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Assessment of Information and Communication Technology in Business Education Programme in Tertiary Institutions in Delta State

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Abstract

The study assessed the availability and utilization of information and communication technology tools for business education programme in tertiary institutions in Delta State. Six research questions were raised to guide the study and two null hypotheses were tested at 0.05 level of significance for the study. The population of the study comprises of the Delta State University of Science and Technology, Ozoro; Delta State University, Abraka Polytechnic, Delta State College of Education, Warri, and Delta State College of Education, Mosogar. The descriptive survey design was used for this study. The instrument used was validated by three experts. Pearson's Product Moment Correlation coefficient was used to compute reliability of the instrument which yielded a correlation coefficient of 0.89. The entire sampled population was used for data analysis. Questionnaire was the instrument used for data collection. Data collected were analyzed using descriptive statistics. The t-test was used to test the hypotheses. From the results of the analysis, it was concluded that *the job performance of secretaries in tertiary??? institutions in Delta State is largely enhance positively by ICT tools utilization in the area of internet, spreadsheet, desktop publishing as well as available hardware while the challenges of ICT Tools pose a danger to business education programme. Respondents did not differ significantly on the utilization of ICT tools for business education programme based on gender and experience. Consequently, it was recommended among others that management of institution and organization should ensure that workable and effective ICT tools are made available to enhance and boost the performance of business education programme in tertiary institution in Delta State. Tertiary Education Trust Fund should assist to organize, seminars, training and re-training programme regularly and also purchase these ICT tools to improve business education performance. Focus should be on the provision of internet services in the institutions.*

Keywords: *Business Education, Programme, ICT Tools, Tertiary Institution, Organization.*

Introduction

In most countries of the world, the information revolution has altered many aspects of life significantly: education, commerce, employment, medicine, security, transportation, and entertainment. Consequently, information and communication technology (ICT) has affected in both good and bad ways- community life, family life, human relationships, education, careers, freedom and democracy Stanford (2015). The future looks bright for office and effective business education programme in the 21st century, as a result of major changes in the way the outside world operates. In the fast changing technological age in which we are, the importance of technological facilities to any business activities and indeed secretarial work in particular cannot be overemphasized and the development of skills cannot be achieved without practical work adequately furnished with the modern technologies. The role of the business education programme has changed over the past decades and management in the business world has changed. Technical advances, new business procedures, and global markets have contributed to the new demands of today.

The changes that have affected business education students in the work place also affect curriculum changes in programs training individuals for the education professionals, the course have only changed in nomenclature and not in scope. Igbinedion (2010) stated that business education which gave birth to office technology and management started in the United States of America in the 17th and 18th centuries, by the 19th and 20th centuries the course expanded rapidly to some developed countries and developing countries. Igbinedion (2010) also explained that business education programmes is a specialized phase of vocational education that prepares students to enter teaching and office occupations as capable and intelligent members of the office force. According to Igbinedion (2010), business function with particular reference to secretarial education has changed everywhere in the world and have undergone a lot of technical changes.

The diversities of these office technologies require the office manager to possess new skills and sub-skills to enable her to be relevant in the modern office work. The role of business education has changed tremendously. (Atakpa 2010), Technology has reshaped the way information is created, stored and disseminated. Business education practitioners are assuming new administrative duties in the electronic office. This new role includes gathering of information, selection of relevant data, incorporating meaningful graphics and presentation of a final report to management. In the new office, business educators must have the ability to make independent decisions and to deal with business internationally. Business professionals are becoming information specialists. Technology is the driving force behind much of the change. Today's business education programmes in addition to word processing are knowledgeable in dealing with voice mail and electronic mail, local area network, budgeting, computer maintenance, desktop publishing, spreadsheets and database applications. The indispensable role of information communication technology forms the bedrock and overall development of any nation. Based on this, great attention is given to the need of information technology to business education programs in higher institutions that would enhance their job performance. The rapid advancement in technologies and new innovations has made tremendous impact on information and communication technology (ICT). Informative tools are application that provide large amounts of information in various forms such as e-business, e-communication, e-purchasing, e-marketing, e-financing, e-learning and e-service and has practically permeated every spheres of human Endeavour. The internet is a huge electronic database and researchers consider the internet as the most significant ICT tool. Apart from created various business needs, wants and challenges and has opened new opportunities like all these make use of electronic devices to conduct business practices on-line. These new opportunities pose enormous challenges to business education programmes.

International Association of Administrative Professionals (IAAP) (2015) the future of information and communication technology will be increasingly mobile with the use of multifunctional wireless office technology and information system such as mobile note-taker, web-based conference services and telecommunicating enabling office workers to perform their duties from virtually everywhere. Thus, it has become imperative that people from all works of life acquire some level of knowledge in the use and application of ICT. They also require skills in planning, organizing, communicating, time management and setting priorities. The nation's line and cry for basic skill had given impetus in the National Policy on education (2014). The first area to be given prominence was the search for technological *know-how*, the second was the pressure on the part of the employers of labour as well as the society in general, for courses that prepare students for jobs that would made them self-reliant as stipulated in the National Policy on Education 2014.

Information and Communication Technology (ICT) is those aspect of scientific, technological and engineering knowledge and administrative methods that are used to access and process information and its application, that is, the interaction between computers and tools with human beings and their social, economic and cultural matters, United Nations Educational, Scientific and Cultural Organization (UNESCO) (2004), Since computer courses are being offered at various levels and different institutions such as Colleges of Education, Polytechnics, Colleges of Technologies and Universities and they produces different personnel to act at different capacities in the field of work where they can contribute their quota to the nations development and business organization. In higher institution, the availability and utilization of computers had added to the training of business education students emerged as the need of human competences and material resources especially the availability of ICT facilities such as word processing, internet facilities like satellite disc, modern, computer private scanning, photocopiers, projectors, storage drive like flash, CD, video/DVD, television. Electronic record management no doubt is quite beneficial to administrative secretaries which include secretarial staff and office technology and management students as it assists them in the effective and efficient management, handling and use of records electronically. However, the management of records via electronic require electronic skills, knowledge and competence well as knowledge of the rudiments of how records are managed in an electronic environment. Igbinedion (2010), job performance is the extent to which the individual tend to maintain the same level of output overtime depending on the intrinsic rewords such as working conditions, status, motivation et cetera.

Statement of the Problem

The world is undergoing a rapid change due to the innovation of ICT as the new evolution continue, in order to cope with the age needs and to know how to assess the available ICT tools in business education programmes, it is an established fact that technology has reshaped the way information is created, stored and disseminated, it is the driving force behind much of the change. Today's business education graduates, in addition to word processing are knowledgeable in using photocopier, printer, computer, fax, voice mail, desktop publishing, spreadsheets database applications and internet. They also require skills in planning, organizing, communicating, time management and setting priorities and assuming new administration in the business world, among Delta State Polytechnic students in Nigeria, business education graduates are becoming information specialists.

The purpose of the study involved the assessment of Information and Communication Technology tools available for business education programmes in tertiary institution in Delta State. Specifically, the study sought to identify the following:

1. To find out the type of ICT tools available for business education programmes in Delta State tertiary institution.
2. The extent to which the available ICT tools are used by business education graduates to enhance their job performance.
3. The extent to which the business education graduates are utilizing these ICT tools extensively to increase their job performance.
4. The extent to which Today's business education graduates in addition to word processing are knowledgeable in dealing with voice mail and electronic mail, local area network, budgeting, computer maintenance, desktop publishing, spreadsheets and database applications in tertiary institutions in Delta State.
5. The extent to which the new opportunities pose enormous challenges to business graduates' job performance in Delta State tertiary institution.
6. The extent to which business education programmes rely on the internet as a virtual textbook and reference library.

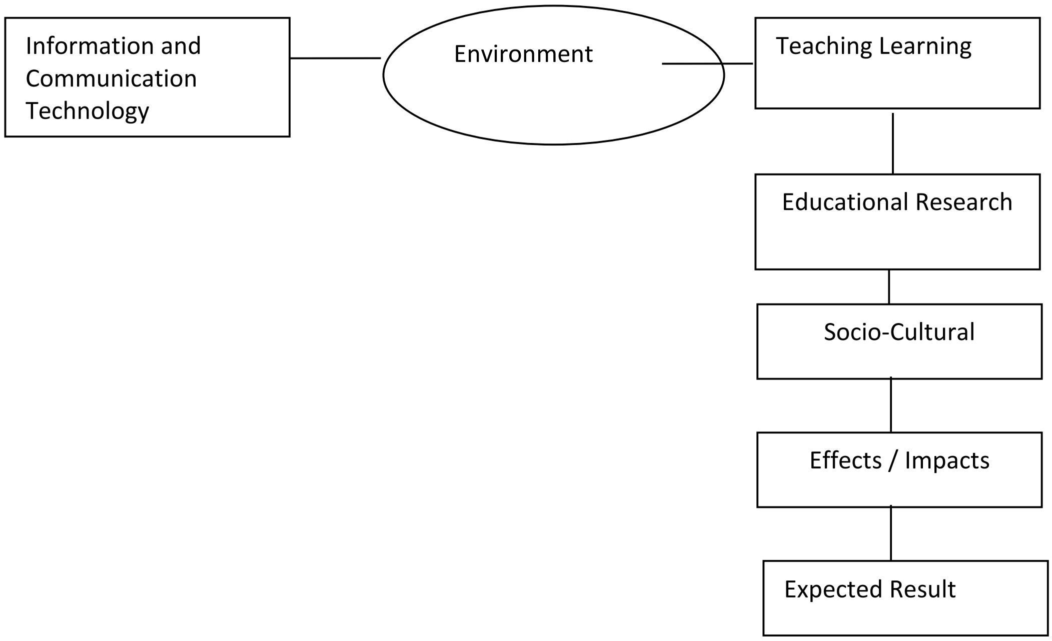

Figure 1: Conceptual model for the relationship between information and communication technology ICT the teaching learning process in some selected tertiary institutions in Delta State

Source: *Desk Research (2024)*

Research Questions

1. Does information and communication technology contribute to teaching learning activities?
2. To what extent does information and communication technology contribute to educational research activities?
3. Does information and communication technology have any impact on the socio-cultural activities of education?
4. What is the level of impact of information and communication on; the teaching learning environment in tertiary institutions in Delta State?

Research Hypotheses

Hypothesis One

Ho: There is no significant relationship between information and communication technology and the teaching learning environment.

Hi: There is significant relationship between information and communication technology and the research environment.

Hypothesis Two

Ho: There is no significance relationship between information and communication technology and educational research environment.

Hi: There is significant relationship between information and communication technology and educational research environment.

Hypothesis Three

Ho: There is no significance relationship between information and communication technology and socio-cultural environment.

Hi: There is significant relationship between information and communication technology and socio-cultural environment.

Literature Review

Concept of Information and Communication Technology

The term information and communication technologies (ICT) refers to forms of technology that are used to transmit, process, store, create, displays, share or exchange information by electronic means. The broad definition of ICT includes such technologies as radio, television, video, DVD, telephone (both fixed line and mobile phones), satellite systems and computer and network hardware and software, as well as the equipment and services associated with these technologies, such as video conferencing, e-mail and blogs. Njoku (2012) opines that ICT as the traditional and modern technologies of disseminating information. The traditional ICT products are the printed page, radio, television films and so on, while the modern technologies include e-mail, voice mail, fax, internet, electronic bulletin boards and cellular telephones. He goes further that communication is essentially central to every human activity. ICT in any giving society are facilities for normalizing, enhancing and improving the communication process in the society. Miller and Akume in Akpomudjere (2014) asserts that the term information and communication technology (ICT) originated from earlier terms such as information technology (IT) and new technologies (NT) which deal with accessing, gathering, manipulating and making available information communication for an enhanced learning and such technologies can be found in a host of devices, software applications, computers and connectivity, access to network, local networking, infrastructure, teleconferencing or web-conferencing among others.

Federal Ministry of Education (2010) refers to information and communication technology as the art and applied sciences that deal with data and information which comprising all equipment and tools (inclusive of traditional technologies of radio, video and television to the newer technologies of computers, hardware, firmware as well as the methods, practices, process, concepts and process. Information and communication technology ICT is technology that supports activities involving information. Such activities include gathering, processing, storing and presenting data. Increasingly these activities also involve collaboration and communication. Hence information technology has become ICT. Information and communication technology, or ICT, is defined as the combination of informatics technology with other related technologies, specifically communication technology. It is a concept which is used to describe the strength and divergent used of computers and telecommunication devices for data and information interchange. ICT provides access to information through scientific convention founded on the forte of computers and telecommunication facility which enables a companies located anywhere in the world has a business link. Information and communication technology (ICT) depends on the local culture and the particular ICT available and how it is configured and managed. Many countries now regard understanding ICT and mastering the basic concepts of ICT as part of the core of education, alongside reading, writing and numeracy.

Concept of Information and Communication Technology in Business Education Programme

The development of business education programme could be traced to the early missionaries who came to Nigeria with the mission to spread the gospel. They recruited and trained some local natives whom they used as interpreters and clerks, Osuala (2018). The European traders who traveled widely through the coasts and creeks of the Niger Delta purely on trade mission, later established trade station at designated points and appointed local trade agents who performed the complex tasks of receiving goods, keeping records of transaction, making payments and rendering accounts to the European trade masters regularly. To a great extent, the quality of trust, confidence and honesty desired of every business professionals seemed to have been associated with the early trade agents who doubled both sales representative and secretaries. The view of Monka (2019), the emergence and subsequent development of office administration and business education programme in Nigeria could be traced to two angles namely, office administration in both private companies and in the civil service. Monka recorded that the earliest European companies such as Royal Niger Company, West African company, the William Brothers and James Pinnock, all establishes trade offices in Lagos and Ibadan to achieve their objectives; these firms depended on the missionaries for trained local natives as interpreters and recording clerks. Ebeku & Ebenezer (2019), outlined that the amalgamation of the four major companies in the then West African into what was known as United African Companies (UAC) boosted the growth and development of secretarial work alongside general increase in trade volume in Nigeria.

The Impact of Information and Communication Technology (ICT) on the Teaching Learning Process.

Learning ICT skills is not sufficient, but using them to improve the teaching and learning environment is the key for pedagogy-technology integration. Understanding the changing role of teachers from instructors to facilitators, teacher-led instruction to learner centered instruction is the key to the successful implementation of pedagogy integration for teacher and learning environment is crucial. Nigerian teachers need to be equipped with the fundamentals of how ICT tools and to have a sufficient understanding of how the integration of these tools in the effective teaching-learning process can be smoothly facilitated. Effort must be oriented towards changing the teachers' mind-set by developing positive attitude towards ICT applications in teaching and learning Shyamal, 2015. Teaching and learning for the effective business education programme should be effectively and efficiently reorganized to reflect the emphasis on the use of ICT in educational service delivery. Information and Communication Technology should be effectively utilized in business activities to match graduate with the current demands of modern organizations. An elaborate use of ICT in business education programme will, in no small measure, assist Nigeria to achieve her vision 2020. According to Shyamal (2015), ICT include all the electronics means for gathering, processing, storing, sharing and distributing information, knowledge and ideas. Information and Communication Technology has integrated the world into a global village thereby making the processing, production, marketing and consumption of knowledge, skills, goods and services very easy without distance barriers.

It encompasses all forms of information delivery systems that use multi-media among others. It is one of the major innovations that are taking place in Nigeria education system, particularly in tertiary education level. The introduction of ICT in teaching and learning methods in Nigeria has affected the whole process of educational service delivery (Eze, 2019).

Integrating Information and Communication Technology as a tool in Research and Socio-Cultural Education

Information and communication technology is an umbrella term that includes any communication device or application, encompassing, radio, television, cellular phones, computer and network hardware and software, satellite systems and as well as the various services and application. Abduluraham (2017) adds that ICT is the integration of data with wired or wireless devices to transforming messages from one point to another across networks linking the various devices to achieve a desired result. It is the process of conveying information through automated electronics devices, such as computer, television, cell phone, electronic mail among others. If Information and Communication Technology can contribute to universal access to education, equity in education, the delivery of equality learning and teaching, teacher's Professional development and more efficient education management, governance and administration. UNESCO (2017) took a holistic and comprehensive approach to promoting ICT in education. Access, inclusion and quality are among the main challenges they can address.

The Organization's Intersectional Platform for ICT in education focuses on these issues through the joint work of three of its sectors: Communication and Information, Education and Science. It has been demonstrated that integrating ICT into education systems can increase the quality of education delivery. All governments aim to provide the most comprehensive education possible for their citizens within the constraints of available finance. Because of the pivotal position of ICT in modern societies, its introduction into tertiary institutions will be highly on any political agenda. In any educational system, the level of available resources places a restriction of the degree to which any new subject can be introduced into the school curriculum, especially where only the most basic facilities have so far been provided. The support services necessary for the effective delivery of an ICT-based curriculum should rank high in any set of government priorities. With a broad base of support, ICT in education will not only be in a position to continue its activities but will be able to develop new approaches and strategies.

Methodology

The study adopted the cross-sectional survey in its investigation of the variables (factors). Primary source of data was generated through structured questionnaire. The population of the study was 100 office personnel randomly selected from the organizations. A sample of fifty (50) respondents was calculated using the Taro Yamen's formula for sample size determination. 36 copies of questionnaire were returned and used for data analysis. The reliability of the instrument was achieved by the use of the Cronbach Alpha coefficient with all the items scoring above 0.07. Data generated were analyzed and presented using both descriptive and inferential statistical techniques. The hypotheses were tested using the chi-square formula.

The tests were carried out at a 0.05 level of significance.

Data Table and Result

Table 1:

S/n	Variables	Research Questions	Response (Optional)	Male	Female	Percentage %	Row Total
1	Information and Communication Technology and the Teaching Learning Process.	Does information and communication technology have any positive effect on the teaching learning process in education?	Yes	10	16	72	26
			No	6	4	28	10
			Column Total	16	20	100	**36**
2	Information and Communication Technology and Educational Research Process.	Does information and communication technology impacts on educational research process?	Yes	20	16	100	36
			No	-	-	-	-
			Column Total	20	16	100	**36**
3	Information and Communication Technology and the Socio-Cultural Education..	Does information and communication technology have any role to play in the socio-cultural aspect of education?	Yes	12	8	56	20
			No	11	5	44	16
			Column Total	23	13	100	**36**

Source: *Field survey 2025.*

Data Analysis and Results

Ho_1: There is no significant relationship between information and communication technology and the teaching learning process in education in tertiary institutions in Delta State.

From table 1 above to get the frequency expected the following formula was used.

$$Fe = \frac{\text{Row total x Column total}}{\text{Grand total}}$$

$$\text{Fe for } 10 = \frac{26 \times 16}{36} = 11.5$$

$$\text{Fe for } 16 = \frac{26 \times 20}{36} = 14.4$$

$$\text{Fe for } 6 = \frac{10 \times 16}{36} = 4.4$$

$$\text{Fe for } 4 = \frac{10 \times 20}{36} = 5.5$$

The Chi-square formula was applied = $\frac{\sum (fo - fe)^2}{fe}$

Fe	Fe	Fo – Fe	$(Fo - Fe)^2$	$X^2 = \frac{\sum (fo - fe)^2}{fe}$
10	11.5	-1.5	2.25	2
16	14.4	1.6	2.56	2
6	4.4	1.6	2.56	2
4	5.5	-1.5	2.25	2
			Calculated value	8

To get the Degree of freedom (Df) we apply the following formula:

(Row -1) (Column -1)

= (2-1) (2-1)

= 1 x 1 =1

Level of significance = 5% (0.05)
Degree of freedom 1 at 5% level of significance = 3.841
Table value = 3.841

Decision – since the calculated value of 8 is greater than the table value of 3.841, we reject the null hypotheses and accept the alternate hypothesis, meaning there is a significant relationship between information and communication technology and the teaching learning process in tertiary institutions in Delta State.

