OBAFEMI AWOLOWO UNIVERSITY

COMPARATIVE EFFICIENCIES OF LIQUID HUMIC SUBSTANCES EXTRACTED FROM RAW AND COMPOSTED AGRO-WASTES ON PHOSPHORUS RELEASE FROM PHOSPHATE ROCK

BY

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A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF DEGREE OF MASTER OF SCIENCE (M. Sc.) IN SOIL SCIENCE

DEPARTMENT OF SOIL SCIENCE AND LAND RESOURCES MANAGEMENT,

FACULTY OF AGRICULTURE,

OBAFEMI AWOLOWO UNIVERSITY,

ILE-IFE, NIGERIA.

2015

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DEGREE: MASTER OF SCIENCE IN SOIL SCIENCE

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DEDICATION

This work is dedicated to God Almighty, the source and giver of all good gifts, and to All who have contributed to the success of this programme.

ACKNOWLEDGEMENTS

I wish to express my sincere and profound gratitude to my supervisor, Dr. (Mrs.) O. O. Adesanwo, for her guidance, firmness and understanding throughout the course of this study. I am much obliged for your incessant, fastidious yet motherly corrections and guidance. I will forever be grateful.

My heart-felt appreciation goes to my Co-supervisor, Dr. (Mrs.) G. O. Ogunlusi, for her willingness and readiness to assist at all times which contributed immensely to the success of this research work. Thank you so much.

I sincerely appreciate the Head of Department of Soil and Science and Land Resources Management, Prof. D. J. Oyedele as well as Professors A. A. Amusan, A. Olayinka, J. A. Adepetu and T. A. Okusami for their professional guidance, fatherly counsel and constructive criticisms all through the period of this research work. Many thanks to Dr. (Mrs.) M. K. Idowu and Dr. S. A. Muda for their invaluable support and encouragement at all times.

With deep sense of appreciation, I acknowledge Baba Wojuade, Messrs M. O. Fadeyibi, M.K. Alofe, R.S. Oyeyemi, Abiodun and Opeyemi. Mesdames Fabode, Baruwa, Olanrewaju and Oyeboade for their support.

To my colleague Fashina Tokunbo Bidemi, I say "thank you" for being a brother and a friend indeed. Your prompt attention, unrelenting effort and contribution to the success of this thesis cannot be measured. I am very grateful. To my senior and my other colleagues, Messers: Azeez, Atoloye, Ojetade, Atere, Akinwumi, Ekundayo, Aduroja Shittu, Olatoberu Tope, and my sisters Ruth Adegbenro, Bola Ogunrewo, Bunmi, Funmi, Adesuwa, Lizzy and many others whose names are not included here, I appreciate your assistance and encouragement.

Great acknowledgements to my parents, Mr. and Mrs. Oluwagbemiga Adeoye, Mr. and Mrs. Felix Molade, for their understanding and immeasurable support (spiritually, morally, financially and otherwise). I also owe an immense debt of gratitude to my brother, Adeoye Oluwatomide, for being there all the way long, for taking time to look through my work and forever reminding me that time is short. Big thanks to my sisters, Adeoye Adetola and Adeoye Omowumi (Mrs) as well as Rev. Frs. Martin Badejo, Felix Emerue, Anthony Omodunbi, Charles Akinloye and Henry Molade, Mrs. Wuraola Odediran, Dr. Akinsomisoye, Dr. Richard Akinwale, Mr. and Mrs. David Alao, the entire Akande and Adeoye families. God bless you all.

I am blessed with the unalloyed friendship, spiritual and financial support, understanding and encouragement of my darling husband, Olayinka Francis Molade. Thank you for believing in me, your sacrifices are invaluable incentives that saw me through.

Above all, to God the Almighty, the most powerful, the most merciful, the Most High - who knows the end from the beginning, I give all the glory and honour.

