of carbonate and bicarbonate was significantly interfere while the presence of sulfate, nitrate and chloride was almost negligible on P removal efficiency. At 10 mg/L the interference of all considered anions was very low but as the concentrations of these competing anions was significantly affected.

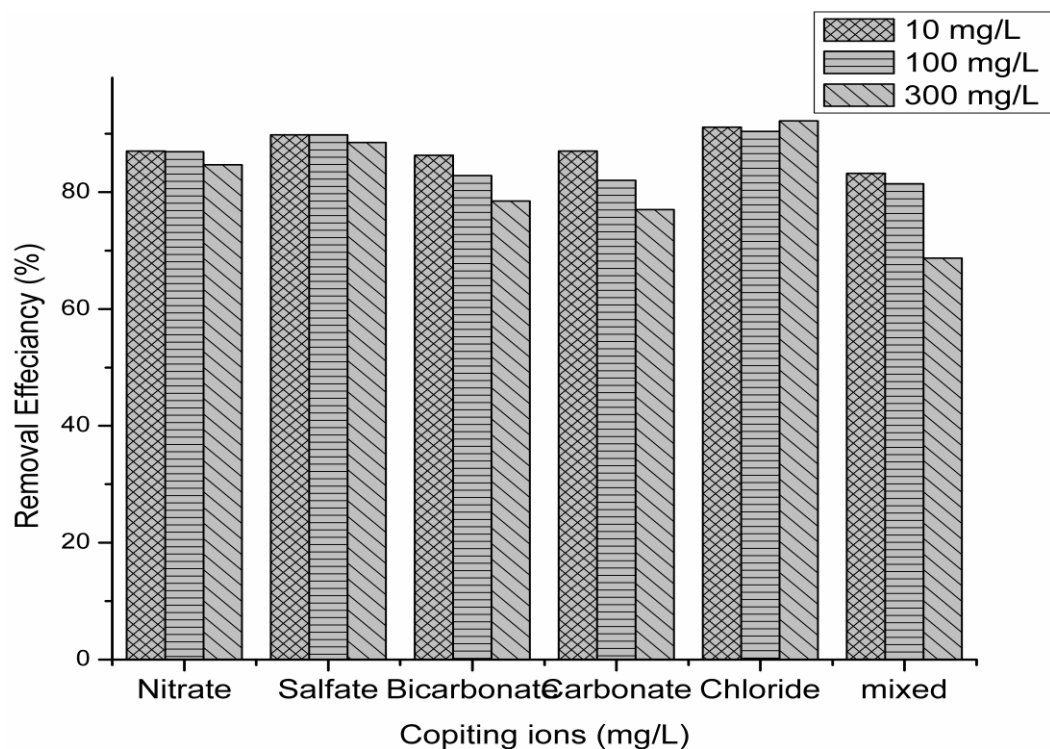


Figure 10: Effect of competing ions on adsorption of phosphate

5.4 Regeneration of adsorbent

The reusability of adsorbent was investigated in two ways. The first method was to know the effect of contact time on regeneration of adsorbent by conducting regeneration process for each agitation time. The result was graphically presented on fig. 11a, it was clear that at short contact time desorption was very low but as a agitation time increases the amount desorbed also increases; For example at time, 5 min amount desorbed was 51 and 62% for 0.1 and 0.2 M NaOH respectively. But at 120 min agitation time amount desorbed was 90 and 99% for 0.1 and 0.2 M NaOH respectively.

The 2nd method of desorption conducted was to check the regenerability of adsorbent for how many times it can be reused by treating with strong acid and base. As it is presented on fig. 11b regenerability was tested for three consecutive cycles. From result obtained it was very effective until third cycle with adsorption/desorption efficiency of greater than 70% even though it needs extra work to know exact life cycle of adsorbent.

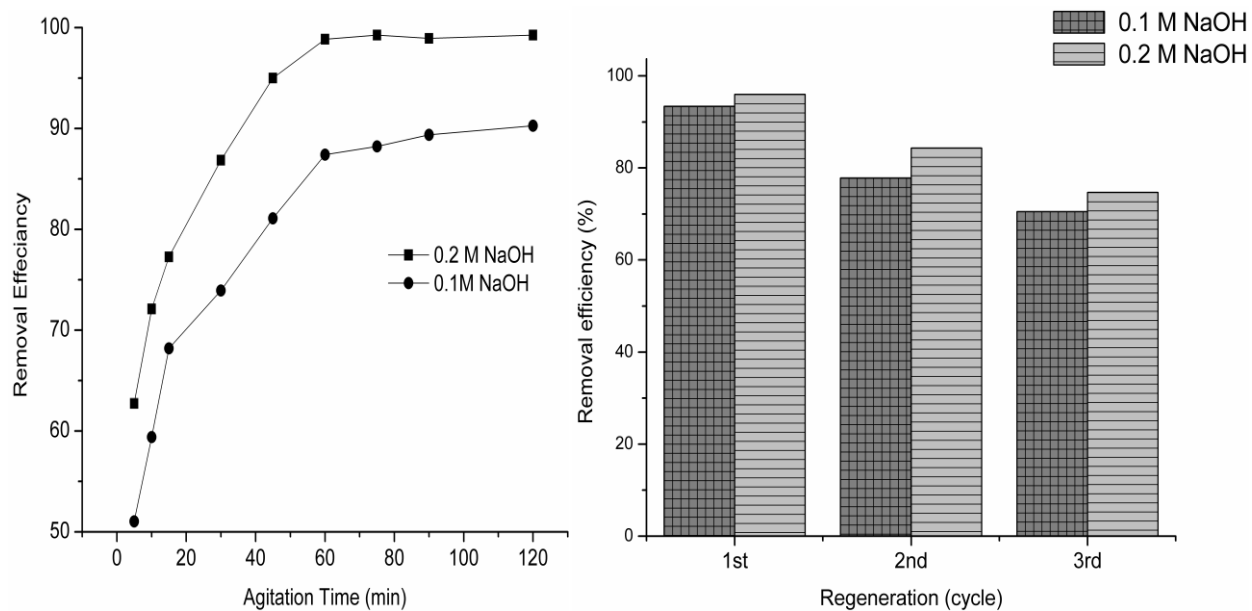


Figure 11: Regenerability of adsorbent (a) effect of agitation time on desorption; (b) amount desorbed with cycle

CHAPTER SIX

Discussion

Physicochemical characteristic

Physicochemical properties of adsorbent are highly affect both negatively and positively the removal efficiency of TMs. High Clay content, CEC, Al^{3+} , Fe^{3+} CaCO_3^{2+} and low organic carbon are factors those increase the removal efficiency of adsorbent (Ackerman et al., 2007; Dowuona et al., 2012; Getahun and Degaga, 2014). According to this finding the outer part of TM has high clay content 58% while, control, external and middle parts contain have 40%, 48.5% and 54.5% respectively. As presented in table 1. The existence of higher concentration of Al^{3+} , Fe^{3+} , CaCO_3^{2+} and clay content in the center of TMs afforded it higher removal efficiency compared with middle, external and control soil which is similar with (Tisdale et al., 1985; Ptáček et al., 2013).