Ho_2: There is no significant relationship between information and communication technology and educational research process in tertiary institutions in Delta State.

From table 1 above to get the frequency expected the following formula was used.

Fe = $\frac{\text{Row total x Column total}}{\text{Grand total}}$

Fe for 20 = $\frac{20 \times 20}{36}$ = 11.1

Fe for 16 = $\frac{16 \times 16}{36}$ = 7.1

Fe for 0 = $\frac{0 \times 20}{36}$ = 0

Fe for 0 = $\frac{0 \times 16}{36}$ = 30

The Chi-square formula was applied = $\frac{\sum (fo - fe)^2}{fe}$

Fe	Fe	Fo – Fe	$(Fo - Fe)^2$	$X^2 = \frac{\sum (fo - fe)^2}{fe}$
20	11.1	8.9	17.8	2
16	7.1	8.9	17.8	2
0	0	0	0	0
0	0	0	0	0
			Calculated value	4

To get the Degree of freedom (Df) we apply the following formula:

(Row -1) (Column -1)

= (2-1) (2-1)

= 1 x 1 =1

Level of significance = 5% (0.05)
Degree of freedom 1 at 5% level of significance = 3.841
Table value = 3.841
Decision – since the calculated value of 4 is greater than the table value of 3.841, we reject the null hypotheses and accept the alternate hypothesis, meaning there is a significant relationship between information and communication technology and educational research activities.

Ho_3: There is no significant relationship between information and communication technology and the socio-cultural aspect of education in tertiary institutions in Delta State.

From table 1 above to get the frequency expected the following formula was used.

$$Fe = \frac{\text{Row total x Column total}}{\text{Grand total}}$$

$$\text{Fe for 12} = \frac{20 \times 23}{36} = 12.7$$

$$\text{Fe for 8} = \frac{20 \times 13}{36} = 7.2$$

$$\text{Fe for11} = \frac{16 \times 23}{36} = 10.2$$

$$\text{Fe for 5} = \frac{16 \times 13}{36} = 5.7$$

The Chi-square formula was applied = $\frac{\sum (fo - fe)^2}{fe}$

Fe	Fe	Fo – Fe	$(Fo – Fe)^2$	$X^2 = \frac{\sum (fo – fe)^2}{fe}$
12	12.7	-0.7	-1.4	1
8	7.2	0.8	1.6	2
11	10.2	0.8	1.6	2
5	5.7	-0.7	-1.4	2
			Calculated value	7

To get the Degree of freedom (Df) we apply the following formula:

(Row -1) (Column -1)

= (2-1) (2-1)

= 1 x 1 =1

Level of significance = 5% (0.05)
Degree of freedom 1 at 5% level of significance = 3.841
Table value = 3.841

Decision – since the calculated value of 7 is greater than the table value of 3.841, we reject the null hypotheses and accept the alternate hypothesis, meaning there is a significant relationship between information and communication technology and the socio-cultural aspect of education.

Discussion of Findings

Based on the data analyzed on this research article, the following findings were deduced;'

Ho$_{1}$: - this hypothesis (variables) is based on the relationship between information and communication technology and teaching learning process. From the data gathered through the questionnaire, 26 respondents representing 72% of the total respondents agree (Yes) that information and communication technology is significant to the performance and efficiency of the teaching learning process in education. 28% of the total respondents disagree (No), representing ten (10) respondents. However, from the above analysis it is agreed that information and communication technology contributes greatly to the teaching learning process.

Ho$_{2}$: - this hypothesis (variables) is based on the relationship between information and communication technology and educational research activities. From data collated in table 1 above, all thirty-six (36) respondents representing 100% agree (Yes) that information and communication technology have a significant relationship with educational research activities. This very much implies that information and communication technology is 100% contributory to educational research activities.

Ho$_{3}$: - this hypothesis (variables) is based on the relationship between information and communication technology and the socio-cultural aspect of education. From data collated in table1 above, 20 respondents representing 56% of the total respondents agree (Yes) that information and communication technology is immensely contributory to the socio-cultural aspect of educational activities. While sixteen (16) of the respondents representing 44% disagree (No). This implies that the alternate hypothesis is accepted and the null hypothesis rejected. Thus, there is a significant relationship between information and communication technology and socio-cultural activities.

Conclusion

This work has been able to present and conclude the fact that information and communication technology is instrumental to the success of educational activities and processes, which could be applied in any dimension of educational activities. It has also proven that information and communication technology is very instrumental and paramount to the socio-cultural aspect of our education. Also this research work has proved that information and communication technology plays an important role in educational research activities. Thus, information and communication technology must be treated properly, if educational set goals and objectives are to be achieved.

Recommendations

Based on the findings of the research work, the following are recommended.

1. That information and communication technology tools should be provided adequately by government and private owned institutions and should be functional.

2. Institutions should evolve the practice and principles or periodically reviewing these information tools to suit and keep abreast with changing educational needs, as this will booster the teaching learning process.

3. Institutions be it government or private owned should ensure that these tools are practically used to enhance the educational quality of graduate students in the labour market.

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School Inspectors Monitoring Services and Teachers Effectiveness in Public Junior Secondary Schools in Rivers State

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Abstract

The study investigated the difference between school inspector's plant monitoring service and its influence on urban and rural teacher's school effectiveness in public junior secondary schools in Rivers state. The study was carried out in Rivers state. The study adopted descriptive research design. Two purposes, specific objectives, research questions and two null hypothesis guided the study. The population of the study comprises of 8, 045 educations in the 23, local government areas in Rivers state. The sample of the study consisted of 804.5, been 10% of the entire population. The researcher structured questionnaire titled school inspectors monitoring service for teacher's effectiveness (SIMSETEIPSO), This instrument was divided into two section, A and B. The A section contains information related to personal data, while B, section is structure in the four point likert scale model, of strongly agreed = 4 points, agreed = 3 points, disagreed =2, strongly disagreed =1point. The research adopted face validation by three experts with a reliability index 0.85. The instrument was administered to the respondents and retrieved by the researcher. The responses were calculated using mean and standard deviation, to determine the significance difference of 3.00 and above as accepted, while 2.99, lower will be rejected, otherwise accepted. The study revealed that school inspectors plant monitoring service to a high extent, influence urban, rural teacher's effectiveness in public secondary school in Rivers State.

Keywords: *School inspectors, monitoring service, Teachers Effectiveness,*

Introduction

The acquisition of knowledge and skills enables individuals to increase their productivity and improve their quality of life. The increase in productivity also leads forwards new sources of earning which enhance the economic growth of a country. Education is the tool for the integration of the individual into a society so that the individual can achieve self-realisation, develop national consciousness, promote unity and strive for social, economic, political, scientific, cultural and technological progress. Education is the aggregate of all the processes by which a child or young adult develops the abilities attitudes and other forms of behaviours which are of positive value to the society in which we live. It is a life-long process. It begins with the birth of a child and ends with his death. It is a continuous process. Continuity is the law of life (Kumar, 2015). Kumar opined that education is not limited to the classroom only. It is not limited to a particular period of life but throughout life. One goes on learning to adjust oneself to the changing patterns of life. Change is the fundamental law of human existence. Life is a continuous process of growth and development and so education is also a continuous process.

Secondary education is the intermediary between primary and tertiary institutions in Nigeria (Federal Republic of Nigeria, 2024). Secondary is an educational institution where the second stage of the three schooling period known as secondary education and usually compulsory up to a specified age takes place. It follows elementary or primary education and is sometimes followed by university education. Secondary education is the education children receive after primary education and before the tertiary stage, (Federal Republic of Nigeria, 2013).

Secondary education is education that normally takes place in secondary schools taking place after primary education and may be followed by higher educational or vocational training. For quality secondary education programme there is need for inspector monitoring services. The inspectors thus, need to be trained in all aspects of school administration and in the area of inspection. They also need to be well–informed about the modern methods in their disciplines, training in effective communication is thus imperative for them to discharge their duties carefully (Mathew,2012). The inspectorate divisions of ministries of education are more direct in terms of contact with the school, the teachers and the pupils. They serve as a bridge between the school and government. They carry out observation, assessment and evaluation of school activities and achievement and provide or proffer solutions to the school problems. They improve the performance of teachers by offering professional encouragement guidance and counselling and by seeing to it that they get whatever in the service training they need to make promises they cannot fulfil to school. The inspector also performs the roles of supervision. The inspector implements the national policy on education in the school. Inspection is a process which strikes to stimulate the schools towards greater achievement of production part of the roles of those engaged in inspection for the purpose of stimulating schools towards greater effectiveness or productivity includes classrooms observation, lesson preparedness to raise the standard of education, through encouraging professional growth and development of teachers by giving them advice and furthermore. The most crucial supervisory activities include giving direction and advice, control simulation of effort towards goals attainment. Observation is part of inspection to determine when correction or adjustment ought to be made in a programme within schools (Anukan, 2019). Ijaiya, (1997), Mwanzi (2015), observed that training of school inspectors was essential as a means of providing them with necessary skills unique to supervise and to facilitate understanding of the modern method of inspection.

The inspectors should endeavour to guide and direct efforts of teachers towards the realization of the goals. This involve the understanding about various factors that motivate teachers acquiring the principles of and method of inspection that are known to be effective in assisting teaching and learning processes. According to Aiyepeku, (2017), identified the role of an inspector as a professional guide, the linkage between the schools and the policies of the ministry of education a professional who monitor the system in order to provide a feed back to the schools and the policy makers who regularly plan for the school system.This interrelationship helps build a strong bond between policy makers and the implementers. School inspectors are to ensure such educational policies, directives seculars and the societal goals and objectives are properly implemented. In Nigeria for example, after independence the leading education philosophy is worth development of the individual and for general development of the society. Which Nigeria still claim to follow. So a Nigeria national curriculum is a document in which the government has put what should be learnt in schools. School inspectors are the ones to ensure that schools follow what have been planned as objectives to be obtained. School inspectors are also expected to provide a continuous checking, reviewing and assessing the attainment and progress of pupils. Just as teaching activities are the core function, school inspector's core function is to inspect the school. It is meaningless for school inspectors to visit the school without checking what is going on in classrooms setting. School inspectors are to ensure that teachers are doing their jobs and that pupils are receiving what they are supposed to acquire as learning experiences.

Tracking institutional development, communication collaboration, sustainability and capacity building within an organisation and with its partners and stakeholders in relation to project implementation monitory, is an activity that involves countries and systematic checking and observing of programme or a project. It involves comparing the present situation with the past in order to find out the extent to which the laid down objectives haves been achieved. Monitoring is done in the education sector to monitor programmes like quality of education. Organizational monitoring is an activity that involves continuous and systematic checking and observing of a program or a project. It involves comparing the present situation with the past in order to find out the extent to which the laid down objectives have been achieved. Monitoring is done in the education sector to monitor programs like quality of education.

In education, two activities take place, these are teaching done by the teachers and learners by the students. Teachers, who teach in secondary schools, are usually degree or diploma holders in education. During training the teacher go through methodologies of teaching and therefore will be versed with good teaching practices. The principle is responsible for monitory and evaluation at the school level to ensure effective teaching and learning is going on (Williams, 2000). Monitoring is the systematic process of collecting analysing and using information to track a programme progress toward reaching its objectives and guide management decisions. Monitoring is an ongoing function that employs the systematic collection of data related to specified indicators. It provides management and the main stake holders of the development intervention with indications of the extent of progress and achievement of expected results and progress with respect to the use of allocated funds. Monitoring provides an early indication of the likely hood that expected results will be attained as well as an opportunity for validating programme theory and logic, making the necessary changes in programme activities and approaches. Monitoring provides essential imputes for evaluation and therefore constitutes part of all overall evaluation process. Organization monitoring tracks institutional development, communication, collaboration, sustainability and capacity building within an organisation and stake holders in relation to project implementation.

Monitoring is a means by which information is gathered, while evaluation is the judgement on the effectiveness of action taken based on the impact on the quality of children learning. In school which have a large population, there heads of departments and heads of subjects who also have a role in monitoring and evaluation of the teaching process. They report their findings every fortnight. There are various activities that are monitored and evaluated in the day to day teaching and learning process. These include teachers prepared documents, the physical attendance of classes by teachers and students reporting time. The learner’s reaction is also used to determine if the students enjoyed the lesson. Therefore, leading to conclusion as to whether learning has taken place or not. Teachers’ effectiveness has never been more important or controversial topic. Teachers are crucial to education system and school are only as good as the teachers within them (Darling – Hammond, 2015). For this study, teacher effectiveness was defined as a teachers ability to utilize approaches, strategies connections to students and a particular set of attitudes that leads to improved student learning and evaluation achievement (Stron,ward , &Grant, 2011). Evaluating the effectiveness of teachers, has changed over time due to increasing state and federal attention to school level accountability for student learning (Goe, Ball & Little,2018). Organisation monitoring goes on all the time, but particularly during speaking activities when the teacher is concerned with the general assessment of the learners performance in relation to general progress or recent language and skills development, (Goe,Bell & Little, 2018).

Monitoring of individual learners takes place during written practice exercises when the aim to point out errors and encourage self-correction, guided practice activities, particularly of the pair work format are monitored for accuracy, while less guided group work an activities are monitoring for task achievement and fluencies. Academic inspection and monitoring refer to the systematic evaluation and supervision of educational evaluation and supervision of educations programs of activities to ensure quality standards and accountability (DEED,2013). Inspection and monitoring are grouped into types, referring to internal inspection, external inspection usually conducted by institution, to evaluate program and activities and external agencies, such as government departments or accreditation bodies to evaluate institutions or programs and per view, involves evaluation by peers or experts in the same field. The components of inspection and monitoring are standards and criteria, according to European Association for Quality Assurance in higher education (EAQA, 2015). Standard are guide line for quality assurance in the European higher education area. Also, United National Educational science and cultural organisation (UNESCO,2018); Global convention on recognition of qualifications of higher education. Academic inspection involves assessing the teaching and learning processes as well as the overall academic environment. Monitoring instruction is an essential aspect of academic inspection.

It involves observing and evaluating the teaching methods and strategies used by instructors to deliver instructions. The purpose of academic inspection and monitoring instruction is to ensure that academic institution institutions meet required standards of education, identifying areas of improvement in teaching and learning, providing feedback to instructors to enhance their teaching methods and promoting accountability and transparency in academic institutions. This research was anchored on the critical theories propounded by the five Frankford school theoreticians: Herbert Marcuse, Theodore Adamo, Maxhortamer, Walter Benjamin and Eric Fromm. This concept was developed from new Marxist philosophy of the Frank school developed in Germany in 1930s. Critical theory calls for educational theory to accept the need to employ interpretative categories in different phenomenon, (Carr & Kemmis, 1986).

Statement of the Problem

Inspection depends heavily on a positive disposition of teachers towards inspectors and inspection. School inspectors have to play that role by ensuring the quality of pupils learning. Early inspectors were drawn from the civil servants and class room teachers due to lack of professionally trained inspectors. The falling standard of education has been a subject of controversy over the years. Some people are of the opinion that it is falling, while others believe that it is improving. However, the service of school inspectors in improving the quality of education has always been over looked by educational researchers and even education managers. In order words they lack of school of school inspectors monitory service should be responsible for deplorable state in terms of infrastructure effective facilities, equipment, teaching staff and students personnel services in the public junior secondary school system in Rivers State.

A common challenge amongst the secondary schools in the state is inadequacy of vital infrastructural facilities such as classroom, laboratory, hostels and staff houses. One other common challenges of secondary school are shortage of essential equipment and materials, such as text books. Lack of Plant monitory and the factors that account for urban and rural teacher's effectiveness makes teaching and learning very difficult. Insufficient number of teaching staff is also a common feature of the secondary schools. Most secondary schools either do not have adequate number of staff or the required type of teachers, Inspectors do not report to the ministry of education on the number and activities of teachers in secondary schools. There is no student personnel service related to feeding, health care, guidance and counselling services.

The inspectors do not care to find out whether all these services are provided to students in secondary school. This is caused by lack of proper inspectorate services. There is the need to train inspectors for their duties if they are to offer inspectorate services and know what they are supposed to do when they go out for inspection. In order to improve the quality education, there should be proper school inspectors monitoring services for the secondary schools; it creates a better atmosphere for teaching and learning in the school.

Aim/Objectives of the Study

The aim of the study was to examine the school inspector's plant monitoring services for teacher's effectiveness in public secondary school in Rivers state. Specifically, the study objective was to:

1. Ascertain the extent school inspector's plant monitory service influence the urban and rural teacher's effectiveness in Public Junior Secondary School in Rivers State.
2. Examine the extent the factors that account for urban and rural school inspectors monitoring services enhance in Public Junior Secondary School in Rivers State.

Research Questions

The following research question guided the study,

1. To what extent do school inspectors plant monitoring service influence urban rural teacher's effectiveness in Public Junior Secondary Schools in Rivers State?
2. To what extent do the factors that account for urban and rural school inspectors, monitoring service enhance teacher's effectiveness in Public Junior Secondary Schools in Rivers State?

Hypotheses

The following null hypotheses guided the study.

1. There is no significant difference in the mean rating of school inspectors on the extent school inspectors' plant monitoring services influence urban and rural teacher's effectiveness in Public Junior Secondary Schools in Rivers State.
2. There is no significant difference in the mean ratings of school inspectors on the extent factors that account for urban and rural inspectors monitoring services effectiveness in Public Junior Secondary Schools in River State.

Methodology

The study, adopted the description survey design. It is a type of design in which the researcher usually has no control over variables of interest being investigated and therefore cannot manipulate them. Usually data are collected after the event or phenomenon under investigation has taken place. Ahiakwo (2003), asserted that descriptive survey, the researcher is interested in drawing current sample, which is a representative of the population, collection of current data and primarily emphasizing the description of current pattern of behaviour of the variables concerned in the study, that allows some degree of generalization to the population. The study was conducted in Public Junior Secondary Schools, in Rivers State. The area of the study comprises of 23 Local Government in Rivers state, Nigeria. The population of the study consisted of all the 8,367 teachers in the, three hundred and twenty-one (321), urban public junior secondary schools in Rivers State. The 5980 comprised the population of teachers in the urban public junior secondary school in urban area, while 2,387 consist of the population of teachers in the Rivers State. The sample of the study comprised of 837, teachers (urban =583, rural =24), representing 10% of the population of the teachers in the public junior secondary schools in rural areas of Rivers state. A stratified random sampling method was adopted. A validated 4point rating scale questionnaire, with 30, item used determined with test-retest method. The instrument was administered to 30, respondents, who are not part of the sample of the study, but were part of the population of the study. The data collected from the two sub- set of administered questionnaire was analysed with the use of Pearson product moment correlation co -efficiency (r), at 0.5, level of significance to determine the reliability index of 0.81(81% percent reliable). The 837 copies of the questionnaire were administered directly by researcher to both teachers and students. Specifically, eight hundred and thirty-seven copies, that were administered, 805 copies representing approximately 89% percent of the total sample of the study were retrieved and used for the study. The arithmetic mean and standard deviation were used to analyse data to answer the research questions and established a criteria mean, while Z-test was used to test the hypothesis as 0.05 level of significance. This is in line with Nzereri, (2010), who ascertained that the population of Z- statistic is appropriate, when the sample size is greater than or equal to thirty. A mean rating that is equal to or greater than 2.9 would be regarded as high extent (HE), 2.49 and below as low extent (LE). The independent Z-test inferential tool was used to test the null hypothesis at 0.5 level of significance and reject calculated value if less than critical table value of 0.05 level of significance.