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LIST OF ABBREVIATIONS

1. FTIR – Fourier Transform Infrared
2. HA – Humic acid
3. HAs - Humic Acids
4. HPLC – High performance Liquid Chromatography
5. IHSS – International Humic Substance Society
6. LHS – Liquid Humic Substances
7. OPR – Ogun Phosphate Rock
8. P - Phosphorus
9. PR – Phosphate Rocks
10. SAW – Solid Agro-wastes
11. RCP – Raw Cocoa Pod
12. CCP – Composted Cocoa Pod
13. RPD - Raw Poultry Dropping
14. CPD – Composted Poultry Dropping
15. RSD – Raw Swine Dung
16. CSD - Composted Swine Dung

APPENDIX

ABSTRACT

The study compared the relative effectiveness of liquid humic substances (LHS) extracted from raw and composted agro-wastes on Phosphorus (P) released from solubilization of Ogun phosphate rock (OPR).

Liquid humic substances were extracted from dried raw and composted agro-wastes (swine dung, cocoa pod husk and poultry dropping) following the International Humic Substance Society (IHSS) standard procedure. Humic acid (HA) were precipitated by adjusting the LHS extracts to pH < 2 with concentrated H_2SO_4. The HAs were characterized using High Performance Liquid Chromatography (HPLC) and Fourier Transform Infrared (FTIR). Kinetics of P released from the dissolution of PR was carried out in duplicates by shaking 10 g OPR in 20 mL dilute LHS (5% volume basis) extracted from the raw and composted agro-wastes. The experiment was repeated with 10 g of raw and composted solid agro-waste (SAW) and 20 mL distilled water. The mixtures were shaken at regular intervals and then filtered. The filtrates were collected over time (2, 4, 6, 8, 10… 48 hrs) and were analyzed for available P using iron oxide-impregnated paper method. An incubation experiment was carried out to further monitor the release of P from OPR (0, 30 and 60 kg P ha^{-1}) added to 100 g of air-dried and sieved soil sample (Iwo soil series) using 20 mL LHS and 10 g SAW separately.

The HPLC chromatograms revealed the major peaks for all the samples at retention time(TR_1) of 1.43 -1.47 minutes with a larger peak area in all the raw than in the composted samples for example, HA in raw cocoa pod covered 67.25% while the composted cocoa pod was 46.57%. Analysis of the FTIR spectra showed that HAs from the raw samples had stronger absorption within the hydrophobic (except for poultry droppings) and hydrophilic signal regions than

composted samples, for example, absorbances of the raw and composted swine dung hydrophobic regions were 0.93 and 0.65 while the hydrophilic regions gave absorbances of 0.70 and 0.50 respectively. Similarly, the HA from raw samples showed stronger absorption for the acidic functional groups than composted samples (raw and composted poultry manure - 3.96, 3.69, cocoa pod - 3.90, 2.71 and swine dung - 2.37, 1.73, respectively). The kinetic results showed initial gradual increase in P concentration in all the treatments before a decline, followed by an increase and the data did not fit into any of the considered kinetic models. The incubation experiment showed higher concentrations of P released with SAW than LHS, there was no significant difference in P concentrations from raw LHS and composted LHS.

Therefore, LHS extracted from raw agro-wastes is recommended for OPR solubilization in order to save time and energy that would have been exerted into composting.

CHAPTER ONE

INTRODUCTION

Maintaining phosphorus (P) in the soil solution is important for sustainable crop production in the tropics. Nigeria soils, being tropical, are highly weathered, leached and have high P-fixation capacities as a result of the activities of aluminum (Al) and oxides of iron which fix P thereby rendering a substantial quantity of P unavailable for plant uptake (Lal, 1990; Adetunji 1995; Formoso, 1999). Phosphorus deficiency is so crucial and has been a major plant growth-limiting factor in West Africa (Sahrawat, *et al*., 1995) and its importance as a yield-limiting factor in many Nigerian soils is well established (Enwezor and Moore, 1966; Udo and Ogunwale, 1977; Adepetu 1983; Adetunji, 1994; Akinrinde *et al.,* 2005; Osundare, 2008). Therefore, the low nutrient status of these soils necessitates frequent application of P fertilizer for intensive cropping systems which is now the practice in Nigeria to ensure growth and adequate food production (Adetunji, 1991; Date *et al*., 1995; Omar, 1998). Rapid population increase, coupled with urban development, compete with agriculture for land use. Therefore, the need to intensify cropping on the available land for crop production informed the need for an imperative, urgent and sustainable means of replenishing soil solution P.