Factors affect adsorptions

Effect of dose: According to the result of this study increasing of TM dose was result with high removal efficiency. This result was expected because as the dose increases the more active site will be available in a solution which is similar with (Baraka et al., 2012; Guan, 2005). From fig.1, it was observed that the adsorption percentage of P ions onto the TM increased rapidly with the increasing of adsorbent concentration. This result is expected because the increase of adsorbent dose leads to greater surface area. When the adsorbent concentration was increased from 0.5 to 50 g/L, the percentage of P adsorption increased from 73.4% to 94.5%. At higher dosage, the equilibrium uptake of P did not increase significantly with increasing TMs dosage. Such behavior is expected because saturation level attained during an adsorption process. This finding also agrees with Kamiyongo et al., (2011) and Mourabet et al., (2011). In general for low adsorbent dose the phosphate uptake capacity is high, because of the better utilization of the available active sites and at high adsorbent dose, too many sites are available for a fixed P ions in the solution (Vyshak and Jayalekshmi, 2014; Mallikarjun and Shashikant, 2010)

Effect of shaking Speed: The result of this study shows that, in batch adsorption system, shaking speed has a significant influence in affecting the external boundary layer and the distribution of the solute in bulky solution. As afforded on fig. 2 from 100 to 200 rpm it increases in its adsorption efficiency, this is due to better contact between adsorbent active site and adsorbate ions which leads to the increase in the diffusion of adsorbate ions onto surface of adsorbent. But

when it increases from 200 to 250 rpm P removal efficiency was start to decrease. Similar finding was also reported by Kebede et al., (2014). Because of better contact between adsorbent and adsorbate the removal of metal ions increased with increases shaking speeds. Due to higher dispersion of adsorbent particles in solution which leads to reduced boundary mass transfer and also it may boost the velocity of particles, so that it increases the percent removal of metal ions (Ragheb, 2013). At high speed desorption may be occur because of over shaking speeds the adsorbent releases the adsorbate.

Effect of Particle Size: Particle size is another important parameter which significantly influences adsorption efficiency of adsorbent (Vyshak and Jayalekshmi, 2014). For this study as plotted on fig. 3 the removal efficiency increased as the particle size decreased. This may be due to the increases of surface area associated with decreased particle size. The presence of large number of smaller particles provides high sorption efficiency with the presence of larger surface area for P ions and it also reduces the external mass transfer resistance (Mohammed and Rashid, 2012; Jamode et al., 2004). This can be pointed to the fact that the smaller adsorbent particles have shortened diffusion paths and increased total surface area, and therefore the ability to penetrate all internal pore structures of adsorbent is very high according to (Gupta et al., 2009). For larger particles, the diffusion opposition to mass transport is higher and the majority of the internal surface of the particle may not be utilized for adsorption and as a result, the amount of P adsorbed is small.

Effect of Contact Time: as a result presented on fig. 1b it was sharply increase starting from 5 to 45 min but after that it was increasing with a little difference above 45 min. Since there is no significant change after 45 min, it was considered as equilibrium with removal efficiency of ~ 96% and maximum adsorption capacity of 0.27 mg/g. As presented on fig. 4b after 45 min it was almost constant this is because, initially the active sites of adsorbent was not occupied and the free ions attached itself on to a free pore sites but as the contact time increase all the active sites are occupied as well as the P ions concentration in the solution gets low which was similar finding with (Kebede et al., 2014; Ragheb, 2013; Riahi et al., 2013).

Adsorption Kinetics: Since adsorbate undergo different molecular stages kinetic studies are important to understand the mechanism of adsorption process. While, it is moving from bulk solution to the adsorbent surface such as movement of adsorbate molecules to the external surface of adsorbent particles, molecular and pore diffusion (Mane and Babu, 2011). The linear

regression correlation coefficient value $R_1^2 = 0.961$ indicates that model cannot be applied to predict the adsorption kinetics. Fig. 4a shows the linear relationship of the graph plot of t/q_t versus time, from which q_e and k can be determined from the slope and intercept, respectively. The linear regression correlation coefficient $R_2^2 = 0.997$ was higher than R_1^2 (Table 5). These results confirm the adsorption data were well represented by the pseudo-second-order kinetic model, indicates the adsorption rate is proportional to the concentration of P. The experimental data reported in Table 5 showed that the TM adsorption is in good agreement with pseudo-second-order kinetic model having the highest R^2 value which was similar with (Ahmad et al., 2014). The value of the mean Gibbs free energy change $\Delta G = -1.12$ kJ/mol computed from eq. 10 was found negative value and necessarily indicate that sorption of P on TM is spontaneous (Weber, 1998).

Effect of pH: Phosphate adsorption works over wide ranges of pH value as plotted in (Fig. 3) it is evident that the adsorption process of P is highly dependent on the pH values of solution. At the two tips the adsorption efficiency of P was decreased while in the middle part it is highly increased which was similar finding with (Huang et al., 2013; Wadood and Sarmad, 2012; Yan et al., 2013) as adsorption depends on pH. The increase of removal efficiency around the neutral is because of high CEC and clay content of the adsorbent as discussed by (Xu et al., 2014).

For this finding as it was observed from Fig. 3 for pH ~ 3, 83.93% and for pH ~ 11 it was 43.01% but at pH ~ 7 its efficiency rise to 95.45%. The decrease in its efficiency at pH increases is because of OH^- ions concentration increases in the solutions which are highly competed with P ions and it binds with active site of adsorbent as reported by (Biswas, 2008b; Rybicki, 1997a; Xu et al., 2014). In addition to this the decrease of removal efficiency at the two tips desorption will be occur at higher alkalinity and dissociation of P species will be expected under strong acidic conditions as it was reported by (Ping et al., 2008).

Other important thing was that the initial and final pH was recorded and for the initial pH of 3 and 11 the final pH recorded after shaking was 4.2 and 8.6 respectively. The importance of recording final pH is used to know safe disposal of final effluent (Yan et al., 2013; Mohammed and Rashid, 2012).

In general, a pH of this adsorbent can be used for value in the range of (3 – 9) with its removal efficiency of over 80% which is reasonable used to remove P from wastewaters before disposal into aquatic environment.

Effects of the Initial Concentrations and Isotherm Adsorption: For this study as presented on fig. 7a the amount adsorbed in (mg/g) was sharp at lower initial concentration and decrease with the increments of initial concentration. The amount of mass loaded on to the solid was increase, to the contrast removal efficiency was decreased. This can be happen because, at low P concentration, the ratio of surface active sites to total P is high and therefore the interaction of adsorbate with the active sites on adsorbent surface was sufficient for efficient P removal which was similar with (Vyshak and Jayalekshmi, 2014; Rout et al., 2014). Moreover these mass loadings show that the higher the concentration of P the greater the mass loading on the solids. For example, the initial concentration of 0.5 to 20 mg/L, the equilibrium adsorption capacities of P ion were 0.05 to 1.20 mg/g, respectively. However, although adsorbed P ion increased from 0.05 mg/L to 1.2 mg/g, the removal ratio decreased from ~ 98% to ~ 62% fig. 7a, which may be due to the ratio between P ion and the available active sites of adsorbent (Chen et al., 2013; Fufa et al., 2013). When the initial P ion concentration was high, active sites were occupied and saturation will be expected. Similar finding was reported by (Hongshao and sanforth, 2001).