Result

Research Question: To what extent does school inspectors plant monitoring service influence urban and rural teachers, effectiveness in public junior secondary schools in Rivers State?

Table 1: Mean and standard deviation scores on the extent school Inspectors plant monitoring service urban and rural teachers, effectiveness in Public Junior Secondary Schools in Rivers State. = (n = 805).

Items Statement	Mean	Urban teachers = 564	Rural teachers =241	Standard deviation	Mean	Remark
Inspectors organize follow up inspection in secondary schools.	2.42	0.87	3.18	0.89	2.80	High extent
Inspector conducts subject inspection secondary school.	2.96	1.15	3.07	0.87	3.02	High extent
Inspectors conducts full inspection in secondary schools	2.97	1.12	3.00	1.09	2.99	High extent
Inspectors conduct full certification inspection in secondary school.	3.77	0.60	3.24	0.96	3.51	High extent
Principals are promoted on the basis of good implementation of the recommendation given by inspection	2.95	0.99	2.83	0.88	3.51	High extent
Total grand. **Mean & standard deviation**	**15.07** **3.01**	**4.73** **0.94**	**15.32** **3.06**	**4.69** **0.93**	**15.21** **3.04**	**High extent**

Source; Field Survey, (2025)

Table 1; this indicates that school inspectors plant monitoring service to a high extent influence urban and rural teacher's effectiveness in public junior secondary schools in Rivers state. This is because the respondents combine mean of urban and rural teachers is 3.01, which were above the criterion mean of 2.5. Both urban and rural teachers have a grand mean of 3.18 and 3.08, while standard deviation was 0.94 and 0.93 respectively. The respondents agreed that teachers comply to organize follow up. Inspectors conduct full inspection services in secondary school teaching. Inspectors conduct certification inspection and promote basis of good implementation of the recommendation given by inspector.

Research Question 2: Mean, and Standard on the extent school inspectors monitoring service influence factor that account for urban and rural teachers' effectiveness in Public Junior Secondary Schools in Rivers State (n=805)

Table 2: Mean and standard deviation scores on the extent school Inspectors plant monitoring service urban and rural teachers, effectiveness in Public Junior Secondary Schools in Rivers State. = (n = 805).

Items	Item Statement	Urban teacher =564	Rural teachers =241	Standard deviation	Mean set	Remarks
Decision making based on inspector's views.	2.66	1.08	3.28	0.71	2.97	High extent
Insufficient regular inspection in schools	2.40	1.03	3.59	0.82	3.00	High extent
Lack of efficiency and effectiveness	3.13	1.07	3.13	0.84	3.13	High extent
Administrative techniques and evaluation.	2.93	1.02	3.24	1.04	3.09	High extent
Poor communication of the result to education	2.88	1.02	3.14	0.99	3.01	High extent
Total grand **Mean & Standard deviation**	**14.00** **2.8**	**5.22** **1.04**	**16.38** **3.27**	**4.4** **0.88**	**15.20** **3.04**	**High extent**

Source: Field Survey, (2025)

Table 2: Indicate that school inspectors monitoring services, influence, factors that account for teacher's effectiveness in urban and rural public junior secondary schools in Rivers state o a high extent. This is because the respondents combine mean of urban and rural teachers is 2.8 which were above the criterion mean of 2.5. Both urban and rural teachers have a grand mean of 3.27 and 3.04, while standard deviation was 1.04 and 0.88 respectively. The respondents agreed that inspectors organise and participate in refresher courses for teachers. Inspectors conduct refresher courses, workshops seminars etc, as a means of implementing the inspection reports. The respondent also agreed that decision making based on secondary school's inspectors and insufficient regular inspection in school.

Hypothesis 1: There is no significant difference in the mean ratings of school inspectors on the extent their plant monitoring services influence urban and rural teacher's effectiveness in Public Junior Secondary Schools in Rivers State.

Table 3: Z-test on the mean ratings of school inspectors on the extent their plant monitoring services influence Urban and rural teacher's effectiveness in public junior secondary schools in Rivers State

Respondents	N	$\overline{X}$	SD	STD error	DF	U	Z-cal	Z-crit	Decision
Urban	564	3.01	0.94	0.005	8.03	0.05	1.71	1.96	Accepted
Rural	241	3.06	0.93						

Source: Field survey, 2025

In table 3, the Z-calculated value of 0.71 is less than Z-critical value of 1.96 at 0.05 levels of significance and 8.03 degrees of freedom. The null hypothesis is accepted indicating there in no significant difference in the mean responses of school inspectors on the extent their plant monitoring services influence urban and rural teacher's effectiveness in Public Junior Secondary Schools in Rivers State.

Hypothesis 2: There is no significant difference in the mean rating s of school inspectors on the extent the factors that account for teacher's effectiveness influence urban and rural teacher's effectiveness in Public Junior Secondary Schools in Rivers State.

Table 4: Z-test on the mean ratings of school inspectors on the extent their plant monitoring services influence urban and rural teacher's effectiveness in public junior secondary schools in Rivers State.

Respondents	n	X	SD	Std Error	DF	A	Z-cal	Z-crit	Decision
Urban teachers	564	2.8	0.98						
Rural teachers				0.005	803	0.05	6.71	1.96	Accepted
	241	3.27	0.88						

Source: Field survey, 2025

From the Z-test in table 10, the Z-calculated value of 1.78 is lesser than z-critical value of 1.96 at 0.05 levels of significance and 803 degrees of freedom. The null hypothesis is accepted. Indicating there is no significant difference in the mean responses of school inspectors on the extent their factors that account for teacher's effectiveness influence urban and rural teacher's effectiveness in Public Junior Secondary Schools in Rivers State.

Discussion of Findings

The results of this study were discussed bases on the research question raised and hypothesis tested.

The result of research question 1 showed that inspectors conduct certification inspection in secondary school. Principals are promoted on basis of good implementation of the recommendations given by inspection. This finding is in agreement with the view of Oyesola (2007), who depicts that school plant enhances better school programmers and the community needs by providing the place for psychological and physical safety for students and teachers enhance the quality and quantity of instruction. School plant availability and utilization include school location, instructional space, administrative space, classroom facilities, recreational facilities which are relevant in teaching and learning depends on the location of structure and facilities within the school environment.

A proper school in terms of location, structure and facilities would encourage effective teaching and enhance better learning environment, is done in the education sector to monitor. During training the teachers go through methodologies of teaching and are therefore well versed with good teaching practices. The principal is responsible for monitoring and evaluation at the school level to ensure effective teaching and learning is going on. In agreement with the view of Goe, Bell and Little (2018) opined that organizational monitoring goes on all the time, but particularly during speaking activities when the teacher is concerned with the general assessment of learner's performance in relation to general progress or recent language and skills development. Monitoring of individual learners take place during written practice exercises. When the aim is to point out errors and encourage self-correction. Guided practice activities, particularly of the pair work format, are monitored for accuracy, while less guided group work activities are monitored for task achievement and fluency. The researcher viewed that monitoring provides essential inputs for evaluation and therefore constitutes part of the overall evaluation process. Monitoring tracks institutional development, communication, collaboration, sustainability and capacity building within an organisation and with it partners and stakeholders in relation to project implementation.

The result of the research question 2, showed that factors that account for urban and rural school inspectors, monitoring services is lack of efficiency and effectiveness Poor communication of the results to education stakeholders and insufficient regular inspection in schools. This finding is in agreement with the view of Musaazi, (2012), who depicts that services in Nigeria. Scrutiny of new textbooks and other teaching materials relating to secondary schools and advising principals and teachers, accordingly. This finding is in agreement with the view of Owoeye and Yara, (2011), who depicts that utilization of resources in education bring about fruitful learning outcomes since resources stimulate students learning as well as motivating them. A common way to examine the utilization of instructional resources is to analyze school expenditure. Instructional resources have been observed as a potent factor to qualitative education. The importance to teaching and learning of the provision of instructional resources cannot be over-emphasized. Facilities and equipment constitute a strategic factor in organizational functioning and determine to a very large extent, the smooth functioning of any social organisation or system including education. Agreeing with Owoeye and Yara, Nwabuzor, (2010), opined that utilization of instructional resources promote effective teaching and learning activities in schools while their inadequacy and /or unavailability may affect the academic performance of the learner negatively. Utilization of instructional resources for the reaching of any subject in the school curriculum, business studies included is very crucial. In agreement with the views of Makewa, Role and Ngussa, (2012), depicts that the use of instructional resources that are related to the basic content of a lesson helps learners to understand a particular lesson. Utilization of instructional resources results to general improvement in teaching of business studies. The researcher viewed that business studies is a very crucial subject and as such instructional resources is very much needed for effective teaching and learning to take place. Instructional resources bring about fruitful learning outcome since pictures and drawings stimulate students learning as well as motivate them, inadequacy and unavailability may affect academic performance of the learners negatively. Utilization of instructional resources results to general improvement in teaching and learning.

Conclusion

Based on the findings of the study, the researcher concludes that as a result of inspection, principals begin to offer periodic positive guidance to experienced teachers. As result of inspection, there is improvement on public attitudes and school discipline. As a result of inspection teachers realize their weakness and improve themselves. Teachers displays a strong sense of financial accountability. The finance committee keep accurate records of meeting held. The financial school policy directs my school towards financial stability. The researcher also concluded that teachers comply to post supervision conferences. Inspectors promote the welfare of all staff members engaged in secondary school teaching. Inspectors attend meetings related to the training of teachers. Inspectors organise and participate in refreshers course workshops, seminars etc as a means of implementing the inspection reports. Scrutiny of new textbooks and other teaching materials relating to secondary schools and advising principals and teachers accordingly. Inspectors conduct certification inspection in secondary schools. Principals are promoted on the basis of good implementation of the recommendations given by inspection. Finally, it was concluded that factors that account for urban and rural school inspectors monitoring services is lack of efficiency and effectiveness. Poor communication of the results to education stakeholders and insufficient regular inspection in schools.

Recommendations

Based on the findings of this study and conclusion made, the following recommendation were put forward by the researcher:

1. Seminars, workshops and conferences should be organised each term at national state and local government levels. This will give each teacher the opportunity to attend at least one staff development programme a year.
2. Teachers should be involved in text books selection. For each subject competencies to be taught should be specified to guide selection of text books. The government should encourage teachers by financing textbook writing.
3. Inspectors should conduct full inspection in order to improve the nature of inspection in secondary schools. In carrying out inspection, inspectors should avoid chances that may lead to conflicts with the teachers as well as principals.
4. After inspection, some form of feedback should be given to teachers in secondary schools.
5. In order to make reliable evaluation of principals and teachers, their behaviour should be observed before making the final judgment.

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Comparative Study of Nano-Particles of Magnesium Oxide and Cow Dung for Hydrocarbon Polluted Soil Remediation

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Abstract

A comparative study of Nano particles of Magnesium Oxide and Cow dung for the remediation of hydrocarbon polluted soil was carried out in this research. The cow dung and loamy soil sample were obtained within Agricultural farm in River State University and the Magnesium Oxide particles were produced in Chemical Engineering laboratory, River State University. 300g of Loamy soil was weighed into 14 rectors. Out of 14 samples, 12 samples containing 300g of loamy soil were polluted with 100ml crude, while the remaining 2 served as control unpolluted soil. The 12 polluted sample were stirred for uniform mixing, 50ml of distill-water were added and stirred then left for 3 days. After 3 days, the samples were taken to the lab to analyze the following parameters; TPH, Bacterial, pH, density, moisture content and particle size. 3 days later the Nano-particles of Magnesium Oxide of masses of 5g, 10g, 15g, 20g, 25g and 30g were introduced into 6 separate reactors and also Cow-dung of masses 5g, 10g, 15g, 20g, 25g and 30g were introduced into 6 separate reactors, 2 samples of polluted soil were set as control. Each of the 14 samples were taken to the lab to analysis the TPH, Bacteria and pH for 1st week – 6th week in 45 days. At the end of the analysis, the percentage degradation of TPH in the 30g loamy soil sample obtained by biological method (cow dung) was 97.49%, 98.12%, 98.25%, 98.78%, 99.11% and 99.66% respectively while chemical method (magnesium oxide) was 91.35%, 93.62%, 97.05%, 98.36%, 98.97% and 99.09% respectively. The first order degradation rate constant, obtained across the treatment options ranged from 0.0159– 0.01243day^{-1} for biological method and 0.00161 – 0.1601day^{-1} for chemical method. The half-life analysis showed that chemical method may take the longest time for TPH to degrade half its initial concentration, and biological method is fastest in the soil samples. Also, the first order rate kinetics performed better than Michaelis-Menten equation. The Chemical method (using Nano-particle) slightly outperformed the biological method (using Cow Dung). Finally, the study showed that Nano-particle can be utilized as an alternative bio-stimulant for crude oil remediation. At the end of the analysis, for 30g mass of loamy soil, the percentage reduction of the pollutant was 99.66% when cow dung was used and 99.09% reduction was realized when Magnesium Oxide was used.

KeyWords: Soil, Hydrocarbon, Remediation, Cow Dung, Magnesium Nano-Particle, Kinetic Models.

Introduction

Oil is a major source of energy in Nigeria and the world in general. Oil being the Main stay of the Nigerian economy plays a vital role in shaping the economic and Political destiny of the country. Although Nigeria's oil industry was founded at the beginning of the century, it was not until the end of the Nigeria Civil War (1967 - 1970) that the oil industry began to play a prominent role in the economic life of the country. Nigeria can be categorized as a country that is primarily rural, which depends on primary product exports (especially oil products). Since the attainment of independence in 1960 it has experienced ethnic, regional and religious tensions, magnified by the significant disparities in economic, educational and environmental development in the south and the north. These could be partly attributed to the major discovery of oil in the country which affects and is affected by economic and social components. Crude oil discovery has had certain impacts on the Nigeria economy both positively and adversely. On the negative side, this can be considered with respect to the surrounding communities within which the oil wells are exploited. Some of these communities still suffer environmental degradation, which leads to deprivation of means of livelihood and other economic and social factors. Although large proceeds are obtained from the domestic sales and export of petroleum products, its effect on the growth of the Nigerian economy as regards returns and productivity is still questionable. Petroleum production facilities generate large quantities of oil wastes from drilling, production and processing activities. According to Odiete (1999), "all activities involved in hydrocarbon production and exploration normally have one impact or the other on the environment". The contamination of the environment by hydrocarbon process occurs through exploitation, transport, and leakage of crude oil storage facilities, which are released into the environment, thereby causing environmental pollution (Moro *et al.,* 2015).

Crude oil pollution in the air occurs via evaporation of volatile components or gas flaring, while on aquatic and land environments it can be via spillage from oil facilities. A study reported that land environment was the most affected of pollution from petroleum industry, mostly from leakage of pipelines, storage tanks and other oil facilities (Nnaji, 2017). Crude oil contains toxic compounds and radioactive elements that are serious health concerns, and also affects plant growth (Oyem & Oyem, 2013). Crude oil pollution, especially on soil, has the ability to bind soil particles together because of low water solubility that could reduce soil nutrients (Wang *et al.,* 2019). Most organic and inorganic chemicals are hazardous to soil, and can cause low yield of agricultural produce (Kuppusamy *et al.*, 2016). Various methods are used for the treatment of petroleum hydrocarbon polluted soil, but the choice of method depends on the cost effectiveness, ability to remove contaminants and availability (Yu *et al.,* 2020). The development of a sustainable method for the removal of petroleum contaminants from the environment is essential. In soil contaminated by petroleum hydrocarbons, methods such as biological, physical and chemical technique can be used to remediate a polluted soil (Yuniati, 2018). Bioremediation is a radiation technique that utilises microorganism or bio-stimulants such as enzymes, spent biomass and fertilizers to remove contaminants from contaminated environment through metabolic process (Kumar *et al.*, 2011). Bioremediation is economical, adaptable, efficient and eco-friendly to the environment (Jeon & Madsen, 2013). Bioremediation can be achieved implemented through bio-stimulation, bio-augmentation and phytoremediation, among others. Bio-stimulation refers to the use of fertilizer, plant and animal wastes, or any other agro based material as amendment agents, to stimulate the growth of microorganisms; while in bio-augmentation bacteria or fungi is directly applied to enhance the degradation rate of pollutant (Varjani & Upasani, 2017). In Phytoremediation, a plant is planted in polluted soil to take up the contaminant as it grows.

Most often, bioremediation process takes place in a system best described as reactor, which can be implemented in batch, or continuous reactors such as the fixed bed, fluidized bed and membrane reactors (Pino-Herrera *et al.,* 2017). The use of bioreactor ensures the growth of microbes necessary for the degradation of contaminants are controlled and monitored, thereby providing the necessary conditions to achieve an optimum process performance (Jeon & Madsen, 2013).

This study adopted the bio-stimulation method, implemented in batch reactor for bioremediation of Total Petroleum Hydrocarbon (TPH) contaminant in polluted loamy soils using Nano Particle and Cow Dung. Soil pollution arising from increasing demand for petroleum and its products has become a common problem in recent years. Soils polluted with petroleum hydrocarbons differ from unpolluted soils and are not able to support adequate crop growth and development. Hence, there is need to treat these soils so as satisfy the food requirement of the ever-growing population and also reduce the impact of crude oil in soil environment. Therefore, capability of Nano Particle and Cow Dung in degrading the (TPH & PAHs) in crude oil polluted loamy soils was investigated. The choice for the use of Nano Particle and Cow Dung as bio-stimulant was based on its essential nutrient, implying that it possesses the ability to stimulate hydrocarbon degrading bacteria necessary for effective bioremediation.

Materials and Methods

The experiments were conducted at the chemical Engineering Laboratory in Rivers State University, Port Harcourt Nigeria.

Materials

The materials used include Volumetric flasks: glass 10 and l00 ml, Agilent 6890 Gas chromatographs with a flame lunation Defector, pH meter with glass electrode, Thermometer, Glass beaker (100ml), Glass rod, Laboratory fume hood, Analytical balance, Glass ware, Mineral salt agar, Distilled water, Petri dishes**,** Scientific Calculator, Cow dung, Nano particle, sieve merge.

Preparation Nano particle

40g sodium hydroxide was dissolved in 250ml distilled water (exothermic reaction, co-precipitate method). 26g of Magnesium (ii) chloride was dissolved in 160ml of distilled water endothermic reaction ‘wet chemical method” both were mixed together to give a light yellowish substance.

6g of iron chloride ($FeCl_3$) was dissolved in 25ml of distilled water 14g of sodium hydroxide little by little to give a dark colour precipitation. Both the nanoparticle (magnesia oxide and fenton) reagent were dried into power form local grams produced 69.48 (magnesium oxide) +74.86 (magnesium oxide) = 144.34 grams.