While nitrogen inputs can be obtained from sources such as biological nitrogen fixation (Ezama *et al.*, 2002), crop residues and other organic sources, appreciable P inputs is often sourced from "imported, scarce and expensive" water soluble P-based mineral fertilizers such as single superphosphates (SSP) and triple superphosphate (TSP) fertilizers by farmers in Nigeria. The average annual importation in the last 5 years was around 560,000 metric tons (Ahmed, 2012) which are often in limited supply as well as very expensive for most farmers and neither can the financial resources in the country sustain importation nor establishment of more fertilizer plants. In addition, recent findings have shown that the excessive use of mineral fertilizers, due to lack of technical know-how on the part of farmers, could be detrimental to the soil and the environment (Sharpely *et al*., 1994; Capenter *et al*., 1998; Ogbodo, 2013; Govinda, 2014) which necessitates the current campaign for a reduced use of agrochemicals and efficient application of natural materials in agro-ecosystems (Rajan *et al.,* 1996). For the aforementioned reasons and many more, the use of mineral fertilizer as a means of maintaining soil fertility is gradually reducing thus necessitating the need for a sustainable, environmental friendly and low-cost alternative. Direct application of Phosphate Rock (PR) as P supplement in soil is globally recognized and has been found to be suitable and effective on acid soils (Khasameh and Doll, 1978; Chien, 1992; Rajan *et al*., 1996; Zapata, 2003; Fankem *et al,* 2006) in Nigeria (Adediran *et al*., 1998; Akande *et al*., 1998). Vast deposits of PR have been discovered in different ecological zones in Nigeria (Adegoke *et al.,* 2003) which are currently being underutilized but can serve as the urgent alternative needed to solve the problem of high cost and scarcity of mineral P fertilizers (Adesanwo *et al.*, 2010). Phosphate rocks are slow-release P fertilizers and due to the extensive time lag needed for their solubilization, numerous studies have been conducted to enhance their rates of dissolution as well as increase their immediate P availability (Kpomblekou *et al*., 1991; Rajan and Watkinson, 1993; Bolland, 1996; Adediran and Sobulo, 1998; Adel *et al*., 2012) such as thermal amendment (Dash *et al*., 1990; Rautaray *et al*., 1995), partial acidulation (Rajan and Marwaha,1993; Menon and Chien, 1996; Chien, 2003), biological methods using microbial organisms (Illmer and schemer, 1992; Goenadi *et al*., 2000; Whitelaw, 2000; Alloush and Clark, 2001; Richardson, 2001; Nahas, 2004; Alikhani *et al*., 2006; Chuang *et* *al*., 2006) as well as the use of liquid humic substances (Martinez *et al*., 1984; Chien and Aviad, 1990; ; Banfield and Hamers, 1997; Chien *et al*., 1999).

Humic substances (HS), derived from plant and animal remains, are the largest constituents of soil organic matter (SOM) and are responsible for many complex chemical reactions in the soil (Stevenson, 1994). Because of their acidic nature as a result of the presence of functional phenolic and carboxylic groups, they have been employed to improve the effectiveness of PR by causing the release of phosphate and calcium ions from apatite (Sinha, 1971; Lobartini *et al*., 1994). Huge quantities of agro-wastes are generated in Nigeria on daily basis and their poor management constitutes great threat to the welfare of the populace. Composting had been found to enhance P release from PR (Kamh *et al*., 1999; Vanlauwe *et al*., 2000a; Horst *et al*., 2001; Akande *et al*., 2006; 2005). However, the bulky nature of the compost, emission of odious gases during composting which also contribute to global warming and long period of the composting process are problems which limit its wide applicability. For instance, cocoa pods take eight months for maturity of its compost. It is then envisaged that since HS are the active components of the organic materials and can be extracted from organic wastes/materials, application of the liquid form of HS extracted from raw and composted agro-wastes should solubilize PR faster than the direct use agro-wastes. Thus, this research work was carried out to test the feasibility of using LHS and to compare the effect of LHS extracted from raw agro-wastes with LHS extracted from composted agro-wastes on the solubilization of PR. Hence, the specific objectives of this study were to