The analysis of equilibrium data is essential to understand the removal process and to be able to compare different adsorbents under different operational conditions. The relationship between various initial P concentration and equilibrium adsorption capacities were investigated. From table 6 it could be found that the equilibrium P adsorption capacities of Control soil, External, Middle and center of TMs found, 0.045 to 0.94, 0.05 to 1.98, 0.049 to 1.09 and 0.048 to 1.04 mg/g, respectively. The P removal capacity of each adsorbent was increase slowly as initial concentration increases; this shows that adsorbent has saturation points.

In order to optimize the design of a P removal system, it is important to establish the most appropriate correlation for the equilibrium curves which describe the relationship between equilibrium residual P in solution (C_e) and equilibrium adsorption capacity (q_e). Langmuir and Freundlich models were applied for the fitting of the experimental data.

From table 4 it could be found that, for control soil, the Langmuir equation represented the poorer fit of experimental data due to the relatively lower $R^2 = 0.732$ compared with that of the Freundlich equation $R^2 = 0.981$. But for others, P removal was much better described using the Langmuir model than the Freundlich one, indicating that the P removal corresponds to a monolayer system which is not open to the formation of a heterogeneous. Previous studies about P removal indicate that, both Langmuir and Freundlich equations were suitable for the

description of P removal by using different adsorbent which agree with (Yan et al., 2013; Zeng et al., 2004). The estimated maximum adsorption capacities (q_{max}) obtained from Langmuir model were 1.277, 1.48, 1.29 and 1.35 mg/g for control soil, external, middle and central part of TMs, respectively.

The values of dimension less Langmuir R_L for control soil, external, middle and center of TM presented on table 6 indicates as the type of isotherm to be favorable which all ranges between $0 < R_L < 1$ (Bhattacharya et al., 2008).

Intraparticle diffusion: From table 4 the intraparticle diffusion rate constant (k_p) value estimated from the slope of plot of q_t versus square root of time was found to be $0.0092 \text{ min}^{1/2}$ for the initial P concentration of 3 mg/L. According to Weber and Morris, (1963), discussion if intraparticle diffusion is a rate controlling step, then the plots should be linear and pass through the origin. So, as shown in fig. 8, the plot is linear but it is not passing through the origin. This indicates that the P adsorption onto TM is complex process and the intraparticle diffusion is not only rate controlling step.

Effect of Temperature: The result indicates that as temperature increases, removal efficiency of adsorbent also increase similar finding was reported by many researchers (Riahi et al., 2013; Dabrowski, 2001; Li et al., 2013; Desta, 2013). According to Chubar et al., (2015) report, increasing the temperature resulted in higher P sorption and this regularity indicates that chemio-sorption was the ruling mechanism of this anion uptake by the investigated material. Another finding was reported that precipitation of Al and Fe is high with increasing of temperature (Rajput et al., 2014).

Effect of Coexisting Anions: The effect of competing anions such as chloride, sulfate, carbonate and bicarbonate those commonly found in wastewater are studied and afforded on fig. 10. As observed from result anions such as Sulfate, Chloride and Nitrate have no significant influence on P adsorption efficiency of adsorbent which is similar finding with (Ren et al., 2012; Kose and Kivanc, 2011). But carbonate and bicarbonate slightly interfere and influence removal efficiency of P. Similarly, Chubar et al., (2009) study of phosphate uptake by HUD and Al-HUD as a function of the initial concentrations of the coexisting ions the uptake of P increased slightly, without any trend, in the presence of chloride, nitrate, or sulfate ions but significantly affected in the presence of carbonate and bicarbonate. Another study state that selectivity of the fluoride adsorption onto three samples was reported as 25 – 50 times greater than phosphate adsorption

(Hamdi and Srasra, 2008). But in this study fluoride is not considered because it is not the problem wastewater.

Also, Panasiuk, (2010) in his study divided co-existing ions into two: those that form outer-sphere complexes (chloride, nitrate, and sulfate) and those that form inner-sphere complexes with binding surfaces, e.g., fluoride. According to the result of this study the quantities of phosphate adsorbed on HUD and Al-HUD decreased from 48.85 and 56.63 mg/g to 35.92 and 29.13 mg/g in the presence of co-existing ions, respectively. The decrease of P sorption in the presence of co-existing ion show that both ions (P and co-existing ions) compete for the same active site of adsorbent.

Regeneration of adsorbent: Desorption of P from the P loaded TMs was evaluated using NaOH solutions with different concentrations. Fig.11 shows the results. It was found that the amount of P desorption increased with the increase of alkalinity. For this study two types of desorption was conducted. The first one was to know effect of time on desorption was analyzed from 5 to 120 min. the result show that desorption depends on both agitation time and strength of alkalinity. For example: for 0.1 and 0.2 M NaOH desorption was ~ 51% and ~ 62% for 5 min and ~ 90% and ~ 99% for 120 min respectively. This shows the agitation time has also play a role for regeneration. The second type of study is what was reported by different researchers for how many times we can use through regenerations. For this by taking 60 min agitation time, 3 mg/L of P concentration, 200 rpm shaking speed and with 0.1 and 0.2 M NaOH was used to test its adsorption/ desorption for three times and it was effective with re-adsorption efficiency of >80% for both alkalinities used after third adsorption/desorption. Similarly, for other adsorbents researchers report as it is possible to use up to 3 to 12 times regenerability with effective re-adsorption efficiency (Koutarou et al., 2015). Chitrakaret al., (2012) used synthetic akaganeite for selective P adsorption from seawater and regenerated with 0.1 M NaOH. They report as almost no loss in capacity after up to 12 adsorption/ desorption cycles. Another research which was conducted to remove P and Ammonium from wastewater using bricks minerals was tested for its regenerability for both pollutants and observed that re-generability was more effective for P than Ammonium (Gu et al., 2013). Also, Genz et al., (2011) studied phosphate adsorption from MBR effluents onto GFH and activated alumina followed by regeneration with 0.6 M NaOH and reported as no decrease in adsorption efficiency after third adsorption-desorption cycles.

In general, adsorption- desorption process can be used as one of resource recovery technology to solve the today's waste disposal problem. So TMs is one of effective low cost locally available adsorbent that can be regenerated for more than three times even though it needs extra study to know its exact adsorption-desorption cycles.

Removal of Phosphate ions from wastewater

By using all optimum and equilibrium conditions that were determined by synthetic aqueous solution except pH, adsorption experiment of P onto TM using wastewater samples. Even though it reduces 9.03 mg/L P ions in the wastewater to 2.13 mg/Lit was reveal from WHO guide line which is 1 mg/L for flow Rivers. But the researcher was try many options to decrease P from wastewater at the optimum conditions by adjusting pH ~ 7 and it was minimize into 1.12 mg/L which was near acceptable. Other option was designed by increasing dose of TM from 10 to 15 g/L which was reduced P ions below WHO guidelines 0.92 mg/L with its removal efficiency of ~94%.

There were many reasons for the decrease of removal efficiency; mainly the existence of competing ions table 4 and real pH of wastewater 5.21 are the main factors. In general the adsorbent was effective to reduce P from wastewater to the level of below its permissible.