Methods

300g of Loamy soil was weighed into 14 rectors. Out of 14 sample reactors, 12 samples containing 300g of loamy soil were polluted with 100ml crude, while the remaining 2 served as control unpolluted soil. The 12 polluted sample were stirred for uniform mixture, 50ml of distill-water were added and stirred then left for 3 days. After 3 days, the samples were taken to the lab to analyze the following parameters; TPH, Bacterial, pH, density, moisture content and particle size. 3 days later the nano-particles of Magnesium Oxide of masses of 5g, 10g, 15g, 20g, 25g and 30g were introduced into 6 separate reactors and also Cow-dung of masses 5g, 10g, 15g, 20g, 25g and 30g were introduced into 6 separate reactors, 2 samples of polluted soil were set as control. Each of the 14 samples were taken to the lab to analysis the TPH, Bacteria and pH for 1^{st} week – 6^{th} week in 45 days.

Physiochemical Properties of the Soil Sample

Physiochemical properties were analyzed; Total Bacterial Count (TBC), Phosphorus content, electrical conductivity, Total Nitrogen Content, Total Organic Carbon

Electrical Conductivity

The electrical conductivity meter was used to measure the electrical conductivity (EC) of the samples. The same procedure stated for pH measurement was used in the determination of EC. However, the EC electrode was thoroughly washed after each reading to avoid cross-contamination and error.

Total Organic Carbon

Total Organic Carbon (TOC) was determined using a method described by Umeda *et al.* (2017). Thus, 1.0g of soil samples was weighed into 250ml beaker, while 10ml of potassium dichromate solution was pipette into beakers and swirled gently to completely wet the soil sample. Thereafter, 20ml of concentrated H_2SO_4 was added using automatic pipette, and gently swirled for one minute to obtain a uniform suspension, as well as for effective and more complete oxidation before allowed to settle for about 30 minutes on asbestos sheet.

On settling, 100ml of distilled water was added followed by addition of 3-4 drops of 0.5 ml diphenylamine indictor. The solution was titrated with 0.5N ferrous sulphate solution until the colour changes from violet to blue and finally bright green colour. The process was repeated on distilled water (blank titration), but without soil to standardize the dichromate. The TOC was calculated according to the formula.

$$TOC = Blank - \frac{Volume\ of\ soil\ Sample \times 0.195}{weight\ \ of\ soil\ sample} \times 100\% \quad (2.1)$$

Total Nitrogen Content

Total nitrogen content was determined using APHA 4500-NO_3B method (APHA, 1998). Thus, 10g of grinded and sieved soil sample containing 10 mg of nitrogen in a dried 500ml Macro-Kjeldahl flask was weighed. It is swirled for about 2 minutes followed by the addition of 20ml of distilled water, and then, allowed to settle for 30 minutes. A tablet of 1g K_2SO_4-H_2O mixture (catalyst), 10g of K_2SO_4 and 30ml concentrated H_2SO_4 were added to prepared sample in the flask and heated cautiously on digestion stand. Upon the notice of water content and frothing, the heating was increased until a clear digest was obtained. The heating was regulated so that H_2SO_4 is about half way up the neck of the flask. After the heating process, the flask was allowed to cool, while 100ml of water was added slowly. The digest was carefully transferred into another clean 750ml Macro-Kjeldahi flask. All soil particles in the original digestion flask were retained due to the severe bumping soil can cause during the Kjeldahl distillation. Soil residue was washed with 50 ml distilled water four times and the aliquant transferred into same flask. Addition of 50ml H_3BO_3 indicator solution into a 500ml Erlenmeyer flask was followed, which was placed under the condenser of distillation apparatus. The 750ml Kjeldahl flask was also attached to the distillation apparatus. About 150ml of 10N NaOH was added into the distillation flask through the opening funnel, and the distillation was stopped after 150ml of the distillate was collected. The NH_4-N in the distillate was determined by titrating with 0.01N standard H_2SO_4 using 25ml burette graduated at 0.1ml intervals. The colour of the end point changed from green to pink. The percentage of nitrogen in the soil was calculated using equation (2.2).

$$N(\%) = \frac{(T - B) \times N \times 1400}{S} \times 100\% \quad (2.2)$$

Where: T = Sample Titration (ml), B = Blank Titration (ml), N = Normality of H_2SO_4 and
S = Sample weight (mg).

Phosphorous Content

Phosphorus content was determined according to APHA method $4500\text{-}PO_4^{3-}$ (APHA, 1998). 1.0g of representative soil sample was weighed into clean extraction flask and 10ml of Bray P-1 extracting solution (0.025N HCl and 0.03N NH_4F) was added and vigorously agitated for 1 minute before being filtered. 5ml of the filtrate was pipette into 25ml volumetric flask and diluted to about 20ml of distilled water, and then, by 4ml of ascorbic acid solution (1.056g ascorbic acid in 200ml molybdate-tartarate solution), which were diluted. The diluted solution was allowed to settle for at least 30 minutes. The recording of data was done after a clear colour has been developed.

Procedure for Total Bacterial Count (TBC) Analysis

Microbiological analysis enumeration of heterotrophic bacteria and fungi was carried out by pour plating technique. This was done by inoculating 0-1ml tenfold seriating diluted sample onto nutrients agar (bacterial), acidified streptomycin (1mg/100ml) (fungal) and mineral salt agar (MSA) (hydrocarbon degraders). The mineral salt media contains the following composition in gram per liter of distilled water, N_aC_L 10g, Mg $S0_4$. $7H_2.0$, 9.42g, K_{CL} 0.29g, $HP0_4$ 1.2g, KH_2P0_4 0.83g, $NaN0_2$ 0.42g, Agar – Agar 16g, pH 7.2 and 2 nill at petrol/Diesel. The inoculated nutrient agar plates were incubated at 37^0C for 24 hours while the potato dextrose Agar plates were incubated at room temperature counted and expressed as colony firming units per gram (Cfu/ml).

3. Results and Discussion

Table 4.1: Physicochemical Properties of 300g Soil Sample before and after Pollution

Parameters	Loamy Soil			
	Before	**After**	**Using Cow Dung**	**Using Magnesium Oxide**
pH	6.5	4.1	6.3	5.9
EC (µS/cm)	352.43	843.61	432.13	567.34
TOC (%)	2.56	5.38	2.3	3.10
P (%)	1.46	0.93	1.8	1.5
N (%)	23.02	0.07	33.00	26.12
K (%)	32.84	1.42	43.61	30.23s
TBC (cfu/ml)	4.98×10^3	2.16×10^2	13.81×10^5	9.51×10^5

The physicochemical properties of loamy soils before and after being polluted by crude oil are shown in Table 3.1. The change in the physicochemical properties of the after pollution shows that crude oil has significant impact on soil. From the analysis, it was shown that pH, phosphorus (P), nitrogen (N), potassium (K) and Total Bateria Counts(TBC) in the soils were reduced after the crude oil pollution. On the other hand, the electrical conductivity (EC) and total organic carbon (TOC) in the soils increased after the pollution.

Table 3 Total Heterotrophic Bacteria Count. The samples were analysed to ascertain the bacteria growth so as to determine the treatment option that has the most influence on TPH degradation under the Nano-particle Also, identification of hydrocarbon degrading bacteria and TPH analysis was conducted by the 7 days mark. The following were identified and isolated as hydrocarbon degrading bacteria in the analysis of bacteria isolates: Nano-particle (*Campylobacter sp*. and *Listeria monocytogenes sp).* The growth analysis of TBC at the various days is shown in Figures 3.1 to 3.2.

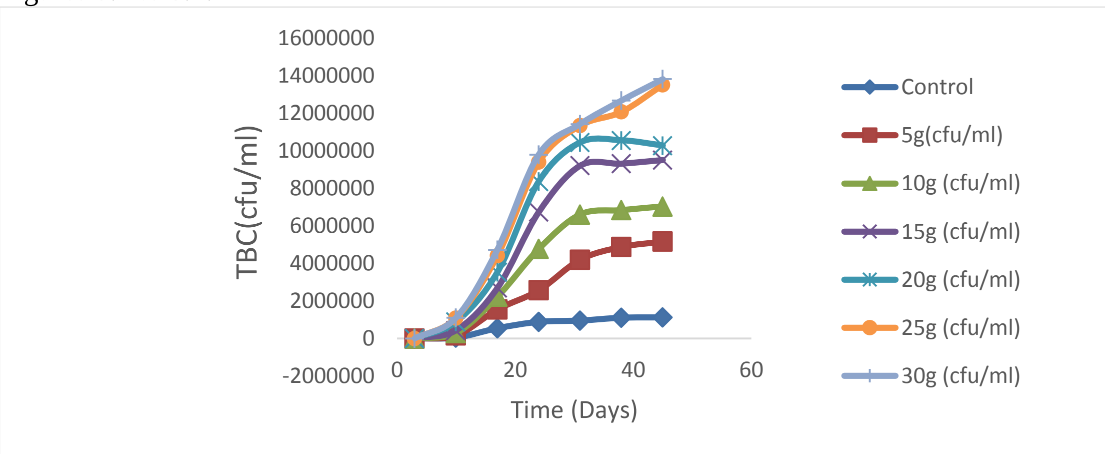


Fig 3:1 TBC Count Variation versus Time in Loamy Soil at Various Weights of Cow Dung Treatment.

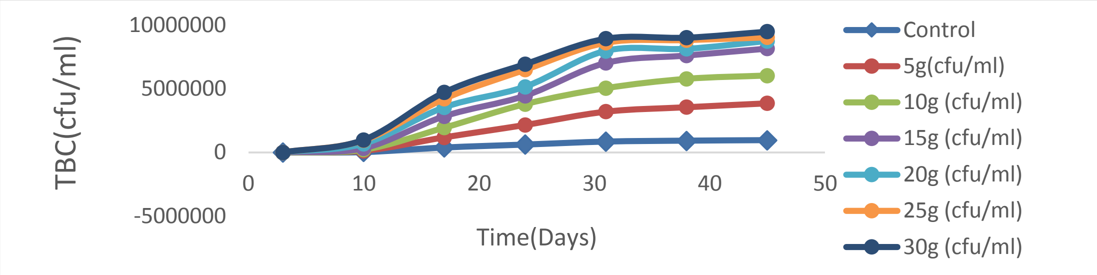
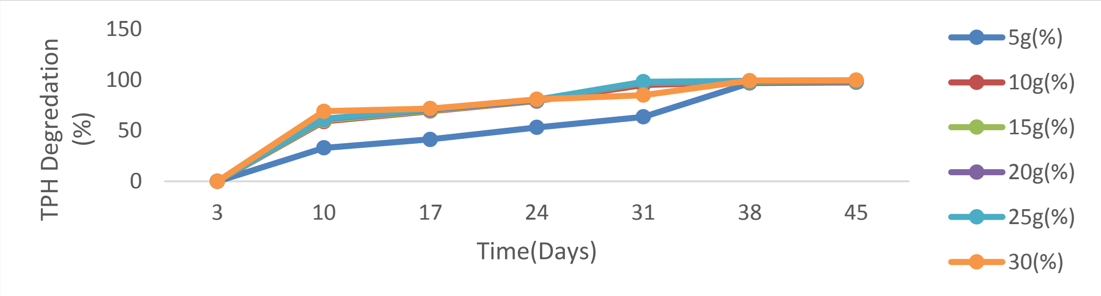


Fig 3:2 TBC Count Variation versus Time in Loamy Soil at Various Weights of Nano-Particle Treatment

TPH Degradation in Soils under the Influence of Treatment.

This study showed that the weight of treatment applied in crude oil contaminated soils has effect on TPH degradation as time of bioremediation increases. Therefore, this section presents the results of the TPH recorded during the investigation periods. Thus, the degradation pattern of TPH in loamy soil under nanoparticle (treatment) compared with control samples as investigated with time at various weights of treatment is shown in Figures 3.3 to 4.12.



TPH Degradation in Loamy Soil versus Time at Various Weights of Nano-Particle Treatment

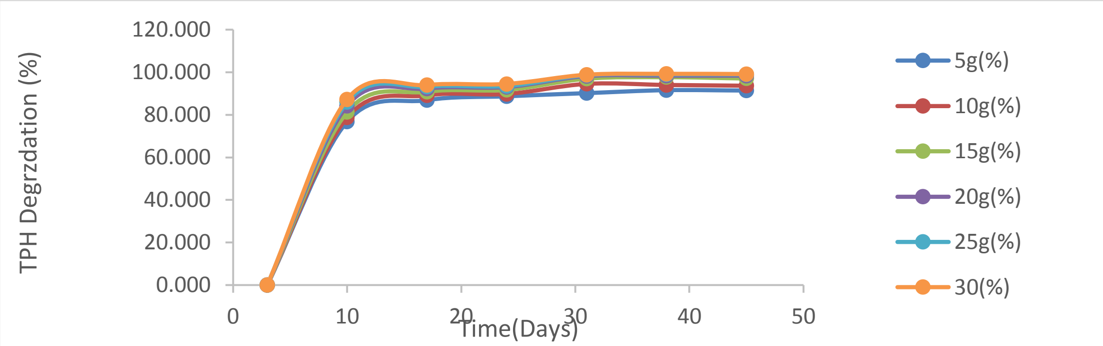


Figure 3.4: TPH Degradation versus Time in Loamy Soil at Various Weights of Cow Dung Treatment

Comparison of Treatment Performance in the Soil.

The performances of nanoparticles and cow dung as bio-stimulant for the degradation of TPH from crude oil polluted loamy soil was compared. Figure 4.13 compared all the treatment options with time at 30g, while Figures 4.14 and 4.15 compared the results obtained at 45th day for the various treatment weights for Cow dung and nanoparticle treatment in the soil samples.

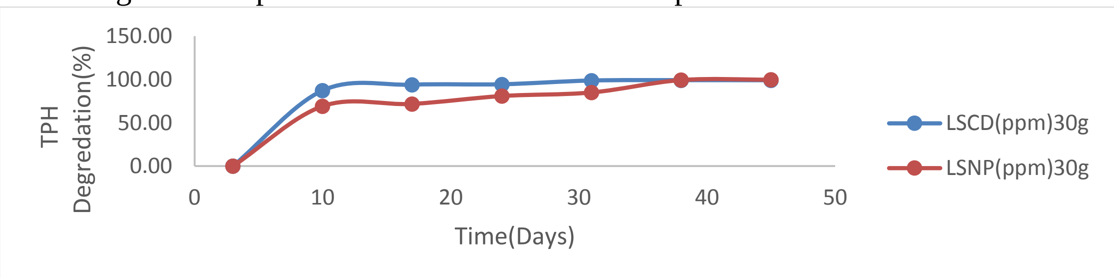


Figure 4.5: Comparison of TPH Removal in the Different Treatment at 30g.

4.5.1 Evaluation of First Order Rate Constant and Half Life

The degradation rate constant in the first order rate kinetic model was determined by comparing Equation (3.16) with the regression equations in Figures 4.19 to 4.24 for the different treatment options. From the determined rate constant, the time taken for the TPH concentration to reduce to half its initial concentration (half-life) was then evaluated.

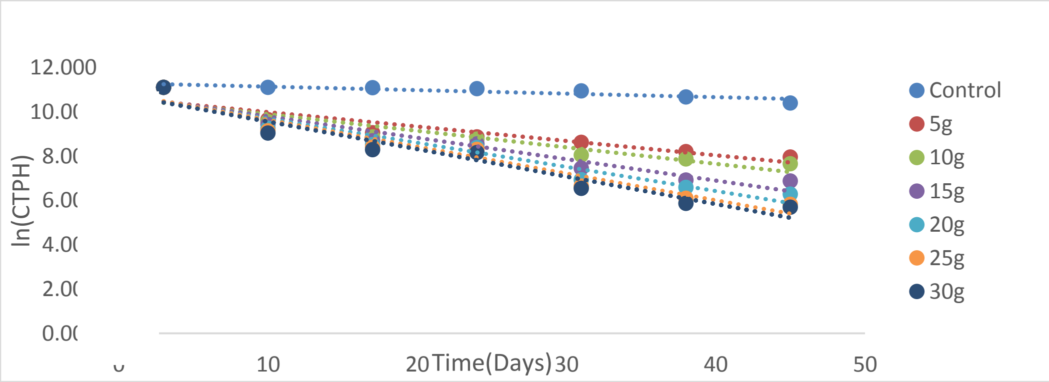


Figure 4.6: Plots for Evaluation of Rate Constant for Cow Dung Treatment in Loamy Soil

Figure 4.6 shows various linear regression equations for the different treatment options in loamy soil under cow dung treatment. From the linear equations on the plot, the degradation rate constant, k_d was determined.

Table 3.2: Rate Constant and Model for Loamy Soil under Cow Dung Treatment

Weight (g)	k (day^{-1})	Predictive Model	$t^{1/2}$ (days)
Control	0.0159	$C_{TPH} = 81570.80e^{-0.0159t}$	43.591
5	0.0651	$C_{TPH} = 42066.21e^{-0.0651t}$	10.646
10	0.0744	$C_{TPH} = 41772.77e^{-0.0744t}$	9.316
15	0.0967	$C_{TPH} = 47667.26e^{-0.0967t}$	7.167
20	0.1091	$C_{TPH} = 48533.04e^{-0.1091t}$	6.352
25	0.121	$C_{TPH} = 51688.99e^{-0.121t}$	5.728
30	0.1243	$C_{TPH} = 49563.01e^{-0.1243t}$	5.576

Table 3.3: Rate Constant and Model for Loamy Soil under Nano-Particle Treatment

Weight (g)	k (day^{-1})	Predictive Model	$t^{1/2}$ (days)
Control	0.0161	$C_{TPH} = 81470.80e^{-0.0161t}$	43.049
5	0.1089	$C_{TPH} = 180412.29e^{-0.1089t}$	6.364
10	0.1197	$C_{TPH} = 121905.32e^{-0.1197t}$	5.790
15	0.1248	$C_{TPH} = 122271.59e^{-0.1248t}$	5.553
20	0.1351	$C_{TPH} = 134995.94e^{-0.1351t}$	5.130
25	0.1446	$C_{TPH} = 147856.87e^{-0.1446t}$	4.793
30	0.1601	$C_{TPH} = 170586.88e^{-0.1601t}$	4.329

Table 3.3. and 3.4 shows the first order kinetic rate model, after inserting the degradation rate constant for the respective treatment option, is also shown in Table the evaluated degradation rate constant, the estimated time at which the TPH concentration would degrade to half its initial concentration is given in Table 4.2 for the respective treatment option. Based on the evaluated time, it will take about 43 days for the TPH concentration to reduce to half its initial concentration if it were allowed to degrade naturally (control sample) in loamy soil, but the addition of 5g cow dung treatment caused the time to reduce to about 6 days to attain 50% degradation, which even reduced further to just about 21 days when the treatment weight increased to 30g. This implied that increase in treatment weight reduces the time at which the TPH degraded to half of its initial concentration. This observation agreed with the work of Ofeogbu *et al*. (2015), for soil amended by cow dung and NPK fertilizer. This reduction in half life was attributed to increase in degradation rate. This is evident in the value of the degradation rate constant, which was lowest in the control sample, but increased as the treatment weight was increased.

Conclusion

The performance of Cow dung and Nano-particle treatment has been investigated for bioremediation of crude oil polluted loamy soil.

The characterized loamy soil before and after pollution showed that the physicochemical properties of the soils changed immediately after polluted by crude oil, and this implied that crude oil has significant impact on soils. Thus pH, phosphorus, nitrogen, potassium and Total Bateria Counts in the soils were reduced after pollution, while electrical conductivity and total organic carbon were increased.

Analysis of bacteria growth for the various treatment options shows that Total Bacteria Count (TBC) in the soil amended with different weights of *cow dung* (treatment) reduced immediately after pollution, but the TBC population increased significantly as time and treatment weight increased. The microbial growth rate attained a stationary state at some point in time, but the bacteria growth in control samples was very slow, indicating that *cow dung* stimulated the growth rate of bacteria in the soil.

The percentage degradation of Total Petroleum Hydrocarbon (TPH) in loamy soils under cow dung and nanoparticle treatment increased with time and treatment weight. There was rapid increase in percentage degradation in the treated soil compared to the gradual increase recorded in the control samples for the various soils. The highest TPH degradation was recorded on the 45th day across the various treatment weights, implying that duration of remediation influenced the degradation efficiency. Also, Treatment improved the degradation rate of TPH in the soils.

Comparison of the different treatment options in remediation of the polluted soils showed that the all the treatment options performed better on the 45th day, but the 30g weight samples performed much better than the other treatment options across the soil types. TPH percentage degradation across the treatment options was highest in Nano-particle treatment soil compared with Cow dung treatment soil. At the end of the analysis, for 30g Nano-particle treatment, the TPH degradation percentages were recorded as 97.48% to 99.66% for Nano-particle, while 91.35% to 99.10% were recorded for Cow dung treatment, respectively. Similarly, the Nano-particle samples slightly edged the Cow dung samples soils, indicating that treatment for bioremediation Nano-particle perform better than Cow dung.

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Extraction of Vegetable Oil from Dacryodes Edulis (African Pear Leaves)

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Abstract
This study was used to investigates the extraction of vegetable oil from African pear leaves (Dacryodes Edulis) using petroleum ether as a solvent. The extraction was conducted maintaining the following controls: temperatures (45 ºC - 60 ºC), times of extraction (20min - 60min), particle sizes (optimal at 1.8 mm), and solvent volumes (300 ml). Physicochemical properties of the oil were analyzed, and oil yield predictions were made using power and kinetic models. Physicochemical analysis classified the oil as a non-drying oil with applications in diverse industries. Optimal conditions for maximum yield were determined, considering factors such as particle size, temperature, extraction time, and solvent volume. Extraction kinetics revealed that both power and first-order kinetic models effectively predicted oil recovery, with the power model exhibiting a slightly better performance. Contributions to knowledge include insights into the extraction of oil from African pear leaves, emphasizing the suitability of petroleum ether as a cost-effective solvent. Recommendations highlight the potential of locally produced pear leaf oil to meet Nigeria's demand for products, reducing dependence on imports. Furthermore, suggestions for equipment upgrades, consistent power supply, and enhanced water availability aim to improve research efficiency. Future research is encouraged to explore the intrinsic behavior of African pear leaf oil for comprehensive characterization and classification, advancing its potential applications.

Keywords*: Oil extraction, petroleum ether, power Log and kinetic models.*

Introduction

Plants contain valuable liquids with applications in medicine and food. Many of these liquids are refined to serve as raw materials for various domestic and industrial products. While most plants offer high nutritional value, the seeds or nuts, often discarded as waste after consuming the edible parts, surprisingly have a high oil content. This oil can be effectively utilized either industrially or domestically as raw materials for producing beauty products or for food processing (Yusuf, 2018). The use of plant oil, commonly referred to as vegetable oil, has been gaining significant attention. From a chemical perspective, vegetable oil is a compound with triglycerides of varying chain lengths, categorized as saturated or unsaturated. Saturated triglycerides consist of single bond compounds of carbon and hydrogen atoms, while unsaturated triglycerides are compounds with double bonds of carbon and hydrogen atoms (Nde and Foncha, 2020).

Vegetable oil is broadly categorized as either edible or non-edible. Edible oils are predominantly employed in food preparation and the manufacturing of pharmaceutical products. On the other hand, non-edible oils are commonly used as raw materials for biodiesel production (Khan et al., 2019), as well as in the manufacturing of soap, perfumes, cosmetics, antioxidants and bioactive compounds (Cortés et al., 2017). Vegetable oils intended for human consumption are extracted from non-harmful sources such as soybean, sunflower, rapeseed, canola, cottonseed, avocado seed, peanut, coconut, shea butter, and palm kernel seed, among other plant seeds (Iddrisu et al., 2019).while non-edible oil from Jatropha curcas L., Pimenta racemosa, Lavender, Calotropis procera, Sterculia apetala, Rhus typhina L. are used to produce biodiesel, perfumes, cosmetics, bio-lubricant and antioxidant among others (Budhwani et al., 2019). Seed oil from edible plants has equally been used by some researchers to produce biodiesel and other non-edible products (Okewale et al., 2020).

This study is driven by the imperative to minimize waste by effectively utilizing abundant and underutilized local raw materials prevalent in many local communities. Seeds from plants such as the African pear leaf are often discarded as waste in the environment. Yet, these leaves may contain essential oils that could be extracted. These oils hold significant value for both domestic and industrial applications. Numerous studies have highlighted that the percentage of oil extracted from plants is influenced by various variables (Agu et al., 2020). Hence, this research delves into the extraction of valuable oil from African pear leaves using the Soxhlet extraction method. The investigation encompasses various extraction temperatures, times, particle sizes, and feed/solvent ratios. Optimizing these parameters is crucial for maximizing the yield of African pear leaf oil, considering both the kinetics and thermodynamics of the extraction process.

Materials and Methods

The experiments were conducted at the Chemical Engineering Laboratory in Rivers State University, Port Harcourt Nigeria.

Materials

The materials used in the experiment include pear leaf, petroleum ether (solvent) with boiling point 45 - 62 ºC.

Volumetric flasks, Soxhlet extractor, steam distillation apparatus, heating mantle, water bath, G-clamp, flasks, beakers, pipette, burette, sample bottle, specific gravity bottle, weighing balance, grinder, Gas chromatography Mass Spectroscopy (GC-MS) detector, pH meter thermometer and stop watch, Scientific Calculator and sieve merge.

Methods

The methods followed were based on Shreves' work (2012). Pear leaf were collected from Agricultural farm in Emu Town, Edo State and transported to the Department of Chemical/Petrochemical Engineering Laboratory, Nkpolu-Oroworukwo Port Harcourt for processing. The sample were weighed, washed, and sundried for 5 weeks. Thereafter, the leaves were ground to powdered form and sieved to particle sizes of 0.8 mm, 1 mm, 1.8 mm, 2 mm and 2.75 mm.

The oil extraction was done using a Soxhlet extractor with petroleum ether as the solvent. The samples were divided to explore the impact of temperature, particle size, extraction time, and solvent volume. Additionally, the pear leaf oil sample was analysed to determine Saponification Value, Acid Value, Iodine Value, Peroxide Value, and Free Fatty Acid. The impact of temperature on pear leaf oil yield was investigated using particle sizes of 0.8 mm, 1 mm, 1.8 mm, 2 mm, and 2.75 mm. Each sample, weighing 50 g, was subjected to extraction in a 500 ml round bottom flask with 300 ml of petroleum ether solvent. The extraction temperatures varied from 45 ºC to 60 ºC.

For each trial, one sample was placed in the thimble of the extractor, and 300 ml of petroleum ether was added to a 500 ml round bottom flask. Heat, set at 45 ºC, was applied using a mantle, and extraction ceased after 20 minutes. The resulting oil-solvent mixture underwent distillation at a temperature range of 45 ºC to 62 ºC. The lower boiling point of petroleum ether allowed it to distil out, leaving only the oil in the flask. The collected oil was weighed to determine the yield.

This process was repeated for the remaining four samples, maintaining the extraction temperature at 45 ºC but varying extraction times to 30, 40, 50, and 60 minutes. Distillation was performed after each extraction to recover the oil, and the yield was calculated for each set of extraction conditions.

Calculation of Oil Yield

The oil yield for each experimental condition was calculated using the formula.

$$Yield\ (\%) = \frac{weight\ of\ pure\ oil\ extracted\ (g)}{weight\ of\ particle\ (g)} \quad (2.1)$$

Characterization of Pear Leaf Oil

The properties of the extracted oil were determined using standard methods described in literature or by the Association of Official Analytical Chemists (AOAC, 2012).

Determination of Saponification Value

The analysis was conducted following the method outlined by the Association of Official Analytical Chemists (AOAC, 2012). In a 250ml conical flask, 4ml of the oil sample was weighed, and 50ml of alcoholic-potassium hydroxide solution was added. The flask with its contents was then heated on a boiling water bath for 30 minutes, with intermittent shaking. To the solution, 1ml of phenolphthalein indicator was added, and titration was performed while hot against hydrochloric acid. A blank titration, containing all the reagents except the sample, was also carried out.

The saponification value (SV) was calculated using the given expression.

$$.\ SV = \frac{(B-S)\times N\times M}{w_o} \quad (2.2)$$

Where,

B = blank titre value
S = sample titre value
N = normality of KOH (0.5 M)
M = molar mass of KOH (56.1)
w_o = weight of oil sample.

Determination of Iodine Value

The Iodine Value was determined following the AOAC method (2012). Approximately 0.35 ml of the sample was accurately weighed into a dry 250 ml conical flask. To this, 20 ml of carbon tetrachloride (CCl4) was added from a dry cylinder, and the flask was shaken to dissolve the oil. A 25 ml aliquot of the solution was pipetted into the flask in a fume cupboard and stoppered with cotton wool moistened with potassium iodide (KI) solution. The flask was left to stand for 30 minutes in the dark.

A blank titration was prepared, including all the reagents except the sample. The liberated iodide was back-titrated with 0.1 N Sodium thiosulphate, using starch solution as an indicator. The blue-black coloration turned colourless, and the titre value was recorded. This blank titration was also conducted.

The Iodine Value (IV) was calculated using the provided equation.

$$IV = \frac{(B-S)\times N\times 12.69}{w_o} \quad (2.3)$$

Where,

B = blank titre value
S = sample titre value
N = normality of sodium thiosulphate
wo = weight of oil sample.

Acid Value

The Acid Value (AV) was calculated using the method described by Warra et al., (2012). Thus, 100 ml of neutral ethyl alcohol was heated with 10 g of the oil sample in 250 ml beaker until the mixture boils. The mixture is then titrated with 0.1 M KOH solution using phenolphthalein as indicator. The content was constantly shaken until the colour changed to pink. The AV is then calculated using the expression:

$$AV = \frac{TV \times N \times M}{w_o} \quad (2.4)$$

Where,
TV = titre value
N = normality of KOH (0.1 M)
M = molar mass of KOH (56.1)
wo = weight of oil sample.
2.5.4 Free Fatty Acid
The free fatty acid was determined according to (AOAC, 2012), This was calculated from the relationship between it and the acid value. The mathematical relation is expressed as:
Free fatty acid = Acid value × 0.503 (2.5)

Determination of Peroxide Value

The analysis, conducted following the method of the Association of Official Analytical Chemists (AOAC, 2012), was carried out in the dark. To begin, 5 g of the oil sample was weighed into a clean, dry boiling tube. Subsequently, 30 ml of a solvent mixture (12 ml acetic acid + 18 ml chloroform) was added to the tube, and the mixture was boiled for 60 seconds. The contents were then poured into a titration flask containing 1 ml of 2% potassium iodide and 30 ml of water.
The resulting solution was titrated against 0.01 N Sodium thiosulphate using 1 ml of 1% starch indicator. The endpoint was indicated by a milky color. A blank titration, excluding the sample, was also performed.

The Peroxide Value (PV) was calculated using the provided equation.

$$Peroxide\ Value\ (PV) = \frac{(S - B) \times N \times (1000)}{w_o} \quad (2.6)$$

Where,
B = blank titre value
S = sample titre value
N = normality of sodium thiosulphate
wo = weight of oil sample

Refractive Index

The refractive index was determined using Abbe Refractometer.

Specific Gravity

The specific gravity was determined according to method described in AOAC (2012). A density bottle was washed with detergent, water and petroleum ether. 100 ml of oil, the sample, and water sample were weighed via the density bottle to determine the respective weight. After recording of the weights, the specific gravity of the oil was then obtained using the expression;

$$Specific\ gravity = \frac{Weight\ of\ Oil}{Weight\ of\ equal\ Volume\ of\ water} \quad (2.7)$$

Colour
The colour was determined by physical observation.

Kinetics and Thermodynamics of Oil Extraction
Various kinetic models have been proposed for the study of oil extraction from plants. In this study, the power model and first order kinetic model were used to study the extraction of pear leaf oil. Also, the thermodynamics of the extraction process was evaluated using established models.

Power Model
The power model that was used in this study has been applied by some researchers in vegetable oil extraction kinetics (Umamaheshwari and Reddy, 2016). This is expressed as:

$$\frac{dY}{dt} = kY^n \tag{2.8}$$

Where,
Rate of oil yield (%/min)
Percentage of oil yield (%)
Extraction time (min)
Extraction rate constant (min-1)
Power index

The rate constant and power index can be determined by taking the logarithm of both sides as follows.

$$\ln\frac{dY}{dt} = \ln k + n\ln Y \tag{2.9}$$

A plot $\ln\frac{dY}{dt}$ against $\ln Y$ gives a slope equivalent to and intercept as k

Now, equation (2.8) can be integrated to predict the yield of oil. After integration, the determined values of the power index and extraction rate constant are substituted into the resulting equation for prediction of oil yield. That is:

$$\int\frac{dY}{Y^n} = k\int dt$$

$$\frac{Y^{1-n}}{1-n} = kt + C \tag{2.10}$$

where C is integration constant.
when t = 0, Y = 0. Then, it implies that C = 0. Therefore, equation (2.10) becomes:

$$\frac{Y^{1-n}}{1-n} = kt \tag{2.11}$$

Or $$Y^{1-n} = (1-n)kt \tag{2.12}$$

Multiplying the powers of both sides of equation (2.12) by $\frac{1}{1-n}$ gives

$$Y = [(1-n)kt]^{\frac{1}{1-n}} \tag{2.13}$$

Equation (2.13) can be simplified to as:

$$Y = \beta t^m \tag{2.14}$$

where: $\beta = (k - nk)^m$ and $m = \frac{1}{1-n}$

In this study, equation (2.14) is used to predict the amount of oil recovered with time. β is the characteristic constant incorporating the active coefficients, while the power index, m, is the diffusion exponent, which indicates the transport mechanism of oil, and it is less than 1 (n <1) in most oil extraction processes.

First Order Kinetic Model

The first order kinetic rate model for leaching process was applied in the work of Jabar et al., (2015) for the extraction *Thevetia peruviana* seeds, and this is stated as follows.

$$\frac{dW_t}{dt} = K\frac{A}{V}(W_e - W_t) \tag{2.15}$$

Where,

Mass of extracted oil at equilibrium (g)
Mass of extracted oil at time t (g)
mass transfer coefficient (cm/min)
A = Area of solid-liquid interface (cm2)
Volume of oil (cm3)
Extraction time (min)

Equation (2.15) can be expressed as:

$$\frac{dW_t}{dt} = K_a(W_e - W_t) \tag{2.16}$$

Where,

$K_a =$ Volumetric mass transfer coefficient (min-1)

Assuming that equilibrium was attained within the period of this experiment, then, equation (2.16) is reduced to:

$$\frac{dW}{dt} = K_a W \tag{2.17}$$

Integration of equation (2.17) and simplification gives;

$$\ln W = K_a t + C \tag{2.18}$$

where C is the constant of integration, which accounts for the initial yield of oil
Expressing equation (2.18) in terms of yield gives;

$$\ln Y = K_a t + C$$ (2.19

A plot of against t gives a slope equivalent to K_a and C as intercept.
To predict the amount of oil yield with time, the exponential of both side of equation (2.19) is taken to give;

$$Y_t = e^{K_a t + C} \tag{2.20}$$

RESULTS AND DISCUSSION

Physicochemical Properties of Pear Leaf Oil

The physicochemical properties of the extracted pear leaf oil are presented in Table 3.1, while the composition of the free fatty acid is presented in Table 3.2.

Table 3.1: Physicochemical Properties of Pear Leaf Oil

Parameter (unit)	Value
Saponification Value (mg KOH/g)	159.27
Iodine value (mg/100 g)	42.34
Acid value (mg KOH/g)	11.71
Free Fatty Acid (mg KOH/g)	4.15
Peroxide value (mg/g)	3.29
Refractive index (-)	1.46
Specific Gravity (-)	0.96
Colour	Light Yellow

The analysis of pear leaf oil's physicochemical properties provides valuable insights into its composition and potential utility. With a saponification value of 159.27 mg KOH/g, the oil may have some limitations for soap making compared to other oils. However, its iodine value falls within the typical range for plant oils, indicating versatility for various applications. The acid value of 11.71 mg KOH/g, although slightly higher than some plant oils, remains within acceptable limits. The free fatty acid value of 4.15 mg KOH/g aligns with recognized standards, suggesting a low risk of enzymatic hydrolysis. Notably, the peroxide value of 3.29 mg/g indicates significant oxidative stability, positioning pear leaf oil as a promising candidate for diverse industrial applications.

In summary, the iodine value indicates that the pear leaf oil can be classified as a non-drying oil, signifying a low presence of unsaturated fatty acids. While the saponification value might not be optimal for soap production, the oil demonstrates suitability for applications in food processing, plasticizers, biodiesel production, skincare products, and bio-lubricants. The low acid value positions the oil as a favourable precursor for creating resins essential for anticorrosion coatings. Furthermore, the peroxide value of 3.29 mg/g underscores the high oxidative stability of the oil, making it well-suited for commercial purposes with reduced risks of rancidity or unpleasant odours. These findings highlight the diverse potential and value of pear leaf oil in various industrial applications.

Table 3.2: Free Fatty Acids of Pear Leaf Oil

Fatty acid	No of Carbon: Bond	Weight (%)
Palmitic	C16:0	10.29
Linoleic	C18:2	18.63
Linolenic		0.76
Palmitoleic	C16:1	0.73
Oleic	C18:1	58.67
Stearic	C18:0	9.72
Myristic	C14:0	0.44

The fatty acid content analysis carried out on the oil revealed the various compositions and percentage of fatty acids in the pear leaf oil.

Yield of Pear Leaf Oil at Different Extraction Times and Temperatures

The experimental investigation recorded the percentage yield of oil from pear leaf at different extraction times and temperatures, while maintaining a constant particle size of 0.8 mm, 1 mm, 1.8 mm, 2 mm, 2.5 mm, and a solvent volume of 300 ml petroleum ether.

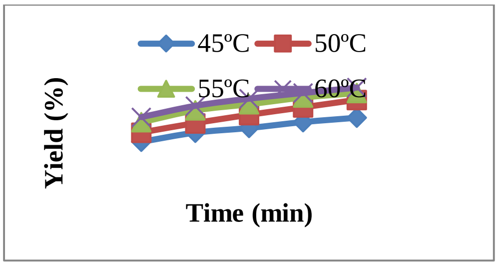

Figure 3.1: Oil Yield versus Extraction Time at Different Temperatures

Figure 3.1 illustrates the profiles of the percentage yield of pear leaf oil obtained through the solvent extraction method at extraction times ranging from 20 to 60 minutes and temperatures ranging from 45 ºC to 60 ºC. The plot indicates that the quantity of pear leaf oil, measured as the percentage of oil recovered after the extraction/distillation processes, increases with prolonged extraction time. Additionally, for a given extraction time, the oil yield rises with an increase in temperature. Specifically, the oil yield obtained between 20 minutes and 60 minutes at a temperature of 45 ºC ranged from 27.29% to 34.58%. Similarly, at temperatures of 50 ºC, 55 ºC, and 60 ºC, the oil yield ranged from 30.04% to 40.02%, 33.22% to 42.12%, and 34.72% to 43.77%, respectively, within the extraction time range of 20 minutes to 60 minutes. Consequently, the highest percentage of oil yield was achieved at a temperature of 60 ºC and an extraction time of 60 minutes.