CHAPTER SEVEN

Conclusion and Recommendation

6.1 Conclusions

Based on the present study, it is clearly shown that TM which abundantly available in tropical and sub-tropical area is an effective adsorbent for the removal of phosphorous from wastewater. The adsorption process is strongly affected by parameters such as time, pH, adsorbent dosage, initial P concentrations and agitation speed. The equilibrium time for P ions is determined as 60 min within ~ 96% of removal efficiency. It was performing within wide pH ranges 3 – 9 with > 80% of adsorption efficiency which is important in practical applications for wastewater released with various pH ranges.

The sorption kinetics was found to follow pseudo-second-order model with $R^2 = 0.997$ rate and the experimental equilibrium sorption data fitted well to Langmuir model (homogeneous) surface with $R^2 = 0.978$ and the equilibrium adsorption, giving a sorption capacity of 1.49 mg/g.

The presences of competing anions (carbonate and bicarbonate) significantly influence P adsorption efficiency while sulfate, chloride and nitrate were interfering slightly. The adsorbent reduce P concentration of real wastewater from 9.03 mg/L to 0.97 mg/L which was below its permissible limits. Regenerability of adsorbent was tested using NaOH solution and the re-adsorption efficiency after third adsorption/desorption was > 73% from the results of this study we concluded that the application of TM for adsorptive removal of P is highly favorable and a spontaneous process. Therefore, it can be likely that termite mound (TM) can be used as a low cost locally available together with highly efficient adsorbent for removal of P from wastewater.

6.2 Recommendations

Based on the results of the study the following recommendations forwarded.

- As TM is widely available and demonstrate satisfactory sorption capacity it can be used for the sorption removal of P.
- Detail characterization of TM using scanning electron microscopy is required for detail understanding of the sorption process.
- P concentrated TMs can be used as soil conditioning to reduce P fixing of soil thus practical applicability requires further investigation.
- Practical applicability of TM for P removal requires further fixed bed column adsorption investigation.

References

- Abbadie, L., Lepage, M. and Roux, X. L. (2009) Soil fauna at the forest-savanna boundary: role of termite mounds in nutrient cycling. *Journal of Chapman and Hall*, 2, 73-82.
- Abdus, N. S. and Itiola, D. A. (2012) Potential application of termite mound for adsorption and removal of Pb(II) from aqueous solutions. *Journal of the Iranian Chemical Society*, 1-12.
- Ackerman, L. I., Wenceslau, G. T., Susan, J. R., Johannes, L. & Erick, F. M. (2007) The impact of mound-building termites on surface soil properties in a secondary forest of Central Amazonia. *Journal of Applied Soil Ecology*, 37, 267-276.
- Ahmad, M. A., Ahmad, N. and Bello, O. S. (2014) Modified durian seed as adsorbent for the removal of methyl red dye from aqueous solutions. *Journal of Appl Water Science*, 1-17.
- Ali, I. and Gupta, V. K. (2007) Advances in water treatment by adsorption technology. *Nature Protocols*, 1, 2261 - 2667.
- Aschale, M., Sileshi, Y., Kelly-Quinn, M. and Hailu, D. (2015) Potentially Toxic Trace Element Contamination of the Little Akaki River of Addis Ababa, Ethiopia. *Journal of Natural Sciences Research* 5, 1-13.
- Baraka, A. M., El-Tayieb, M. M., Shafai, M. E. and Mohamed, N. Y. (2012) Sorptive Removal of Phosphate From Wastewater Using Activated Red Mud. *Australian Journal of Basic and Applied Sciences*, 6, 500-510.
- Bignell, D. E. and Eggleton, P. (2000a) *Termites: Evolution, Sociality, Symbioses, Ecology*. *Journal of Kluwer Academic Publishers*, 7, 363-387.
- Bignell, E. and Eggleton, P. (2000b) *Termites: Evolution, Sociality, Symbioses, Ecology*. *Journal of Applied Soil Ecology*, 12, 363-387.
- Biswas, B. K. (2008a) Removal and recovery of arsenic and phosphorus by means of adsorption onto orange waste, an available agricultural by-product. *Journal of Chemical Engineering*, 12, 78-89.
- Biswas, B. K. (2008b) Removal and recovery of arsenic and phosphorus by means of adsorption onto orange waste, an available agricultural by-product. *Chemical Engineering*. Saga University, Japan.
- Boller, M. (1993) Removal of organic matter by physic-chemical mechanism in wastewater treatment plants. *Journal of Water Sci. Tech*, 27, 167-183.

- Bowden, L., Jarvis, A., Younger, P. and Johnson, A. (2009) Phosphorus Removal from Waste Waters Using Basic Oxygen Steel Slag. *Journal of Environ. Sci. Technol* 43, 2476-2481.
- Chen, J., Cai, Y., Clark, M. and Yu, Y. (2013) Equilibrium and Kinetic Studies of Phosphate Removal from Solution onto a Hydrothermally Modified Oyster Shell Material. *PLOS ONE*, 8.
- Chubar, N., Szlachta, M. and Gerda, V. (2015) Phosphate Adsorption By The Mixed Inorganic Ion Exchanger Based On Fe_ Mn Hydrous Oxides Equilibrium And Ftir Studies. *Environmental Science and Technolo*, 5.
- Dabrowski, A. (2001) Adsorption from theory to practice. *Advances in Colloid and Interface Science*, 93, 135-224.
- Debelo, D. G. and Degaga, E. G. (2014) Studies on Ecology of mound-building termites in the Central rift valley of Ethiopia *International Journal of Agricultural Sciences* ISSN 4 326-333.
- Desta, M. B. (2013) Batch Sorption Experiments: Langmuir and Freundlich Isotherm Studies for the Adsorption of Textile Metal Ions onto Teff Straw (*Eragrostis tef*) Agricultural Waste. *Journal of Thermodynamics*, 2013, 7.
- Dowuona, G. N. N., Atwere, P., Dubbin, W., Nude, P. M., Mutala, B. E., Nartey, E. K. and Heck, R. J. (2012) Characteristics of termite mounds and associated acrisols in the coastal savanna zone of Ghana and impact on hydraulic conductivity 4, 423-437.
- Dursun, S., Guclu, D. and Bas, M. (2006a) Phosphate removal by using activated red mud from Seydisehir Aluminium Factory in Turkey. *Journal of Int. Environmental Application & Science*, 1, 98-106.
- Dursun, S., Guclu, D. and Bas, M. (2006b) Phosphate removal by using activated red mud from Seydisehir Aluminium Factory in Turkey. *J. Int. Environmental Application & Science*, , 1, 98-106.
- Fufa, F., Alemayehu, E. and Lennartz, B. (2013) Defluoridation of Groundwater Using Termite Mound. *Water Air Soil Pollut*, 224, 1552- 1567.
- Getahun, D. D. and Degaga, E. G. (2014) Termite species composition in the central rift valley of Ethiopia. *Journal of Agriculture and Biology Journal of North America*, 5, 123-134.

- Grassi, M., Kaykioglu, G., Belgiorno, V. and Lofrano, G. (2012) Removal of Emerging Contaminants from Water and Wastewater by Adsorption Process. IN 2006 (Ed.) Emerging Compounds Removal from Wastewater. Corlu-Tekirdag, Turkey.
- Gu, D., Zhu, X., Vangosay, T., Huanga, M., Song, L. and He, Y. (2013) Phosphorous and Nitrogen removal using novel porous bricks incorporated with waste and minerals. *Journal of Environmental study*, 22, 1349-1356.
- Guan, X. (2005) Adsorption of phosphates and Organic Acids On Aluminum hydroxides in Aquatic Environment - mechanisms and Interactions. Civil Engineering. Hong Kong, Hong Kong University of Science and Technology.
- Guppy, C. N., Menzies, N. W., Moody, P. W. and Blamey, F. P. C. (2005) Competitive sorption reactions between phosphorus and organic matter in soil: a review. *Australian Journal of Soil Research* 43, 189-202.
- Haddis, A., Getahun, T., Mengistie, E., Jemal, A., Smets, I. and Bruggen, B. V. D. (2014) Challenges to surface water quality in mid-sized African cities: conclusions from Awetu-Kito Rivers in Jimma, south-west Ethiopia. *Water and Environment*, 28, 173-182.
- Hadgu, F. (2014) Study of phosphorus adsorption and its relationship with soil properties, analyzed with Langmuir and Freundlich models. *Journal of Agriculture, Forestry and Fisheries*, 3, 40-51.
- Hadgu, F., Gebrekidan, H., Kibret, K. and Birruyitaferu (2014) Study of phosphorus adsorption and its relationship with soil properties, analyzed with Langmuir and Freundlich models. *Journal of Agriculture, Forestry and Fisheries*, 3, 40-51.
- Hamdi, N. and SrasRA, E. (2008) Sorption of Phosphate from Acidic Wastewater into Three Tunisian Type Clay Soils. *Journal of Water Chemistry and Technology*, 30, 374-384.
- Hardy, F. (1995) Some aspects of tropical soils. *journal International Congo Soil Science*, 2, 156-163.
- Harrell, D. L. and Wang, J. J. (2006) Fractionation and sorption of inorganic phosphorus in Louisiana calcareous soils *Journal of Soil Science*, 173, 39-51.
- Harris, W. G. (2002) Phosphate minerals Madison Wisconsin, Soil Science Society of American Inc.
- Henze, M. (2008) *Biological Wastewater Treatment*, London, UK, Published by IWA Publishing

- Huang, C. P. (1975) Adsorption of phosphate at hydrous $t\text{-Al}_2\text{O}_3$. *Journal of Colloid Interface Science*, 53 175-186.
- ILEC (2009) Survey of the State of the World's Lakes. Technical report, International Lake Environment Committee.
- Itanna, F., Olssonb, M. and Stahrc, K. (2011) Effect of Land Use Changes on Soil Carbon Status of Some Soil Types in the Ethiopian Rift Valley. *Journal of the Dryland*, 4, 289-299.
- Jamode, A. V., Sapkal, V. S., Jamode, V. and Jarvi, A. (2004) Defluoridation of water using inexpensive adsorbents. *Journal of Indian Institute of Science*, 84, 163-171.
- Jouquet, P., Boulain, N., Gignoux, J. and Lepage, M. (2004) Association between subterranean termites and grasses in a West African savanna: spatial pattern analysis shows a significant role for *Odontotermes n. pauperans*. *Journal of Applied Soil Ecology*, 27, 99-118.
- Kebede, B., Beyene, A., Fufa, F., Megersa, M. and Behm, M. (2014) Experimental evaluation of sorptive removal of fluoride from drinking water using iron ore. *Journal of Appl Water Sci*, 9.
- Konate, S., Roux, X. L., Tessier, D. and Lepage, M. (1999) Influence of large termitaria on soil characteristics, soil water regime and tree leaf shedding pattern in a West Africa savanna. *Journal of Plant Soil*, 206, 47-60.
- Kose, T. E. and KIVANC, B. (2011) Adsorption of phosphate from aqueous solutions using calcined waste eggshell. *Chemical Engineering Journal* 178, 34- 39.
- Koutarou, A., Seigo, U., Harada, H., Oura, S., Biswas, B. K., Watari, T. and Mitoma, Y. (2015) Simultaneous solidification of potassium and phosphorus using rice straw charcoal and saturated phosphorus adsorbent. *Int J Recycl Org Waste Agricult* 4, 67-72.
- Lagergren, S. (1898) About The Theory of So-Called Adsorption of Soluble Substances. *Kungliga Svenska Ventenskapsakademiens Handlingar*, 24, 1-39.
- Lamoureux, S. and O'kane, A. M. (2012) Effects of termites on soil cover system performance. *Journal of Australian Centre for Geomechanics*, 2, 433.
- Li, M., Whelan, M. J., Wang, G. Q. and White, S. M. (2013) Phosphorus sorption and buffering mechanisms in suspended sediments from the Yangtze Estuary and Hangzhou Bay, China. *Journal of Biogeosciences*, 10, 3341-3348.

- Liu, Y., Villalba, G., Ayres, R. U. and Schroder, H. (2014) Global Phosphorus Flows and Environmental Impacts from a Consumption Perspective. *Journal of Industrial Ecology*, 12, 231-247.
- Maduakor, H., An. Okere, A. and Onyeaunoro, C. (1995) Termite mounds in relation to the surrounding soils in the forest and derived savannas zones of southeastern Nigeria. *Journal of Biol Fertil Soils*, 20, 157-162.
- Mallikarjun.S.D and Shashikant.R.Mise (2010) A Batch Study of P Phosphate Adsorption Characteristics on Clay Soil. *International Journal of Research in Engineering and Technology*, 338- 342.
- Millus, G. (2009) *Phosphorous, Agricultural and Environment*, London, LEWIS.
- MOWIE (2015) *Urban Wastewater Management Strategy*. Addis Ababa, Ethiopia, Berehan ena Selam press agency.
- Onyango, M. S., Kuchar, D., Kubota, M. and Matsuda, H. (2007) Adsorptive Removal of Phosphate Ions from Aqueous Solution Using Synthetic Zeolite. *Journal of Ind. Eng. Chem. Res.*, 46, 894-900.
- Panasiuk, O. (2010) *Phosphorus Removal and Recovery from Wastewater using Magnetite*. *Industrial Ecology*,. Stocholm, Royal Institute of Technology.
- Pena, F. and Torrent, J. (1990) Predicting Phosphate Sorption in the Soil of Mediterranean Regions. *Journal of Fertilizer Research*, 23 173-179.
- Ping, N., Hans-J'Org, B., Bing, L., Xiwu, L. and Yong, Z. (2008) Phosphate removal from wastewater by model-La(III) zeolite adsorbents. *Journal of Environmental Sciences* 20, 670-674.
- Ptáček, P., Brandštetr, J., Šoukal, F. and Opravil, T. (2013) Investigation of Subterranean Termites Nest Material Composition, Structure and Properties.
- Ragheb, S. M. (2013) Phosphate removal from aqueous solution using slag and fly ash. *HBRC Journal*, 9, 270-275.
- Rajput, A., Panhwar, Q. A., Naher, U. A., Rajput, S., Hossain, E. and Shamshuddin, J. (2014) Influence of Incubation Period, Temperature and Different Phosphate Levels on Phosphate Adsorption in Soil *American Journal of Agricultural and Biological Sciences* 2, 251-260.