The observations reveal that even within the chosen extraction time range, the percentage of oil yield continued to increase. Notably, between 50 minutes and 60 minutes of extraction time, especially at extraction temperatures of 55 ºC and 60 ºC, the difference in the amount of oil recovered was only about 3 – 4%. This suggests that if the extraction process were extended beyond 60 minutes, it could potentially lead to a higher yield of the oil. The findings indicate the sensitivity of the extraction process to both time and temperature, with the potential for further enhancement of oil yield with extended extraction durations. Though, some studies have reported insignificant yield of oil at about 60 minutes of extraction.

Yield of Pear Leaf Oil at Different Particle Sizes and Temperatures

The experimental study further explored the percentage oil yield from pear leaf at different particle sizes and temperatures, with the extraction time and solvent volume held constant at 60 minutes and 150 ml, respectively.

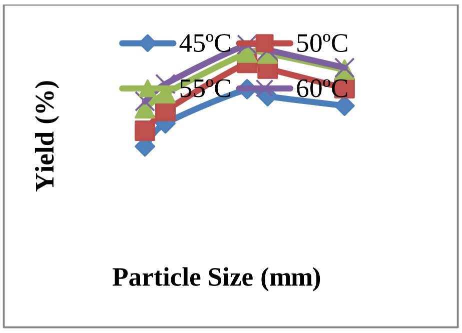

Figure 3.2: Oil Yield versus Particle Size at Different Temperatures

The study delved into the impact of particle size on pear leaf oil yield, encompassing sizes ranging from 0.8 to 2.75 mm. Different extraction temperatures were considered for each particle size, spanning from 45 ºC to 60 ºC at 5 ºC intervals. As illustrated in Figure 3.2, the pear leaf oil yield exhibited an upward trend with an increase in particle size, ranging from 0.8 to 1.8 mm. However, this trend reversed as the particle size further expanded to 2.75 mm, irrespective of the extraction temperature. Specifically, within the 0.8 to 1.8 mm particle size range, the oil yield increased from 22.74% to 34.58%, 25.99% to 40.02%, 30.64% to 42.13%, and 32.05% to 43.77% at temperatures of 45 ºC, 50 ºC, 55 ºC, and 60 ºC, respectively. Conversely, enlarging the particle size from 1.8 to 2.75 mm resulted in a decline in oil yield from 34.58% to 31.14%, 40.02% to 34.78%, 42.13% to 38.62%, and 43.77% to 39.03% at temperatures of 45 ºC, 50 ºC, 55 ºC, and 60 ºC, respectively.

This suggests that the maximum oil recovery from pear leaves was achieved with a particle size of 1.8 mm. Therefore, it is anticipated that at smaller particle sizes, the yield would be maximal due to the increased surface area. However, an unexpected result was observed as the lowest oil yield was recorded at the 0.8 mm particle size.

Yield of Pear Leaf Oil at Different Volume of Solvent and Temperatures

The experimental investigation of pear leaf oil yield involved varying solvent volumes and temperatures, while maintaining a constant extraction time of 60 minutes and particle size of 1.8 mm.

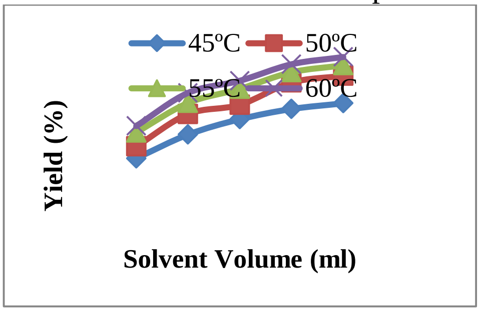

Figure 3.3: Oil Yield versus Solvent Volume at Different Temperatures

Figure 3.3 displays the variations in the percentage yield of pear leaf oil during solvent extraction, considering different solvent volumes (ranging from 150 to 350 ml) and temperatures (from 45 ºC to 60 ºC). The figure 3.3 illustrates an upward trend in the percentage of pear leaf oil with increasing solvent volume and extraction temperature. Specifically, elevating the solvent volume from 150 to 350 ml resulted in an increased oil yield at different temperatures, indicating a positive correlation between solvent volume, extraction temperature, and the yield of pear leaf oil.

Kinetic Analysis of Oil Extraction from Pear Leaf

The extraction of vegetable oil from plant seeds and leaves has been extensively explored through the application of mathematical expressions. To effectively utilize these models, it is essential to evaluate the constant coefficients using experimental data. In this study, the constant parameters in the mentioned kinetic models are determined based on the experimental data acquired, and the plots presented here facilitate this determination.

Evaluation of Power Model Constants

The power index (n) and the constant coefficient (k) were derived from the experimental data. Subsequently, the experimental results were fitted into equation (2.9) and plotted, as illustrated in Figure 3.4 at temperatures ranging from 45 to 60 ºC.

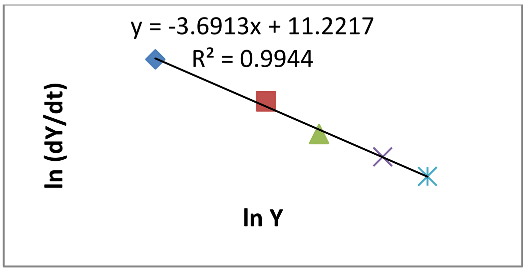

Figure 3.4: Plot for Evaluation of Power Index and Constant Coefficient at 45 ºC

Figure 3.4 displays the plot of the natural logarithm of the time rate of change in pear leaf oil yield against the natural logarithm of the yield at an extraction temperature of 45 ºC. Utilizing the power model, as simplified into equation (2.9), the index (n) and the constant coefficient (k) were determined by comparing the linear regression equation in Figure 3.4 with equation (2.9). Consequently, from the linear equation in Figure 4.4, it was found that \(n = -3.6913 \) and \(\ln k = 11.2217 \).
Hence, k = 74733.20 min^{-1}. By substituting into equation (2.14), the percentage yield of oil from the pear leaf at 45 ºC, can be expressed as: $Y = 14.6019t^{0.21}$.

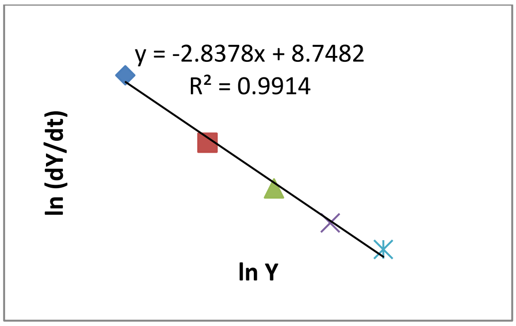

Figure 3.5: Plot for Evaluation of Power Index and Constant Coefficient at 50 ºC

In Figure 3.5, the plot depicts the natural logarithm of the time rate of change in pear leaf oil yield against the natural logarithm of the yield at an extraction temperature of 50 ºC. By applying the power model as simplified into equation (2.9), the index (n) and the constant coefficient (k) were determined by comparing the linear regression equation in Figure 3.5 with equation (2.9). Therefore, from the linear equation, n = -2.8378 and ln$k$ = 8.7482. Hence, k = 6299.49 min^{-1}. By substituting into equation (2.14), the percentage yield of oil from the pear leaf at 50 ºC, can be expressed as: $Y = 13.7937t^{0.26}$.

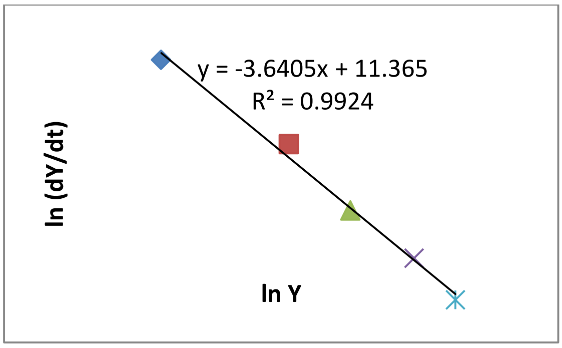

Figure 3.6: Plot for Evaluation of Power Index and Constant Coefficient at 55 ºC

In Figure 3.6, the graph depicts the natural logarithm of the time rate of change in pear leaf oil yield against the natural logarithm of yield at an extraction temperature of 55 ºC. Utilizing the power model simplified into equation (2.9), the obtained values for the index, n, and the constant coefficient, k, were derived by comparing the linear regression equation in Figure 4.6 with equation (2.9). Consequently, from the linear equation, the values were determined as n = -3.6405 and lnk = 11.3650, leading to k = 86249.60 min^{-1}. Through substitution into equation (2.14), the percentage yield of oil from the pear leaf at 55 ºC can be expressed as:.: $Y = 17.0809t^{0.22}$.

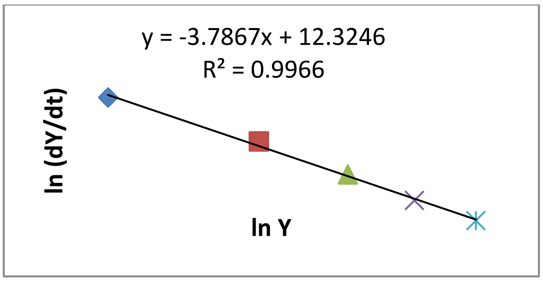

Figure 3.7: Plot for Evaluation of Power Index and Constant Coefficient at 60 ºC

In Figure 3.7, the graph illustrates the natural logarithm of the time rate of change in pear leaf oil yield against the natural logarithm of yield at an extraction temperature of 60 ºC. Employing the power model and simplifying it into equation (2.9), the index, n, and the constant coefficient, k, were determined by comparing the linear regression equation in Figure 3.7 with equation (2.9). As a result, from the linear equation, the values were found to be n = -3.7867 and lnk = 12.3245, leading to k = 225155 min^{-1}.

Evaluation of First Order Kinetic Constant

Similar to the power model, the constants in the first-order kinetics were established by fitting the experimental data into equation (2.19). The results were then plotted, as depicted in Figure 3.8, for different temperatures.

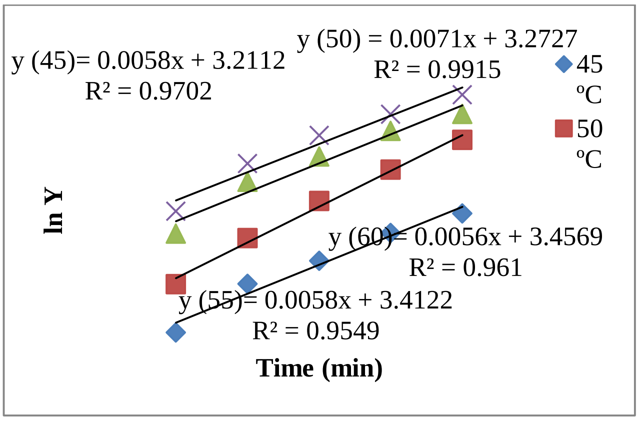

Figure 3.8: Plot for Evaluation of First Order Kinetic Rate Constant

In figure 3.8, the linear graphs depict the natural logarithm of pear leaf oil yield plotted against extraction time across temperatures ranging from 45 ºC to 60 ºC. The determination of the volumetric mass transfer coefficient, Ka, and the constant, C, was accomplished by comparing the linear equations in figure 3.8 with equation (2.19). Consequently, the obtained Ka values are 0.0058, 0.0071, 0.0058, and 0.0056 min^{-1} at temperatures of 45 ºC, 50 ºC, 55 ºC, and 60 ºC, respectively. Additionally, the corresponding C values are 3.2112, 3.2727, 3.4122, and 3.4569 at the respective temperatures.

Although the first-order kinetic model, which includes the equilibrium yield, has been applied in oil extraction, equilibrium was not achieved within the specified extraction variables. Therefore, the equilibrium yield has been neglected in this study. Some reports suggest that the kinetic constant in the first-order rate equation, when incorporated with equilibrium yield, is a function of extraction temperature, and the kinetic constant increases with temperature. By substituting Ka and C into equation (2.20), the percentage yield of oil from the pear leaf oil at various temperatures can be expressed and used for prediction.

Comparison of Kinetic Model Prediction of the Extracted Oil

The predictive accuracy of the first-order kinetic and power models was assessed at a temperature of 60 ºC, and the results were compared with the measured percentage of pear leaf oil yield, as illustrated in Figure 3.9.

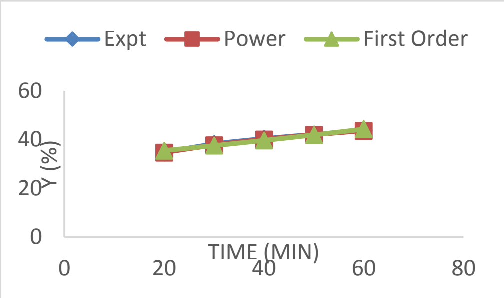

Figure 3.9: Comparison of the Degree of Model Predictions

The experimentally obtained percentage of pear leaf oil yield was compared with the values predicted by both the power and kinetic models, using the determined constants through subsequent substitutions. Figure 3.9 depicts the profiles of the percentage yield against extraction time, demonstrating the effectiveness of both models in predicting oil yield, with over 95% agreement with the experimental values. The deviation between the values predicted by the power model and the experiment ranged from 0.12% to 1.10%, while the deviation between the values predicted by the first-order kinetic model and the experiment ranged from 0.34% to 2.18%. This suggests a slight advantage of the power model over the first-order kinetic model.

Thermodynamic Analysis of Oil Extraction from Pear Leaf

Thermodynamics plays a pivotal role in comprehending heat transfer systems, and its relevance to oil extraction is notable due to the involved heating, leading to the exchange and transfer of heat from the solvent to the solid leaf particles. In the context of oil extraction, thermodynamics entails scrutinizing the process's state in terms of enthalpy and entropy.

The thermodynamic analysis initiates with the assessment of the equilibrium constant using equation (2.24), following the calculation of the constant K through equation (2.25). Subsequently, the thermodynamic parameters, specifically enthalpy and entropy, are determined based on the linear equation presented in Figure 3.10.

Conclusion

The investigation into the extraction of vegetable oil from pear leaves, employing petroleum ether as a solvent, covered a comprehensive exploration of factors such as temperatures, extraction times, particle sizes, and solvent volumes. Additionally, the study delved into the physicochemical properties of the oil, utilizing power and kinetic models for oil yield assessment. Thermodynamic properties were also scrutinized to gain insights into the heat dynamics, feasibility, and disorderliness of the extraction process.

Physicochemical analysis unveiled that the oil falls into the category of non-drying oils, as indicated by its iodine value. The saponification value suggested limitations for soap production but showcased potential applications across various industries. A low acid value highlighted the suitability of pear leaf oil as a precursor for synthesizing resins for anticorrosion coatings. Furthermore, the peroxide value attested to the oil's high oxidative stability, making it commercially viable without the risk of rancidity or offensive odours.

The analysis demonstrated that the percentage yield of pear leaf oil responds positively to increased extraction time, temperature, and solvent volume. However, specific particle sizes, particularly those below 1mm and above 2mm, were identified as potential factors leading to a decrease in oil yield. The optimal conditions for achieving maximum yield were pinpointed as a particle size of 1.8 mm, a temperature of 60 ºC, an extraction time of 60 min, and a solvent volume of 400ml.

In terms of extraction kinetics, both the power and first-order kinetic models exhibited efficacy in predicting the percentage of recovered oil. Notably, the power model displayed a slightly superior performance. This comprehensive understanding of influential factors and optimal conditions contributes significantly to the efficient extraction of pear leaf oil, providing valuable insights for practical applications across various industries.

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Investigating the effect of Using Cow Dung and Water Leaf on Bioremediation of Crude Oil Polluted Soil

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Abstract
This study investigated the use of fresh Talinum triangular (Water-leaves) and fresh cow dung for bioremediation of crude oil-polluted soils. Water leaves and cow dung were used as bio-stimulant for remediation of crude oil polluted soil. The physicochemical properties of the soils before and after pollution were analyzed. Also, the Total Heterotrophic Bacteria count (THB) and Total Petroleum Hydrocarbons (TPH) content were analyzed every 7 days for 35 days. The results obtained from the physicochemical analysis showed that there was an increase in the pH of the soils after contamination, while there were decreases in the soils' moisture content, total organic carbon, total nitrogen, and phosphorus contents, which differ remarkably from the control samples, implying that the water leaves and cow dung treatments after pollution were effective. Also, as time and treatment weights were increased, the percentage degradation of TPH in the soil increased. Thus, the 150g weight samples exhibited the best performance on the 35th day, consistently demonstrating superior efficacy across various soil types. Waterleaf treatment outperformed Cow dung treatment in terms of TPH percentage degradation. Specifically, 150g Waterleaf treatment resulted in degradation percentages ranging from 81.27% to 89.50%, while Cow dung treatment achieved percentage of 72.24% to 86.88%. Further examination of TPH degradation rate constants and half-lives for Waterleaf and Cow dung treatments revealed distinct patterns. Waterleaf treatment displayed higher degradation rate constants (ranging from 0.0043 to 0.057 day^-1 for Cow dung and 0.0043 to 0.0509day^-1 for Waterleaf), corroborating its superior TPH removal efficiency. Half-life analysis indicated that Cow dung required more time for TPH to degrade to half its initial concentration, while Waterleaf treatment exhibited faster degradation. Conversely, the variation of Michaelis-Menten constants showed no clear pattern. In terms of model performance, the first-order kinetic rate model demonstrated better congruence between experimental TPH concentrations and the Michaelis-Menten equation.

Keywords: *Soil, Hydrocarbon, Remediation, Cow Dung, Water-leaves and kinetic models.*

Introduction
The Environment was created to serve man and other living things with benefits. Energy related environmental problems, including oil spills, air pollution, flooding and deforestation have become a threat to world's biodiversity and delicate ecosystems. Oil spill occurs more frequently in developing countries such as Nigeria and have been the cause of severe environmental damage.

For example, spills in Rivers and other water bodies in the creeks have caused damages to swamp itself, hurt the local fishing communities, covered beaches with crude, and greatly polluted the coastal soils. Although most environmental pollution was not deliberate, it is the human quest for good living and advancement in technology that brought about the operations of petroleum industries, including exploring, production (extraction), storing, transporting, and refining of crude oil and the storing, distribution, and handling of products that are potential soil contaminates (oily sludge). Accidental spills of crude oil and petroleum products during the handling, storing, and transporting operations are the principal causes of the formation of oil sludge in large quantities (Ehirim et al., 2020).

Petroleum production facilities generate large quantities of oily wastes from drilling, production, and processing activities. All activities involved in hydrocarbon production and exploration normally have one impact or the other on the environment. The contamination of the environment by hydrocarbon processing occurs through exploitation, transport, and leakage of crude oil storage facilities, which are released into the environment, thereby causing environmental pollution. Crude oil pollution in the air occurs via evaporation of volatile components or gas flaring, while in aquatic and land environments it can occur via spillage from oil facilities. A study reported that the land environment was the most affected by pollution from the petroleum industry, mostly from leakage of pipelines, storage tanks, and other oil facilities (Nnaji, 2017). Crude oil contains toxic compounds and radioactive elements that can cause challenges to the health and also affect plant growth. Crude oil pollution, especially on soil, can bind soil particles together because of low water solubility which could reduce soil nutrients. Most organic and inorganic chemicals are hazardous to soil and can cause low yield of agricultural produce (Kuppusamy et al., 2016).

Bioremediation is a radiation technique that utilizes microorganisms or bio-stimulants such as enzymes, spent biomass, and fertilizers to remove contaminants from a contaminated environment through a metabolic process. Bioremediation is economical, adaptable, efficient, and eco-friendly to the environment (Jeon & Madsen, 2013). Bioremediation can be implemented through bio-stimulation, bio-augmentation, and phytoremediation, among others. Bio-stimulation refers to the use of fertilizer, plant and animal wastes, or any other agro-based material as amendment agents, to stimulate the growth of microorganisms; while in bio-augmentation bacteria or fungi are directly applied to enhance the degradation rate of pollutants (Varjani & Upasani, 2017). In Phytoremediation, a plant is planted in polluted soil to take up the contaminant as it grows.
Soil pollution arising from increasing demand for petroleum and its products has become a common problem in recent years. Soils polluted with petroleum hydrocarbons differ from unpolluted soils and do not support adequate crop growth and development. Hence, the need to treat these soils, and also reduce the negative impacts of the crude oil on the environment. Therefore, the capability of *cow dung and water leaf* to degrade the TPH in crude oil-polluted loamy soil is investigated. The choice for the using of *cow dung and water leaf* as bio-stimulant is based on their nutritional quality implying that they possess the ability to stimulate hydrocarbon-degrading bacteria necessary for effective bioremediation.

Materials and Methods

A collection of loamy soil samples was procured from Ugwuaji Community within Enugu State. In parallel, samples of waterleaf and cow dung were acquired from the Agriculture farm at Rivers State University. The aforementioned specimens were meticulously stored within appropriate containers. Additionally, a representative crude oil sample was sourced from the Port-Harcourt Refinery, situated in Rivers State.

The assembled samples were subsequently transported to the Chemical/Petrochemical Laboratory within the premises of Rivers State University in Port Harcourt, for comprehensive analysis. The waterleaf, cow dung, and soil samples were subjected to specific preparatory procedures to facilitate subsequent processing stages.

Materials

The materials used in the experiment include Volumetric flasks: glass 10 and l00 ml, Agilent 6890 Gas chromatographs with a flame lunation Defector, pH meter with glass electrode, Thermometer, Glass beaker (100ml), Glass rod, Laboratory fume hood, Analytical balance, Glass ware, Mineral salt agar, Distilled water, Petri dishes**,** Scientific Calculator, Cow dung, Nano particle, sieve merge.

Methods

A total of 4 kilograms of soil samples were utilized for the study. Cow dung and waterleaf specimens were procured from the agriculture farm at Rivers State University. Ten empty batch reactors were employed, loaded with 400 grams of soil samples. The samples were left in the reactors for three days. Subsequently, seven reactors were subjected to pollution by introducing 200 milliliters of crude oil into each reactor. The mixture was thoroughly blended to ensure homogeneity, after which the reactors were left undisturbed for an additional three-day period. Among the reactors, Reactor 1 was the control and remained devoid of crude oil and nutrients. Reactor 2, also a control, contained 2400 grams of slit loam soil within a plastic batch reactor. Before pollution and post-pollution, all samples were subjected to thorough analysis. To ensure uniform crude oil concentration within the soil samples, the polluted samples were meticulously mixed and left undisturbed for three days to facilitate settling. Following a three-day soil settlement period, soil treatment was initiated, involving the application of treatments ranging from 10 to 50 grams of cow dung and waterleaf.

The physicochemical attributes of loamy soils were assessed both before and after pollution. These attributes encompassed pH, particle size distribution, electrical conductivity, nitrogen content, total organic carbon content, and phosphorus content. Additionally, the study involved the analysis of Total Bacterial Count (TBC) and Total Petroleum Hydrocarbon at 7-day intervals during the treatment phase.

Determination of Total Petroleum Hydrocarbon

The analysis of the Total Petroleum Hydrocarbon was done using a Gas Chromatography — Flame Ionization Detector Model HP 5890 series II, U.S.A. This analysis was done in the Endpoint laboratory. Total Petroleum Hydrocarbon was obtained using a calibrated graph as a reference.

Soil pH Analysis

A quantity of 20 grams of air-dried soil with a particle size of 2mm was precisely weighed and placed into a beaker. Subsequently, 50 milliliters of distilled water were introduced into the beaker, and a thorough mixing was performed using a glass rod for approximately 5 minutes. The mixture was then left undisturbed for thirty minutes.

During this interval, the pH meter was activated for 15 minutes. The glass electrode within the pH meter underwent standardization using a pH 7 standard buffer solution. This calibration procedure also involved either pH 4 or pH 9.2 buffer solutions. The glass electrodes were then immersed into the beakers containing the soil-water suspension, all while ensuring continuous stirring. As the pH value was detected, the pH meter was switched to the pH reading mode. Following a 30-second stabilization period, the pH value was meticulously recorded to the nearest 0.1 unit.

After recording, the pH meter was placed in standby mode, and the electrodes were gently extracted from the soil suspension. They were subsequently cleansed using distilled water. To ensure accuracy, the electrodes were rinsed and carefully dried using filter paper before the next determination.

Standardization of the glass electrodes was performed after every ten determinations. During periods of inactivity, the electrodes were immersed in distilled water. The reference electrode was consistently maintained with saturated potassium chloride in contact with solid potassium chloride crystals.

The range pH is classified at

i. Less than 4.5 is extremely acidic
ii. 4.6 to 5.2 strongly acidic
iii. 5.3 to 6.0 moderately acidic
iv. 6.1 to 6.5 slightly acidic
v. 6.6 to 7.0 neutral
vi. 7.1 to 7.5 slightly alkaline
vii. 7.6 to 8.3 moderately alkaline
viii. 8.4 to 9.0 strongly alkaline
ix. Greater than 9.0 is extremely alkaline

Electrical Conductivity

The electrical conductivity meter was used to measure the electrical conductivity (EC) of the samples. The same procedure stated for pH measurement was used in the determination of EC. However, the EC electrode was thoroughly washed after each reading to avoid cross-contamination and error.

Total Organic Carbon

Total Organic Carbon (TOC) was determined using a method described by Umeda et al. (2017). Consequently, a mass of 1.0 grams of the soil samples was meticulously measured and placed within a 250ml beaker. the volume of 10ml from the potassium dichromate solution was carefully transferred into the beaker and then swirled gently to ensure complete saturation of the soil sample. 20 ml of the concentrated H_2SO_4 was introduced into the beaker with an automatic pipette. The mixture was then gently swirled for one minute, achieving a uniform suspension and an enhanced and thorough oxidation process. Following this, the mixture was allowed to settle for approximately 30 minutes on an asbestos sheet.

Once the settling had occurred, 100ml of distilled water was added to the mixture. This was promptly followed by 3 to 4 drops of a diphenylamine indicator solution measuring 0.5ml. The resulting solution was titrated using a 0.5N ferrous sulfate solution. Titration continued until the observable color transitioned from violet to blue, eventually reaching a vivid green hue.

This procedure was replicated using distilled water (a blank titration) but without soil. This blank titration served the purpose of standardizing the potassium dichromate solution. The TOC was calculated according to the formula.

$$TOC = Blank - \frac{volume of\ soil\ sample titre \times 0.195}{weight\ of\ soil\ sample} \times 100\% \qquad (2.1)$$

Total Nitrogen Content

The determination of total nitrogen content was conducted in accordance with the APHA 4500-NO3B method (APHA, 1998). To begin, a sample of soil, ground, and sieved, weighing 10g and containing approximately 10 mg of nitrogen, was measured and placed within a dried 500ML Macro-Kjeldahl flask. The contents were gently swirled for approximately 2 minutes. Following this, 20ml of distilled water were added to the flask, after which the mixture was allowed to settle for a duration of 30 minutes.

Into the prepared sample in the flask, a tablet of 1g K_2SO_4-H_2O mixture (acting as a catalyst), 10g of K_2SO_4, and 30 ml of concentrated H_2SO_4 were introduced. The flask was placed cautiously on a digestion stand and subjected to controlled heating. As signs of water content and frothing became apparent, the heat intensity was elevated until a clear digest was achieved.

The regulation of heating ensured that the level of H_2SO_4 in the flask remained approximately halfway up the neck. Once the heating process concluded, the flask was allowed to cool, and a gradual addition of 100ml of water followed.

The obtained digest was meticulously transferred into another clean 750ml Macro-Kjeldahl flask, while any sand particles present in the original digestion flask were retained. This precautionary step was taken to prevent severe bumping that sand particles might cause during the subsequent Kjeldahl distillation. The sand residue was washed using 50ml of distilled water in four iterations, and the collected aliquots were then added to the same flask.

Subsequently, 50ml of H_3BO_3 indicator solution was introduced into a 500ml Erlenmeyer flask. This flask was positioned beneath the condenser of the distillation apparatus. Simultaneously, the 750ml Kjeldahl flask was attached to the distillation apparatus. Through a funnel-like opening, approximately 150ml of 10N NaOH was carefully added to the distillation flask. The distillation process was halted once 150ml of distillate had been collected.

The ammonium nitrogen (NH_4-N) in the distillate was quantified through titration, employing a 0.01N standard H_2SO_4 solution. The titration process was carried out using a 25ml burette calibrated with intervals of 0.1ml. The color of the endpoint changed from green to pink. The percentage of nitrogen in the soil was calculated using equation (3.2).

$$N(\%) = \frac{(T - B) \times N \times 1400}{S} \times 100\% \quad (2.2)$$

Where: T = Sample Titration (ml), B = Blank Titration (ml), N = Normality of H_2SO_4 and
S = Sample weight (mg).

Phosphorous Content

Phosphorus content was determined according to APHA method $4500 - PO_4^{3-}$ (APHA, 1998). 1.0g of representative soil sample was weighed into a clean extraction flask and 10 ml of Bray P-1 extracting solution (0.025N HCl and 0.03N NH_4F) was added and vigorously agitated for 1 minute before being filtered. 5ml of the filtrate was pipette into 25ml volumetric flask and diluted to about 20ml of distilled water, and then, by 4ml of ascorbic acid solution (1.056g ascorbic acid in 200ml molybdate-tartrate solution), which were diluted. The diluted solution was allowed to settle for at least 30 minutes. The recording of data was done after a clear colour had been developed.

Procedure for Total Bacterial Count (TBC) Analysis

Microbiological analysis enumeration of heterotrophic bacteria and fungi was carried out by pour plating technique. This was done by inoculating 0-1ml tenfold seriating diluted sample onto nutrients agar (bacterial), acidified streptomycin (1mg/100ml) (fungal), and mineral salt agar (MSA) (hydrocarbon degraders).

Total Petroleum Hydrocarbon (TPH) Analysis

The determination of Total Petroleum Hydrocarbons (TPH) was conducted using Gas Chromatography-Flame Ionization Detector (GC-FID). The protocol for TPH analysis is elucidated as follows:

Initially, the soil sample was carefully poured into a 1-liter separation funnel. Subsequently, 50 ml of methylene chloride was introduced into the sample bottle. The bottle was sealed and agitated for 30 seconds to ensure the inner surface was evenly coated. The solvent was then transferred from the sample bottle to the separation funnel. The funnel was shaken for 2 minutes, with intermittent venting to release excess pressure.

The organic layer was allowed to separate from the aqueous phase for a minimum of 10 minutes. The methylene chloride was extracted into a 250ml flask. A second volume of 60 ml of methylene chloride was added to the sample bottle. Rinsing of the separation funnel and the column was performed using 25ml of the solvent, directing the reinstate into the extract. This extraction process was repeated a second time, and the extracts from both repetitions were combined in an Erlenmeyer flask.

The third extraction followed the same procedure. The extracts obtained from all three extractions were filtered through a drying column comprising packed cotton wool, anhydrous sodium sulfate, and silica. The resultant extract was collected in a vial and subsequently concentrated. Concentration was achieved by boiling down the extract using nitrogen gas, ultimately reducing it to a volume of 1.0ml.

The concentrated extract was then mixed with 1.0 ml of the solvent. From this mixture, a volume of 1.0ml was injected into the gas chromatograph equipped with a flame ionization detector for TPH analysis.
The residual TPH percentage at any time was calculated using Equation (2.3).

$$TPH_R(\%) = \frac{TPH_i - TPH_f}{TPH_i} \times 100\% \quad (2.3)$$

Where: TPH_R is the residual TPH percentage with time, TPH_i is the initial concentration of TPH, and is the concentration of TPH measured with time.

3. RESULTS AND DISCUSSION

Investigations on the efficacy of cow dung and water leaves in bioremediation of crude oil-polluted soil have been carried out and the results are presented in this chapter.

3.1 Influence of Treatment on the Soil Physicochemical Properties

The behavior of the polluted soils after application of the cow dung and water leaves over the investigative period was studied through some of the soils' physicochemical properties, which were as shown in Figures 3.1 through 3.5.

3.1.1 influence of Treatment on the Soil pH

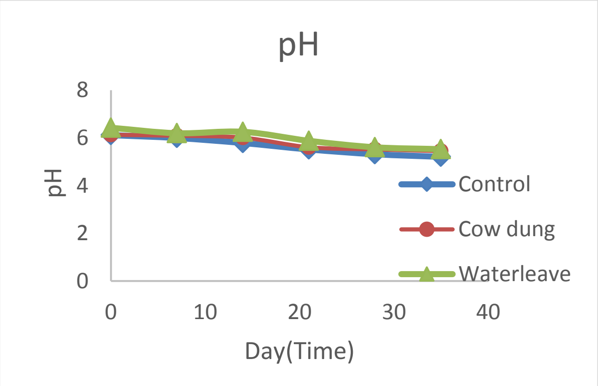


Figure 3:1: Variation of pH in Loamy Soil with Treatment

Figure 3.1 shows the variation of pH in crude oil-polluted loamy soil treated with cow dung and water leaves. There were changes from the initial conditions of the soil after pollution with crude oil. These physicochemical changes in the soils from their initial conditions have been attributed to the crude oil introduction. Thus, the pH of silt loam soil after pollution decreased from its initial condition of 5.01 to 5.4 in the control sample (CL), 5.23 in the sample treated with water leave particles (WL) and 5.11 in the sample treated with cow dung (CD) up to the seventh (7th) day of treatment, which then gradually increased to 5.4 in control sample, 6.53 in sample treated with water leave and 6.0 in sample treated with cow dung at the 35th day. Again, the increase in pH of soil samples with no treatment was low compared to the samples with treatment.

Influence of Treatment on the Soil Moisture Content

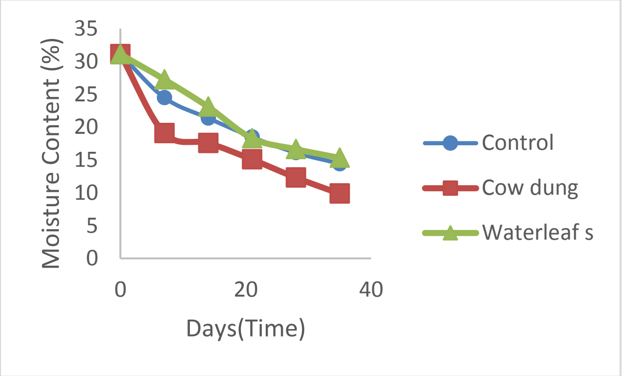


Figure 3.2: Variation of Moisture Content in Silt Loam Soil with Treatment

Figure 3.2 shows the variation in moisture content of crude oil-polluted loamy soil with treated and untreated samples. Unlike the soils' pH, moisture content decreases with time for both control and treated samples. Thus, moisture content decreases with time for both control and treated samples. Similarly, the moisture content in silt loam soil after pollution decreased from 31.12% to 14.45% in the control sample (CL), 15.34% in the sample treated with water leaves (WL) and 14.67% in the sample treated with cow dung (CD) at the end of the 35day treatment Again, the soil with no water leave treatment recorded moisture content than the other soil samples. The trends in moisture content obtained in this study are similar to those reported in a previous work (Umeda et al., 2017).

Influence of Treatment on the Soil Total Organic Carbon

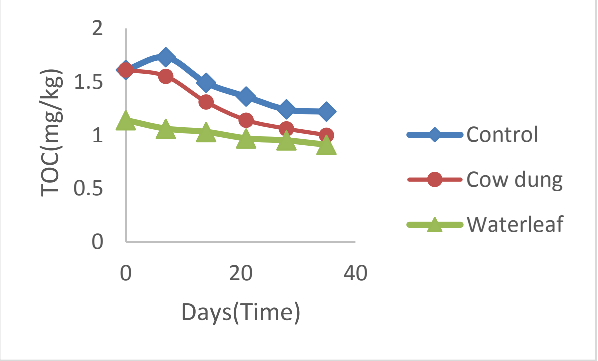


Figure 3.3: Variation of TOC in Silt Loam Soil with Treatment

Figure 3.3 shows the trends in TOC across the treatment samples. Like the soil's moisture content, the total organic carbon decreases. However, the TOC in the control samples were higher than samples with treatment. The TOC in silt loam soil before pollution was 1.61mg/kg, but at the end of the investigation (35 days), it decreased to 1.22mg/kg, 0.91mg/kg water leave and 1mglkg cow dung, treatment with water leave and treatment with cow dung respectively. Again, silt loam soil with no treatment recorded a higher concentration of TOC than the treated samples.

Influence of Treatment on the Soil Total Nitrogen

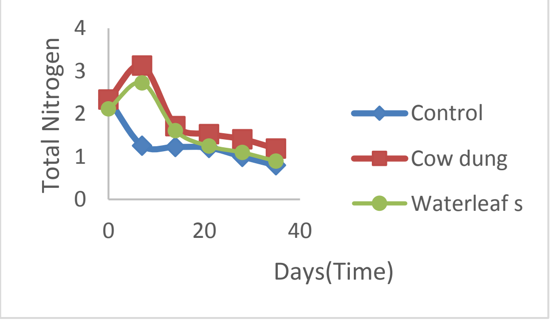


Figure 3.4: Variation of Total Nitrogen in Silt Loam Soil with Treatment

Variation in total nitrogen of treated and untreated crude oil polluted silt loam soil is shown in Figure 4.4. Again, total nitrogen in the treated soil initially increased within the first 7 days, and thereafter decreased gradually till the end of the investigation, on the contrary, there was no increase of total nitrogen at the first seen (7) days in the control sample. This is because addition of treatment improved the content of nitrogen in the polluted soil samples. The total nitrogen in silt loam soil before pollution was 2.34mg/kg, but after 35days of investigation, it decreased to 0.6mg/kg, while water leave treatment and cow dung treatment samples respectively (Table 4.4 of Appendix A), representing 80% and 90% reduction of total nitrogen in the respective soil samples. Total nitrogen content was most produced in the soil treated with cow dung, the control sample which has limited nitrogen production also does not contain the necessary nitrogen supplying nutrient to cause a speedy degradation of TPH in soil.