- Ren, Z., Shao, L. and Zhang, G. (2012) Adsorption of Phosphate from Aqueous Solution Using an Iron–Zirconium Binary Oxide Sorbent. *Journl Water Air Soil Pollut* 223, 4221-4231.
- Riahi, K., Chaabane, S. and Thayer, B. C. B. (2013) A kinetic modeling study of phosphate adsorption onto *Phoenix dactylifera* L. date palm fibers in batch mode. *Journal of Saudi Chemical Society*, 10.
- Rout, P. R., Bhunia, P. and Dash, R. R. (2014) Modeling isotherms, kinetics and understanding the mechanism of phosphate adsorption onto a solid waste: Ground burnt patties *Journal of Environmental Chemical Engineering* 9.
- Rupela, O. P., Humayun, P., Venkateswarlu, B. and Yadav, A. K. (2006) Comparing conventional and organic farming crop production systems: inputs, minimal treatments and data needs. *Journal of National Center for Organic Farming (NCOF)*, 23, 103-115.
- Rybicki, S. (1996) Advanced wastewater treatment. In Plaza, E., Levlin, E. and Hultman, B. (Eds.) *Phosphorous removal from wastewater*. Stockholm Royal Institute of Technology.
- Rybicki, S. (1997a) Advanced Wastewater Treatment. In Plaza, E., Levlin, E. & Hultman, B. (Eds.) *Phosphorus Removal From Wastewater*. Stockholm Royal Institute Of Technology.
- Rybicki, S. (1997b) Advanced wastewater treatment. In E. Plaza, E. Levlin & Hultman, B. (Eds.) *Phosphorus removal from wastewater*. Stockholm Royal Institute of Technology.
- Sanchez, P. A. and Uehara, G. (1980) Management considerations for acid soils with high phosphorus fixation capacity, ASA, Madison, WI.
- Semhi, K., Chaudhuri, S., Claurer, N. and Boeglin, J. L. (2008) Impact of termite activity on soil environment: a perspective from their soluble chemical components. *Journal of the Iranian Chemical*, 21, 331-444.
- Singh, S., G, S. and A., B. (2012) Physicochemical Determination of Pollutants in wastewater in Dheradun. *Curr World Environ*, 7, 133-138.
- Soils, P. and Torrent, J. (1989) Phosphate sorption by calcareous Vertisols and inceptisols of Spain *Soil Science Society American Journal*, 53, 456-459.
- Spellman, F. R. (Ed.) (2003) *Handbook of Water and Wastewater Treatment Plant Operations*, Boca Raton London New York Washington, D.C., LEWIS PUBLISHERS.

- Sreenivasuju, A., Sundaram, E. V. and Reddy, M. K. (1999) Phosphate adsorption studies using carbon prepared from stem bark of Eucalyptus teriticornis Smith Indian Journal of Chemical Technology 6, 256-262.
- Stephenson, T., Lester, J. N. and Perry, R. (1985) Advanced wastewater treatment for biological phosphorus removal, UK, Selper Ltd.
- Mohammed, T. W. and Rashid, S. A. (2012) Phosphorus Removal from Wastewater Using Oven-Dried Alum Sludge. International Journal of Chemical Engineering, 2012, 11.
- Tekalign, M. and Haque, I. (2007) Phosphorus status of some Ethiopian soils Sorption characteristics. Journal of Plant and Soil, 102, 261-266.
- Tilahun, A., Kebede, F., Yamoah, C., Erens, H., Mujinya, B. B., Verdood, A. and Ranst, E. V. (2012) Quantifying the masses of Macrotermes subhyalinus mounds and evaluating their use as a soil amendment. Journal of Agriculture, Ecosystems and Environment 157, 54-59.
- Tisdale, S. L., Nelson, W. L. and Beaton, J. D. (1985) Soil Fertility and Fertilizers, New York, USA, Macmillan Publishing Company.
- Tomar, M. (1999) Quality Assessment Of Water And Wastewater Boka Rato London New York Washington, D.C., LEWIS.
- Troeh, Frederick and Thompson, L. M. (1993) Soils and Soil Fertility, New York, NY, Oxford University Press.
- Tsadilas, C. D., Samaras, V. and Dimoyiannis, D. (1996) Phosphate sorption by red Mediterranean soils from Greece. Comm. Soil Sci. Plant Analysis, 27, 2279-2293.
- Voundi, N. J. C., Demeyer, A., Baert, G., Verloo, M. G. and Van Ranst, E. (1997) Chemical fertility aspects influenced by the mineralogical composition of some acid tropical soils of the forest zone in Central Cameroon Journal of Agrochemicals, 41, 209-220.
- Vyshak, R. S. and Jayalekshmi, S. (2014) Soil - An Adsorbent for Purification of Phosphate Contaminated Water. Int. J. Struct. & Civil Engg. Res. , 3, 66-78.
- White, R. E. (1980) Retention and release of phosphate by soil and soil constituents. Society of Chemical Industry, 2, 71-114.
- WHO (1997) Department of Public Works Bureau of Sanitation. Industrial Waste Management Division. Los Angeles Press Agency, Produced by City of Los Angeles.

- Xu, N., Yin, H., Chen, Z., Liu, S., Chen, M. and Zhang, J. (2014) Mechanisms of phosphate retention by calcite: effects of magnesium and pH. *Journal of Soils Sediments* 14, 495-503.
- Yan, Y., Sun, X., Ma, F., Li, J., Shen, J., Han, W., Liu, X. and Wang, L. (2013) Removal of phosphate from wastewater using alkaline residue
- Zeng, L., Li, X. and Liu, J. (2004) Adsorptive removal of phosphate from aqueous solutions using iron oxide tailings. *Journal of Water Research*, 38, 1318--1326.
- Zhang, G. Y., Zhang, X. N. and Yu, T. R. (1987) Adsorption of sulphate and fluoride by variable charge Soils. *Journal of Soil Science*, 38, 29-38.

Annex I: Batch Experiments Procedure

(Ali and Gupta, 2007)

Conversion of reactive materials into adsorbents

1. Collect selected material and sieve to remove other particles such as stone, soil, paper etc.
2. Wash with distilled H₂O and dry in an oven at 100°C for about 2 h.
3. Carbonize organic precursors by heating to 400–800°C for 5 –24 h.
4. Treat with hydrogen peroxide at 60°C for 24 h to remove adhered organic matter.
5. Wash with distilled H₂O three times to remove hydrogen peroxide and dry in an oven at 100°C for ~ 2 h.
6. Heat to 500°C in a furnace for 6 –12 h to activate the adsorbent.
7. Determine density, porosity and ignition loss by the usual methods
8. Establish the stability of the adsorbent by suspending in ddH₂O, HCl and NaOH (0.1 to 1.0 M) for about 1–2 h.
9. Establish mineral and crystal structure by X-ray diffractometry and Scanning electron microscope (SEM), using published methods
10. Carry out elemental analysis by chemical methods, as described
11. Collect adsorbent of different particle sizes by sieving and keep in vacuum desiccators. At this stage, the adsorbent is ready for water purification.

Batch experiments

12. Use a 50-ml Erlenmeyer flask to carry out batch experiments in a thermostatic shaking water bath. Take a known amount of pollutant in 10–25 ml H₂O and add a dose of adsorbent. The dose of adsorbent depends on the type of adsorbent and adsorbate. However, a suggested starting point is 0.5 g/L. Alter the pH of the solution using HCl or NaOH.
13. Agitate flask mechanically in a water bath at desired temperature. Normally temperature is fixed between 25 and 35°C for 1– 3 h.
14. Repeat Steps 12 – 13 to optimize concentration of pollutant, pH, adsorbent dose, temperature and contact time after varying their values.
15. Centrifuge or filter the mixture and determine the concentration of pollutant in the aqueous phase.