Influence of Treatment on the Soil Phosphorus Content

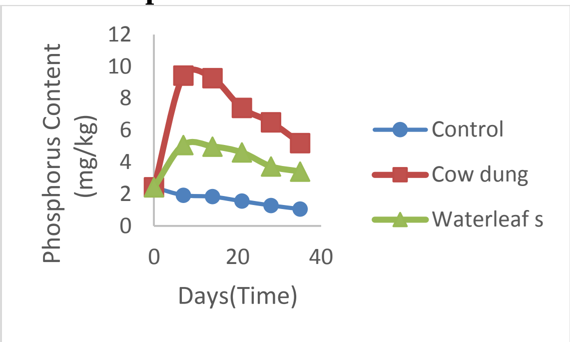


Figure 3.5: Variation of Phosphorus Content in Silt Loam Soil with 150g Treatment

Figure 4.5 shows the variation in phosphorus content of treated and untreated silt loam soil samples. The phosphorus content in the soil with water leaves and cow dung initially increased within the first 7 days before decreasing till the end of the investigation. As in total nitrogen, the initial increase in phosphorus content within the first 7 days was not observed in the control sample. However, from the analysis, phosphorus content in silt loam soil before pollution was 2.42mg/kg, but on the 35th day after pollution, it decreased to 1.06mg/kg, water leaves 5.2mg/kg and 3.41mg/kg cow dung treatment samples respectively.

Total Heterotrophic Bacteria Count

Analysis carried out on hydrocarbon bacteria was carried out on the soils before pollution to identify micro-organisms present. Also, as the experiment was in progress, the control and treatment samples were subjected to analysis to monitor the THB growth in the soils. the following micro-organisms were identified: Bacillus species, Pseudomonas species, and Proteus species. The Bacillus species with colonies in white color, have pointed edged center, and measure about 1-2cm. The Pseudomonas species appeared to be swarming in colonies, whose color can be described as green color with circular edges. Also, the Proteus species are flat with swarming colonies,

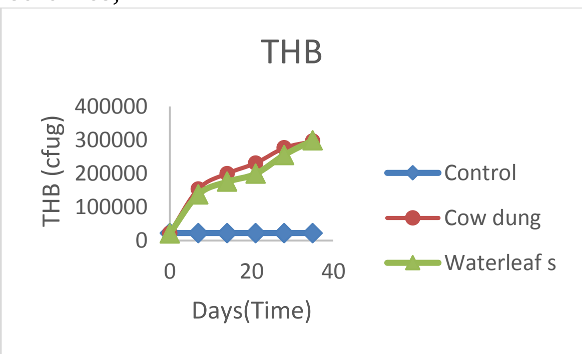


Figure 3.6: TBC Count Variation versus Time in Loamy Soil at Treatment of 150g Waterleaf and Cow Dung

Figure 3.6 depicts the Total Bacteria Count (TBC) dynamics within Loamy soil subjected to varying amendments of Waterleaf treatment weights over an extended period. Much like the preceding experiment involving Cow dung treatment, the introduction of the treatment led to a rapid elevation in the TBC populace within the soil, with a proportional amplification linked to treatment weight. Around the 35th day, the growth rates of microorganisms across all specimens started to approach a state of relative stability. This stabilization trend persisted in samples containing 50 to 150g even after the 35th day. As before, the untreated control sample of Loamy soil exhibited gradual bacterial proliferation.

The findings revealed that the Total Bacteria Counts within Loamy soil treated with Waterleafs exhibited an upward trajectory across the range of treatment variations. Specifically, the counts ranged from 21700 cfu/g for the control sample to 21813 cfu/g, water leaves 21700 cfu/g to 298754 cfu/g, and cow dung 298754 cfu/g, the samples treated with 150g of Waterleafs and cow dung, respectively. The graphical data aptly illustrate that the water leave-treated samples displayed higher TBC values compared to the soils treated with cow dung. A presentation of the Total Bacteria Count (TBC) recorded over time for Loamy soil under the both treatments.

TPH Degradation in Soils under the Influence of Treatment

This study underscores the influence of treatment weight applied in crude oil-contaminated soils on the degradation of Total Petroleum Hydrocarbons (TPH) as bioremediation progresses over time. Consequently, this section presents the outcomes of TPH degradation observed during the investigation periods. The degradation pattern of TPH in loamy soil treated with Waterleaf s is compared with control samples across various treatment weights and time intervals, as depicted in.

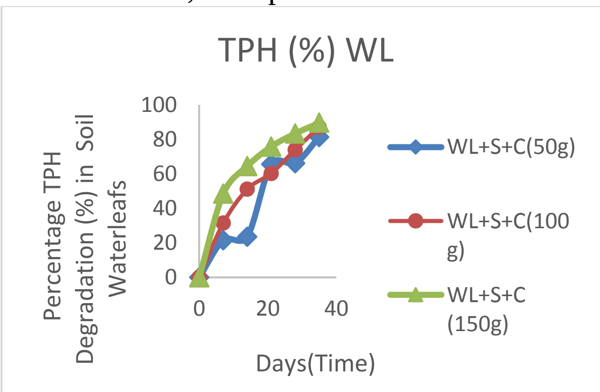


Figure 3.7: TPH Degradation in Loamy Soil versus Time at Various Weights of Waterleaf Treatment

Figure 3.7 portrays the degradation process of Total Petroleum Hydrocarbons (TPH) within loamy soil when subjected to Waterleaf treatment. The profiles of TPH percentage degradation within the loamy soil distinctly demonstrate that an extended time frame corresponds to an augmented percentage of degradation. This correlation directly implies a diminishing concentration of TPH over time. The graph also conveys that while the TPH percentage degradation rate did not display a substantial enhancement with higher treatment weights, the 50g, 100g, and 150g treatments exhibited similar levels of efficacy.

As a consequence of the comprehensive experimental study encompassing 35 days, the TPH percentage degradation within the loamy soil was quantified at 81.27%, 87.07%, and 89.50%, for treatment weights of 50g, 100g, and 150g, respectively. A comprehensive compilation of the TPH analysis results for loamy soil treated with Waterleafs. Notably, the most substantial TPH degradation was observed on the 35th day across varying treatment weights, highlighting the profound influence of the remediation duration on removal efficiency. The results obtained in this study are similar to the reported effect of treatment on crude oil-polluted soil. However, observed that a high concentration of crude oil in soil can negatively affect TPH degradation efficiency. The 5g sample recorded the poorest TPH degradation rate. This implied that the treatment contained nutrients that stimulated the hydrocarbon-degrading bacteria.

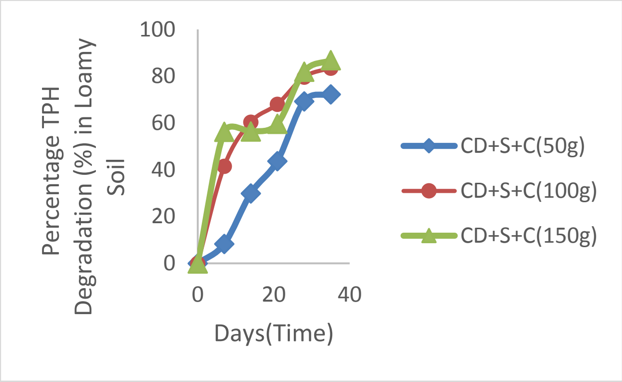
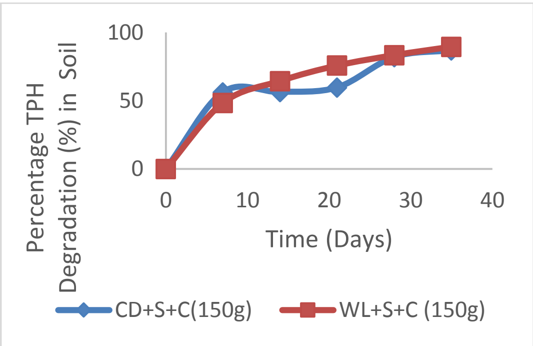


Figure 3.8: TPH Degradation versus Time in Loamy Soil at Various Weights of Cow Dung Treatment

Figure 3.8 portrays the profiles of TPH percentage degradation within Loamy soil subjected to Cow dung treatment. Analogous to the trends observed in Loamy soil treated with Waterleafs, the TPH degradation percentage within Loamy soil exhibited a proportional augmentation with an elongated duration of remediation. Furthermore, an incremental increase in the rate of TPH degradation was noticeable as the treatment weight was elevated. The control sample, similar to the Waterleaf treatment scenario, also demonstrated a reduction in TPH concentration over time, yet at a comparatively slower rate of degradation. The findings revealed that on the 35th day of the experimental study, the recorded TPH degradation percentages within Loamy soil across the spectrum of treatment options were as follows: 72.25%, 83.49%, and 86.89% for treatment weights of 50g, 100g and 150g, respectively. A comprehensive compilation of the TPH analysis results for Loamy soil treated with Cow dung.

Evaluation of Treatment Performance in the Soil

The effectiveness of water leaves and Cow dung as bio-stimulants for TPH degradation in crude oil-contaminated Loamy soil was compared. Figure 3.13 provides a comparison of all treatment options over time at a treatment weight of 150g. Meanwhile, Figure 3.5 presents a comparison of the outcomes obtained on the 35th day across various treatment weights for Cow dung and



waterleaf treatments in the soil samples.

Figure 3.9: Comparison of TPH Removal in the Different Treatment at 150g.

Figure 3.9 illustrates the juxtaposition of TPH percentage degradation between Cow dung treatment and Waterleaf treatment for loamy soil, both carried out using a treatment weight of 150g. As evident from the depicted profiles, the TPH percentage degradation in the Cow dung-treated sample slightly surpassed that of the sample treated with Waterleafs. Additionally, the degradation rate demonstrated a more rapid advancement with a steeper slope in the Cow dung-treated samples compared to the samples treated with Waterleafs.

Evaluation of TPH Degradation Rate Constants

The degradation of TPH in soil was further studied using the first-order kinetic model, which has been generally used for evaluation of crude oil degradation rate in soil.

Evaluation of First Order Rate Constant and Half-Life

The assessment of the degradation rate constant, employing the first-order rate kinetic model, entailed a juxtaposition between Equation (2.16) and the regression equations outlined in Figures 3.9 to 3.24, encompassing a range of treatment options. By utilizing the determined rate constant, the duration necessary for the TPH concentration to diminish to fifty percent of its initial concentration (commonly known as the half-life) was subsequently evaluated.

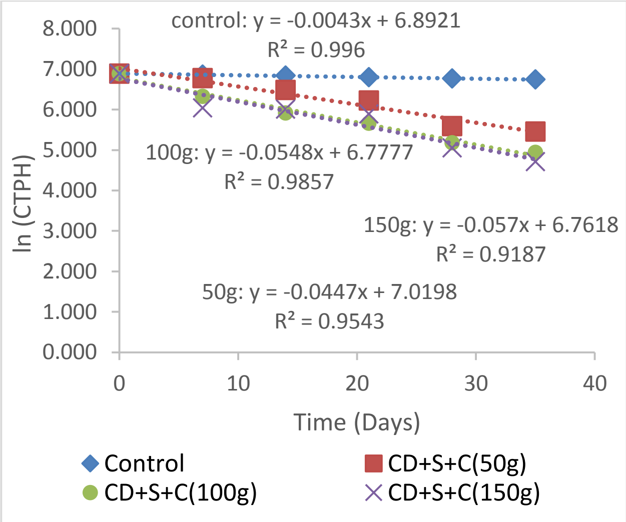


Figure 3.9: Plots for Evaluation of Rate Constant for Cow Dung Treatment in Loamy Soil

Figure 3.9 presents a series of distinctive linear regression equations that characterize various treatment scenarios applied to Loamy soil during Cow dung treatment. The degradation rate constant, referred to as Ks, was derived from these linear equations illustrated in the plot. This process involved a comparison between the provided equations in Figure 3.9 and Equation (2.16). Subsequently, the identified rate constant, together with the initial TPH concentration, was incorporated into Equation (2.17) to generate the final predictive model used for estimating residual TPH levels within the soil. Notably, the degradation rate constant exhibited variability in correspondence with treatment weight. A compilation of the obtained degradation rate constants can be found in Table 3.1. The first-order kinetic rate model, which integrates the degradation rate constants for the respective treatment options, is also documented in Table 3.1.

Utilizing the calculated degradation rate constants, the projected timeframe for the TPH concentration to decrease to half of its initial concentration is meticulously detailed in Table 3.1 for the respective treatment alternatives. Accordingly, considering the evaluated timeframes, the intrinsic degradation process (control sample) within the Loamy soil would demand approximately 161 days to achieve a 50% reduction in TPH concentration. However, the introduction of 50g of Cow dung treatment reduced this duration to about 15 days to attain 50% degradation. Furthermore, this period significantly diminished to 12 days as the treatment weight escalated to 100g, it held steady at 12 days even for 150g treatment. This observation underscores the notion that an increase in treatment weight leads to a notable reduction in the time required for TPH to degrade to half its initial concentration. This observation indicates that augmenting treatment weight leads to a reduction in the time required for TPH to degrade to half of its initial concentration.

Table 3.1: Rate Constant and Model for Loamy Soil under Cow dung Treatment

Weight (g)	k (day^{-1})	Predictive Model	$t^{1/2}$ (days)
Control	0.0043	$C_{TPH} = 984.47e^{-0.004t}$	161.186
50g	0.047	$C_{TPH} = 1118.6e^{-0.047t}$	14.7468
100g	0.0548	$C_{TPH} = 878.05e^{-0.055t}$	12.6478
150g	0.057	$C_{TPH} = 864.2e^{-0.057t}$	12.1596

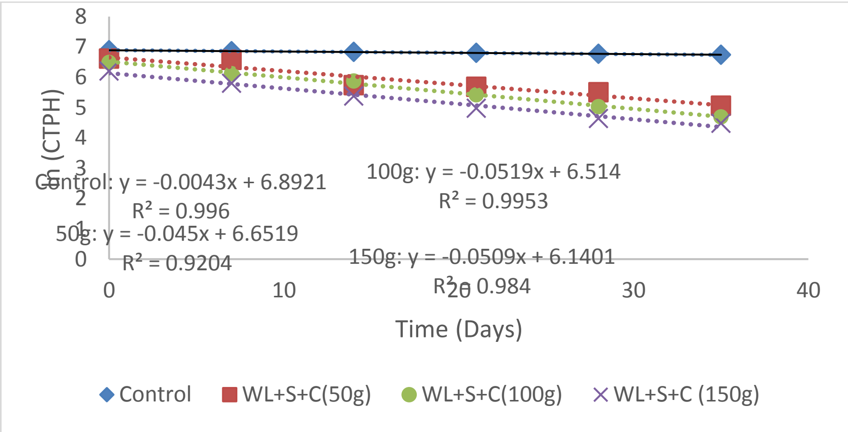


Figure 3.10: Plots for Evaluation of Rate Constant for Waterleaf Treatment in Loamy Soil

Figure 3.10 exhibits an array of unique linear regression equations signifying diverse treatment scenarios applied to Loamy soil during Waterleaf treatment. The determination of the degradation rate constant, designated as Ks, was derived from these linear equations featured on the plot. This determination entailed comparing the provided equations in Figure 3.10 with Equation (3.16). Subsequently, the established rate constant, coupled with the initial TPH concentration, was integrated into Equation (3.17) to yield the conclusive model utilized for projecting residual TPH levels within the Loamy soil. Noteworthy is the variability observed in the degradation rate constant, which correlates with the treatment weight. The tabulated degradation rate constants are available in Table 3.2. Furthermore, Table 3.2 provides the first-order kinetic rate model, encompassing the degradation rate constants unique to each treatment option.

Once again, by relying on the calculated degradation rate constants, the anticipated timeframe for the TPH concentration to decrease to half of its initial concentration within Loamy soil treated with Waterleafs is outlined in Table 3uhuvnnvvn.2. According to the analyzed timeframes, the investigation disclosed that without any amendment, approximately 161 days would be required for the TPH concentration to achieve 50% degradation in Loamy soil undergoing natural degradation (control sample). With the introduction of 50g of Waterleaf's treatment, this timeframe would be reduced to roughly 15 days to attain 50% degradation. This duration further diminishes to around 13 days when the treatment weight is escalated to 100g and holds steady for 150g treatment. Once more, the augmentation of treatment weight results in a shorter period needed for TPH to degrade to half of its initial concentration.

Notably, the pace of degradation, and consequently the degradation rate constant, exhibited its lowest value in the control sample under the Waterleaf treatment but showed an increase as the treatment weight was elevated. Intriguingly, the half-life in Loamy soil under both Cow dung and Waterleaf treatment was nearly identical in the control sample.

Table 4.2: Rate Constant and Model for Loamy Soil under Waterleaf Treatment

Weight (g)	*k* (day^{-1})	Predictive Model	$t^{1/2}$ (days)
Control	0.0043	$C_{TPH} = 984.47e^{-0.0043t}$	161.186
50g	0.045	$C_{TPH} = 774.25e^{-0.045t}$	15.4022
100g	0.0519	$C_{TPH} = 674.52e^{-0.0519t}$	13.3545
150g	0.0509	$C_{TPH} = 464.1e^{-0.0509t}$	13.6169

Conclusion

The study's main focus was on assessing the effectiveness of Cow dung and Waterleaf treatments for remediating crude oil-contaminated loamy soil. Water leaves and cow dung were used fresh and silt loams soil were used for this study. The physicochemical properties of the soils before and after pollution were analyzed. Also, the Total Heterotrophic Bacteria count (THB) and Total Petroleum Hydrocarbons (TPH) content were analyzed every 7 days for 35 days. The results obtained from the physicochemical analysis showed that there was an increase in the pH of the soils after contamination, while there were decreases in the soils' moisture content, total organic carbon, total nitrogen, and phosphorus contents, which differ remarkably from the control samples, implying that the water leaves and cow dung treatments after pollution were effective. Also, as time and treatment weights were increased, the percentage degradation of TPH in the soil increased. Thus, the 150g weight samples exhibited the best performance on the 35th day, consistently demonstrating superior efficacy across various soil types. Waterleaf treatment outperformed Cow dung treatment in terms of TPH percentage degradation. Specifically, 150g Waterleaf treatment resulted in degradation percentages ranging from 81.27% to 89.50%, while Cow dung treatment achieved percentage of 72.24% to 86.88%. Further examination of TPH degradation rate constants and half-lives for Waterleaf and Cow dung treatments revealed distinct patterns. Waterleaf treatment displayed higher degradation rate constants (ranging from 0.0043 to 0.057 day^-1 for Cow dung and 0.0043 to 0.0509day^-1 for Waterleaf), corroborating its superior TPH removal efficiency. Half-life analysis indicated that Cow dung required more time for TPH to degrade to half its initial concentration, while Waterleaf treatment exhibited faster degradation. Conversely, the variation of Michaelis-Menten constants showed no clear pattern. In terms of model performance, the first-order kinetic rate model demonstrated better congruence between experimental TPH concentrations and the Michaelis-Menten equation. Comparing diverse treatment options for soil remediation, the 150g weight samples exhibited the best performance on the 35th day, consistently demonstrating superior efficacy across various soil types. Waterleaf treatment outperformed Cow dung treatment in terms of TPH percentage degradation. Specifically, 150g Waterleaf treatment resulted in degradation percentages ranging from 81.27% to 89.50%, while Cow dung treatment achieved percentages of 72.24% to 86.88%.

Further examination of TPH degradation rate constants and half-lives for Waterleaf and Cow dung treatments revealed distinct patterns. Waterleaf treatment displayed higher degradation rate constants (ranging from 0.0043 to 0.057 day^-1 for Cow dung and 0.0043 to 0.0509 day^-1 for Waterleaf), corroborating its superior TPH removal efficiency. Half-life analysis indicated that Cow dung required more time for TPH to degrade to half its initial concentration, while Waterleaf treatment exhibited faster degradation. Conversely, the variation of Michaelis-Menten constants showed no clear pattern.

In terms of model performance, the first kinetic rate model demonstrated better congruence between experimental TPH concentrations and the Michaelis-Menten equation.

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