16. Calculate the amount of pollutant adsorbed from the aqueous solution by determining the equilibrium concentration in solution. Kinetic studies
17. Set up 50-ml Erlenmeyer flasks containing various amounts of standard solutions of pollutant and shake in a thermostatic shaking water bath.
18. Add a known amount of adsorbent to each flask.
19. Allow flasks to agitate mechanically in the water bath at a constant temperature. Contact time, temperature and other conditions should be selected based on preliminary experiments.
20. Centrifuge the mixture at pre-decided time intervals and analyze the concentration of pollutant in the supernatant. Adsorbent particle size is an important variable in deciding centrifugation timings. Normally, this varies from 30 to 60 min at 5,000–100,000g.
21. Determine the equilibrium concentration (C_e) and time to reach equilibrium.
22. Calculate thermodynamic parameters as detailed in the introduction and run adsorption models.

ANNEX II Tables contain more information's

Table 5: Effect of agitation time on P adsorption

Time (min)	Co = 2.82 mg/L			Co = 9.52 mg/L			pH	
	Ce (mg/L)	qe (mg/g)	A (%)	Ce (mg/L)	qe (mg/g)	A%	pH _i	pH _f
5	0.78	0.20	72.30	3.02	0.65	68.26	7.00	5.92
10	0.72	0.21	74.48	2.21	0.73	76.80	7.12	5.9
15	0.70	0.21	74.98	1.82	0.77	80.92	7.00	5.75
30	0.50	0.23	82.15	1.49	0.80	84.35	6.97	5.42
45	0.44	0.24	84.28	1.16	0.84	87.82	7.02	5.52
60	0.13	0.27	95.36	0.95	0.86	90.01	7.04	5.21
75	0.12	0.27	95.84	1.00	0.85	89.52	6.99	5.42
90	0.12	0.27	95.90	0.89	0.86	90.65	7.21	5.39
120	0.11	0.27	96.12	0.96	0.86	89.88	7.08	5.22

Table 6: Effect of pH on Phosphate adsorption

pH _i	C _o (mg/L)	C _e (mg/L)			q _e (mg/g)	A(%)	pH _f
		Trail 1	Trail 2	Average			
3.02	2.901	0.535	0.400	0.279	0.244	83.93	3.99
3.99	2.901	0.260	0.177	0.219	0.269	92.49	5.11
5.20	2.901	0.168	0.235	0.201	0.271	93.08	5.72
6.11	2.901	0.183	0.180	0.181	0.273	93.76	5.83
7.00	2.901	0.121	0.144	0.133	0.278	95.45	5.89
8.12	2.901	0.233	0.102	0.168	0.274	94.24	5.82
8.89	2.901	0.503	0.479	0.491	0.242	83.12	6.82
9.98	2.901	0.597	0.764	0.680	0.223	76.63	7.81
10.87	2.901	1.740	1.577	1.658	0.125	43.01	8.01

Table 7 Effect of adsorbent dose on adsorption

Dose (g)	C _o (mg/L)	C _e (mg/L)	q _e (mg/g)	A(%)	pH	
					pH _i	pH _f
2	2.901	0.773	0.213	73.36	6.98	5.86
5	2.901	0.293	0.052	86.40	7.03	5.84
10	2.901	0.223	0.027	92.30	7.11	5.93
15	2.901	0.213	0.018	92.65	7.04	5.98
20	2.901	0.228	0.013	92.14	7.01	6.01
30	2.901	0.154	0.009	94.68	7.20	6.24
50	2.901	0.153	0.005	94.74	7.12	6.54

Table 8 Effect of control soil on Phosphate adsorption

C _o (mg/L)	C _e (mg/L)	q _e (mg/L)	Freundlich isotherm		Langmuir Isotherm			A(%)	pH	
			q _{e, cal}	SSE	q _{e, cal}	R _L	SSE		pH _i	pH _f
0.49	0.04	0.05	0.01	0.0011	0.03	0.79	0.0004	92.12	6.99	6.35
0.97	0.11	0.09	0.03	0.0032	0.07	0.65	0.0002	88.37	7.02	6.44
2.91	1.19	0.17	0.18	0.0000	0.38	0.38	0.0450	58.99	7.04	5.99
4.96	2.10	0.29	0.27	0.0002	0.48	0.27	0.0368	57.65	7.00	5.93

9.50	4.54	0.50	0.49	0.0000	0.58	0.16	0.0067	52.20	7.01	5.71	
14.15	7.56	0.66	0.73	0.0048	0.62	0.11	0.0013	46.58	7.05	5.244.91	
19.40	9.93	0.95	0.90	0.0025	0.64	0.09	0.0940	48.83	6.99		
			Sum	0.0117				Sum	0.1843		

Table 9: Effect of Center soil on Phosphate adsorption

Co (mg/L)	C _e (mg/L)	q _e (mg/L)	Freundlich isotherm		Langmuir isotherm		A (%)	pH		
			q _{e, cal}	SSE	q _{e, cal}	SSE		pH _i	pH _f	
0.49	0.025	0.047	0.008	0.0015	0.004	0.0019	94.93	6.98	6.84	
0.97	0.085	0.088	0.022	0.0045	0.012	0.0058	91.21	6.97	6.79	
2.91	1.001	0.191	0.165	0.0007	0.141	0.0025	65.61	7.01	6.25	
4.96	2.124	0.284	0.306	0.0005	0.288	0.0000	57.18	7.10	5.88	
9.50	4.271	0.523	0.545	0.0005	0.544	0.0004	55.04	7.04	5.41	
14.15	6.456	0.769	0.766	0.0000	0.774	0.0000	54.36	6.98	5.01	
19.40	9.120	1.028	1.018	0.0001	1.020	0.0001	52.99	7.10	4.92	
			Sum	0.0077			Sum	0.0107		

Table 10: Effect of Middle of TM on Phosphate adsorption

Co (mg/L)	C _e (mg/L)	q _e (mg/L)	Freundlich isotherm		Langmuir isotherm			A (%)	pH	
			q _{e, cal}	SSE	q _{e, cal}	RL	SSE		pH _i	pH _f
0.49	0.010	0.048	0.067	0.0004	0.008	0.775	0.0016	97.92	7.12	6.94
0.97	0.029	0.094	0.104	0.0001	0.021	0.637	0.0053	97.05	7.05	6.90
2.91	0.387	0.252	0.312	0.0035	0.240	0.368	0.0001	86.70	7.05	5.83
4.96	0.790	0.417	0.421	0.0000	0.411	0.255	0.0000	84.08	7.10	5.84
9.50	2.257	0.724	0.656	0.0046	0.739	0.152	0.0002	76.24	7.12	5.42
14.15	4.800	0.935	0.903	0.0010	0.956	0.107	0.0005	66.07	7.09	5.40
19.40	8.410	1.099	1.144	0.0020	1.077	0.080	0.0005	56.65	6.99	5.11
			Sum	0.0117			Sum	0.0082		

Table 11: Effect of Outer part of TM on Phosphate adsorption

Co (mg/L)	C _e (mg/L)	q _e (mg/L)	Freundlich isotherm		Langmuir isotherm			A (%)	pH	
			q _{e, cal}	SSE	q _{e, cal}	R _L	SSE		pH _i	pH _f
0.49	0.01	0.05	0.09	0.0019	0.01	0.72	0.0015	98.34	7.01	6.88
0.97	0.02	0.09	0.14	0.0022	0.03	0.57	0.0044	97.44	7.04	6.93
2.91	0.33	0.26	0.39	0.0182	0.31	0.30	0.0025	88.54	7.00	6.01
4.96	0.66	0.43	0.51	0.0069	0.50	0.20	0.0056	86.72	7.06	5.77
9.50	1.39	0.81	0.69	0.0151	0.77	0.12	0.0014	85.37	7.04	5.31
14.15	2.85	1.13	0.91	0.0474	1.02	0.08	0.0112	79.87	6.98	5.01
19.40	7.43	1.20	1.33	0.0177	1.27	0.06	0.0047	61.68	7.01	5.20
			Sum	0.1094		Sum	0.0313			

Table 12 Effect of shaking speed on Phosphate adsorption

Shaking speed Rpm	Co (mg/L)	C _e (mg/L)			q _e (mg/g)	%A
		Trail 1	Trail 2	Average		
100	2.901	0.750	0.796	0.773	0.213	73.36
150	2.901	0.393	0.439	0.416	0.248	85.66
200	2.901	0.146	0.178	0.162	0.274	94.42
250	2.901	0.215	0.285	0.250	0.265	91.39

Table 13 Effect of particle size on Phosphate adsorption

P. Size (mm)	Co (mg/L)	C _e (mg/L)	q _e (mg/g)	A (%)	pH	
					pH _i	pH _f
<0.075	2.91	0.097	0.281	96.68	7.08	5.43
0.075-0.425	2.91	0.240	0.267	91.76	7.12	5.61
0.425-2	2.91	0.414	0.250	85.78	7.02	5.55
>4.75	2.91	0.442	0.247	84.81	6.89	5.47

Table 14 Effect of thermodynamics on Phosphate adsorption for 25 oC

Co (mg/L)	Ce (mg/g)	A (%)	$q_{e,exp}$ (mg/g)	Freundlich Isotherm		Langmuir isotherm		
				$q_{e,cal}$ (mg/g)	SSE	$q_{e,cal}$ (mg/g)	R_L (L/g)	SSE
0.479	0.479	96.33	0.046	0.066	3.6E-05	0.011	0.846	0.002
0.974	0.974	91.07	0.089	0.181	1.0E-03	0.052	0.730	0.001
2.808	2.808	82.45	0.232	0.336	4.6E-03	0.258	0.484	0.000
4.503	4.503	78.84	0.355	0.500	4.5E-03	0.434	0.369	0.010
9.515	9.515	77.35	0.736	0.705	7.9E-03	0.736	0.217	0.001
14.728	14.728	74.02	1.090	1.012	4.7E-02	0.968	0.152	0.005
19.716	19.716	59.21	1.167	1.463	1.5E-02	1.232	0.118	0.002
					8.0E-02	0.020		

Table 15: Effect of thermodynamics on Phosphate adsorption for 35 oC

Co (mg/L)	Ce (mg/g)	%A	$q_{e,exp}$ (mg/g)	Freundlich Isotherm		Langmuir isotherm		
				$q_{e,cal}$ (mg/g)	SSE	$q_{e,cal}$ (mg/g)	R_L (L/g)	SSE
0.479	0.006	98.769	0.047	0.052	3.5E-04	0.007	0.740	0.002
0.974	0.057	94.141	0.092	0.121	8.0E-03	0.068	0.584	0.001
2.808	0.229	91.835	0.258	0.299	6.1E-03	0.243	0.327	0.000
4.503	0.563	87.496	0.394	0.422	1.1E-02	0.493	0.233	0.010
9.515	1.220	87.182	0.829	0.647	1.5E-02	0.796	0.125	0.001
14.728	2.750	81.330	1.198	0.874	3.5E-02	1.127	0.085	0.005
19.716	6.311	67.989	1.340	1.290	1.5E-02	1.386	0.065	0.002
					9.1E-02	0.020		

Table 16 Effect of thermodynamics on Phosphate adsorption for 35 oC

Co (mg/g)	Ce (mg/L)	%A	$q_{e,exp}$ (mg/g)	Freundlich Isotherm		Langmuir isotherm		
				$q_{e,cal}$ (mg/g)	SSE	$q_{e,cal}$ (mg/g)	R_L (L/g)	SSE
0.479	0.003	99.31	0.048	0.051	1.4E-05	0.004	0.740	0.002
0.974	0.049	94.95	0.092	0.170	6.0E-03	0.059	0.584	0.001
2.808	0.382	86.41	0.243	0.421	3.2E-02	0.368	0.327	0.016
4.503	0.395	91.24	0.411	0.427	2.8E-04	0.378	0.233	0.001

9.515	0.732	92.31	0.878	0.562	1.0E-01	0.589	0.125	0.084
14.728	1.544	89.51	1.318	0.783	2.9E-01	0.895	0.085	0.179
19.716	4.972	74.78	1.474	1.316	2.5E-02	1.323	0.065	0.023
					4.5E-01			0.306

Table 17 Effect of co-existing ions on Phosphate adsorption

Anions		Nitrate	Sulfate	Bicarbonate	Carbonate	Chloride	Mixed
0	A	93.27	93.27	93.27	93.27	93.27	93.27
10	(%)	87.04	89.83	85.76	89.98	90.63	83.10
100		86.90	89.80	82.84	89.25	87.10	81.90
300		84.67	88.74	82.36	93.07	91.88	68.74

Table 18 Effect of agitation time on Phosphate desorption

Co (mg/L)	Time (min)	Regeneration for 0.2 M NaOH			Regeneration for 0.1 M NaOH		
		q _e (mg/g) desorbed	q _e (mg/g) desorbed	(%) Desorbed	q _e (mg/g) desorbed	q _e (mg/g) desorbed	(%) Desorbed
9.52	5	0.65	0.406	62.72	0.331	0.406	51.04
9.52	10	0.73	0.526	72.11	0.433	0.526	59.40
9.52	15	0.77	0.594	77.28	0.524	0.594	68.19
9.52	30	0.80	0.696	86.87	0.592	0.696	73.93
9.52	45	0.83	0.794	95.23	0.676	0.794	81.10
9.52	60	0.86	0.849	98.84	0.751	0.849	87.40
9.52	75	0.86	0.850	99.27	0.755	0.850	88.23
9.52	90	0.86	0.852	98.93	0.769	0.852	89.37
9.52	120	0.86	0.856	99.26	0.779	0.856	90.28

Table 19 Regeneration of adsorbent by cycle using 0.1 and 0.2 M of NaOH

Cycle	Adsorption (%)		Desorption (%)	
	TM			
	0.1 M	0.2 M	0.1 M	0.2 M
1	94.41	93.90	93.34	99.98
2	88.24	86.31	85.56	89.65
3	84.94	81.12	74.74	84.22
4	78.65	73.54	-	-